BRUSSELATOR AS A REACTION-DIFFUSION SYSTEM

By

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BONAFIDE CERTIFICATE

Certified that this dissertation titled **BRUSSELATOR AS A REACTION-DIFFUSION SYSTEM** is the bonafide work of **Mr. RAJEEV SINGH** who carried out the project under my supervision.

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Abstract

In this work we study the Brusselator model, which is a minimal mathematical model for chemical oscillations. We first review the mean-field analysis for the model and the traditional way of adding the effect of diffusion.

We argue that the mean-field analysis does not capture the stochasticity which is present in any chemical system. Also the usual way of taking diffusion into account does not capture the diffusion. So one should work with the stochastic description of the system.

To this end we study the master equation for the brusselator system using the technique of second quantization method and numerical simulation.

In the second quantization method, after reviewing the method we derive the effective hamiltonian and effective action for the brusselator system. It is found that the effective action can not be used to obtain the differential equation for the field by integration.

The numerical simulation is carried out for various parameter values and we find a transition, which is different from the transition in the mean-field analysis, for small system sizes we looked at. The effect of system size is qualitatively studied.

Future directions for understanding non-equilibrium chemical phenomena at microscopic level is proposed.

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Chapter 1

Introduction

The phenomena of chemical oscillations is a remarkable non-equilibrium behaviour. Under suitable conditions, some chemical systems show a periodic change in the concentration of the species involved. It was initially observed in a system where the oscillating species had a characteristic colour. The oscillations were then seen as a periodic change in the colour of the chemical system.

1.1 Historical Perspective

Some landmarks

- The first homogeneous isothermal chemical oscillation was observed by *William C. Bray* in 1921 [1, 2]. The bray reaction consists of reaction between iodate, iodine and hydrogen peroxide. The concentrations of oxygen and iodine showed approximate periodicity during evolution.

- In 1950, *Boris Pavlovich Beluosov* observed chemical oscillation while investigating a solution of bromate, citric acid and ceric ions (Ce^{4+}). He carefully studied the system and in 1951 submitted his discovery for publication, which was rejected. His work was rejected by a number of journals and hence it was known only in Moscow for a long time. In 1958, his work got published in the abstracts of a conference on Radiation Biology. Later it was published in Russian as well as translated in English [9].

- In 1961, *Anaton Zhabotinsky* started studying the same system. In 1968 he presented some of his results at a conference on 'Biological and Biochemical Oscillators' in Prague.

- In 1970, *Zaikin* and *Zhabotinsky* used ferroin catalyst alone without cerium. They studied unstirred solution in layers and discovered propagating chemical waves.

- In 1980, Lenin prize was awarded to Beluosov, Zhabotinsky, Krinsky, Ivanitsky and Zaikin for discovery and study of the BZ system. Beluosov was already dead in 1970.

Objections

Chemical oscillations was not recognized at first. People simply did not believe that chemical oscillations are possible. At that time it was a general belief that *truly homogeneous oscillating reactions are impossible*. Lots of people claimed that the Bray reaction is not a homogeneous reaction. Also it was claimed that oscillations in a chemical reaction are due to heterogeneous phenomena like bubble formation or presence of small particles. But the most serious of the objections was that *spontaneous temporal self-organization violates second law of thermodynamics*. We shall look at this argument carefully.

1.2   Second Law of Thermodynamics

Second law of thermodynamics is one of the most sacred law in natural sciences. It decides the direction in which a spontaneous change can occur. It says that the entropy of the universe increases for a spontaneous change, i.e.

$$\Delta S_{total} > 0.$$

For an isolated system, the entropy or equivalently Gibbs free energy changes monotonically in a spontaneous process.

Misleading analogy

An oscillating chemical reaction is analogous to a pendulum which passes through its equilibrium position during oscillation. Similarly an oscillating chemical reaction passes through its equilibrium point (equilibrium concentration for all the components) during oscillation. The entropy and the Gibbs free energy being state functions oscillate during the process. But this is in conflict with second law and hence chemical oscillations are impossible.

Resolution

When a chemical system oscillates it never passes through its equilibrium point. The system consists of a number of components. Let us for simplicity of argument assume that only two components are oscillating. When the concentration of one of the component is at its equilibrium value, the other one is far from equilibrium and hence the total system is far from equilibrium. While evolving the other concentration can reach its equilibrium value but by that time the first one can change to a value far from equilibrium. This cycle is possible as during the cycle the entropy does not reach its maxima. In fact the entropy increases by small amounts after each cycle, and hence reaches its maximum value only after few cycles. This argument can be generalised for the case when more than two components are oscillating.

Important points

- As the system evolves the entropy of the system increases. So after a long time the system will eventually reach equilibrium. Thus the oscillatory behaviour is a *transient phenomena for closed systems*, on the way to equilibrium.

- A chemical process would mean that some reactant is getting converted into product. An important point about the closed chemical system is that it is the intermediate products which can oscillate. The *essential* initial reactants monotonically decrease and the final products monotonically increase.

1.3   Some Experimental Results

- Ecological systems with a predator and a prey show oscillation in their populations. Laboratory experiments involving paramecia (predator) and yeast (prey) have been studied and oscillation in population is observed. These systems are modeled by Lotka-Volterra model.

- Bray reaction i.e. the reaction between iodate, iodine and hydrogen peroxide show oscillation in the concentration. This reaction was reported by Bray in 1921 but was looked upon with suspicion. Careful experiments have been carried out and it is shown that the oscillation observed are genuine oscillations.

- The Beluosov-Zhabotinsky (BZ) reaction and its variants have been studied in great detail. After some initial difficulties when this reaction was known to more people, serious research began. The first of the reactions were done in beaker in which the oscillations were seen as a transience phenomena. Later people employed *continuous-flow stirred tank reactors* (CSTR) to study the system. CSTR is an open system which thoroughly mixes the reactants. The flow rates of CSTR are the control parameters for the system. People were able to obtain sustained oscillations for many chemical reactions. Reactions in CSTR can be thought of as zero dimensional system. Typical oscillations look as shown in fig. (1.1). (For reference see [12].)

- The BZ reactions were also done in narrow tubes and propagating chemical waves were observed (see fig. (1.2)). A narrow tube is an unstirred system and diffusion plays an important role in the transport of the reactants. A thin tube is viewed as a one dimensional system.

- These reactions are also carefully done on a Petri-dish. The control parameters are the diffusion constants which are controlled by using suitable substrate. Target patterns and spiral waves are observed (see fig (1.3)). Petri-dish is a two dimensional closed system.

- Careful arrangements have been done to obtain what can be called *continuously fed unstirred reactor* (CFUR), using gel to take care of the fluid motion and allow only

FIG. 1.1. Typical experimental records of oscillatory behaviour in the Belousov–Zhabotinskii reaction: (a) platinum electrode which responds primarily to the Ce^{3+}/Ce^{4+} couple; (b) bromide-sensitive electrode measuring $\ln[Br^-]$.
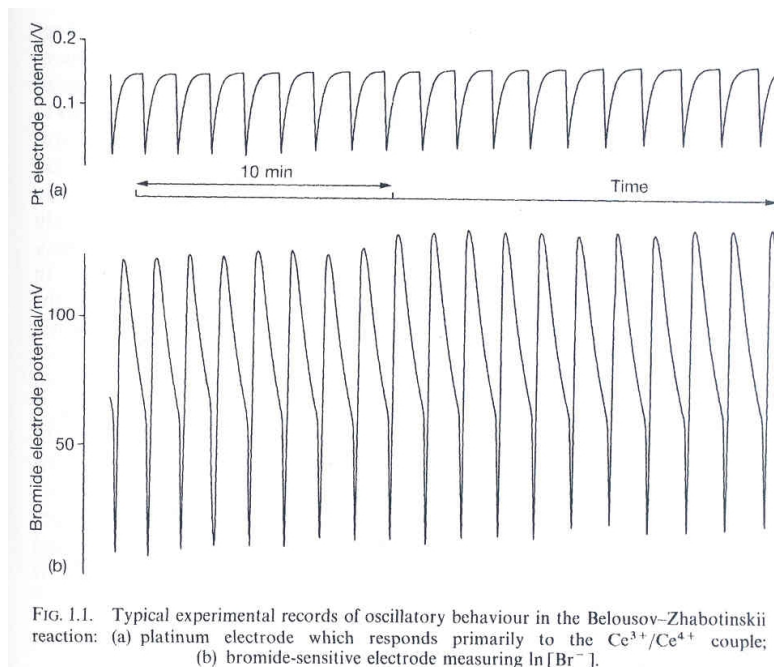
Figure 1.1: Typical experimental record of oscillatory behaviour (p 3, ref. [12])

00:00   03:00   04:00   04:35   04:45   05:05
minutes
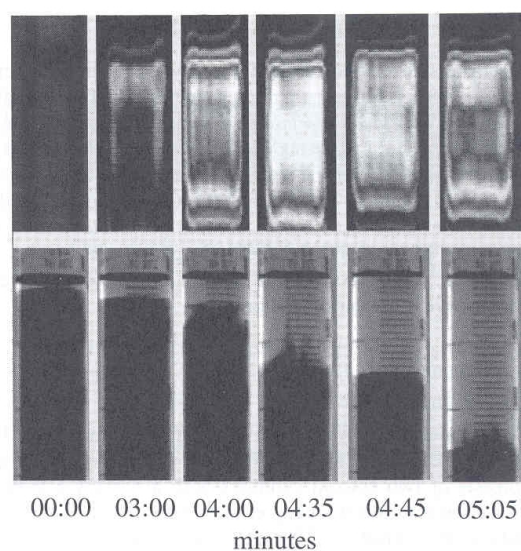
Figure 3.8 Simultaneous visible and IR images of fronts in the bromate–sulfite system (Nagy et al., 1995) propagating in a 100-mL graduated cylinder.

Figure 1.2: Propagating fronts (p 59, ref. [8])
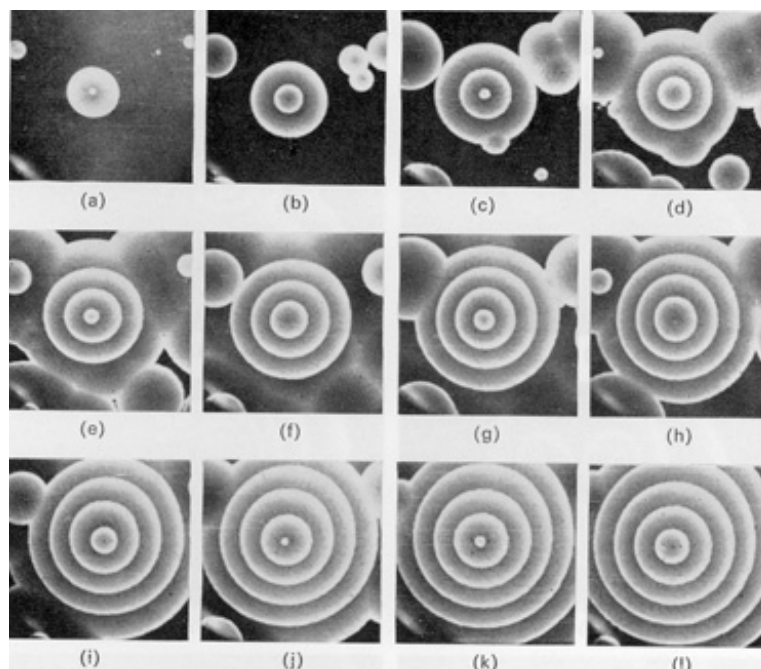
Figure 1.3: Concentric chemical waves forming target patterns (ref. [17])

diffusion as means of transport. This acts as an open system of higher dimensions. Patterns are observed here as well.

- Mixed mode oscillations (fig 1.4), bursting oscillations (fig 1.5), quasi-periodicity (fig 1.6), intermittency (fig 1.7) and chaos are also observed in open chemical systems for suitable parameters.

- Effect of gravity, electric and magnetic fields are also studied experimentally on travelling chemical waves.

- Coupled chemical oscillators have also been studied and the phenomena of entrainment, oscillator death, rythmogenesis, birythmicity, compound oscillations, bursting and chaotic oscillations are observed.

- Interference of target patterns and spiral waves is also studied experimentally.

- Chlorine dioxide iodine malonic acid (CDIMA) reaction has shown Turing patterns experimentally.

For an excellent review of the experimental aspects of chemical oscillations see [8].
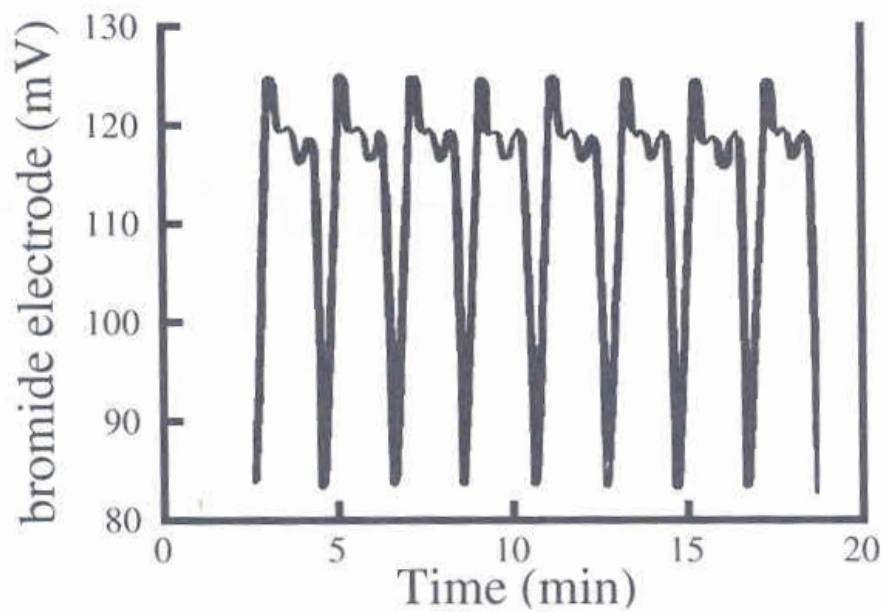
Figure 1.4: Mixed-mode oscillations (p 164, ref. [8])
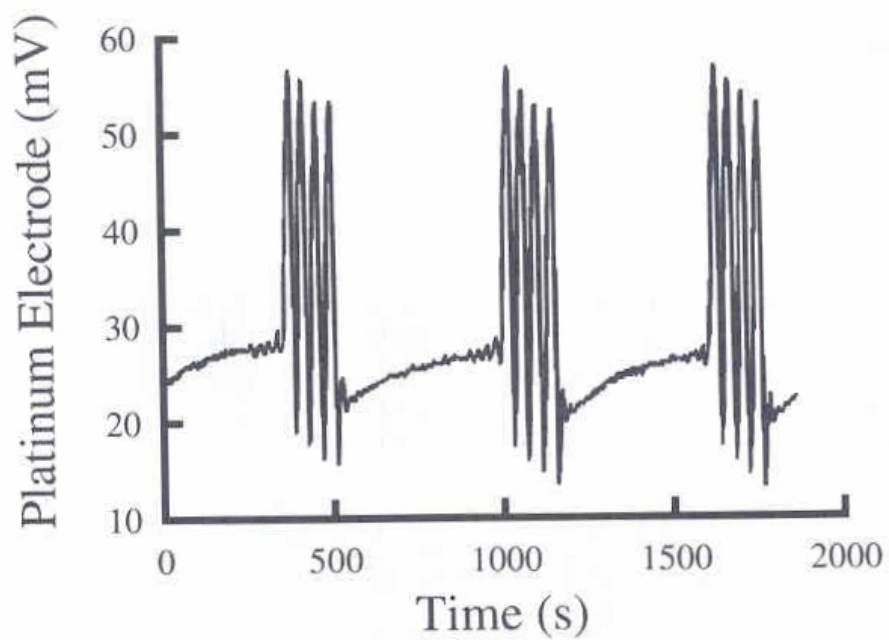
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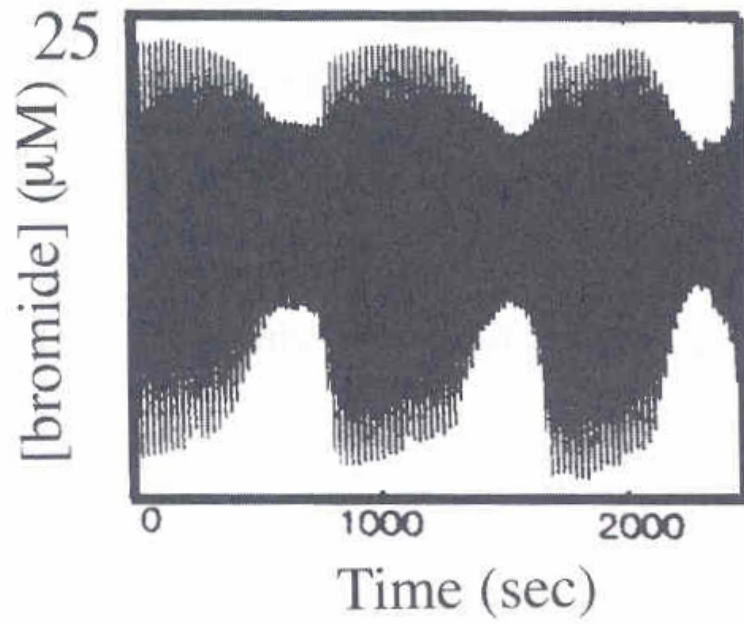
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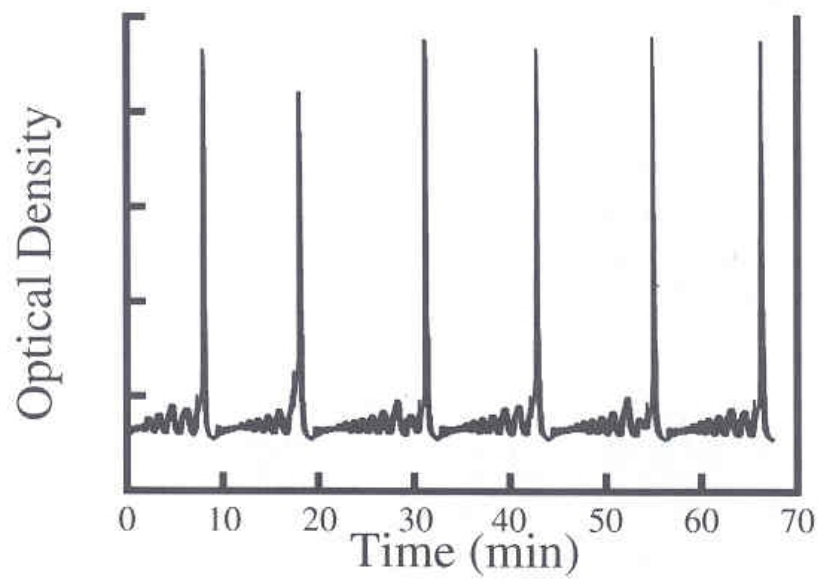
Figure 1.7: Intermittency (p 184, ref. [8])

1.4   The Beluosov-Zhabotinsky (BZ) Reaction

1.4.1   FKN Mechanism

The mechanism for the BZ reaction as given by Field, Körös and Noyes (FKN) in 1972 is given here (refer to [12]).

The mechanism can be divided into three overall processes

1. The first process consists of three steps which result in reduction of bromate to bromine. The bromide ion acts as the reducing agent. The three steps are

$$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr \tag{1.1a}$$

$$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr \tag{1.1b}$$

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \tag{1.1c}$$
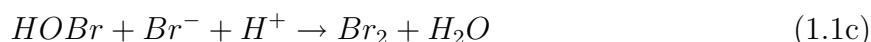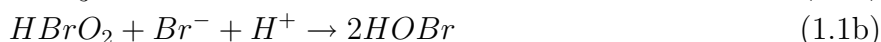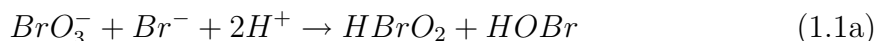
   The overall stoichiometry of the first process is obtained by taking eqn. (1.1a)+eqn. (1.1b)+3 eqn. (1.1c), which gives

$$\boxed{BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O} \tag{1.2}$$
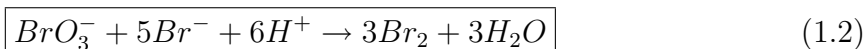
2. The second process becomes important when the concentration of Br^- becomes low. This again has three steps which are

$$BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2 + H_2O \tag{1.3a}$$

$$BrO_2 + Ce(III) + H^+ \rightarrow Ce(IV) + HBrO_2 \tag{1.3b}$$

$$2HBrO_2 \rightleftharpoons HOBr + BrO_3^- + H^+ \tag{1.3c}$$
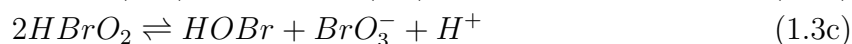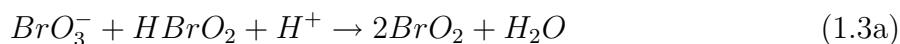
   The first two steps [eqn. (1.3a) and eqn. (1.3b)] together constitute an auto-catalytic sequence, which is obtained taking eqn. (1.3a)+2 eqn. (1.3b)

$$BrO_3^- + 3H^+ + 2Ce(III) + HBrO_2 \rightarrow H_2O + 2Ce(IV) + 2HBrO_2.$$
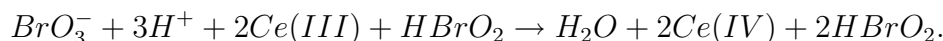
   The rate of this process accelerates and the cerium catalyst gets converted to its oxidized form, as a result of auto-catalysis. *There is a sharp colour change.*

   The overall stoichiometric of this process is obtained by taking 2 eqn.(1.3a)+ 4 eqn.(1.3b)+ eqn. (1.3c)

$$\boxed{BrO_3^- + 4Ce(III) + 5H^+ \rightarrow 4Ce(IV) + HOBr + 2H_2O} \tag{1.4}$$
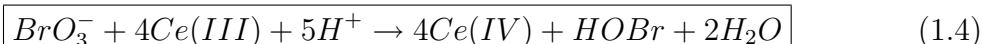
3. The following three steps constitute the third process

$$MA \rightarrow \text{enol} \tag{1.5a}$$

$$\text{enol} + Br_2 \rightarrow BrMA + H^+ + Br^- \tag{1.5b}$$

$$2Ce(IV) + BrMA + MA \rightarrow 2Ce(III) + fBr^- + \text{other products} \tag{1.5c}$$
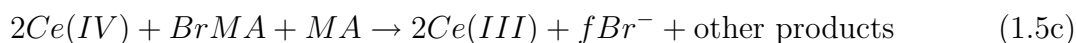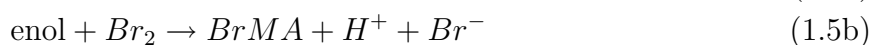
   Eqn. (1.5c) is not well understood, hence we have the factor f and the term 'other products'.

1.4.2 Oregonator

The oregonator is a mathematical model which captures the essence of the FKN mechanism. It was developed by Field and Noyes at University of Oregon in 1974. The idea is to make suitable approximations and reduce the number of variables in the model. To obtain the oregonator model we make the following approximations

1. The change in concentrations of BrO_3^-, H^+ and the organic species is so small during the process that we assume them to be constant.

2. The concentration of BrO_2 changes so rapidly than the species we are interested in, that we assume the concentration of BrO_2 to be constant, equal to its average value.

Let us denote the required concentrations as following

$$[HBrO_2] = X, \qquad [Br^-] = Y, \qquad [Ce(IV)] = Z,$$
$$[HOBr] = P, \qquad [BrO_3^-] = A, \qquad \text{[organic species]} = B$$

The oregonator model is then given by

$$A + Y \rightarrow X + P$$
$$X + Y \rightarrow 2P$$
$$A + X \rightarrow 2X + 2Z$$
$$2X \rightarrow A + P$$
$$B + Z \rightarrow \frac{1}{2}fY$$
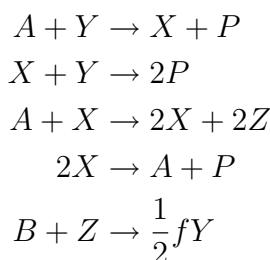
where f is an adjustable stoichiometric factor.

1.4.3 Brusselator

This model was proposed by Prigogine and Lefever in 1968 and was given its name by Tyson in 1973. The brusselator system is given by

$$A \rightarrow X$$
$$B + X \rightarrow Y + D$$
$$2X + Y \rightarrow 3X$$
$$X \rightarrow E$$
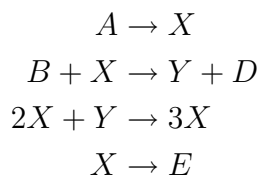
This model is the subject of study in this work.

The brusselator is the minimal mathematical model that can incorporate the oscillating behaviour, as we show in the next section. This model is usually studied in the mean-field approximation. The mean-field approximation neglects the effect of fluctuations and correlations. We wish to study the system taking into account the fluctuations and correlations, hence we study the master equation approach to the model.

1.5   Can bimolecular reactions show oscillations?

This question can be answered by a result due to Hanusse (1972) which was re-derived and extended by Tyson and Light (1973). We follow the analysis given in [14].

Claim. It is impossible to have a limit cycle surrounding an unstable node or focus in a reaction sequence involving two variable intermediates if the reaction steps are uni- and bimolecular.

Proof. Let X and Y denote the concentrations of the two variable intermediates. Then,

$$\frac{dX}{dt} = f(X,Y), \qquad \frac{dY}{dt} = g(X,Y)$$

If the reaction steps are restricted to be only uni- or bimolecular, then f and g can only have terms that are utmost second order in X, Y. The most general expressions for f and g are

$$f(X,Y) = A_1 + B_1 X + C_1 Y + D_1 X^2 + E_1 Y^2 + F_1 XY$$
$$g(X,Y) = A_2 + B_2 X + C_2 Y + D_2 X^2 + E_2 Y^2 + F_2 XY$$

where A's and B's are constants.
The fixed points $(X^\star, Y^\star)$ are given by $f(X^\star, Y^\star) = g(X^\star, Y^\star) = 0$. This implies

$$X^\star \left(B_1 + D_1 X^\star + F_1 Y^\star \right) = - \left(A_1 + C_1 Y^\star + E_1 Y^{\star 2} \right) \tag{1.6}$$

$$Y^\star \left(C_2 + E_2 Y^\star + F_2 X^\star \right) = - \left(A_2 + B_2 X^\star + D_2 X^{\star 2} \right) \tag{1.7}$$

Expanding about the fixed point, the Jacobian matrix M is given by

$$M(X,Y) \equiv \begin{bmatrix} \frac{\partial f}{\partial X} & \frac{\partial f}{\partial Y} \\ \frac{\partial g}{\partial X} & \frac{\partial g}{\partial Y} \end{bmatrix}$$
$$= \begin{bmatrix} B_1 + 2D_1 X + F_1 Y & C_1 + 2E_1 Y + F_1 X \\ B_2 + 2D_2 X + F_2 Y & C_2 + 2E_2 Y + F_2 X \end{bmatrix}$$

At fixed point, it becomes

$$M(X^\star, Y^\star) = \begin{bmatrix} B_1 + 2D_1 X^\star + F_1 Y^\star & C_1 + 2E_1 Y^\star + F_1 X^\star \\ B_2 + 2D_2 X^\star + F_2 Y^\star & C_2 + 2E_2 Y^\star + F_2 X^\star \end{bmatrix}$$

The trace of the Jacobian matrix at the fixed point is given by

$$T = - \left(\frac{\left(A_1 + C_1 Y^\star + E_1 Y^{\star 2} \right)}{X^\star} - D_1 X^\star + \frac{\left(A_2 + B_2 X^\star + D_2 X^{\star 2} \right)}{Y^\star} - E_2 Y^\star \right) \tag{1.8}$$

The list of all possible uni- and bimolecular reactions and their contributions to the various reaction constants is given in table (1.1). The table gives the sign of each constant in eqn. (1.8). Every term inside bracket in eqn. (1.8) is positive, hence we get

$$\boxed{T < 0}$$

Let λ_1 and λ_2 be the two eigenvalues of $M(X^\star, Y^\star)$. Then $T = \lambda_1 + \lambda_2$. The λ's determine the stability of the fixed point, and in this case we have only following three possibilities

1. Both λ_1 and λ_2 are real and negative. Then the fixed point is a stable fixed point.

2. Both λ_1 and λ_2 are real and, $\lambda_1 > 0$ and $\lambda_2 < 0$ such that $\lambda_1 + \lambda_2 < 0$. Then the fixed point is a saddle point. There is result which says that *there can not be a limit cycle enclosing a saddle point.*

3. λ_1 and λ_2 are complex conjugates of one another, in which case real part of both λ_1 and λ_2 is negative and the fixed point is a stable spiral.

It is clear that we can not have a limit cycle in this case. Hence oscillations are not possible in a chemical system involving only two variable intermediates with reaction steps only uni- or bimolecular.

Thus if one wants to construct a model for oscillating chemical reactions with two intermediate species, one requires at least a trimolecular step. The *brusselator* is a minimal model which involving a tri-molecular step. We show the existence of a limit cycle for suitable parameter range for the brusselator later.

Table 1.1: Contribution of all possible uni- and bimolecular reactions to the reaction constants.

Step	Contribution to dX/dt (if $\neq 0$)	Contribution to dY/dt (if $\neq 0$)
$A \rightarrow$	$A_1 > 0$	$A_2 > 0$
$X \rightarrow$	B_1?	$B_2 > 0$
$Y \rightarrow$	$C_1 > 0$	C_2?
$2X \rightarrow$	$D_1 < 0$	$D_2 > 0$
$2Y \rightarrow$	$E_1 > 0$	$E_2 < 0$
$X + Y \rightarrow$	F_1?	F_2?

Chapter 2

Two Dimensional Flows

Before we start analysing the rate equations for the brusselator system, which are particular case of two-dimensional flow equations, we wish to briefly review the physics of two-dimensional flows. In this chapter, we follow the treatment given in [15].

2.1 Linear Systems

A two-dimensional linear system is given by

$$\dot{x} = ax + by$$
$$\dot{y} = cx + dy \tag{2.1}$$

where x and y are the system variables, a, b, c, d are constants and $\dot{x}$, $\dot{y}$ stands for time-derivative of x, y. Eqn. (2.1) can be written in a compact matrix form as following

$$\dot{X} = AX \tag{2.2}$$

where

$$A = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \text{ and } X = \begin{pmatrix} x \\ y \end{pmatrix} \tag{2.3}$$

The fixed point of eqn. (2.2) is given by setting $\dot{X} = 0$, which gives $X = 0$ if determinant of A is not zero.

It is instructive to find what are called *straight line trajectories*: i.e. trajectories which always remain on some straight line in the phase space (here 2-dimensional space of x and y). These trajectories are given by

$$X = e^{\lambda t} V \tag{2.4}$$

where $V \neq 0$ is some fixed vector to be determined, and λ is a growth rate also to be determined.

To find V and λ, we substitute eqn. (2.4) in eqn. (2.2) to get

$$AV = \lambda V \tag{2.5}$$

The above equation is simply is the eigen-equation for the matrix A, λ being an eigenvalue of A and V being the corresponding eigenvector. The solution for λ is given by the characterstic equation which reads

$$
\begin{aligned}
det(A - \lambda\mathbb{1}) &= 0 \\
\Rightarrow \lambda^2 - \tau\lambda + \Delta &= 0
\end{aligned}
\tag{2.6}
$$

where

$$
\begin{aligned}
\tau &= trace(A) = a + d \\
\Delta &= det(A) = ad - bc
\end{aligned}
$$

Then

$$
\lambda_1 = \frac{\tau + \sqrt{\tau^2 - 4\Delta}}{2}, \qquad \lambda_2 = \frac{\tau - \sqrt{\tau^2 - 4\Delta}}{2}
\tag{2.7}
$$

are the solutions to eqn. (2.6). Typically, $\lambda_1 \neq \lambda_2$, in which case the corresponding eigenvectors V_1 and V_2 are linearly independent (by a theorem in linear algebra). Then any initial condition $X(0)$ can be written as a linear combination of eigenvectors, i.e.

$$
X(0) = c_1 V_1 + c_2 V_2
\tag{2.8}
$$

where c_1 and c_2 are constants. The solution is then given by

$$
X(t) = c_1 e^{\lambda_1 t} V_1 + c_2 e^{\lambda_2 t} V_2.
\tag{2.9}
$$

The asymptotic behaviour of the flow depends on the eigenvalues λ_1 and λ_2. The following cases are possible:

Case I: Both λ_1 and λ_2 are real and negative

In this case, $X(t) \to 0$ in the limit $t \to \infty$. The the fixed point $X = 0$ is a stable fixed point. The condition for this case to occur is

$$
\tau < 0 \quad \text{and} \quad \tau^2 > 4\Delta.
\tag{2.10}
$$

using eqn. (2.7).

Case II: Both λ_1 and λ_2 are real and positive

In this case, $X(t) \to \infty$ in the limit $t \to \infty$. The the fixed point $X = 0$ is a unstable fixed point. Using eqn. (2.7), we get

$$
\tau > 0 \quad \text{and} \quad \tau^2 > 4\Delta.
\tag{2.11}
$$

Case III: Both λ_1 and λ_2 are real and of opposite sign

Using eqn. (2.9), we see that the trajectory decays exponentially along one eigenvector whereas grows exponentially along the other. The fixed point in this case is called saddle point.

The condition for this case to occur is

$$\Delta < 0 \tag{2.12}$$

since the determinant is the product of eigenvalues.

Case IV: λ_1 and λ_2 are complex conjugates with negative real part

In this case the trajectory spirals into the fixed point asymptotically. The fixed point is called stable spiral in this case.

It occurs when
$$\tau < 0 \quad \text{and} \quad \tau^2 < 4\Delta. \tag{2.13}$$

Case V: λ_1 and λ_2 are complex conjugates with positive real part

In this case the trajectory spirals out of the fixed point and asymptotically go to infinity. The fixed point is called unstable spiral in this case.

It occurs when
$$\tau > 0 \quad \text{and} \quad \tau^2 < 4\Delta. \tag{2.14}$$

The following figure summarises all the cases considered:
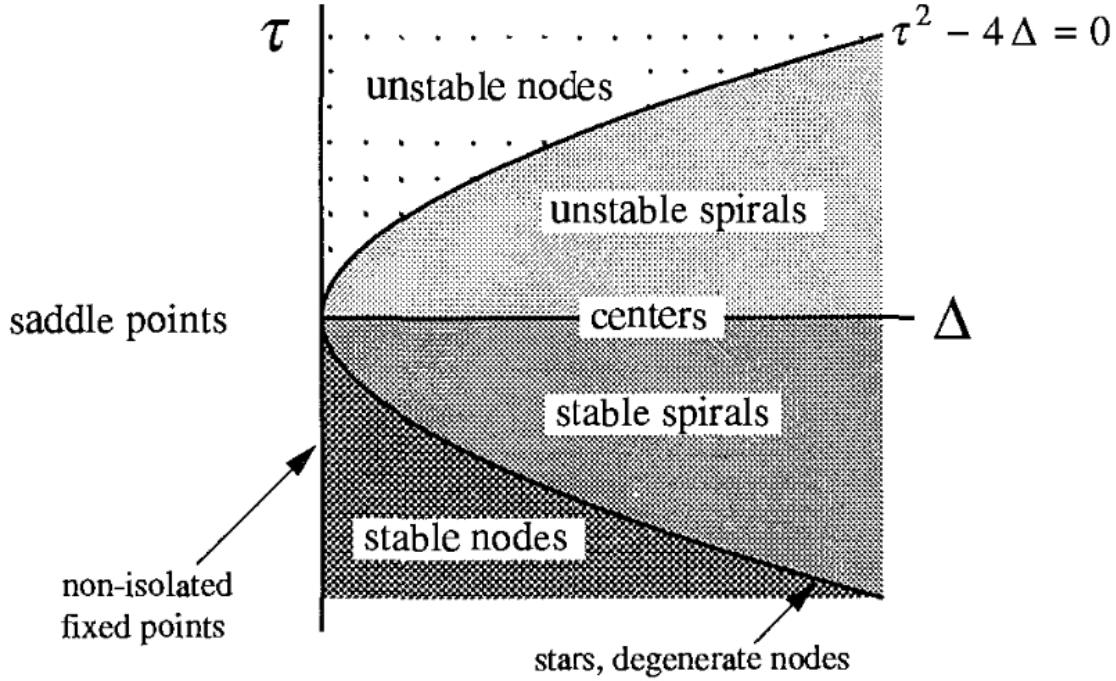
Figure 2.1: Summary of stability analysis. (p 137, [15])

2.2 Nonlinear Systems

A two-dimensional nonlinear system is given by

$$\dot{X} = f(X, Y)$$
$$\dot{Y} = g(X, Y)$$

$$(2.15)$$

where X and Y are system variables and $f(X, Y)$ and $g(X, Y)$ are general nonlinear functions of X and Y.

The fixed points are obtained by setting $\dot{X} = \dot{Y} = 0$. Let $(X^\star, Y^\star)$ be a fixed point, then very close to the fixed point i.e.

$$X = X^\star + x$$
$$Y = Y^\star + y$$

$$(2.16)$$

the dynamics is given by linearised equations

$$\dot{x} = \frac{\partial f(X^\star, Y^\star)}{\partial X} x + \frac{\partial f(X^\star, Y^\star)}{\partial Y} y$$

$$(2.17)$$

$$\dot{y} = \frac{\partial g(X^\star, Y^\star)}{\partial X} x + \frac{\partial g(X^\star, Y^\star)}{\partial Y} y$$

which can be written in compact form as

$$\begin{pmatrix} \dot{x} \\ \dot{y} \end{pmatrix} = M(X^\star, Y^\star) \begin{pmatrix} x \\ y \end{pmatrix} \tag{2.18}$$

where

$$M(X^\star, Y^\star) = \begin{pmatrix} \frac{\partial f(X^\star, Y^\star)}{\partial X} & \frac{\partial f(X^\star, Y^\star)}{\partial Y} \\ \frac{\partial g(X^\star, Y^\star)}{\partial X} & \frac{\partial g(X^\star, Y^\star)}{\partial Y} \end{pmatrix} \tag{2.19}$$

is called the Jacobian matrix.

Eqn. (2.18) is analogous to eqn. (2.2) for the linear system. The analysis for the linear system is carried over to the nonlinear system close to the fixed point with $M(X^\star, Y^\star)$ replacing A.

Note: For a nonlinear system, there can be multiple fixed points. Linear stability analysis should be done for all the fixed points separately. The result of the linear stability analysis is valid only for a small region close to the fixed point. In general, we can not solve the nonlinear equations explicitly. Linear stability analysis enables us to characterise all the fixed points in the phase space of the nonlinear system, and give us a qualitative understanding of the dynamics.

We now mention few important results without proof, which would be useful for our purpose.

2.2.1 Existence and Uniqueness Theorem

Consider the initial value problem $\dot{X} = F(X), X(0) = X_0$, where X is a n-dimensional vector and $F(X)$ is a n-dimensional function of X, i.e. F consists of n functions of X. Suppose that F is continuous and that all its partial derivatives $\partial F_i / \partial X_j$, $i, j = 1, 2, \cdots, n$, are continuous for X in some open connected set D. Then for $X_0 \in D$, the initial value problem has a solution $X(t)$ on some time interval $(-\tau, \tau)$ about $t = 0$, and the solution is unique.

An immediate consequence of this theorem is that different trajectories cannot intersect, because if they did then at th point of intersection the uniqueness will not hold anymore.

2.2.2 Poincaré- Bendixson Theorem

For vector fields on the plane, if a trajectory is confined to a closed, bounded region and there are no fixed points in the region, then the trajectory must eventually approach a closed orbit.

It follows from this theorem that if one is able to construct a trapping region around an unstable fixed point or unstable spiral, then this theorem guarantees the existence of a limit cycle. We make use of this theorem in proving the existence of limit cycle for the rate equation of the brusselator system later.

Chapter 3

Brusselator - A Mean Field Approach

The brusselator is a system of chemical reactions which can be written in a simplified form as

$$\phi \xrightarrow{J_{in}} X$$
$$2X + Y \xrightarrow{\lambda_1} 3X$$
$$X \xrightarrow{\lambda_2} Y \tag{3.1}$$
$$X \xrightarrow{J_{out}} \phi$$

where X, Y are two intermediate species of chemicals.

3.1 Analysis using mean-field approximation and non-linear dynamics

In the mean-field approximation, it is assumed that there is no fluctuation or correlations. This approximation is usually valid for large system size. The dynamics of concentration is given by

$$\frac{dX}{dt} = J_{in} + \lambda_1 \ X^2 \ Y - \lambda_2 \ X - J_{out} \ X \equiv f\left(X, Y\right)$$
$$\frac{dY}{dt} = -\lambda_1 \ X^2 \ Y + \lambda_2 \ X \equiv g\left(X, Y\right) \tag{3.2}$$

where X and Y denote the mean-concentration of the two species in the system.

Fixed points:

Fixed points $(X^\star, Y^\star)$ are given by $\dot{X} = \dot{Y} = 0$. This gives

$$J_{in} + \lambda_1 \ X^{2\star} \ Y^\star - \lambda_2 \ X^\star - J_{out} \ X^\star = 0$$
$$-\lambda_1 \ X^{2\star} \ Y^\star + \lambda_2 \ X^\star = 0$$

There is a unique solution

$$X^\star = \frac{J_{in}}{J_{out}} \tag{3.3a}$$

$$Y^\star = \frac{\lambda_2}{\lambda_1} \frac{J_{out}}{J_{in}} \tag{3.3b}$$

To study the behaviour of the system, we will linearize eqn. (3.2) around the fixed point, i.e., we substitute

$$X = X^\star + x \text{ and } Y = Y^\star + y$$

in eqn. (3.2) and neglect the higher order terms in x and y.

$$\frac{dx}{dt} = (2 \lambda_1 X^\star Y^\star - \lambda_2 - J_{out}) x + \lambda_1 X^{\star\, 2} y$$

$$\frac{dy}{dt} = (-2 \lambda_1 X^\star Y^\star + \lambda_2) x - \lambda_1 X^{\star\, 2} y$$

These equations can be written in a compact form as

$$\frac{d}{dt} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} 2 \lambda_1 X^\star Y^\star - \lambda_2 - J_{out} & \lambda_1 X^{\star\, 2} \\ -2 \lambda_1 X^\star Y^\star + \lambda_2 & -\lambda_1 X^{\star\, 2} \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} \tag{3.4}$$

The matrix above is the *Jacobian matrix* at $(X^\star, Y^\star)$. Let us denote it by $M(X^\star, Y^\star)$. Substituting for $X^\star$ and $Y^\star$ we get

$$M(X^\star, Y^\star) = \begin{bmatrix} \lambda_2 - J_{out} & \lambda_1 \, (J_{in}/J_{out})^2 \\ -\lambda_2 & -\lambda_1 \, (J_{in}/J_{out})^2 \end{bmatrix} \tag{3.5}$$

The determinant of the Jacobian matrix at the fixed point is

$$\Delta \equiv det\,[M(X^\star, Y^\star)]$$

$$= \lambda_1 \, J_{out} \left(\frac{J_{in}}{J_{out}} \right)^2 > 0$$

The positive value of the determinant rules out the possibility of having a saddle point. The trace of the Jacobian matrix is

$$\tau = Tr\,[M(X^\star, Y^\star)]$$

$$= \lambda_2 - J_{out} - \lambda_1 \left(\frac{J_{in}}{J_{out}} \right)^2$$

Since the determinat is positive, hence the stability of the fixed point can be established just by looking at the sign of trace:

Case I: The fixed point is *stable* if the trace is negative, i.e.

$$\tau < 0 \Rightarrow \lambda_2 < J_{out} + \lambda_1 \left(\frac{J_{in}}{J_{out}} \right)^2$$

Case II: The fixed point is *unstable* if the trace is positive, i.e.

$$\tau > 0 \Rightarrow \lambda_2 > J_{out} + \lambda_1 \left(\frac{J_{in}}{J_{out}}\right)^2$$

Hence, we define the critical point as

$$\boxed{\lambda_{2c} = J_{out} + \lambda_1 \left(\frac{J_{in}}{J_{out}}\right)^2} \tag{3.6}$$

The fixed point is stable if $\lambda_2 < \lambda_{2c}$ and is unstable if $\lambda_2 > \lambda_{2c}$.

Eigenvalues of M

The characterstic equation is given by

$$det\,[M - \Lambda\,I] = 0$$

where Λ gives the eigenvalues and I is the 2×2 identity matrix.

$$\Rightarrow \Lambda = \frac{\left\{\lambda_2 - J_{out} - \lambda_1\,(J_{in}/J_{out})^2\right\} \pm \sqrt{\left\{\lambda_2 - J_{out} - \lambda_1\,(J_{in}/J_{out})^2\right\}^2 - 4\,\lambda_1\,J_{out}\,(J_{in}/J_{out})^2}}{2} \tag{3.7}$$

The square root term above if real, is certainly less than the first term, since

$$4\,\lambda_1\,J_{out}\,(J_{in}/J_{out})^2 > 0.$$

Hence the real part of both the eigenvalues will have the same sign as the first term. This implies that the stability is still decided by the critical point we found earlier [in eqn. (3.6)]. The square root term tells us whether the fixed point is ordinary fixed point or spiral. The fixed point will be an ordinary fixed point if

$$\left\{\lambda_2 - J_{out} - \lambda_1\,(J_{in}/J_{out})^2\right\}^2 - 4\,\lambda_1\,J_{out}\,(J_{in}/J_{out})^2 \geq 0$$

$$\Rightarrow \lambda_2 \geq J_{out} + \lambda_1\,(J_{in}/J_{out})^2 + 2\,\sqrt{\lambda_1\,J_{out}}\,(J_{in}/J_{out})$$
$$\text{or } \lambda_2 \leq J_{out} + \lambda_1\,(J_{in}/J_{out})^2 - 2\,\sqrt{\lambda_1\,J_{out}}\,(J_{in}/J_{out}). \tag{3.8}$$

Hence the stability analysis gives us the following information:
Case I: The fixed point is *stable fixed point* if

$$\lambda_2 \leq J_{out} + \lambda_1\,(J_{in}/J_{out})^2 - 2\,\sqrt{\lambda_1\,J_{out}}\,(J_{in}/J_{out})$$

Case II: The fixed point is *stable spiral* if

$$J_{out} + \lambda_1\,(J_{in}/J_{out})^2 - 2\,\sqrt{\lambda_1\,J_{out}}\,(J_{in}/J_{out}) < \lambda_2 < J_{out} + \lambda_1\,(J_{in}/J_{out})^2$$

Case III: The fixed point is *unstable spiral* if

$$J_{out} + \lambda_1 \ (J_{in}/J_{out})^2 < \lambda_2 < J_{out} + \lambda_1 \ (J_{in}/J_{out})^2 + 2 \ \sqrt{\lambda_1 \ J_{out}} \ (J_{in}/J_{out})$$

Case IV: The fixed point is *unstable fixed point* if

$$\lambda_2 \geq J_{out} + \lambda_1 \ (J_{in}/J_{out})^2 + 2 \ \sqrt{\lambda_1 \ J_{out}} \ (J_{in}/J_{out})$$

Construction of Trapping Region

Now we present an algorithm to construct a trapping region aroung the fixed point in the most general case. We also show that such algorithm always work, and hence show the existence of a trapping region around the fixed point. Refer to fig.(3.1) in order to follow the algorithm.
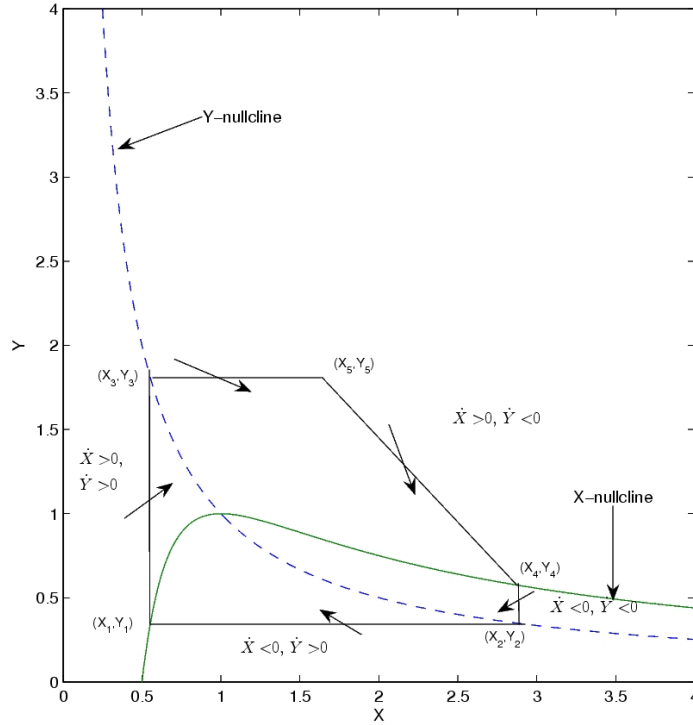
Figure 3.1: X and Y nullclines and the trapping region.

Step 1: Choose $Y = \epsilon > 0$.

Step 2: The curves in phase space (XY-plane) on which $\dot{X} = 0$ ($\dot{Y} = 0$) is called the X (Y)-*nullcline*.

X-nullcline:

$$J_{in} + \lambda_1 \, X^2 \, Y - \lambda_2 \, X - J_{out} \, X = 0$$
$$\Rightarrow \lambda_1 \, Y \, X^2 - (\lambda_2 + J_{out}) \, X + J_{in} = 0$$
$$\Rightarrow Y = \frac{(\lambda_2 + J_{out}) \, X - J_{in}}{\lambda_1 \, X^2} \tag{3.9a}$$

$$\text{Also, } X = \frac{(\lambda_2 + J_{out}) \pm \sqrt{(\lambda_2 + J_{out})^2 - 4 \, \lambda_1 \, Y \, J_{in}}}{2 \, \lambda_1 \, Y} \tag{3.9b}$$

Y-nullcline:

$$- \lambda_1 \, X^2 \, Y + \lambda_2 \, X = 0$$
$$\Rightarrow X = 0 \text{ or } XY = \frac{\lambda_2}{\lambda_1} \tag{3.10}$$

Find the points on X-nullcline for which $Y = \epsilon$, which can be found using eqn.(3.9b)

$$X_\pm = \frac{(\lambda_2 + J_{out}) \pm \sqrt{(\lambda_2 + J_{out})^2 - 4 \, \lambda_1 \, \epsilon \, J_{in}}}{2 \, \lambda_1 \, \epsilon}$$

Let us define the point:

$$(X_1, Y_1) = \left(\frac{(\lambda_2 + J_{out}) - \sqrt{(\lambda_2 + J_{out})^2 - 4 \, \lambda_1 \, \epsilon \, J_{in}}}{2 \, \lambda_1 \, \epsilon}, \epsilon \right)$$

Step 3: Starting from (X_1, Y_1) draw a line parallel to X-axis to meet the Y-nullcline at (X_2, Y_2), given by eqn.(3.10)

$$(X_2, Y_2) = \left(\frac{\lambda_2}{\lambda_1 \, \epsilon}, \epsilon \right)$$

Step 4: Starting from (X_1, Y_1) draw a line parallel to Y-axis to meet the Y-nullcline at the point (X_3, Y_3) given by eqn.(3.10)

$$(X_3, Y_3) = \left(X_1, \frac{\lambda_2}{\lambda_1 \, X_1} \right).$$

Step 5: Starting from (X_2, Y_2) draw a line parallel to Y-axis to meet the X-nullcline at the point (X_4, Y_4) given by eqn.(3.9a)

$$(X_4, Y_4) = \left(X_2, \frac{(\lambda_2 + J_{out}) \, X_2 - J_{in}}{\lambda_1 \, X_2^2} \right).$$

Step 6: Starting from (X_3, Y_3) draw a line parallel to X-axis and draw another line passing through (X_4, Y_4) with slope -1 to intersect at (X_5, Y_5). These lines are given by the following equations and the solution of these equations gives the point (X_5, Y_5).

$$Y = Y_3 \qquad\qquad\qquad\qquad\text{(the line parallel to the } X \text{ - axis)}$$
$$X + Y = X_4 + Y_4 \qquad\qquad\qquad\qquad\text{(the line with slope -1)}$$

$$\Rightarrow X_5 = X_4 + Y_4 - Y_3$$

So we get, $(X_5, Y_5) = (X_4 + Y_4 - Y_3, Y_3)$

Claim: We now claim that the region we have constructed above is *trapping region* provided $X_5 > X^\star$.

We first show that it is always possible to choose ϵ such that the above condition is satisfied and then we show that the region constructed above is indeed a trapping region.

Proof that it is always possible to choose ϵ such that the above condition is satisfied

Let us evaluate X_5,

$$X_5 = X_4 + Y_4 - Y_3$$
$$= X_2 + \frac{(\lambda_2 + J_{out})\, X_2 - J_{in}}{\lambda_1\, X_2^2} - \frac{\lambda_2}{\lambda_1\, X_1}$$
$$= \frac{\lambda_2}{\lambda_1\, \epsilon} + \frac{(\lambda_2 + J_{out})}{\lambda_1}\, \frac{\lambda_1\, \epsilon}{\lambda_2} - \frac{J_{in}}{\lambda_1}\left(\frac{\lambda_1\, \epsilon}{\lambda_2}\right)^2$$
$$\qquad - \frac{\lambda_2}{\lambda_1}\, \frac{2\, \lambda_1\, \epsilon}{(\lambda_2 + J_{out}) - \sqrt{(\lambda_2 + J_{out})^2 - 4\, \lambda_1\, \epsilon\, J_{in}}}$$
$$= \frac{\lambda_2}{\lambda_1\, \epsilon} + \frac{(\lambda_2 + J_{out})\, \epsilon}{\lambda_2} - \frac{J_{in}\, \lambda_1 \epsilon^2}{\lambda_2^2} - \frac{2\, \lambda_2\, \epsilon}{(\lambda_2 + J_{out})\left[1 - \left\{1 - \frac{4\, \lambda_1\, \epsilon\, J_{in}}{(\lambda_2 + J_{out})^2}\right\}^{1/2}\right]}$$
$$= \frac{\lambda_2}{\lambda_1\, \epsilon} + \frac{(\lambda_2 + J_{out})\, \epsilon}{\lambda_2} - \frac{J_{in}\, \lambda_1 \epsilon^2}{\lambda_2^2} - \frac{2\, \lambda_2\, \epsilon}{(\lambda_2 + J_{out})\left[1 - \left\{1 - \frac{1}{2}\frac{4\, \lambda_1\, \epsilon\, J_{in}}{(\lambda_2 + J_{out})^2} + \cdots\right\}\right]}$$
$$\approx \frac{\lambda_2}{\lambda_1\, \epsilon} + \frac{(\lambda_2 + J_{out})\, \epsilon}{\lambda_2} - \frac{J_{in}\, \lambda_1 \epsilon^2}{\lambda_2^2} - \frac{2\, \lambda_2\, \epsilon}{\frac{2\, \lambda_1\, \epsilon\, J_{in}}{(\lambda_2 + J_{out})}} \qquad \text{(assuming } \epsilon \text{ to be very small)}$$
$$\approx \frac{\lambda_2}{\lambda_1\, \epsilon} + \frac{(\lambda_2 + J_{out})\, \epsilon}{\lambda_2} - \frac{J_{in}\, \lambda_1 \epsilon^2}{\lambda_2^2} - \frac{\lambda_2\, (\lambda_2 + J_{out})}{\lambda_1\, J_{in}}$$

Since we have assumed ϵ to be very small, the first term in the above expression dominates. In fact, ϵ can be chosen such that X_5 is larger than any number we wish. In particular ϵ can be chosen to be so that X_5 is larger than $X^\star$.

Proof that the region constructed by the above algorithm is a trapping region

The region constructed by the above algorithm has five sides. It is trivial to see that the sides parallel to X-axis and Y-axis have desired direction of flow of trajectories just by looking at the fig.(3.1) and the sign of $\dot{X}$ and $\dot{Y}$ in various regions. The only non-trivial part is the side with slope -1.

Let us look at the expression for the slope of trajectories

$$
\begin{aligned}
\frac{dY}{dX} &= \frac{\dot{Y}}{\dot{X}} \\
&= \frac{-\lambda_1 \, X^2 \, Y + \lambda_2 \, X}{J_{in} + \lambda_1 \, X^2 \, Y - \lambda_2 \, X - J_{out} \, X} \\
&= \frac{J_{in} - J_{out} \, X - (J_{in} + \lambda_1 \, X^2 \, Y - \lambda_2 \, X - J_{out} \, X)}{J_{in} + \lambda_1 \, X^2 \, Y - \lambda_2 \, X - J_{out} \, X} \\
&= \frac{J_{out} \, [(J_{in}/J_{out}) - X]}{J_{in} + \lambda_1 \, X^2 \, Y - \lambda_2 \, X - J_{out} \, X} - 1 \\
&= \frac{J_{out} \, (X^\star - X)}{J_{in} + \lambda_1 \, X^2 \, Y - \lambda_2 \, X - J_{out} \, X} - 1
\end{aligned}
$$

In the region where we have drawn the line with slope -1, $\dot{X} > 0$ i.e. the denominator of the first term above is positive. Now the first term in the above expression is negative if $X > X^\star$ as $J_{out} > 0$. Thus for $X > X^\star$, $dY/dX < -1$ and as shown by the arrow in the figure the trajectories come inside through the line with slope -1. Hence, the region constructed by us is indeed trapping region provided $X_5 > X^\star$.

We have shown that the unstable fixed point would necessarily mean the existence of limit cycle. We can solve eqn. (3.2) numerically for given value of the parameters. Numerical solutions for two set of parameters are shown in figs. (3.4 and 3.5), showing stable spiral and unstable spiral giving rise to a limit cycle. For the parameter set considered, we have

$$
\begin{aligned}
\lambda_{2c} &= J_{out} + \lambda_1 \left(\frac{J_{in}}{J_{out}} \right)^2 \\
&= 2 + 1 \left(\frac{2}{2} \right)^2 \\
&= 3
\end{aligned}
$$
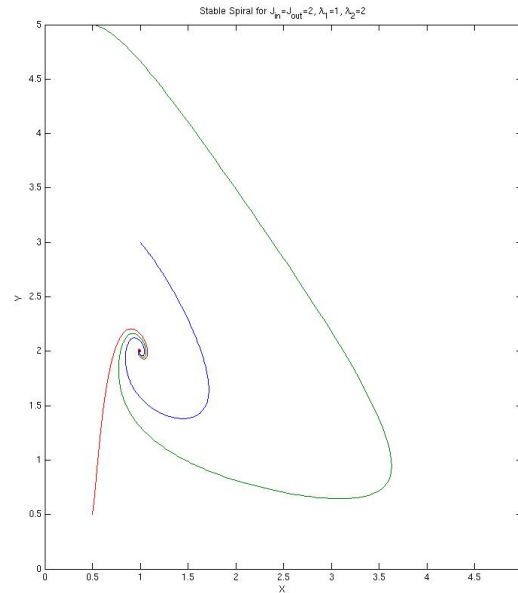
Figure 3.2: Stable spiral for parameter set: $J_{in} = J_{out} = 2$, $\lambda_1 = 1$, $\lambda_2 = 2$.
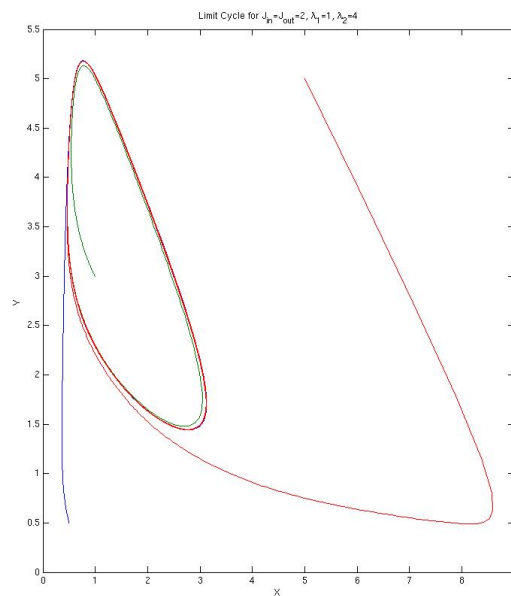
Figure 3.3: Limit cycle for parameter set: $J_{in} = J_{out} = 2$, $\lambda_1 = 1$, $\lambda_2 = 4$.

3.2 Brusselator as a Reaction-Diffusion System

Typical way of studying spatially extended reaction-diffusion system is to add diffusion terms $(D\nabla^2)$ to the rate equation. Let us also analyse spatially extended brusselator system by adding diffusion terms to the eqn. (3.2) as following:

$$\frac{\partial X}{\partial t} = J_{in} + \lambda_1 \ X^2 \ Y - \lambda_2 \ X - J_{out} \ X + D_X \nabla^2 X \tag{3.11a}$$

$$\frac{\partial Y}{\partial t} = -\lambda_1 \ X^2 \ Y + \lambda_2 \ X + D_Y \nabla^2 Y \tag{3.11b}$$

The uniform steady state solution to above equations is the same as that for the zero dimensional case, i.e.

$$X^\star = \frac{J_{in}}{J_{out}} \text{ and } Y^\star = \frac{\lambda_2}{\lambda_1} \ \frac{J_{out}}{J_{in}}$$

We will say that this solution lies on the *thermodynamic branch.*

Since we are considering spatially extended system, we need to specify appropriate boundary conditions (b.c.). We consider the *periodic boundary condition.* In 1-dim, periodic b.c. is given by

$$X(l) = X(0) \text{ and } Y(l) = Y(0) \tag{3.12}$$

where l is the length of the 1-dim system. Two different boundary conditions namely Dirichlet's b.c. and No-flux b.c. have been considered in [14].

Linear Stability Analysis

We can linearize the system by assuming small fluctuations near the thermodynamic branch, i.e.

$$X = X^\star + x \text{ and } Y = Y^\star + y$$

Substituting in eqns (3.11a and 3.11b) and neglecting higher order terms in x and y, just as we did for eqn. (3.2), we get eqns similar to eqn (3.4)

$$\frac{\partial}{\partial t} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} 2 \ \lambda_1 \ X^\star \ Y^\star - \lambda_2 - J_{out} + D_X \nabla^2 & \lambda_1 \ X^{\star \ 2} \\ -2 \ \lambda_1 \ X^\star \ Y^\star + \lambda_2 & -\lambda_1 \ X^{\star \ 2} + D_Y \nabla^2 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} \tag{3.13}$$

$$= \mathcal{L} \ \begin{bmatrix} x \\ y \end{bmatrix}$$

where

$$\mathcal{L} = \begin{bmatrix} 2 \ \lambda_1 \ X^\star \ Y^\star - \lambda_2 - J_{out} + D_X \nabla^2 & \lambda_1 \ X^{\star \ 2} \\ -2 \ \lambda_1 \ X^\star \ Y^\star + \lambda_2 & -\lambda_1 \ X^{\star \ 2} + D_Y \nabla^2 \end{bmatrix}$$

$$= \begin{bmatrix} \lambda_2 - J_{out} + D_X \nabla^2 & \lambda_1 \ (J_{in}/J_{out})^2 \\ -\lambda_2 & -\lambda_1 \ (J_{in}/J_{out})^2 + D_Y \nabla^2 \end{bmatrix} \tag{3.14}$$

where eqn (3.5) has been used to simplify the last step.

The boundary conditions (eqn 3.12) in terms of x and y are

$$x(l) = x(0) \text{ and } y(l) = y(0) \tag{3.15}$$

The operator $\mathcal{L}$ in eqn (3.14) is called a *parabolic operator*. The eigenvalues and the eigenvectors of this operator determine the asymptotic behaviour of eqn (3.13).

Let the eigenequation for $\mathcal{L}$ be

$$\mathcal{L} \begin{bmatrix} u_m \\ v_m \end{bmatrix} = \omega_m \begin{bmatrix} u_m \\ v_m \end{bmatrix}, \tag{3.16}$$

then the general solution to eqn (3.13) is given by

$$\begin{bmatrix} x \\ y \end{bmatrix} = \sum_m a_m \, e^{\omega_m t} \begin{bmatrix} u_m \\ v_m \end{bmatrix}. \tag{3.17}$$

In 1-dim, we have

$$\nabla^2 = \frac{d^2}{dr^2}, \qquad 0 \le r \le l.$$

The eigenfunctions of ∇^2 with the given b.c.'s are trigonometric functions. Hence the eigenfunctions of $\mathcal{L}$ are

$$\begin{bmatrix} u_m \\ v_m \end{bmatrix} = \begin{bmatrix} C_1 \\ C_2 \end{bmatrix} \sin(m \, \pi \, r / l + \phi), \qquad m = 1, 2, 3, \ldots. \tag{3.18}$$

The eigenequation for $\mathcal{L}$ becomes

$$\begin{bmatrix} \lambda_2 - J_{out} - D_X \, m^2\pi^2/l^2 & \lambda_1 \, (J_{in}/J_{out})^2 \\ -\lambda_2 & -\lambda_1 \, (J_{in}/J_{out})^2 - D_Y \, m^2\pi^2/l^2 \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \end{bmatrix} = \omega_m \begin{bmatrix} C_1 \\ C_2 \end{bmatrix}$$

$$\Rightarrow \begin{bmatrix} \alpha_m & A^2 \\ -B & -\beta_m \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \end{bmatrix} = \omega_m \begin{bmatrix} C_1 \\ C_2 \end{bmatrix} \tag{3.19}$$

where

$$A^2 = \lambda_1 \, (J_{in}/J_{out})^2$$
$$B = \lambda_2$$
$$\alpha_m = \lambda_2 - J_{out} - D_X \, m^2\pi^2/l^2$$
$$\beta_m = \lambda_1 \, (J_{in}/J_{out})^2 + D_Y \, m^2\pi^2/l^2 \tag{3.20}$$

The eigenvalues (ω_m) are given by

$$\begin{vmatrix} \alpha_m - \omega_m & A^2 \\ -B & -\beta_m - \omega_m \end{vmatrix} = 0$$

$$\Rightarrow \omega_m^2 - (\alpha_m - \beta_m)\omega_m - \alpha_m \, \beta_m + A^2 \, B = 0 \tag{3.21a}$$

$$\Rightarrow \omega_m = \frac{1}{2} \left[\alpha_m - \beta_m \pm \sqrt{(\alpha_m + \beta_m)^2 - 4 \, A^2 \, B} \right] \tag{3.21b}$$

Case I: *Real Eigenvalues*
Eigenvalues are real if

$$(\alpha_m + \beta_m)^2 - 4\ A^2\ B \geq 0$$

$$\Rightarrow \lambda_2^2 - 2\ \lambda_2 \left[\lambda_1\ \left(\frac{J_{in}}{J_{out}}\right)^2 + J_{out} + (D_X - D_Y)\frac{m^2\pi^2}{l^2} \right]$$

$$+ \left[\lambda_1\ \left(\frac{J_{in}}{J_{out}}\right)^2 - J_{out} - (D_X - D_Y)\frac{m^2\pi^2}{l^2} \right]^2 \geq 0 \qquad (3.22)$$

The zeroes of the expression on L.H.S. of eqn (3.22) are

$$\lambda_2 = \frac{1}{2} \left\{ 2\ \left[\lambda_1\ \left(\frac{J_{in}}{J_{out}}\right)^2 + J_{out} + (D_X - D_Y)\frac{m^2\pi^2}{l^2} \right] \right.$$

$$\pm \left(4\ \left[\lambda_1\ \left(\frac{J_{in}}{J_{out}}\right)^2 + J_{out} + (D_X - D_Y)\frac{m^2\pi^2}{l^2} \right]^2 \right.$$

$$\left. \left. -4\ \left[\lambda_1\ \left(\frac{J_{in}}{J_{out}}\right)^2 - J_{out} - (D_X - D_Y)\frac{m^2\pi^2}{l^2} \right]^2 \right)^{\frac{1}{2}} \right\}$$

$$= \lambda_1\ \left(\frac{J_{in}}{J_{out}}\right)^2 + J_{out} + (D_X - D_Y)\frac{m^2\pi^2}{l^2} \pm \sqrt{2\ \lambda_1\ \left(\frac{J_{in}}{J_{out}}\right)^2 2\left[J_{out} + (D_X - D_Y)\frac{m^2\pi^2}{l^2} \right]}$$

Thus eqn (3.22) becomes

$$\lambda_2 \leq \lambda_1\ \left(\frac{J_{in}}{J_{out}}\right)^2 + J_{out} + (D_X - D_Y)\frac{m^2\pi^2}{l^2}$$

$$- 2\sqrt{\lambda_1\ \left(\frac{J_{in}}{J_{out}}\right)^2 \left[J_{out} + (D_X - D_Y)\frac{m^2\pi^2}{l^2} \right]} \equiv \lambda_{2c}^{(1)}$$

$$\text{or } \lambda_2 \geq \lambda_1\ \left(\frac{J_{in}}{J_{out}}\right)^2 + J_{out} + (D_X - D_Y)\frac{m^2\pi^2}{l^2}$$

$$+ 2\sqrt{\lambda_1\ \left(\frac{J_{in}}{J_{out}}\right)^2 \left[J_{out} + (D_X - D_Y)\frac{m^2\pi^2}{l^2} \right]} \equiv \lambda_{2c}^{(1')} \qquad (3.23)$$

To satisfy the above inequality, we must have

$$J_{out} + (D_X - D_Y)\frac{m^2\pi^2}{l^2} \geq 0$$

$$\Rightarrow D_Y - D_X \leq J_{out}\,\frac{l^2}{m^2\pi^2} \tag{3.24}$$

If eqn (3.24) is not satisfied then eqn (3.22) holds for all values of λ_2. Thus the eigenvalues are necessarily real if

$$D_Y - D_X > J_{out}\,\frac{l^2}{\pi^2}.$$

If the eigenvalues are real, then both the eigenvalues are negative only if the trace of $\mathcal{L}$ is negative and the determinant of $\mathcal{L}$ is positive, i.e.

$$\alpha_m - \beta_m < 0 \text{ and } -\alpha_m\,\beta_m + A^2\,B > 0$$

Trace condition:

$$\alpha_m - \beta_m < 0$$

$$\Rightarrow \lambda_2 < J_{out} + \lambda_1\,\left(\frac{J_{in}}{J_{out}}\right)^2 + (D_X + D_Y)\,\frac{m^2\pi^2}{l^2} \equiv \lambda_{2c}^{(2)} \tag{3.25}$$

Determinant condition:

$$-\alpha_m\,\beta_m + A^2\,B > 0$$

$$\Rightarrow \lambda_2 < J_{out} + \frac{D_X}{D_Y}\,\lambda_1\,\left(\frac{J_{in}}{J_{out}}\right)^2 + D_X\,\frac{m^2\pi^2}{l^2} + J_{out}\,\lambda_1\,\left(\frac{J_{in}}{J_{out}}\right)^2\,\frac{l^2}{D_Y m^2\pi^2} \equiv \lambda_{2c}^{(3)} \tag{3.26}$$

Case II: *Complex Eigenvalues*
We have complex eigenvalues if eqn (3.24) is satisfied and eqn (3.23) is not. The real part of both the complex eigenvalues is negative if the trace of $\mathcal{L}$ is negative, i.e. eqn (3.25) is satisfied.

We summarise the results of linear stability analysis in Table 3.1.

Table 3.1: Summary of linear stability analysis. (T=Satisfied, F=Unsatisfied)

Eqn (3.24)	Eqn (3.23)	Eqn (3.25)	Eqn (3.26)	Nature of eigenvalues
T	T	T	T	Real and both negative
T	T	F	—	Real and at least one positive
T	T	—	F	Real and at least one positive
T	F	T	—	Complex conjugate with real part negative
T	F	F	—	Complex conjugate with real part positive
F	—	T	T	Real and both negative
F	—	F	—	Real and at least one positive
F	—	—	F	Real and at least one positive

- The eigenmodes for which the real part of both the eigenvalues are negative will decay in time.

- The eigenmodes with real part of both eigenvalues positive will give rise to *spatio-temporal pattern*.

- The case corresponding to a positive and a negative eigenvalue will also have some asymptotic behaviour and not give any spatio-temporal pattern.
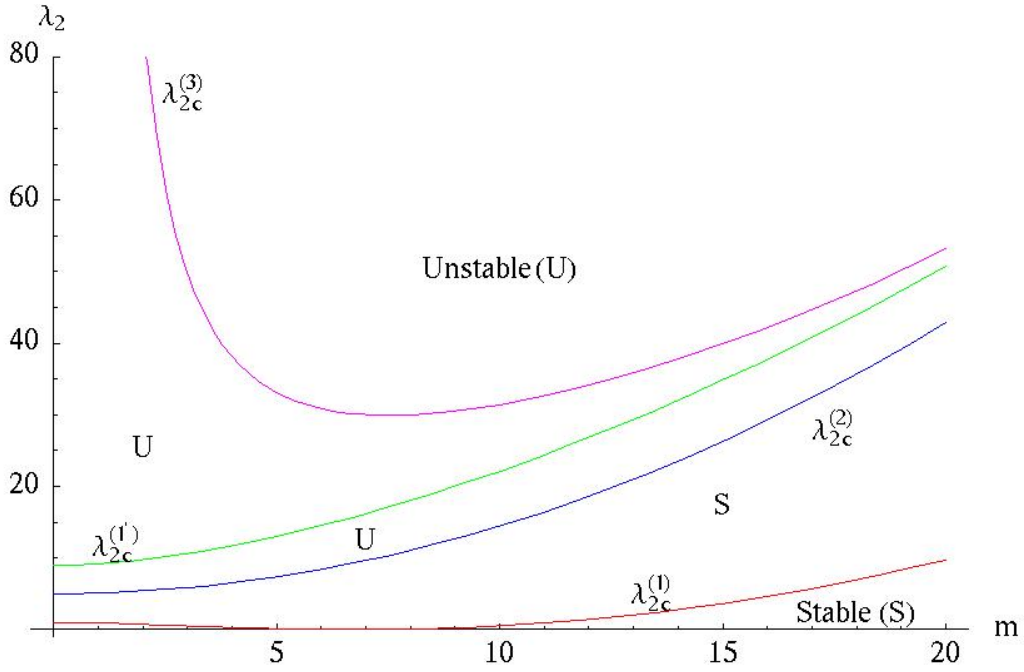
Figure 3.4: Plots with parameters $A = 2$, $l = 1$, $D_X = 8 \times 10^{-3}$ and $D_Y = 1.6 \times 10^{-3}$.
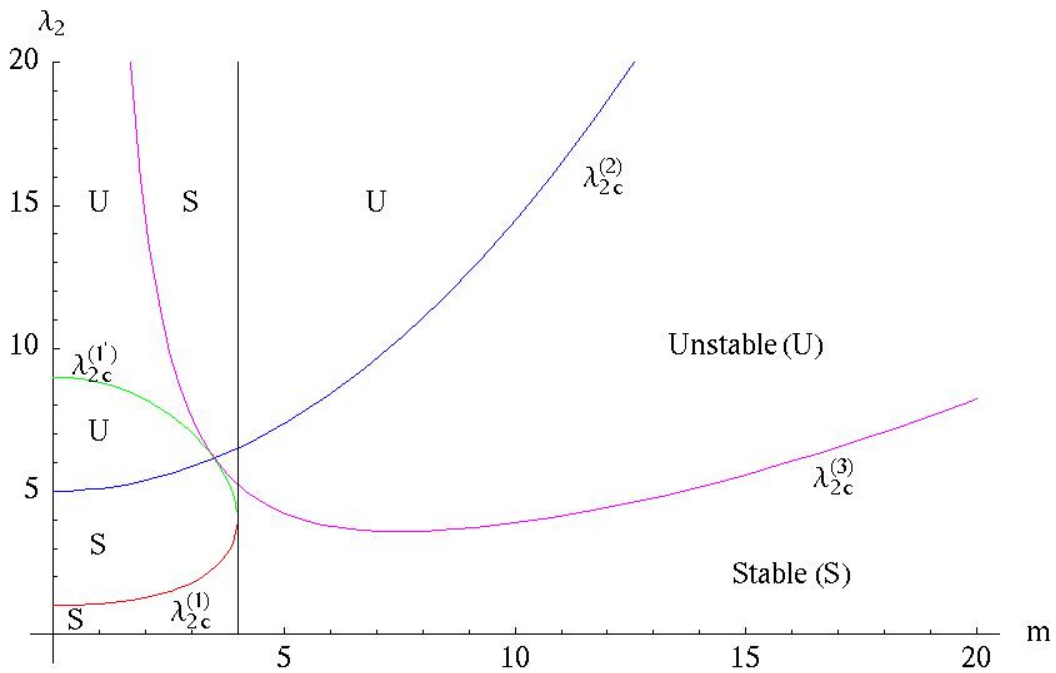
Figure 3.5: Plots with parameters $A = 2$, $l = 1$, $D_X = 1.6 \times 10^{-3}$ and $D_Y = 8 \times 10^{-3}$.

3.2.1 Turing Instability

Equations (3.23), (3.24), (3.24) and (3.25) depend on the diffusion constants D_X and D_Y. A mode that is stable in absence of diffusion may become unstable in presence of it. Instabilities induced by the presence of diffusion are called *Turing Instabilities*.

3.3 Critique of the mean-field approximation

- The mean-field approximation is usually valid for well mixed systems. But, in general we are interested in system which is not homogeneous and has spatial dependence.

- The chemical reactions are stochastic in nature, hence their dynamics should be handled properly including the effect of stochasticity. This is possible by treating the master equation for the chemical system.

Chapter 4

Brusselator - A Master Equation Approach

Master equation is the time evolution equation for the probability of the microstates being occupied. Generically, it can be written as

$$\frac{dP(\alpha;t)}{dt} = \sum_{\beta} R_{\beta\to\alpha} \; P(\beta;t) - \sum_{\beta} R_{\alpha\to\beta} \; P(\alpha;t),$$

where α, β denote microstates and $R_{\alpha\to\beta}$ denote the rate of transition from the microstate α to the microstate β.

- The first term above is called the *gain term* whereas the second term is called the *loss term*.

- The master equation is not one equation, rather it is a set of equations one for each microstate.

4.1   Why Master Equation?

- All non-equilibrium processes are stochastic, hence a correct description of them would be in terms the probabilities of their microstates.

- Chemical processes are inherently stochastic and master equation is a natural description for them. See [13] for an extensive summary of stochastic approach to chemical kinetics.

- The rate equations are deterministic and do not take into account the fluctuations and correlations, whereas master equation does. For most chemical reaction these are not important and one gets the deterministic equation from the stochastic formulation (see [13]). However, the fluctuations and correlations become important near chemical instabilities and the rich behaviour is captured by the stochastic formulation and the master equation.

- Traditionally the effect of diffusion is accounted for by including a $D\,\nabla^2$ term in the rate equation. One would like to derive a more concrete way of including the effect of diffusion. This is typically done by treating the diffusion process as simple hopping on a lattice model. One gets the correct form of the diffusion term by taking the continuum limit of the lattice model afterwards. This issue is quite important because there have been deviations from the traditional method in the past.

4.2   Master Equation for some simple processes

4.2.1   Death: $A \rightarrow \phi$

The simplest stochastic process one can think of is that of the radioactive decay, where the atoms of radioactive species, say A, decay spontaneously with a rate λ. The microstate is simply the number of radioactive species left, n. In a small time dt, the probability of one atom decaying is $\lambda\,dt$. The probability of more than one atom decaying is $O(\lambda^2)$. Hence the elementary stochastic step is that of one particle decaying.

If there are n atoms, the probability of one atom decaying in time dt is $n\,\lambda\,dt$. The master equation for the process becomes

$$\frac{dP(n;t)}{dt} = (n+1)\,\lambda\,P(n+1;t) - n\,\lambda\,P(n;t).$$

The first term in the above equation corresponds to one decay taking a state with $(n+1)$ atoms to n atoms and hence is a gain term. Whereas the second term takes a state with n atoms to one with $(n-1)$ atoms and hence is a loss term.

This example also illustrates that the phenomenology involved in writing the master equation is at a more fundamental level directly at the level of the microscopic description of the process.

4.2.2   Coagulation Process: $A + A \rightarrow A$

The microstate is again the number of A's left. If λ is the rate associated with the process, the master equation is given by

$$\frac{dP(n;t)}{dt} = \binom{n+1}{2}\,\lambda\,P(n+1;t) - \binom{n}{2}\,\lambda\,P(n;t),$$

where $\binom{n}{2}$ is the no. of ways of choosing 2 objects out of n objects. Here it means the total no. of ways in which an elementary process can occur if there are n A's. Similar combinatorial factors will come for more complicated processes.

4.2.3   Creation of a particle: $\phi \rightarrow A$

If λ is the rate of creation then the master equation is

$$\frac{dP(n;t)}{dt} = \lambda\,P(n-1;t) - \lambda\,P(n;t).$$

Note that there is no combinatorial factor involved. This signifies the fact that the process of creation of particle is independent of the number of particles already present.

Other terms in the expression are as for the above equations and we shall no more explicitly mention them unless needed.

4.2.4   Process $X \to Y$

Let us now consider the simplest case involving two different species. The process involves one species getting converted to another. The microstate is given by an ordered pair of numbers, (n_X, n_Y) where n_X and n_Y are no. of X and Y particles present. If the rate of conversion is λ then the master equation is given by

$$\frac{dP(n_X, n_Y; t)}{dt} = (n_X + 1) \; \lambda \; P(n_X + 1, n_Y - 1; t) - n_X \; \lambda \; P(n_X, n_Y; t).$$

4.2.5   Process $2X + Y \to 3X$

We choose this process because it appears as one of the elementary processes in the brusselator model. Like above the microstate is given by (n_X, n_Y) and if the rate is λ the master equation is

$$\frac{dP(n_X, n_Y; t)}{dt} = \binom{n_X - 1}{2} \; (n_Y + 1) \; \lambda \; P(n_X - 1, n_Y + 1; t) - \binom{n_X}{2} \; n_Y \; \lambda \; P(n_X, n_Y; t).$$

The combinatorial factor is the number of ways of choosing 2 X and a Y.

4.2.6   Hopping between two sites

This stochastic process is very important as it is the elementary model for diffusion. The microstate is given by (n_1, n_2) where 1 and 2 label the two sites. If λ is the rate of hopping from one site to another and it is same for both sites, then the master equation is

$$\frac{dP(n_1, n_2; t)}{dt} = (n_1 + 1) \; \lambda \; P(n_1 + 1, n_2 - 1; t) + (n_2 + 1) \; \lambda \; P(n_1 - 1, n_2 + 1; t)$$
$$- n_1 \; \lambda \; P(n_1, n_2; t) - n_2 \; \lambda \; P(n_1, n_2; t).$$

where first term is the gain term due to hopping from site 1 to site 2, second term is the gain term due to hopping from site 2 to site 1, third term is the loss term due to hopping from site 1 to site 2 and fourth term is the loss term due to hopping from site 2 to site 1.

4.3   Master Equation for Brusselator

To define the brusselator system stochastically, we begin to define the model on a d-dimensional lattice. On each lattice site we have a brusselator system given by eqns. (3.1),

(??), (??) and (??). Apart from these reactions, the particles can diffuse on the lattice. The process of diffusion in our model is a *random walk* on the lattice.

Let (X_i, Y_i) denote the no. of X and Y species at the i-th site, and $(\{X\}, \{Y\})$ denote the full system i.e. the no. of X and Y species on all the lattice points. Then, at i-th site, we have the following elementary processes going on

$$\phi \xrightarrow{J_{in}} X_i \tag{4.1a}$$

$$2X_i + Y_i \xrightarrow{\lambda_1} 3X_i \tag{4.1b}$$

$$X_i \xrightarrow{\lambda_2} Y_i \tag{4.1c}$$

$$X_i \xrightarrow{J_{out}} \phi \tag{4.1d}$$

$$X_j \xrightarrow{D_X} X_i \tag{4.1e}$$

$$X_i \xrightarrow{D_X} X_j \tag{4.1f}$$

$$Y_j \xrightarrow{D_Y} Y_i \tag{4.1g}$$

$$Y_i \xrightarrow{D_Y} Y_j \tag{4.1h}$$
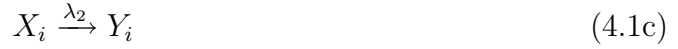
where j is one of the nearest neighbours of i.
The master equation for the process will be

$$
\begin{aligned}
\frac{dP(\{X\}, \{Y\})}{dt} =& J_{in} \sum_i [P(X_i - 1, Y_i) - P(X_i, Y_i)] \\
&+ \lambda_1 \sum_i \left[\binom{X_i - 1}{2} (Y_i + 1) P(X_i - 1, Y_i + 1) - \binom{X_i}{2} Y_i \, P(X_i, Y_i) \right] \\
&+ \lambda_2 \sum_i [(X_i + 1) P(X_i + 1, Y_i - 1) - X_i \, P(X_i, Y_i)] \\
&+ J_{out} \sum_i [(X_i + 1) P(X_i + 1, Y_i) - X_i \, P(X_i, Y_i)] \\
&+ D_X \sum_{\langle i,j \rangle} [(X_i + 1) P(X_i + 1, X_j - 1, Y_i, Y_j) \\
&\qquad\qquad + (X_j + 1) P(X_i - 1, X_j + 1, Y_i, Y_j) \\
&\qquad\qquad\quad - X_i \, P(X_i, X_j, Y_i, Y_j) - X_j \, P(X_i, X_j, Y_i, Y_j)] \\
\\
&+ D_Y \sum_{\langle i,j \rangle} [(Y_i + 1) P(X_i, X_j, Y_i + 1, Y_j - 1) \\
&\qquad\qquad + (Y_j + 1) P(X_i, X_j, Y_i - 1, Y_j + 1) \\
&\qquad\qquad\quad - Y_i \, P(X_i, X_j, Y_i, Y_j) - Y_j \, P(X_i, X_j, Y_i, Y_j)] \tag{4.2}
\end{aligned}
$$

where in each bracket the first term is the gain term for i-th site and the second term is the loss term for it. In the diffusion terms, the first two terms correspond to gain terms and the

last two terms correspond to the loss terms. $\langle i, j \rangle$ stands for the nearest neighbour pairs. For the sake of notational convenience, the argument of P on R.H.S. consists of the numbers which change during an elementary step.

4.4 Methods of Analysis

The master equation contains the full information about a stochastic process. Most of the times it is not solvable and many times it is intractable even numerically. We shall employ two schemes to analyse this master equation.

1. *Second quantization representation*: This method was originally proposed by Doi and also developed Zeldovich (refer to [6, 7, 18]). It was further developed by a no. of people but we shall closely follow the scheme and notation of John Cardy (refer to [5, 4, 3, 16]). In this method an effective hamiltonian is derived, whose equation of motion is the master equation. Then the standard schemes of second quantisation including renormalization group is used.

2. *Numerical simulation*: We will use Monte-Carlo simulation to study the master equation. We will use a particular algorithm proposed by Daniel T. Gillespie (refer to [10], [11]).

Chapter 5

Second Quantization Method

In this method we introduce creation and annihilation operators corresponding to the classical particles involved. Any elementary step of a stochastic process consists of change in no. of some particles at various sites. Then an effective hamiltonian is found whose equation of motion (like *Schrödinger equation*) is the master equation.

The general scheme of the method goes as following:

- The microstates for any stochastic process on a lattice is given by the occupation numbers $\{n\} \equiv \{n_1,\ n_2, \ldots\}$ of each site. Let $P(\{n\},\ t)$ denote the probability of the microstates at time t.

- Introduce annihilation and creation operators $\{a_i,\ a_i^\dagger\}$ for each lattice site, where i is the lattice site index. Let these operators follow the commutation relations given by

$$\left[a_i,\ a_j^\dagger\right] = \delta_{ij}. \tag{5.1}$$

These commutation relations can be realized by the following formal relations

$$a_i = \frac{\partial}{\partial a_i^\dagger} \qquad \text{and} \qquad a_i^\dagger = -\frac{\partial}{\partial a_i} \tag{5.2}$$

Note the negative sign in the second relation above.

- Define the vaccum state $(|0\rangle)$ by

$$a_i \,|0\rangle = 0 \qquad \forall\ i \tag{5.3}$$

- The microstate $\{n_1,\ n_2, \ldots\}$ is given by the state

$$|n_1,\ n_2, \ldots\rangle \equiv a_1^{\dagger\ n_1}\ a_2^{\dagger\ n_2}\ \ldots\ |0\rangle \tag{5.4}$$

- Let us denote a general state $|\psi(t)\rangle$ as

$$\begin{aligned}
|\psi(t)\rangle &= \sum_{n_1,\ n_2,\ldots} P(n_1,\ n_2, \ldots; t)\ |n_1,\ n_2, \ldots\rangle \\
&= \sum_{n_1,\ n_2,\ldots} P(n_1,\ n_2, \ldots; t)\ a_1^{\dagger\ n_1}\ a_2^{\dagger\ n_2} \ldots\ |0\rangle
\end{aligned} \tag{5.5}$$

- Then the master equation is completely equivalent to the Schrödinger-like equation

$$\frac{d}{dt}|\psi(t)\rangle = -H|\psi(t)\rangle \tag{5.6a}$$

$$\Rightarrow |\psi(t)\rangle = e^{-Ht}|\psi(0)\rangle \tag{5.6b}$$

where H is an operator given in terms of the a's and $a^\dagger$'s. We shall call H as the effective Hamiltonian for the given master equation. Here eqn. (5.6b) is the formal solution to the eqn. (5.6a).

We introduce the idea of this method by considering a no. of elementary steps. The full brusselator system will consist of these steps and we will combine the result obtained for the individual systems to analyse the full system.

5.1 Effective Hamiltonian for the elementary steps

5.1.1 Simple Hopping

Consider just two sites (1, 2) and hopping $1 \to 2$ at rate D. Then, the master equation for this process is

$$\frac{dP(n_1, n_2; t)}{dt} = D\ (n_1 + 1)\ P(n_1 + 1, n_2 - 1; t) - D\ n_1\ P(n_1, n_2; t) \tag{5.7}$$

Let us define creation and annihilation operators as following

$$\begin{aligned}
a_1^\dagger &= \text{Creation operator for site 1} \\
a_1 &= \text{Annihilation operator for site 1} \\
a_2^\dagger &= \text{Creation operator for site 2} \\
a_2 &= \text{Annihilation operator for site 2}
\end{aligned} \tag{5.8}$$

The vaccum ($|0\rangle$) is the state with no particles in either site 1 or 2. The state with n_1 particles at site 1 and n_2 particles at site 2, denoted as $|n_1,\ n_2\rangle$, is given by eqn. (5.4)

$$|n_1,\ n_2\rangle \equiv a_1^{\dagger\ n_1}\ a_2^{\dagger\ n_2}\ |0\rangle \tag{5.9}$$

And a general state $|\psi(t)\rangle$ is given by eqn. (5.5) as

$$\begin{aligned}
|\psi(t)\rangle &= \sum_{n_1,\ n_2} P(n_1,\ n_2; t)\ |n_1,\ n_2\rangle \\
&= \sum_{n_1,\ n_2} P(n_1,\ n_2; t)\ a_1^{\dagger\ n_1}\ a_2^{\dagger\ n_2}\ |0\rangle
\end{aligned} \tag{5.10}$$

Then,

$$
\begin{aligned}
\frac{d|\psi(t)\rangle}{dt} &= \sum_{n_1,\,n_2} \frac{dP(n_1,\,n_2;t)}{dt}\, a_1^{\dagger\ n_1}\, a_2^{\dagger\ n_2}\, |0\rangle \\
&= \sum_{n_1,\,n_2} \left[D\,(n_1+1)\,P(n_1+1,n_2-1;t) - D\,n_1\,P(n_1,n_2;t) \right] a_1^{\dagger\ n_1}\, a_2^{\dagger\ n_2}\, |0\rangle
\end{aligned}
$$

[using eqn. (5.7)]

$$
\begin{aligned}
&= D \sum_{n_1,\,n_2} \left[P(n_1+1,n_2-1;t)\,\left\{(n_1+1)\,a_1^{\dagger\ n_1}\right\}\, a_2^{\dagger\ n_2} \right. \\
&\qquad\qquad\qquad\qquad \left. - P(n_1,n_2;t)\,\left\{n_1\, a_1^{\dagger\ n_1}\right\}\, a_2^{\dagger\ n_2} \right] |0\rangle \\
&= D \sum_{n_1,\,n_2} \left[P(n_1+1,n_2-1;t)\,\left\{\frac{\partial}{\partial a_1^{\dagger}}\, a_1^{\dagger\ (n_1+1)}\right\}\, a_2^{\dagger\ n_2} \right. \\
&\qquad\qquad\qquad\qquad \left. - P(n_1,n_2;t)\, a_1^{\dagger}\,\left\{\frac{\partial}{\partial a_1^{\dagger}}\, a_1^{\dagger\ n_1}\right\}\, a_2^{\dagger\ n_2} \right] |0\rangle \\
&= D \sum_{n_1,\,n_2} \left[P(n_1+1,n_2-1;t)\, a_1\, a_1^{\dagger\ (n_1+1)}\, a_2^{\dagger\ n_2} \right. \\
&\qquad\qquad\qquad\qquad \left. - P(n_1,n_2;t)\, a_1^{\dagger}\, a_1\, a_1^{\dagger\ n_1}\, a_2^{\dagger\ n_2} \right] |0\rangle
\end{aligned}
$$

[using eqn. (5.2)]

$$
\begin{aligned}
&= D \left[a_1\, a_2^{\dagger} \sum_{n_1,\,n_2} P(n_1+1,n_2-1;t)\, a_1^{\dagger\ (n_1+1)}\, a_2^{\dagger\ (n_2-1)}\, |0\rangle \right. \\
&\qquad\qquad\qquad \left. - a_1^{\dagger}\, a_1 \sum_{n_1,\,n_2} P(n_1,n_2;t)\, a_1^{\dagger\ n_1}\, a_2^{\dagger\ n_2}\, |0\rangle \right]
\end{aligned}
$$

$$
= D\,\left(a_1\, a_2^{\dagger} - a_1^{\dagger}\, a_1\right) |\psi(t)\rangle \tag{5.11}
$$

On comparing with eqn. (5.6a), we get the effective Hamiltonian as

$$
H_{1\to 2} = -D\,\left(a_1\, a_2^{\dagger} - a_1^{\dagger}\, a_1\right) \tag{5.12}
$$

Similarly for the hopping $2 \to 1$ with the same constant D, we will get

$$
H_{2\to 1} = -D\,\left(a_2\, a_1^{\dagger} - a_2^{\dagger}\, a_2\right) \tag{5.13}
$$

The master equation for the two-way hopping $1 \leftrightarrow 2$ will be

$$
\begin{aligned}
\frac{dP(n_1,n_2;t)}{dt} =\;& D\,(n_1+1)\,P(n_1+1,n_2-1;t) - D\,n_1\,P(n_1,n_2;t) \\
& + D\,(n_2+1)\,P(n_1-1,n_2+1;t) - D\,n_2\,P(n_1,n_2;t)
\end{aligned} \tag{5.14}
$$

And the effective Hamiltonian will be given by the sum of eqns. (5.12) and (5.13)

$$
\begin{aligned}
H_{1\leftrightarrow 2} &= H_{1\rightarrow 2} + H_{2\rightarrow 1} \\
&= -D \left(a_1 \, a_2^\dagger - a_1^\dagger \, a_1 \right) - D \left(a_2 \, a_1^\dagger - a_2^\dagger \, a_2 \right) \\
&= -D \left(a_1 \, a_2^\dagger - a_1^\dagger \, a_1 + a_2 \, a_1^\dagger - a_2^\dagger \, a_2 \right) \\
&= -D \left[\left(a_2^\dagger - a_1^\dagger \right) a_1 - \left(a_2^\dagger - a_1^\dagger \right) a_2 \right] \\
&= -D \left(a_2^\dagger - a_1^\dagger \right) (a_1 - a_2) \\
&= D \left(a_2^\dagger - a_1^\dagger \right) (a_2 - a_1)
\end{aligned}
\tag{5.15}
$$

Generalising the above result for a lattice, we get the Hamiltonian

$$
\boxed{H = D \sum_{\langle i,\, j \rangle} \left(a_i^\dagger - a_j^\dagger \right) (a_i - a_j)}
\tag{5.16}
$$

where $\langle i,\, j \rangle$ represents all pairs $i,\, j$ between which hopping is allowed. The process described by this Hamiltonian is the microscopic version of *diffusion*. This will be our model for diffusion on a lattice.

5.1.2   Creation of a particle ($\phi \rightarrow A$)

Let us consider a stochastic process such that the end result of an elementary step is an increase in the no. of particle A by one. If we are interested in particle A alone, then the elementary step would be creation of the particle.

If J_{in} is the rate of creation and n denotes the no. of particles, then the master equation for the process is given by

$$
\frac{dP(n;t)}{dt} = J_{in} \, P(n-1;t) - J_{in} \, P(n;t).
\tag{5.17}
$$

Let a, $a^\dagger$ and $|0\rangle$ be respectively the annihilation operator, creation operator and the vaccum for our system. Let the general state be given by

$$
\begin{aligned}
|\psi(t)\rangle &= \sum_n P(n;t) \, |n\rangle \\
&= \sum_n P(n;t) \, a^{\dagger \, n} \, |0\rangle
\end{aligned}
\tag{5.18}
$$

Then,

$$
\begin{aligned}
\frac{d|\psi(t)\rangle}{dt} &= \sum_n \frac{dP(n;t)}{dt} \ a^{\dagger \ n} \ |0\rangle \\
&= \sum_n \left[J_{in} \ P(n-1;t) - J_{in} \ P(n;t) \right] \ a^{\dagger \ n} \ |0\rangle \qquad \text{[using eqn. (5.17)]} \\
&= J_{in} \ \sum_n \left[a^{\dagger} \ P(n-1;t) \ a^{\dagger \ (n-1)} - P(n;t) \ a^{\dagger \ n} \right] \ |0\rangle \\
&= J_{in} \ \left[a^{\dagger} \ |\psi(t)\rangle - |\psi(t)\rangle \right] \\
&= J_{in} \ \left(a^{\dagger} \ - 1 \right) \ |\psi(t)\rangle
\end{aligned}
\tag{5.19}
$$

The effective hamiltonian for the process is given by eqn. (5.6a) as

$$
H_{\phi \to A} = -J_{in} \ \left(a^{\dagger} - 1 \right) = J_{in} \ \left(1 - a^{\dagger} \right)
\tag{5.20}
$$

For a lattice where a particle can be created at each site with rate J_{in}, the effective Hamiltonian will be

$$
\boxed{H = J_{in} \ \sum_i \left(1 - a_i^{\dagger} \right)}
\tag{5.21}
$$

where i denotes the lattice site label.

5.1.3 Annihilation of a particle $(A \to \phi)$

Just as a particle can be created in an elementary step of a stochastic process, it can get annihilated also.

If J_{out} is the rate of annihilation and n is the no. of particle A, then the master equation for the process is given by

$$
\frac{dP(n;t)}{dt} = J_{out} \ (n+1) \ P(n+1;t) - J_{out} \ n \ P(n;t).
\tag{5.22}
$$

Let a, $a^{\dagger}$ and $|0\rangle$ be respectively the annihilation operator, creation operator and the vaccum

for our system. Let the general state be given by eqn. (5.18). Then,

$$
\frac{d|\psi(t)\rangle}{dt} = \sum_n \frac{dP(n;t)}{dt} \, a^{\dagger \, n} \, |0\rangle
$$

$$
= \sum_n \left[J_{out} \, (n+1) \, P(n+1;t) - J_{out} \, n \, P(n;t) \right] \, a^{\dagger \, n} \, |0\rangle
$$

[using eqn. (5.22)]

$$
= J_{out} \, \sum_n \left[P(n+1;t) \, (n+1) \, a^{\dagger \, n} - P(n;t) \, n \, a^{\dagger \, n} \right] \, |0\rangle
$$

$$
= J_{out} \, \sum_n \left[P(n+1;t) \, \frac{\partial}{\partial a^\dagger} \, a^{\dagger \, (n+1)} - P(n;t) \, a^\dagger \, \frac{\partial}{\partial a^\dagger} a^{\dagger \, n} \right] \, |0\rangle
$$

$$
= J_{out} \, \sum_n \left[P(n+1;t) \, a \, a^{\dagger \, (n+1)} - P(n;t) \, a^\dagger \, a \, a^{\dagger \, n} \right] \, |0\rangle
$$

[using eqn. (5.2)]

$$
= J_{out} \, \left(a - a^\dagger \, a \right) \, |\psi(t)\rangle \tag{5.23}
$$

The effective hamiltonian for the process is given by eqn. (5.6a) as

$$
H_{A \to \phi} = -J_{out} \, \left(a - a^\dagger \, a \right) = J_{out} \, \left(a^\dagger - 1 \right) \, a \tag{5.24}
$$

For a lattice where a particle can be annihilated at each site with rate J_{out}, the effective Hamiltonian will be

$$
\boxed{H = J_{out} \, \sum_i \left(a_i^\dagger - 1 \right) \, a_i} \tag{5.25}
$$

where i denotes the lattice site label.

5.1.4   Process $X \to Y$ with rate λ_2

This is one of the elementary steps involved in the brusselator model. The probability distribution here would be the joint probability distribution $P(X, Y; t)$, where X and Y are the number of X type and Y type species. To save notation we use the symbol X for both the name of the species as well as the no. of it. The difference would be clear from the context.

The master equation for this process is

$$
\frac{dP(X,Y;t)}{dt} = \lambda_2 \, (X+1) \, P(X+1, Y-1; t) - \lambda_2 \, X \, P(X,Y;t) \tag{5.26}
$$

To represent this process, we would need an annihilation and creation operators for both X (say a_X and $a_X^\dagger$) and Y (say a_Y and $a_Y^\dagger$). Let the vaccum be represented by $|0\rangle$. The state with X no. of X species and Y no. of Y species would be given by

$$
|X, \, Y\rangle = a_X^{\dagger \, X} \, a_Y^{\dagger \, Y} \, |0\rangle \tag{5.27}
$$

A general state $|\psi(t)\rangle$ is given by

$$\begin{aligned}
|\psi(t)\rangle &= \sum_{X,Y} P(X,Y;t) \, |X, \, Y\rangle \\
&= \sum_{X,Y} P(X,Y;t) \, a_X^{\dagger \, X} \, a_Y^{\dagger \, Y} \, |0\rangle
\end{aligned} \tag{5.28}$$

Then,

$$\begin{aligned}
\frac{d|\psi(t)\rangle}{dt} &= \sum_{X, \, Y} \frac{dP(X,Y;t)}{dt} \, a_X^{\dagger \, X} \, a_Y^{\dagger \, Y} \, |0\rangle \\
&= \sum_{X, \, Y} [\lambda_2 \, (X+1) \, P(X+1,Y-1;t) - \lambda_2 \, X \, P(X,Y;t)] \, a_X^{\dagger \, X} \, a_Y^{\dagger \, Y} \, |0\rangle
\end{aligned}$$

[using eqn. (5.26)]

$$\begin{aligned}
&= \lambda_2 \, \sum_{X, \, Y} \left[P(X+1,Y-1;t) \, (X+1) \, a_X^{\dagger \, X} \, a_Y^{\dagger \, Y} \right. \\
&\qquad\qquad\qquad\qquad \left. -P(X,Y;t) \, X \, a_X^{\dagger \, X} \, a_Y^{\dagger \, Y} \right] |0\rangle \\
&= \lambda_2 \, \sum_{X, \, Y} \left[P(X+1,Y-1;t) \, \frac{\partial}{\partial a_X^\dagger} \, a_X^{\dagger \, (X+1)} \, a_Y^{\dagger \, Y} \right. \\
&\qquad\qquad\qquad\qquad \left. -P(X,Y;t) \, a_X^\dagger \, \frac{\partial}{\partial a_X^\dagger} \, a_X^{\dagger \, X} \, a_Y^{\dagger \, Y} \right] |0\rangle \\
&= \lambda_2 \, \sum_{X, \, Y} \left[P(X+1,Y-1;t) \, a_X \, a_X^{\dagger \, (X+1)} \, a_Y^{\dagger \, Y} \right. \\
&\qquad\qquad\qquad\qquad \left. -P(X,Y;t) \, a_X^\dagger \, a_X \, a_X^{\dagger \, X} \, a_Y^{\dagger \, Y} \right] |0\rangle
\end{aligned}$$

[using eqn. (5.2)]

$$= \lambda_2 \, \left(a_X \, a_Y^\dagger - a_X^\dagger \, a_X \right) \, |\psi(t)\rangle \tag{5.29}$$

The effective hamiltonian for the process is given by eqn. (5.6a) as

$$H_{X \to Y} = -\lambda_2 \, \left(a_X \, a_Y^\dagger - a_X^\dagger \, a_X \right) = \lambda_2 \, \left(a_X^\dagger - a_Y^\dagger \right) a_X \tag{5.30}$$

For a lattice where the process $X \to Y$ takes place at each site with rate λ_2, the effective Hamiltonian will be

$$\boxed{H = \lambda_2 \, \sum_i \left(a_{X_i}^\dagger - a_{Y_i}^\dagger \right) a_{X_i}} \tag{5.31}$$

where i denotes the lattice site label.

5.1.5 Process $2X + Y \rightarrow 3X$ with rate λ_1

This is another elementary step involved in the brusselator model. As in previous section the probability distribution here would be the joint probability distribution $P(X, Y; t)$.

The master equation for this process is

$$\frac{dP(X, Y; t)}{dt} = \lambda_1 \frac{(X-1)(X-2)}{2} (Y+1) P(X-1, Y+1; t)$$
$$- \lambda_1 \frac{X(X-1)}{2} Y P(X, Y; t). \qquad (5.32)$$

Let the operators and vaccum be defined as in previous section, and the general state be given by eqn. (5.28). Then,

$$\frac{d|\psi(t)\rangle}{dt} = \sum_{X, Y} \frac{dP(X, Y; t)}{dt} a_X^{\dagger X} a_Y^{\dagger Y} |0\rangle$$

$$= \sum_{X, Y} \left[\lambda_1 \frac{(X-1)(X-2)}{2} (Y+1) P(X-1, Y+1; t) \right.$$
$$\left. - \lambda_1 \frac{X(X-1)}{2} Y P(X, Y; t) \right] a_X^{\dagger X} a_Y^{\dagger Y} |0\rangle$$
$$\text{[using eqn. (5.32)]}$$

$$= \frac{\lambda_1}{2} \sum_{X, Y} \left[P(X-1, Y+1; t) (X-1)(X-2) a_X^{\dagger X} (Y+1) a_Y^{\dagger Y} \right.$$
$$\left. - P(X, Y; t) X(X-1) a_X^{\dagger X} Y a_Y^{\dagger Y} \right] |0\rangle$$

$$= \frac{\lambda_1}{2} \sum_{X, Y} \left[P(X-1, Y+1; t) a_X^{\dagger 3} \frac{\partial^2}{\partial a_X^{\dagger 2}} a_X^{\dagger (X-1)} \frac{\partial}{\partial a_Y^{\dagger}} a_Y^{\dagger (Y+1)} \right.$$
$$\left. - P(X, Y; t) a_X^{\dagger 2} \frac{\partial^2}{\partial a_X^{\dagger 2}} a_X^{\dagger X} a_Y^{\dagger} \frac{\partial}{\partial a_Y^{\dagger}} a_Y^{\dagger Y} \right] |0\rangle$$

$$= \frac{\lambda_1}{2} \sum_{X, Y} \left[P(X-1, Y+1; t) a_X^{\dagger 3} a_X^2 a_X^{\dagger (X-1)} a_Y a_Y^{\dagger (Y+1)} \right.$$
$$\left. - P(X, Y; t) a_X^{\dagger 2} a_X^2 a_X^{\dagger X} a_Y^{\dagger} a_Y a_Y^{\dagger Y} \right] |0\rangle$$
$$\text{[using eqn. (5.2)]}$$

$$= \frac{\lambda_1}{2} \left(a_X^{\dagger 3} a_X^2 a_Y - a_X^{\dagger 2} a_X^2 a_Y^{\dagger} a_Y \right) |\psi(t)\rangle \qquad (5.33)$$

The effective hamiltonian for the process is given by eqn. (5.6a) as

$$H_{2X+Y \to 3X} = -\frac{\lambda_1}{2} \left(a_X^{\dagger\,3} a_X^2 a_Y - a_X^{\dagger\,2} a_X^2 a_Y^\dagger a_Y \right)$$

$$= -\frac{\lambda_1}{2} a_X^{\dagger\,2} \left(a_X^\dagger - a_Y^\dagger \right) a_X^2 a_Y$$

$$= \frac{\lambda_1}{2} a_X^{\dagger\,2} \left(a_Y^\dagger - a_X^\dagger \right) a_X^2 a_Y \tag{5.34}$$

For a lattice where the process $2X + Y \to 3X$ takes place at each site with rate λ_1, the effective Hamiltonian will be

$$\boxed{H = \frac{\lambda_1}{2} \sum_i a_{X_i}^{\dagger\,2} \left(a_{Y_i}^\dagger - a_{X_i}^\dagger \right) a_{X_i}^2 a_{Y_i}} \tag{5.35}$$

where i denotes the lattice site label.

5.1.6 Effective Hamiltonian for the Brusselator system

Combining all the elementary steps from above, the effective Hamiltonian for the brusselator system is given by

$$H = \sum_i \left[J_{in} \left(1 - a_{X_i}^\dagger \right) + \frac{\lambda_1}{2} a_{X_i}^{\dagger\,2} \left(a_{Y_i}^\dagger - a_{X_i}^\dagger \right) a_{X_i}^2 a_{Y_i} \right.$$

$$\left. + \lambda_2 \left(a_{X_i}^\dagger - a_{Y_i}^\dagger \right) a_{X_i} + J_{out} \left(a_{X_i}^\dagger - 1 \right) a_{X_i} \right]$$

$$+ \sum_{\langle i,\,j \rangle} \left[D_X \left(a_{X_i}^\dagger - a_{X_j}^\dagger \right) \left(a_{X_i} - a_{X_j} \right) + D_Y \left(a_{Y_i}^\dagger - a_{Y_j}^\dagger \right) \left(a_{Y_i} - a_{Y_j} \right) \right] \tag{5.36}$$

5.2 Comparison with Second Quantization Method of the Quantum Theory

One should bear in mind various things while working with the second quantization method for classical stochastic process discussed here. There are some immediate differences with the second quantization method of the quantum theory:

- Unlike Schrödinger equation, there is no factor of 'i' in eqn. (5.6a).

- The effective Hamiltonian operator (H) is generally not hermitian.

- The most important difference is in the calculation of expectation value. The expectation value of an operator $\hat{O}$ when the system is in state $|\psi\rangle$ is not $\langle\psi|\hat{O}|\psi\rangle$, like in quantum theory, because $\langle\psi|\hat{O}|\psi\rangle$ is bilinear in probabilities, $P(\{n_i\})$.

- An observable in the classical stochastic process, say $O(\{n_i\})$, can be represented by an operator, $\hat{O}$, which is diagonal in the Fock basis, by the prescription of substituting $(a_i^\dagger\, a_i)$ in place of n_i.

- To define an expression for the expectation value in terms of operators and vectors in our setup, let us define a *projection state* $\langle\mathcal{P}|$ with following properties

$$\langle\mathcal{P}|a_i^\dagger = \langle\mathcal{P}| \tag{5.37}$$

$$\text{and, } \langle\mathcal{P}|0\rangle = 1 \tag{5.38}$$

The above eqns. can be satisfied by defining $\langle\mathcal{P}|$ as

$$\langle\mathcal{P}| = \langle 0|e^{\sum_i a_i} \tag{5.39}$$

Proof: Expanding the L.H.S. of eqn. (5.37), we get

$$\langle\mathcal{P}|a_i^\dagger = \langle 0|e^{\sum_i a_i}a_i^\dagger$$
$$= \langle 0|e^{a_i}a_i^\dagger e^{\sum_{j\neq i} a_j}$$

Now,

$$e^a a^\dagger = \left[e^a, a^\dagger\right] + a^\dagger e^a$$
$$= \left[e^a, -\frac{\partial}{\partial a}\right] + a^\dagger e^a \qquad\qquad \text{[using eqn. 5.2]}$$
$$= \left[\frac{\partial}{\partial a}, e^a\right] + a^\dagger e^a$$
$$= \frac{\partial}{\partial a}e^a - e^a\frac{\partial}{\partial a} + a^\dagger e^a$$
$$= e^a\frac{\partial}{\partial a} + e^a - e^a\frac{\partial}{\partial a} + a^\dagger e^a$$
$$= e^a + a^\dagger e^a$$
$$\Rightarrow e^a a^\dagger = (1 + a^\dagger)e^a \tag{5.40}$$

Using this result, we get

$$\langle\mathcal{P}|a_i^\dagger = \langle 0|\, (1 + a_i^\dagger)\, e^{a_i}\, e^{\sum_{j\neq i} a_j}$$
$$= \langle 0|\, e^{\sum_i a_i} \qquad\qquad \text{[since } \langle 0|a_i^\dagger = 0]$$
$$= \langle\mathcal{P}|$$

Simplifying L.H.S. of eqn. (5.38), we get

$$\langle\mathcal{P}|0\rangle = \langle 0|e^{\sum_i a_i}|0\rangle$$
$$= \langle 0|\left(1 + \sum_i a_i + \cdots\right)|0\rangle$$
$$= 1 \qquad\qquad \text{[since } a_i|0\rangle = 0]$$

- For a classical stochastic process, the expectation value of an observable $O(\{n_i\})$ is defined as

$$\langle O \rangle = \sum_{\{n_i\}} P(\{n_i\}; t) \, O(\{n_i\})$$

Since $\langle \mathcal{P} | \prod_{\{n_i\}} a_i^{\dagger \, n_i} |0\rangle = 1$ using eqns. (5.37) and (5.38), let us multiply the above equation by it on R.H.S. Here we have the freedom to choose the set $\{n_i\}$ which we choose to be the same as the one on which summation is carried over, i.e.

$$\begin{aligned}
\langle O \rangle &= \sum_{\{n_i\}} P(\{n_i\}; t) \, O(\{n_i\}) \langle \mathcal{P} | \prod_{\{n_i\}} a_i^{\dagger \, n_i} |0\rangle \\
&= \sum_{\{n_i\}} P(\{n_i\}; t) \, \langle \mathcal{P} | O(\{n_i\}) \prod_{\{n_i\}} a_i^{\dagger \, n_i} |0\rangle \\
&= \sum_{\{n_i\}} P(\{n_i\}; t) \, \langle \mathcal{P} | O(\{n_i\}) |n_1, n_2, \cdots \rangle \\
&= \sum_{\{n_i\}} P(\{n_i\}; t) \, \langle \mathcal{P} | \widehat{O} |n_1, n_2, \cdots \rangle
\end{aligned}$$

where $\widehat{O}$ is an operator obtained by replacing n_i by $a_i^{\dagger} a_i$ in $O(\{n_i\})$. It is important to note here that the operator $\widehat{O}$ is independent of the indices n_i, hence we get

$$\langle O \rangle = \langle \mathcal{P} | \widehat{O} | \psi(t) \rangle \tag{5.41}$$
$$= \langle \mathcal{P} | \widehat{O} \, e^{-Ht} | \psi(0) \rangle$$

where we have used eqns. (5.5) and (5.6b).

- Putting $O = 1$ in eqn. (5.41) we get

$$\langle \mathcal{P} | \psi(t) \rangle = \langle \mathcal{P} | e^{-Ht} | \psi(0) \rangle = 1. \tag{5.42}$$

This equation means that the total probability is conserved during the time evolution given by eqn. (5.6a).

- Putting $t = 0$ in eqn. (5.42) we get

$$\langle \mathcal{P} | \psi(0) \rangle = 1.$$

Since the above equation and eqn. (5.42) are true for all $|\psi(0)\rangle$, we must have

$$\langle \mathcal{P} | H = 0. \tag{5.43}$$

- If H is written in normal ordered form, i.e. all $a^{\dagger}$'s are to the left of all a's, then eqns. (5.37) and (5.43) implies that H should vanish if all the $a^{\dagger}$'s are replaced by 1.

5.3   Doi's Shift

Using eqns. (5.39) and (5.41), we have

$$\langle O \rangle = \langle 0| e^{\sum_i a_i} \, \widehat{O} \, e^{-Ht} |\psi(0)\rangle.$$

The factor $e^{\sum_i a_i}$ can be commuted through the operators to get

$$\langle O \rangle = \langle 0| \widehat{O}_{shifted} \, e^{-H_{shifted}t} \, e^{\sum_i a_i} |\psi(0)\rangle \tag{5.44}$$

where the shifted operators are obtained from the unshifted ones by substituting $(1 + a_i^\dagger)$ in place of $a_i^\dagger$. This step follows by using eqn. (5.40). This shifting is known as the *Doi's shift*.

For our brusselator system, the shifted hamiltonian is obtained from eqn. (5.36) as

$$
\begin{aligned}
H_{shifted} = \sum_i & \left[-J_{in} \, a_{X_i}^\dagger + \frac{\lambda_1}{2} \left(1 + a_{X_i}^\dagger \right)^2 \left(a_{Y_i}^\dagger - a_{X_i}^\dagger \right) a_{X_i}^2 \, a_{Y_i} \right. \\
& \left. + \lambda_2 \left(a_{X_i}^\dagger - a_{Y_i}^\dagger \right) a_{X_i} + J_{out} \, a_{X_i}^\dagger \, a_{X_i} \right] \\
+ \sum_{\langle i,\, j \rangle} & \left[D_X \left(a_{X_i}^\dagger - a_{X_j}^\dagger \right) \left(a_{X_i} - a_{X_j} \right) + D_Y \left(a_{Y_i}^\dagger - a_{Y_j}^\dagger \right) \left(a_{Y_i} - a_{Y_j} \right) \right] \tag{5.45}
\end{aligned}
$$

5.4   Coherent State Representation

Coherent states are the right eigenstates of the annihilation operator corresponding to a harmonic oscillator. Let us denote a coherent state by $|\phi\rangle$, then

$$a \, |\phi\rangle = \phi \, |\phi\rangle$$

A useful form for the coherent states is

$$|\phi\rangle = N(\phi) \, e^{\phi a^\dagger} \, |0\rangle.$$

We can explicitly check that the state given above is a coherent state:

$$
\begin{aligned}
a \, |\phi\rangle &= N(\phi) \, a \, e^{\phi a^\dagger} \, |0\rangle \\
&= N(\phi) \left[a, \, e^{\phi a^\dagger} \right] |0\rangle && [\text{since } a|0\rangle = 0] \\
&= N(\phi) \left[\frac{\partial}{\partial a^\dagger}, \, e^{\phi a^\dagger} \right] |0\rangle && [\text{using eqn. (5.2)}] \\
&= N(\phi) \, \phi \, e^{\phi a^\dagger} \, |0\rangle \\
&= \phi \, |\phi\rangle
\end{aligned}
$$

Since the overall phase of a state vector is not meaningful, we can choose $N(\phi)$ to be real. The normalisation constant $N(\phi)$ is fixed by demanding

$$1 = \langle \phi | \phi \rangle$$

$$= N^2(\phi) \langle 0 | e^{\phi^\star a} e^{\phi a^\dagger} | 0 \rangle$$

$$= N^2(\phi) \left\langle 0 \left| \sum_{m=0}^{\infty} \frac{\phi^{\star m} a^m}{m!} \sum_{n=0}^{\infty} \frac{\phi^n a^{\dagger n}}{n!} \right| 0 \right\rangle$$

$$= N^2(\phi) \sum_{m,n=0}^{\infty} \frac{\phi^{\star m} \phi^n}{m! \, n!} \langle 0 | a^m a^{\dagger n} | 0 \rangle$$

Now for $m \neq n$,

$$\langle 0 | a^m a^{\dagger n} | 0 \rangle = 0.$$

While for $m = n$, we have

$$
\begin{aligned}
\langle 0 | a^n a^{\dagger n} | 0 \rangle &= \left\langle 0 \left| a^{n-1} \left[a, a^{\dagger n} \right] \right| 0 \right\rangle && [\text{since } a|0\rangle = 0] \\
&= \langle 0 | a^{n-1} \, n \, a^{\dagger (n-1)} | 0 \rangle && [\text{using eqn. (5.2)}] \\
&= n \, \langle 0 | a^{n-1} a^{\dagger (n-1)} | 0 \rangle \\
&= n(n-1) \, \langle 0 | a^{n-2} a^{\dagger (n-2)} | 0 \rangle \\
&\quad \vdots \\
&= n!
\end{aligned}
$$

Thus we have

$$\boxed{\langle 0 | a^m a^{\dagger n} | 0 \rangle = n! \, \delta_{m,n}} \tag{5.46}$$

Substituting in the equation above for determining $N(\phi)$, we get

$$
\begin{aligned}
1 &= N^2(\phi) \sum_{m,n=0}^{\infty} \frac{\phi^{\star m} \phi^n}{m! \, n!} n! \, \delta_{m,n} \\
&= N^2(\phi) \sum_{n=0}^{\infty} \frac{|\phi|^{2n}}{n!} \\
&= N^2(\phi) \, e^{|\phi|^2} \\
\Rightarrow N(\phi) &= e^{-\frac{1}{2} |\phi|^2} \tag{5.47}
\end{aligned}
$$

Thus the normalised coherent state is given by

$$|\phi\rangle = e^{-\frac{1}{2} |\phi|^2 + \phi a^\dagger} \, |0\rangle \tag{5.48}$$

5.4.1   Projection state

The projection state $\langle \mathcal{P}|$ defined in eqn. (5.39) is also a coherent state as

$$\langle \mathcal{P}| = \langle 0|e^a$$
$$= e^{\frac{1}{2}} \langle 1| \tag{5.49}$$

since eqn. (5.48) $\Rightarrow |1\rangle = e^{-\frac{1}{2}+a^\dagger} |0\rangle$.

5.4.2   Inner product between two coherent states

For later use let us evaluate the expression for inner product between two coherent states.

$$\langle \phi_1|\phi_2 \rangle = \left\langle 0 \left| e^{-\frac{1}{2}|\phi_1|^2 + \phi_1^\star a} \; e^{-\frac{1}{2}|\phi_2|^2 + \phi_2\, a^\dagger} \right| 0 \right\rangle$$

$$= e^{-\frac{1}{2}|\phi_1|^2 - \frac{1}{2}|\phi_2|^2} \left\langle 0 \left| e^{\phi_1^\star a} \; e^{\phi_2\, a^\dagger} \right| 0 \right\rangle$$

$$= e^{-\frac{1}{2}|\phi_1|^2 - \frac{1}{2}|\phi_2|^2} \left\langle 0 \left| \sum_{m=0}^{\infty} \frac{\phi_1^{\star m}\, a^m}{m!} \; \sum_{n=0}^{\infty} \frac{\phi_2^n\, a^{\dagger n}}{n!} \right| 0 \right\rangle$$

$$= e^{-\frac{1}{2}|\phi_1|^2 - \frac{1}{2}|\phi_2|^2} \sum_{m,n=0}^{\infty} \frac{\phi_1^{\star m}\, \phi_2^n}{m!\, n!} \, \langle 0|a^m\, a^{\dagger n}|0\rangle$$

$$= e^{-\frac{1}{2}|\phi_1|^2 - \frac{1}{2}|\phi_2|^2} \sum_{m,n=0}^{\infty} \frac{\phi_1^{\star m}\, \phi_2^n}{m!\, n!} \, n!\, \delta_{m,n} \qquad \text{[using eqn. (5.46)]}$$

$$= e^{-\frac{1}{2}|\phi_1|^2 - \frac{1}{2}|\phi_2|^2} \sum_{n=0}^{\infty} \frac{\phi_1^{\star n}\, \phi_2^n}{n!}$$

$$= e^{-\frac{1}{2}|\phi_1|^2 - \frac{1}{2}|\phi_2|^2} \, e^{\phi_1^\star\, \phi_2}$$

$$\Rightarrow \langle \phi_1|\phi_2 \rangle = e^{-\frac{1}{2}|\phi_1|^2 - \frac{1}{2}|\phi_2|^2 + \phi_1^\star\, \phi_2} \tag{5.50}$$

5.4.3   Resolution of identity in terms of coherent states

Let us first evaluate a complex integral.

$$\frac{1}{\pi\,m!}\int d^2z\;e^{-|z|^2}\;z^{\star m}\;z^n = \frac{1}{\pi\,m!}\int_0^\infty r\;dr\int_0^{2\pi} d\theta\;e^{-r^2}\;r^{m+n}\;e^{i\,\theta\,(n-m)}$$

$$[z = r\,e^{i\,\theta}]$$

$$= \frac{1}{\pi\,m!}\int_0^\infty r\;dr\;e^{-r^2}\;r^{m+n}\;2\;\pi\;\delta_{m,n}$$

$$= \frac{\delta_{m,n}}{m!}\int_0^\infty d(r^2)\;e^{-r^2}\;\left(r^2\right)^m$$

$$= \frac{\delta_{m,n}}{m!}\;\Gamma(m+1)\qquad\qquad[\text{since }\Gamma(n+1)\equiv\int_0^\infty dt\;t^n e^{-t}]$$

$$= \frac{\delta_{m,n}}{m!}\;m!\qquad\qquad\qquad[\text{since }\Gamma(n+1)=n!]$$

$$= \delta_{m,n}\tag{5.51}$$

Resolution of identity in terms of number states is given by

$$\mathbb{1} = \sum_n \frac{1}{n!}\;|n\rangle\langle n|$$

$$= \sum_{m,n}\frac{1}{n!}\;|n\rangle\langle m|\;\delta_{m,n}$$

$$= \sum_{m,n}\frac{1}{n!}\;|n\rangle\langle m|\;\frac{1}{\pi\,m!}\int d^2\phi\;e^{-|\phi|^2}\;\phi^{\star m}\;\phi^n\qquad\qquad[\text{using eqn. (5.51)}]$$

$$= \sum_{m,n}\frac{1}{\pi}\int d^2\phi\;e^{-\frac{1}{2}|\phi|^2}\;\frac{\phi^n}{n!}\;|n\rangle\langle m|\;\frac{\phi^{\star m}}{m!}\;e^{-\frac{1}{2}|\phi|^2}$$

$$= \int \frac{d^2\phi}{\pi}\;|\phi\rangle\langle\phi|.\tag{5.52}$$

5.5   Path Integral Formulation

5.5.1   Single Species Stochastic Process in 0-dimension

For simplicity we first derive the path integral formulation for a single species stochastic process on a single lattice site. This would avoid unnecessary complication in notation which is present for the full brusselator system.

Let the effective hamiltonian for the process be H. Let a, $a^\dagger$ and $|0\rangle$ denote the annihilation operator, creation operator and vaccum respectively. The state of the system is given by eqn. (5.5) and the time-evolution is given by eqns. (5.6a) and (5.6b).

To derive the path integral formulation we start from eqn. (5.6b)

$$|\psi(t)\rangle = e^{-Ht} \, |\psi(0)\rangle \tag{5.53}$$

Let us divide the time 0 to t in N intervals of Δt, i.e.

$$\Delta t = \frac{t}{N} \tag{5.54}$$

We are ultimately interested in the limit $\Delta t \to 0$. Eqn. (5.53) can be written as

$$|\psi(t)\rangle = \lim_{\Delta t \to 0} \, e^{-H N \Delta t} \, |\psi(0)\rangle$$

$$= \lim_{\Delta t \to 0} \, e^{-H \Delta t} \, e^{-H \Delta t} \cdots e^{-H \Delta t} \, |\psi(0)\rangle \tag{5.55}$$

Inserting the resolution of identity (eqn. (5.52)) between every time slice in above equation, we get

$$|\psi(t)\rangle = \lim_{\Delta t \to 0} \, \int \frac{d^2\phi_t}{\pi} \, |\phi_t\rangle\langle\phi_t| \, e^{-H \Delta t} \, \int \frac{d^2\phi_{t-\Delta t}}{\pi} \, |\phi_{t-\Delta t}\rangle\langle\phi_{t-\Delta t}| \, e^{-H \Delta t}$$

$$\int \frac{d^2\phi_{t-2\Delta t}}{\pi} \, |\phi_{t-2\Delta t}\rangle\langle\phi_{t-2\Delta t}| \, e^{-H \Delta t}$$

$$\vdots$$

$$\int \frac{d^2\phi_{\Delta t}}{\pi} \, |\phi_{\Delta t}\rangle\langle\phi_{\Delta t}| \, e^{-H \Delta t} \, \int \frac{d^2\phi_0}{\pi} \, |\phi_0\rangle\langle\phi_0|\psi(0)\rangle$$

$$= \lim_{\Delta t \to 0} \, \mathcal{N}^{-1} \int \left(\prod_{\tau=0}^{t} d^2\phi_\tau \right) \, |\phi_t\rangle\langle\phi_t| \, e^{-H \Delta t} \, |\phi_{t-\Delta t}\rangle\langle\phi_{t-\Delta t}| \, e^{-H \Delta t} \, |\phi_{t-2\Delta t}\rangle$$

$$\cdots \, \langle\phi_{\Delta t}| \, e^{-H \Delta t}|\phi_0\rangle\langle\phi_0|\psi(0)\rangle$$

$$= \lim_{\Delta t \to 0} \, \mathcal{N}^{-1} \int \left(\prod_{\tau=0}^{t} d^2\phi_\tau \right) \, |\phi_t\rangle \left[\prod_{\tau=\Delta t}^{t} \langle\phi_\tau| \, e^{-H \Delta t}|\phi_{\tau-\Delta t}\rangle \right] \, \langle\phi_0|\psi(0)\rangle \tag{5.56}$$

where $\mathcal{N}$ is the normalisation constant.

Let $O(n)$ is an observable, then the corresponding operator $\widehat{O}$ is defined by replacing n by $a^\dagger a$ in $O(n)$. The expectation value is given by eqn. (5.41) as

$$\langle O \rangle = \langle \mathcal{P} | \widehat{O} | \psi(t) \rangle$$

$$= e^{\frac{1}{2}} \, \langle 1 | \widehat{O} | \psi(t) \rangle$$

$$= \mathcal{N}^{-1} \lim_{\Delta t \to 0} \int \left(\prod_{\tau=0}^{t} d^2 \phi_\tau \right) \langle 1 | \widehat{O} | \phi_t \rangle \left[\prod_{\tau=\Delta t}^{t} \langle \phi_\tau | \, e^{-H \, \Delta t} | \phi_{\tau - \Delta t} \rangle \right] \langle \phi_0 | \psi(0) \rangle \qquad (5.57)$$

where we have absorbed the factor $e^{\frac{1}{2}}$ in the normalisation constant.
We shall now evaluate each term in the above equation one by one.
Let us first evaluate the middle term:

$$\langle \phi_\tau | \, e^{-H \, \Delta t} | \phi_{\tau - \Delta t} \rangle = \langle \phi_\tau | \, \left[\mathbb{1} - H \, \Delta t + O(\Delta t^2) \right] | \phi_{\tau - \Delta t} \rangle$$

$$= \langle \phi_\tau | \phi_{\tau - \Delta t} \rangle - \langle \phi_\tau | \, H \, | \phi_{\tau - \Delta t} \rangle \, \Delta t + O(\Delta t^2)$$

$$= \langle \phi_\tau | \phi_{\tau - \Delta t} \rangle - \langle \phi_\tau | \, H \, (\phi_\tau^\star, \phi_{\tau - \Delta t}) \, | \phi_{\tau - \Delta t} \rangle \, \Delta t + O(\Delta t^2)$$

$$= \langle \phi_\tau | \phi_{\tau - \Delta t} \rangle - H \, (\phi_\tau^\star, \phi_{\tau - \Delta t}) \, \langle \phi_\tau | \phi_{\tau - \Delta t} \rangle \, \Delta t + O(\Delta t^2)$$

$$= \langle \phi_\tau | \phi_{\tau - \Delta t} \rangle \, \left[1 - H \, (\phi_\tau^\star, \phi_{\tau - \Delta t}) \, + O(\Delta t^2) \right]$$

$$= \langle \phi_\tau | \phi_{\tau - \Delta t} \rangle \, e^{-H(\phi_\tau^\star, \phi_{\tau - \Delta t}) \, \Delta t} \qquad (5.58)$$

where $H \, (\phi_\tau^\star, \phi_{\tau - \Delta t})$ is obtained by replacing a by $\phi_{\tau - \Delta t}$ and $a^\dagger$ by $\phi_\tau^\star$ in the normal ordered form. Now,

$$\langle \phi_\tau | \phi_{\tau - \Delta t} \rangle = e^{-\frac{1}{2}|\phi_\tau|^2 - \frac{1}{2}|\phi_{\tau - \Delta t}|^2 + \phi_\tau^\star \, \phi_{\tau - \Delta t}} \qquad \text{[using eqn. (5.50)]}$$

$$= e^{\frac{1}{2}(|\phi_\tau|^2 - |\phi_{\tau - \Delta t}|^2)} \, e^{-|\phi_\tau|^2 + \phi_\tau^\star \, \phi_{\tau - \Delta t}}$$

$$= e^{\frac{1}{2}(|\phi_\tau|^2 - |\phi_{\tau - \Delta t}|^2)} \, e^{-\phi_\tau^\star \, (\phi_\tau - \phi_{\tau - \Delta t})} \qquad (5.59)$$

Now,

$$\prod_{\tau=\Delta t}^{t} \langle\phi_\tau| \, e^{-H\,\Delta t}|\phi_{\tau-\Delta t}\rangle = \prod_{\tau=\Delta t}^{t} \langle\phi_\tau|\phi_{\tau-\Delta t}\rangle \, e^{-H(\phi_\tau^\star,\phi_{\tau-\Delta t})\,\Delta t} \qquad \text{[using eqn. (5.58)]}$$

$$= \prod_{\tau=\Delta t}^{t} e^{\frac{1}{2}(|\phi_\tau|^2-|\phi_{\tau-\Delta t}|^2)} \, e^{-\phi_\tau^\star\,(\phi_\tau-\phi_{\tau-\Delta t})} \, e^{-H(\phi_\tau^\star,\phi_{\tau-\Delta t})\,\Delta t}$$

$$\text{[using eqn. (5.59)]}$$

$$= \left[\prod_{\tau=\Delta t}^{t} e^{\frac{1}{2}(|\phi_\tau|^2-|\phi_{\tau-\Delta t}|^2)}\right]\left[\prod_{\tau=\Delta t}^{t} e^{-\phi_\tau^\star\,(\phi_\tau-\phi_{\tau-\Delta t})} \, e^{-H(\phi_\tau^\star,\phi_{\tau-\Delta t})\,\Delta t}\right]$$

$$= e^{\frac{1}{2}\,\sum_{\tau=\Delta t}^{t}(|\phi_\tau|^2-|\phi_{\tau-\Delta t}|^2)} \, e^{-\sum_{\tau=\Delta t}^{t}[\phi_\tau^\star\,(\phi_\tau-\phi_{\tau-\Delta t})+H(\phi_\tau^\star,\phi_{\tau-\Delta t})\,\Delta t]}$$

$$= e^{\frac{1}{2}\,[|\phi_t|^2-|\phi_{t-\Delta t}|^2+|\phi_{t-\Delta t}|^2-|\phi_{t-2\Delta t}|^2+\cdots+|\phi_{\Delta t}|^2-|\phi_0|^2]}$$

$$e^{-\sum_{\tau=\Delta t}^{t}[\phi_\tau^\star\,(\phi_\tau-\phi_{\tau-\Delta t})+H(\phi_\tau^\star,\phi_{\tau-\Delta t})\,\Delta t]}$$

$$= e^{\frac{1}{2}\,(|\phi_t|^2-|\phi_0|^2)} \, e^{-\sum_{\tau=\Delta t}^{t}[\phi_\tau^\star\,(\phi_\tau-\phi_{\tau-\Delta t})+H(\phi_\tau^\star,\phi_{\tau-\Delta t})\,\Delta t]} \qquad (5.60)$$

Let us now evaluate the first term in eqn. (5.57). If the operator $\widehat{O}$ is written in normal ordered form, it can be made a function of a by simply substituting 1 in place of $a^\dagger$, as $\langle 1| \, a^\dagger = \langle 1|$. We get on further evaluation

$$\langle 1|\widehat{O}|\phi_t\rangle = O(\phi_t) \, \langle 1|\phi_t\rangle$$

$$= O(\phi_t) \, e^{-\frac{1}{2}1^2-\frac{1}{2}|\phi_t|^2+\phi_t}$$

$$= O(\phi_t) \, e^{-\frac{1}{2}-\frac{1}{2}|\phi_t|^2+\phi_t} \qquad (5.61)$$

where $O(\phi_t)$ is obtained by substituting 1 in place of $a^\dagger$ and ϕ_t in place of a in the operator $\widehat{O}$ written in normal ordered form.

Let us now evaluate the last term in eqn. (5.57). To be specific, let us assume the initial distribution to be *Poisson*, i.e.

$$P(n;0) = \frac{\bar{n}_0^n}{n!} \, e^{-\bar{n}_0} \qquad (5.62)$$

$$\Rightarrow |\psi(0)\rangle = \sum_n P(n;0) \ |n\rangle$$

$$= \sum_n \frac{\bar{n}_0^n}{n!} \ e^{-\bar{n}_0} \ a^{\dagger \, n}|0\rangle$$

$$= e^{-\bar{n}_0} \ e^{\bar{n}_0 \ a^{\dagger}}|0\rangle$$

$$= e^{-\bar{n}_0} \ |\bar{n}_0\rangle \tag{5.63}$$

Now,

$$\langle \phi_0|\psi(0)\rangle = e^{-\bar{n}_0} \ \langle \phi_0|\bar{n}_0\rangle$$

$$= e^{-\bar{n}_0} \ e^{-\frac{1}{2}|\phi_0|^2 - \frac{1}{2}|\bar{n}_0|^2 + \phi_0^{\star} \, \bar{n}_0} \tag{5.64}$$

Substituting eqns. (5.60), (5.61) and (5.64) in eqn. (5.57) and absorbing all the constants in the normalisation factor, we get

$$\langle O \rangle = \mathcal{N}^{-1} \lim_{\Delta t \to 0} \int \left(\prod_{\tau=0}^{t} d^2\phi_\tau \right) \ O(\phi_t) \ e^{-\frac{1}{2}|\phi_t|^2 + \phi_t}$$

$$e^{\frac{1}{2} \ (|\phi_t|^2 - |\phi_0|^2)} \ e^{-\sum_{\tau=\Delta t}^{t} [\phi_\tau^{\star} \ (\phi_\tau - \phi_{\tau-\Delta t}) + H(\phi_\tau^{\star}, \phi_{\tau-\Delta t}) \ \Delta t]}$$

$$e^{-\frac{1}{2}|\phi_0|^2 + \phi_0^{\star} \, \bar{n}_0}$$

$$= \mathcal{N}^{-1} \lim_{\Delta t \to 0} \int \left(\prod_{\tau=0}^{t} d^2\phi_\tau \right) \ O(\phi_t) \ e^{\phi_t} \ e^{-|\phi_0|^2} \ e^{\phi_0^{\star} \, \bar{n}_0}$$

$$\exp \left\{ - \sum_{\tau=\Delta t}^{t} [\phi_\tau^{\star} \ (\phi_\tau - \phi_{\tau-\Delta t}) + H \left(\phi_\tau^{\star}, \phi_{\tau-\Delta t} \right) \ \Delta t] \right\}$$

$$= \mathcal{N}^{-1} \lim_{\Delta t \to 0} \int \left(\prod_{\tau=0}^{t} d^2\phi_\tau \right) \ O(\phi_t) \ e^{\phi_t} \ e^{-|\phi_0|^2} \ e^{\phi_0^{\star} \, \bar{n}_0}$$

$$\exp \left\{ - \sum_{\tau=\Delta t}^{t} \left[\phi_\tau^{\star} \left(\frac{\phi_\tau - \phi_{\tau-\Delta t}}{\Delta t} \right) \ \Delta t + H \left(\phi_\tau^{\star}, \phi_{\tau-\Delta t} \right) \ \Delta t \right] \right\} \tag{5.65}$$

$$= \mathcal{N}^{-1} \int \mathcal{D}\phi \ \mathcal{D}\phi^{\star} \ O[\phi(t)] \ e^{\phi(t)} \ e^{-|\phi(0)|^2} \ e^{\phi^{\star}(0) \, \bar{n}_0}$$

$$\exp \left\{ - \int_0^t dt' \left[\phi^{\star}(t') \ \frac{\partial \phi(t')}{\partial t'} + H \left[\phi^{\star}(t'), \phi(t') \right] \right] \right\} \tag{5.66}$$

[where we have taken the limit $\Delta t \to 0$]

$$= \mathcal{N}^{-1} \int \mathcal{D}\phi \ \mathcal{D}\phi^{\star} \ O[\phi(t)] \ \exp \left\{ -S \left[\phi^{\star}, \phi \right]_0^t \right\} \tag{5.67}$$

where

$$S\left[\phi^{\star},\phi\right]_0^{t_f} = -\left[\phi(t_f) \ -|\phi(0)|^2 \ +\phi^{\star}(0) \ \bar{n}_0\right] + \int_0^{t_f} dt \left\{\phi^{\star}(t) \ \frac{\partial\phi(t)}{\partial t} + H\left[\phi^{\star}(t),\phi(t)\right]\right\}$$

$$= -\left[\phi(t_f) \ +\phi^{\star}(0) \ \left\{\bar{n}_0 - \phi(0)\right\}\right] + \int_0^{t_f} dt \left\{\phi^{\star}(t) \ \partial_t\phi(t) + H\left[\phi^{\star}(t),\phi(t)\right]\right\} \quad (5.68)$$

Important points to note

- In taking the limit $\Delta t \to 0$, we have replaced both $\phi_\tau^{\star}$ and $\phi_{\tau-\Delta t}$ by $\phi^{\star}(t')$ and $\phi(t')$. Hence whenever a term contains both $\phi^{\star}(t')$ and $\phi(t')$, $\phi^{\star}(t')$ would be considered to be at a later time than $\phi(t')$.

- The measure is defined as

$$\mathcal{D}\phi \ \mathcal{D}\phi^{\star} = \lim_{\Delta t \to 0} \prod_{\tau=0}^{t} d^2\phi_\tau \qquad (5.69)$$

- The normalisation constant is determined by taking $O(n)$ to be 1 in eqn. (5.67).

$$1 = \mathcal{N}^{-1} \int \mathcal{D}\phi \ \mathcal{D}\phi^{\star} \ 1 \ \exp\left\{-S\left[\phi^{\star},\phi\right]_0^t\right\}$$

$$\Rightarrow \mathcal{N} = \int \mathcal{D}\phi \ \mathcal{D}\phi^{\star} \ \exp\left\{-S\left[\phi^{\star},\phi\right]_0^t\right\} \qquad (5.70)$$

Initial Term

The integral over $\phi_0^{\star}$ in eqn. (5.65) can be done, to obtain

$$\int d\phi_0^{\star} \ e^{-|\phi_0|^2} \ e^{\phi_0^{\star} \bar{n}_0} = \int d\phi_0^{\star} \ \exp\left\{\phi_0^{\star} \ (\bar{n}_0 - \phi_0)\right\}$$

$$= \delta\left(\bar{n}_0 - \phi_0\right) \qquad (5.71)$$

Now the integral over ϕ_0 can also be done which would enforce the initial condition in the integrand. Hence the term $\left[\phi^{\star}(0) \ \{\bar{n}_0 - \phi(0)\}\right]$ can be dropped from the action (eqn. (5.68)), with the constraint on the field $\phi(0) = \bar{n}_0$.

But a path integral with such an implied constraint is not directly amenable to a perturbation expansion.

Scheme for perturbative calculation

The part of action S which is bilinear in fields, i.e. $\propto \phi^{\star}\phi$ is chosen as reference action and solved exactly. Remaining terms are treated perturbatively. In the perturbation calculation, a term would be zero if every ϕ in it cannot be paired up with a $\phi^{\star}$ at an earlier time.

In the exponential of $\phi^{\star}(0)\phi(0)$, every term except the first one vanishes, because there is no $\phi^{\star}$ earlier to $t = 0$. This is equivalent to dropping $|\phi(0)|^2$ from the action.

So, we are left with $e^{-\bar{n}_0\phi^{\star}(0)}$ as the initial term.

Final term

The term $\phi(t_f)$ in the action (eqn. (5.68)) can be taken care of by performing the following shift in the field:

$$\phi^\star(t) = 1 + \bar{\phi}(t)$$

$$\Rightarrow \int_0^{t_f} dt \, \phi^\star(t) \, \partial_t\phi(t) = \int_0^{t_f} dt \, \left(1 + \bar{\phi}(t)\right) \, \partial_t\phi(t)$$

$$= \phi(t_f) - \phi(0) + \int_0^{t_f} dt \, \bar{\phi}(t) \, \partial_t\phi(t) \tag{5.72}$$

The action in terms of shifted field becomes

$$S\left[\bar{\phi}, \phi\right]_0^{t_f} = -\left[\phi(0) + \left(1 + \bar{\phi}(0)\right) \bar{n}_0\right] + \int_0^{t_f} dt \left\{\bar{\phi}(t) \, \partial_t\phi(t) + H\left[\bar{\phi}(t), \phi(t)\right]\right\}$$

We can again drop the $\phi(0)$ from the action as there is no $\bar{\phi}$ before $t = 0$. The term $\bar{n}_0$ can be absorbed in the normalisation constant. Hence, our action reduces to

$$\boxed{S\left[\bar{\phi}, \phi\right]_0^{t_f} = -\bar{\phi}(0) \, \bar{n}_0 + \int_0^{t_f} dt \left\{\bar{\phi}(t) \, \partial_t\phi(t) + H\left[\bar{\phi}(t), \phi(t)\right]\right\}} \tag{5.73}$$

where $H\left[\bar{\phi}(t), \phi(t)\right]$ is obtained by substituting $1 + \bar{\phi}(t)$ in place of $a^\dagger$ and $\phi(t)$ in place of a.

5.5.2 Single Species Stochastic Process in d-dimension

Since we have worked out the essential steps for the derivation of the path integral formulation for the simpler case of 0-dimension, it will not be difficult to generalise it for d-dimensions.

Let the effective hamiltonian for the process be H. Let a_i, $a_i^\dagger$ and $|0\rangle$ denote the annihilation operators , creation operators and vaccum respectively. The subscript i denotes the label for the lattice site.

The resolution of identity (eqn. (5.52)) in terms of coherent states for each lattice is

$$\mathbb{1} = \bigotimes_i \left[\int \frac{d^2\phi_i}{\pi} \, |\phi_i\rangle\langle\phi_i|\right]$$

$$= \int \left(\prod_i \frac{d^2\phi_i}{\pi}\right) |\{\phi\}\rangle\langle\{\phi\}| \tag{5.74}$$

where $|\{\phi\}\rangle = \otimes_i |\phi_i\rangle$.

The path integral expression analogous to eqn. (5.56) for the 0-dimensional case becomes

$$|\psi(t)\rangle = \lim_{\Delta t \to 0} \mathcal{N}^{-1} \int \left(\prod_{\tau=0}^t \prod_i d^2\phi_{i,\tau}\right) |\{\phi\}_t\rangle \left[\prod_{\tau=\Delta t}^t \prod_i \langle\phi_{i,\tau}| \, e^{-H \, \Delta t}|\phi_{i,\tau-\Delta t}\rangle\right] \langle\{\phi\}_0|\psi(0)\rangle \tag{5.75}$$

The operator, $\widehat{O}$, corresponding to an observable $O(\{n\})$ is obtained by replacing n_i by $a_i^\dagger a_i$. The expectation value, eqn. (5.57), is given by

$$\langle O \rangle = \mathcal{N}^{-1} \lim_{\Delta t \to 0} \int \left(\prod_{\tau=0}^{t} \prod_i d^2\phi_{i,\tau} \right) \langle \{1\} | \widehat{O} | \{\phi\}_t \rangle$$

$$\left[\prod_{\tau=\Delta t}^{t} \prod_i \langle \phi_{i,\tau} | e^{-H\,\Delta t} | \phi_{i,\tau-\Delta t} \rangle \right] \langle \{\phi\}_0 | \psi(0) \rangle \quad (5.76)$$

The middle term of the above equation is given by

$$\prod_{\tau=\Delta t}^{t} \prod_i \langle \phi_{i,\tau} | e^{-H\,\Delta t} | \phi_{i,\tau-\Delta t} \rangle = \exp \left\{ \frac{1}{2} \sum_i \left(|\phi_{i,t}|^2 - |\phi_{i,0}|^2 \right) \right\}$$

$$\exp \left\{ - \sum_{\tau=\Delta t}^{t} \left[\sum_i \phi_{i,\tau}^\star \left(\phi_{i,\tau} - \phi_{i,\tau-\Delta t} \right) \right. \right.$$

$$\left. \left. + H\left(\{\phi_\tau^\star\}, \{\phi_{\tau-\Delta t}\} \right)\,\Delta t \right] \right\}$$
$$(5.77)$$

We have made use of eqn. (5.60) to get the above equation.
The first term in eqn. (5.76) is becomes

$$\langle \{1\} | \widehat{O} | \{\phi\}_t \rangle = \langle \{1\} | O(\{\phi\}_t) | \{\phi\}_t \rangle$$

$$= O(\{\phi\}_t)\, \langle \{1\} | \{\phi\}_t \rangle$$

$$= O(\{\phi\}_t)\, \prod_i \exp \left\{ -\frac{1}{2} - \frac{1}{2} |\phi_{i,t}|^2 + \phi_{i,t} \right\}$$

$$\propto O(\{\phi\}_t)\, \exp \left\{ \sum_i \left[-\frac{1}{2} |\phi_{i,t}|^2 + \phi_{i,t} \right] \right\} \quad (5.78)$$

where we have made use of eqn. (5.61).
Assuming the initial distribution to be *Poisson*, we get for the third term in eqn.(5.76)

$$\langle \{\phi\}_0 | \psi(0) \rangle \propto \prod_i \exp \left\{ -\frac{1}{2} |\phi_{i,0}|^2 + \phi_{i,0}^\star\, \bar{n}_0 \right\}$$

$$\propto \exp \left\{ \sum_i \left[-\frac{1}{2} |\phi_{i,0}|^2 + \phi_{i,0}^\star\, \bar{n}_0 \right] \right\} \quad (5.79)$$

where we have used eqn. (5.64).

Substituting eqns. (5.77), (5.78) and (5.79) in eqn. (5.76) and absorbing all the constants in the normalisation constant, we get

$$\langle O \rangle = \mathcal{N}^{-1} \lim_{\Delta t \to 0} \int \left(\prod_{\tau=0}^{t} \prod_i d^2\phi_{i,\tau} \right) O(\{\phi\}_t) \; \exp\left\{ \sum_i \left[\phi_{i,t} - |\phi_{i,0}|^2 + \phi_{i,0}^\star \, \bar{n}_0 \right] \right\}$$
$$\exp\left\{ -\sum_{\tau=\Delta t}^{t} \left[\sum_i \phi_{i,\tau}^\star \left(\phi_{i,\tau} - \phi_{i,\tau-\Delta t} \right) \right.\right.$$
$$\left.\left. + H\left(\{\phi_\tau^\star\}, \{\phi_{\tau-\Delta t}\}\right) \; \Delta t \right] \right\} \tag{5.80}$$

$$= \mathcal{N}^{-1} \int \left(\prod_i \mathcal{D}\phi_i \, \mathcal{D}\phi_i^\star \right) O[\{\phi(t)\}] \; \exp\left\{ \sum_i \left[\phi_i(t) - |\phi_i(0)|^2 + \phi_i^\star(0) \, \bar{n}_0 \right] \right\}$$
$$\exp\left\{ -\int_0^t dt' \left[\sum_i \phi_i^\star(t') \, \frac{\partial \phi_i(t')}{\partial t'} + H\left[\{\phi^\star(t')\}, \{\phi(t')\}\right] \right] \right\} \tag{5.81}$$

$$= \mathcal{N}^{-1} \int \left(\prod_i \mathcal{D}\phi_i \, \mathcal{D}\phi_i^\star \right) O[\{\phi(t)\}] \; \exp\left\{ -S\left[\{\phi^\star\}, \{\phi\}\right]_0^t \right\} \tag{5.82}$$

where

$$S\left[\{\phi^\star\}, \{\phi\}\right]_0^{t_f} = -\sum_i \left[\phi_i(t_f) - |\phi_i(0)|^2 + \phi_i^\star(0) \, \bar{n}_0 \right]$$
$$+ \int_0^{t_f} dt \left[\sum_i \phi_i^\star(t) \, \frac{\partial \phi_i(t)}{\partial t} + H\left[\{\phi^\star(t)\}, \{\phi(t)\}\right] \right]$$

We argued that term containing $\phi(0)$ can be dropped from the action as we don't have $\phi^\star$ for $t < 0$. Hence, we get

$$S\left[\{\phi^\star\}, \{\phi\}\right]_0^{t_f} = -\sum_i \left[\phi_i(t_f) + \phi_i^\star(0) \, \bar{n}_0 \right] + \int_0^{t_f} dt \left[\sum_i \phi_i^\star(t) \, \frac{\partial \phi_i(t)}{\partial t} + H\left[\{\phi^\star(t)\}, \{\phi(t)\}\right] \right]$$

Shifting field $\phi^\star$ to $1 + \bar{\phi}$, we get

$$S\left[\{\bar{\phi}\}, \{\phi\}\right]_0^{t_f} = -\sum_i \left[\phi_i(0) + \{1 + \bar{\phi}_i(0)\} \, \bar{n}_0 \right]$$
$$+ \int_0^{t_f} dt \left[\sum_i \bar{\phi}_i(t) \, \frac{\partial \phi_i(t)}{\partial t} + H\left[\{\bar{\phi}(t)\}, \{\phi(t)\}\right] \right]$$

See eqns. (5.72) and (5.73). Again we can drop the term with $\phi(0)$ and the constant to get

$$S\left[\{\bar{\phi}\}, \{\phi\}\right]_0^{t_f} = -\sum_i \bar{\phi}_i(0)\, \bar{n}_0 + \int_0^{t_f} dt \left[\sum_i \bar{\phi}_i(t)\, \frac{\partial \phi_i(t)}{\partial t} + H\left[\{\bar{\phi}(t)\}, \{\phi(t)\}\right]\right]$$

Continuum Limit

We take the continuum limit by the following scheme

$$\sum_i \to \int \frac{d^d x}{h^d}$$

$$\phi_i(t) \to h^d\, \phi(\vec{x}, t) \tag{5.83}$$

$$\bar{\phi}_i(t) \to \bar{\phi}(\vec{x}, t)$$

where h is the lattice constant.

Let us assume that the stochastic process we are describing consists of the same set of elementary processes at each lattice site and diffusion (i.e. hopping) to nearest neighbours. Let us also assume that the rate constants and the diffusion constants are site independent. Then the full hamiltonian can be split into two parts as following

$$H = H_{diffusion} + H_{reaction}$$

where for a system with one species and diffusion constant D

$$\begin{aligned}
H_{diffusion} &= D \sum_{\langle i,j \rangle} (\bar{\phi}_i - \bar{\phi}_j)(\phi_i - \phi_j) \\
&= D \int \frac{d^d x}{h^d}\, \{h \nabla \bar{\phi}(\vec{x})\} \cdot \{h \nabla \phi(\vec{x})\, h^d\} \qquad \text{[taking continuum limit]} \\
&= D\, h^2 \int d^d x\, \nabla \bar{\phi}(\vec{x}) . \nabla \phi(\vec{x}) \\
&= -D\, h^2 \int d^d x\, \bar{\phi}(\vec{x})\, \nabla^2 \phi(\vec{x}). \tag{5.84}
\end{aligned}$$

where in the last step we have done integration by parts and neglected the boundary terms. The reaction part of the hamiltonian can be written as

$$\begin{aligned}
H_{reaction} &= \sum_i H_i' \\
&= \int \frac{d^d x}{h^d}\, H'(\vec{x})
\end{aligned}$$

where H'_i is the reaction part hamiltonian at i-th lattice site.

Substituting in the expression for the action, we get the action in the continuum limit as

$$
\begin{aligned}
S\left[\bar{\phi}, \phi\right]_0^{t_f} = & -\int \frac{d^d x}{h^d} \; \bar{\phi}(\vec{x}; 0) \; \bar{n}_0 \\
& + \int_0^{t_f} dt \int \frac{d^d x}{h^d} \; \left[\bar{\phi}(\vec{x}; t) \; \frac{\partial \phi(\vec{x}; t)}{\partial t} \; h^d - D \; h^{d+2} \; \bar{\phi}(\vec{x}) \; \nabla^2 \phi(\vec{x}) + H'(\vec{x})\right] \\
= & -\int \frac{d^d x}{h^d} \; \bar{\phi}(\vec{x}; 0) \; \bar{n}_0 \\
& + \int_0^{t_f} dt \int d^d x \; \left[\bar{\phi}(\vec{x}; t) \; \frac{\partial \phi(\vec{x}; t)}{\partial t} - D \; h^2 \; \bar{\phi}(\vec{x}) \; \nabla^2 \phi(\vec{x}) + \frac{1}{h^d} H'(\vec{x})\right]
\end{aligned}
$$

We shall redefine all the constants so as to absorb all the factors of h, after which we get for action

$$
\boxed{S\left[\bar{\phi}, \phi\right]_0^{t_f} = -\int d^d x \; \bar{\phi}(\vec{x}; 0) \; \bar{n}_0 + \int_0^{t_f} dt \int d^d x \left[\bar{\phi}(\vec{x}; t) \; (\partial_t - D \; \nabla^2) \; \phi(\vec{x}; t) + H'(\vec{x})\right]}
$$

(5.85)

5.5.3 Multiple Species Stochastic Process in d-dimension

The action given in eqn. (5.85) can be readily generalised to the case of multiple species. Let us directly write the action of a stochastic process involving multiple species.

$$
\begin{aligned}
S\left[\bar{\phi}_1, \phi_1, \bar{\phi}_2, \phi_2, \cdots\right]_0^{t_f} = & -\int d^d x \; \left[\bar{\phi}_1(\vec{x}; 0) \; \bar{n}_{0,1} + \bar{\phi}_2(\vec{x}; 0) \; \bar{n}_{0,2} + \cdots\right] \\
& + \int_0^{t_f} dt \int d^d x \Big[\bar{\phi}_1(\vec{x}; t) \; (\partial_t - D \; \nabla^2) \; \phi_1(\vec{x}; t) \\
& \qquad\qquad + \bar{\phi}_2(\vec{x}; t) \; (\partial_t - D \; \nabla^2) \; \phi_2(\vec{x}; t) \\
& \qquad\qquad \vdots \\
& \qquad\qquad + H'(\vec{x})\Big]
\end{aligned}
$$

(5.86)

5.6 Effective Action for the Brusselator System in d-dimensions

Using eqns. (5.86) and (5.36), the effective action for the brusselator system is given by

$$
\begin{aligned}
S\left[\bar{\phi}_X, \phi_X, \bar{\phi}_Y, \phi_Y\right]_0^{t_f} = &-\int d^d x \left[\bar{\phi}_X(\vec{x}, 0)\ \bar{n}_X + \bar{\phi}_Y(\vec{x}, 0)\ \bar{n}_Y\right] \\
&+ \int_0^{t_f} dt \int d^d x \Big[\bar{\phi}_X \left(\partial_t - D_X \nabla^2\right) \phi_X \\
&\qquad\qquad + \bar{\phi}_Y \left(\partial_t - D_Y \nabla^2\right) \phi_Y \\
&\qquad\qquad - J_{in}\ \bar{\phi}_X \\
&\qquad\qquad + \frac{\lambda_1}{2} \left(1 + \bar{\phi}_X\right)^2 \left(\bar{\phi}_Y - \bar{\phi}_X\right) \phi_X^2\ \phi_Y \\
&\qquad\qquad + \lambda_2 \left(\bar{\phi}_X - \bar{\phi}_Y\right)\ \phi_X \\
&\qquad\qquad + J_{out}\ \bar{\phi}_X\ \phi_X\Big]
\end{aligned}
\tag{5.87}
$$

This action can be used in a perturbative expansion to calculate the expectation value of any observable.

If the action is linear or quadratic in the $\bar{\phi}$ fields then it is possible to derive the differential equation obeyed by the ϕ fields by integration. But the action for the brusselator system turns out to be cubic in $\bar{\phi}_X$ field. Hence rate equations or mean-field equations can not be derived from this action.

5.7 Summary

- In this chapter, we mapped the master equation to the second quantization formalism.

- We derived the effective hamiltonian and discussed the important differences of the formalism from the usual quantum theory.

- We then derived expressions for the expectation value of the observables.

- We obtained the path integral formalism for the process and derived the expression for effective action.

- The action for the brusselator turned out to be cubic in one of the $\bar{\phi}$ fields, hence the differential equations for ϕ could not be derived by integration.

Chapter 6

Direct Simulation of the Master Equation

In 1976, Daniel T. Gillespie gave an algorithm for direct simulation of the master equation [10, 11]. In this chapter, we briefly describe the algorithm and summarise the result of simulation.

6.1 The Gillespie Algorithm

Step 1: Calculate the rate of each of the elementary steps of the stochastic process. Denote the total rate by r_{total}. Set the time to 0.

Step 2: Increment the time by an amount dt, where dt is drawn from an exponential distribution

$$P(dt) = \frac{1}{r_{total}} \exp(-r_{total} \ dt)$$

This can be done by drawing a random number, η_1, from uniform distribution $(0, 1)$ and putting

$$dt = \frac{1}{r_{total}} \ \ln\left(\frac{1}{\eta_1}\right).$$

Step 3: Call another random number, η_2, between 0 and 1, and choose one of the elementary steps weighted by their individual rates.

Step 4: Perform the elementary step.

Step 5: Update the individual rates and the total rate according to the change.

Step 6: Repeat steps 2 through 5, till the desired time is reached.

This algorithm gives one realisation of the stochastic time evolution of the master equation. Various quantities of interest can be calculated with the time evolution.

6.2   Brusselator System in 0-dimension

The elementary steps for the brusselator system in 0-dimension are given by eqn. (3.1) as following —

$$\phi \xrightarrow{J_{in}} X$$

$$2X + Y \xrightarrow{\lambda_1} 3X$$

$$X \xrightarrow{\lambda_2} Y$$

$$X \xrightarrow{J_{out}} \phi$$
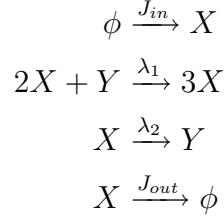
Let r_1, r_2, r_2 and r_4 be the individual rates of the above steps respectively. Then,

$$r_1 = J_{in}$$

$$r_2 = \lambda_1 \begin{pmatrix} X \\ 2 \end{pmatrix} Y$$

$$= \frac{\lambda_1 \; X \; (X - 1) \; Y}{2}$$

$$r_3 = \lambda_2 \; X$$

$$r_4 = J_{out} \; X$$

where X and Y are the no. of X and Y species respectively.

6.3   Results of Simulation

We start off by setting the time scale for the simulation. This we have achieved by setting $J_{out} = 0.1$. Then we varied various parameters and looked at the time evolution.

From fig. (6.1) to fig. (6.6), we choose $\lambda_1 = 0.01$ and $J_{in} = 7.0$. According to eqn. (3.6), the critical value of λ_2 for which transition occurs is

$$\lambda_{2c} = J_{out} + \frac{\lambda_1}{2} \left(\frac{J_{in}}{J_{out}} \right)^2 \tag{6.1}$$

$$= 0.1 + \frac{0.01}{2} \left(\frac{7.0}{0.1} \right)^2$$

$$= 24.6 \tag{6.2}$$

Note the factor of 2 with λ_1, which is because of difference between reaction rates in the rate equation [eqn. (3.2)]and the master equation [eqn. (4.2)].

In the background of stochastic noise, one finds fixed point [fig. (6.1)] and limit cycle [fig. (6.3)]. But the transition is not sharp as predicted by the mean-field analysis. Rather we find a long region of intermittent behaviour [fig. (6.2)] during the transition from fixed point to limit cycle.
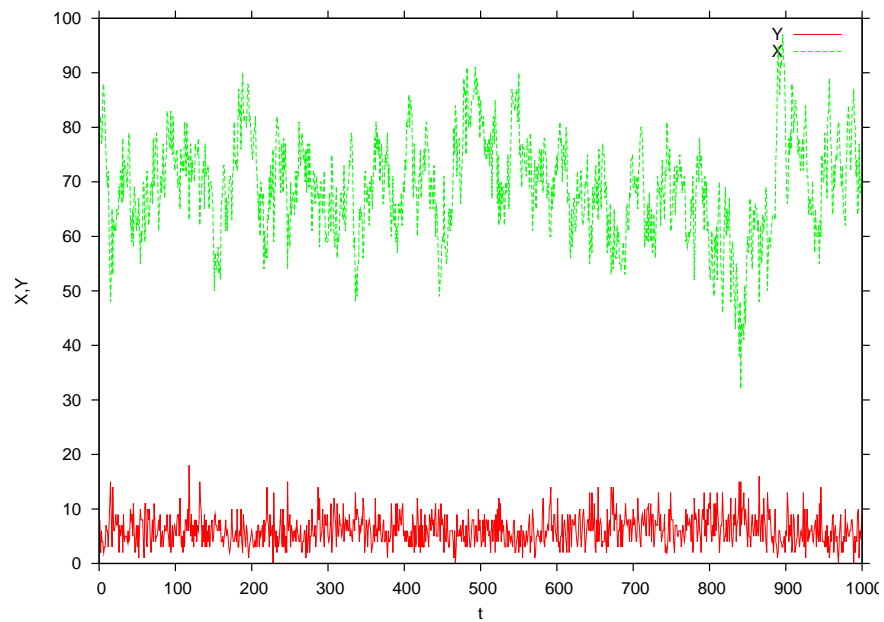
Figure 6.1: Time evolution corresponding to a fixed point. Parameter set: $\lambda_1 = 0.01$, $\lambda_2 = 2$, $J_{in} = 7.0$, $J_{out} = 0.1$
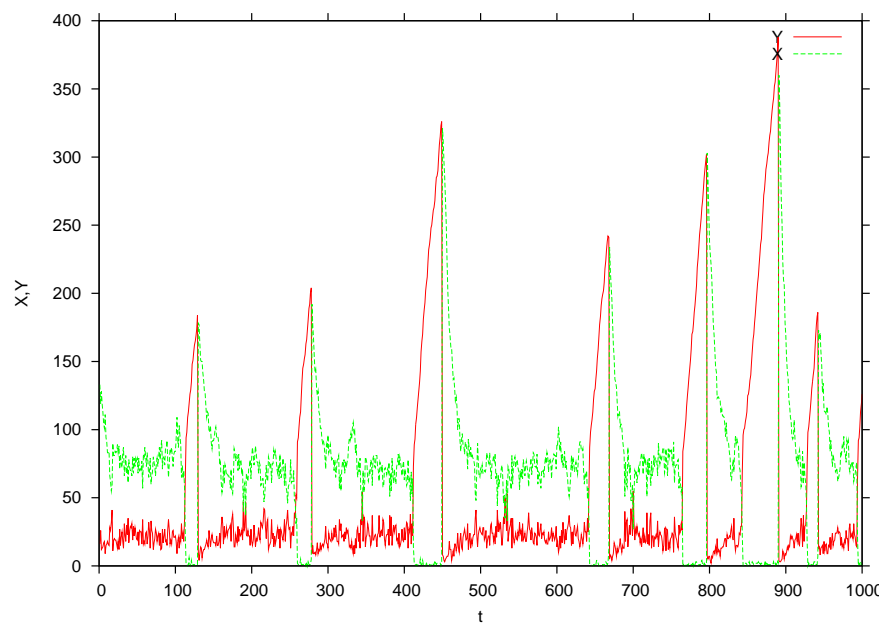
Figure 6.2: Time evolution corresponding to intermittent behaviour. Parameter set: $\lambda_1 = 0.01$, $\lambda_2 = 8$, $J_{in} = 7.0$, $J_{out} = 0.1$
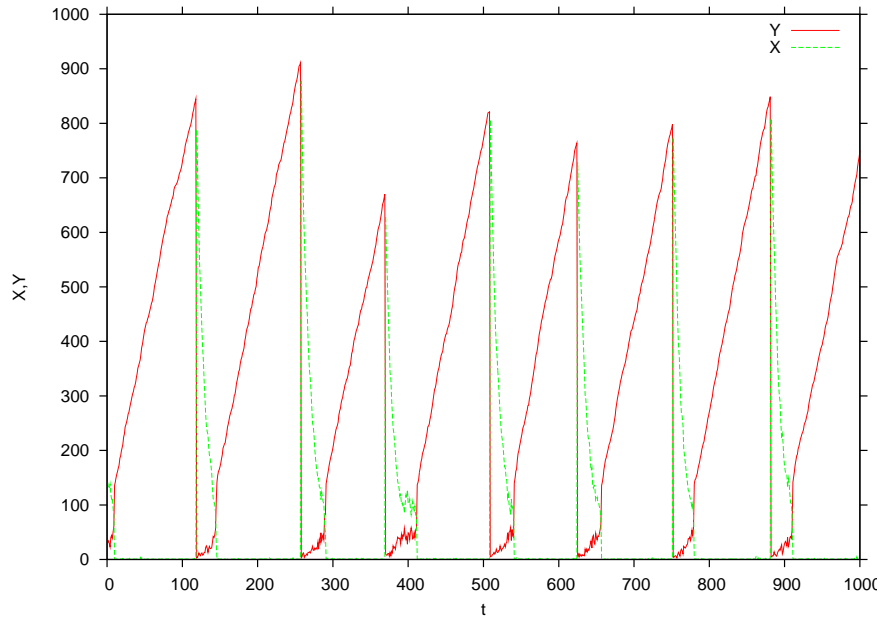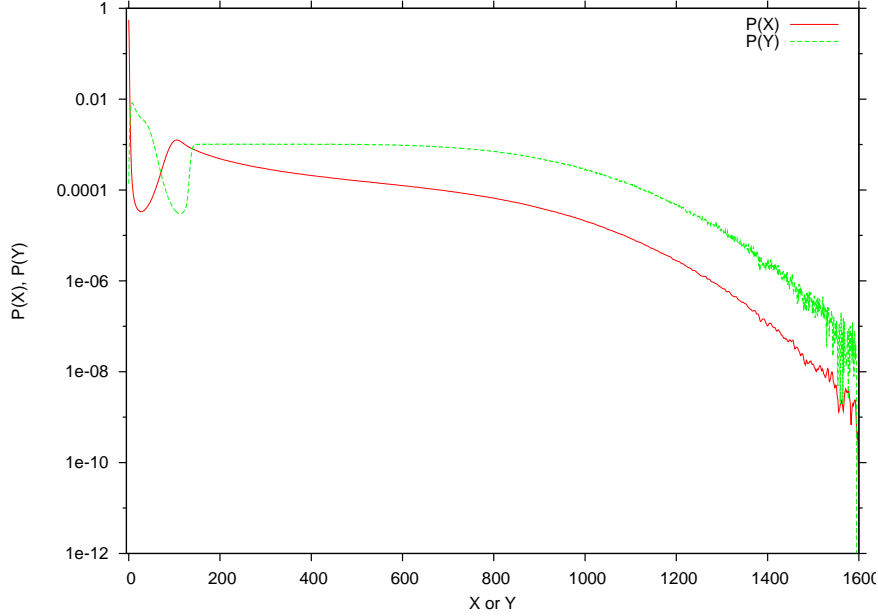
Figure 6.3: Time evolution corresponding to limit cycle. Parameter set: $\lambda_1 = 0.01$, $\lambda_2 = 22$, $J_{in} = 7.0$, $J_{out} = 0.1$

We calculate the probability for different values of X and Y by measuring the time spent at the values [figs. (6.4), (6.5) and (6.6)]. We observe a qualitative change in the probability distribution. For the fixed point [fig. (6.4)] the probability has a maxima at the classical values of the fixed point given by eqn. (3.3a) and (3.3b). The maxima for $P(X)$ gradually shifts at $X = 0$, whereas $P(Y)$ develops a plateau [figs. (6.5) and (6.6)].
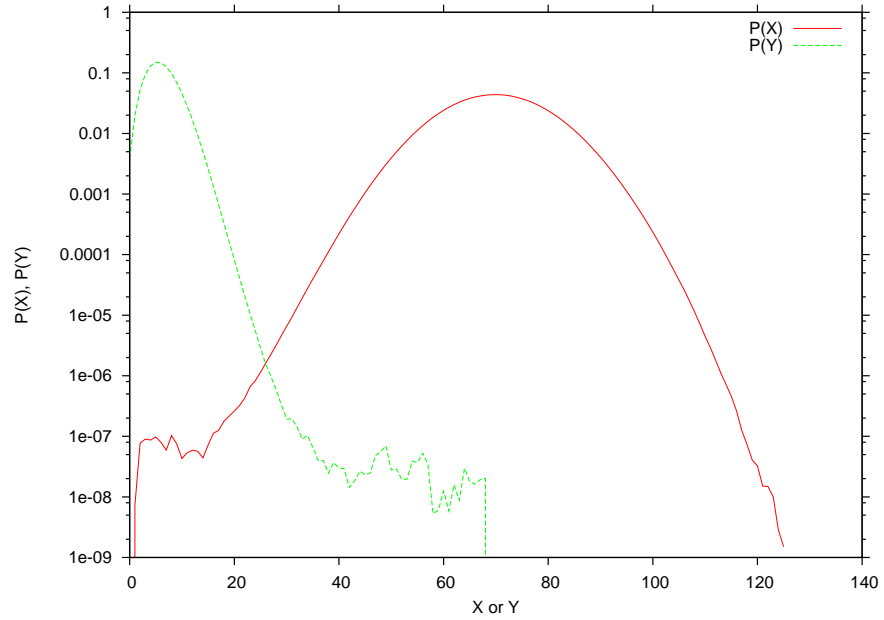
Figure 6.4: Probabilities corresponding to a fixed point. Parameter set: $\lambda_1 = 0.01$, $\lambda_2 = 2$, $J_{in} = 7.0$, $J_{out} = 0.1$
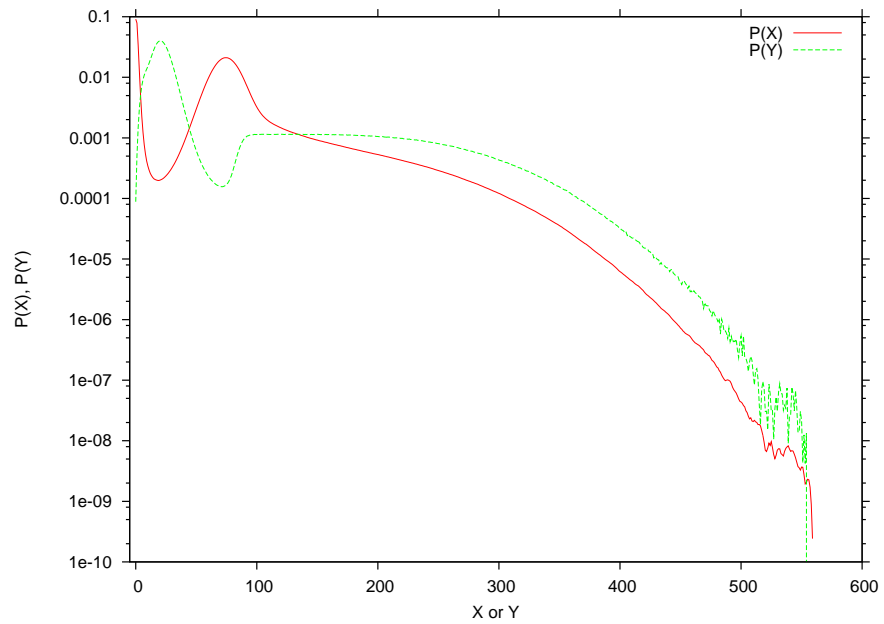
Figure 6.5: Probabilities corresponding to intermittent behaviour. Parameter set: $\lambda_1 = 0.01$, $\lambda_2 = 8$, $J_{in} = 7.0$, $J_{out} = 0.1$

Figure 6.6: Probabilities corresponding to limit cycle. Parameter set: $\lambda_1 = 0.01$, $\lambda_2 = 22$, $J_{in} = 7.0$, $J_{out} = 0.1$

In order to characterise the phase transition, we take λ_2 to be the control variable and define a number of order parameters as following:

No. of spikes : X becomes much larger than its mean for a short time during the intermittent behaviour and limit cycle. This is seen as a spike in the time series of X and Y. During the time evolution we count the number of times the spike is seen.

$\mathbf{P}(X = 0)$ **:** During the time evolution we directly measure the probability of X taking the value 0.

$\mathbf{P}(X = 1)$ **:** During the time evolution we directly measure the probability of X taking the value 1.

$\mathbf{X}_{mean}$ **:** During the time evolution we directly measure the mean value of X.

$\mathbf{X}_{var}$ **:** During the time evolution we directly measure the variance in the value of X.

$\mathbf{T}_{mean}$ **:** Time interval between each spike is called period, denoted by T. We calculate the mean of the period during the time evolution.

$\mathbf{T}_{var}$ **:** This is the variance in the period (defined above).

$(X_{max})_{mean}$ **:** At each spike X takes a peak value. We call this value as X_{max}. The mean of this value is calculated.

$(X_{max})_{var}$ **:** This is the variance in the peak value of X at each spike.

$\mathbf{d}T_{mean}$ **:** Just before X takes its peak value, it remains close to zero for some time. During each cycle, the time X spends close to zero is denoted by dT. To determine this value we use a cutoff in X. The mean of this value is measured during the time evolution.

$\mathbf{d}T_{var}$ **:** This is the variance of the time X spends near zero in each cycle.

We find the value of each of the order parameter mentioned above for various system sizes. We define the system size to be the mean value of X. Since we have fixed J_{out} to set the time scale, we change J_{in} to change the system size. For sake of comparison, we keep the value of λ_{2c} given by eqn. (6.1) fixed. This we achieve by choosing λ_1 suitably. We have chosen six values of X_{mean}. The following table gives the values of the parameters used for the simulation:

Table 6.1: Values of parameters used for simulation

$\mathbf{J}_{in}$	$\mathbf{J}_{out}$	λ_1	λ_{2c}	$\mathbf{X}_{mean}$
7.0	0.1	0.01	24.6	70
15.0	0.1	0.002178	24.6025	150
30.0	0.1	0.000544	24.58	300
60.0	0.1	0.0001361	24.598	600
120.0	0.1	0.0000340278	24.6	1200
240.0	0.1	0.00000850694	24.6	2400

All the order parameter mentioned above are plotted with the control variable in the remaining figures below.
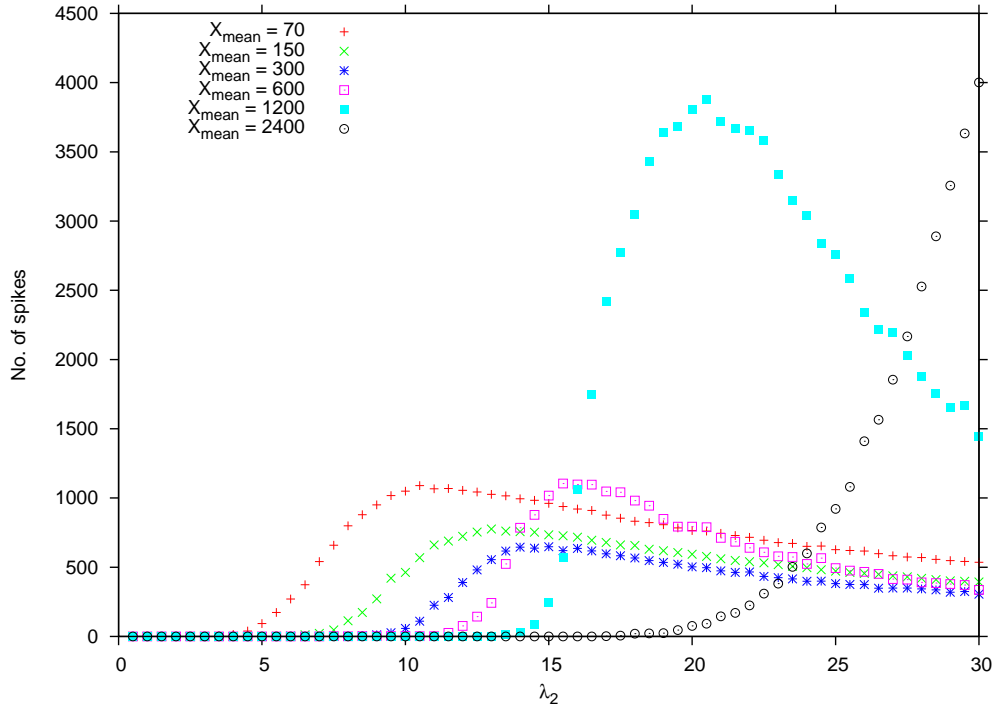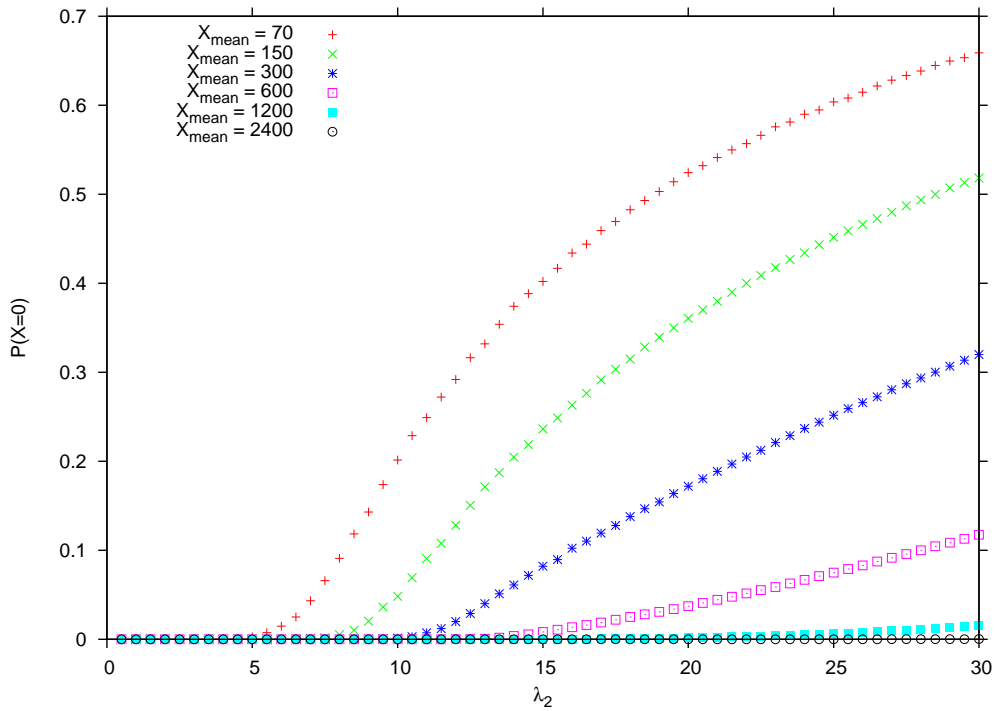
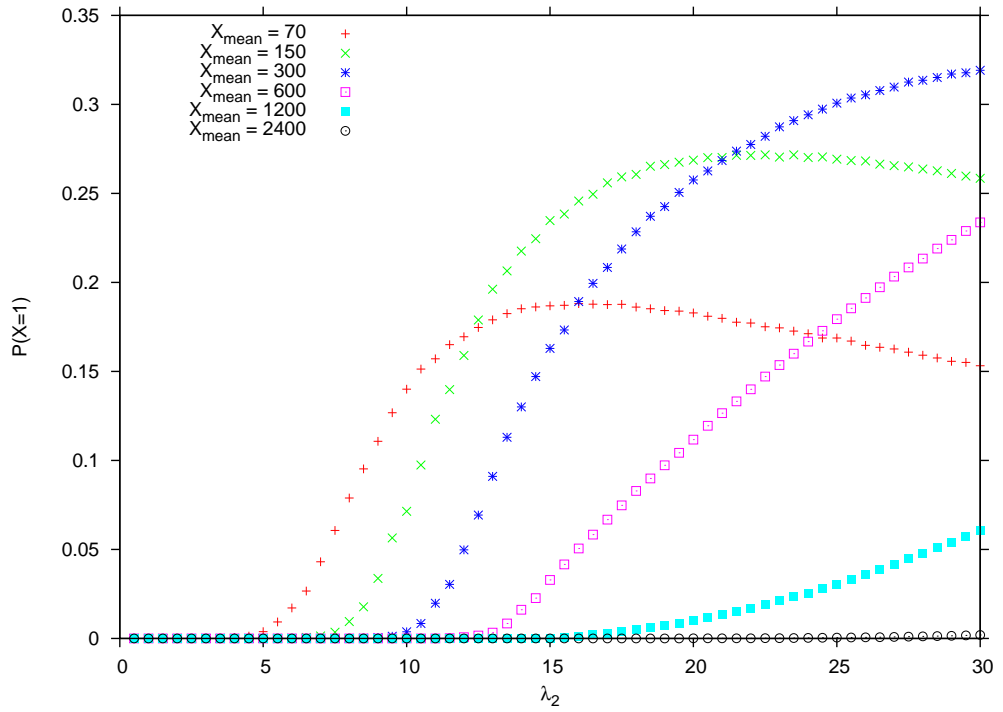Figure 6.7: No. of spikes vs. λ_2

Figure 6.8: $P(X = 0)$ vs. λ_2

Figure 6.9: $P(X = 1)$ vs. λ_2
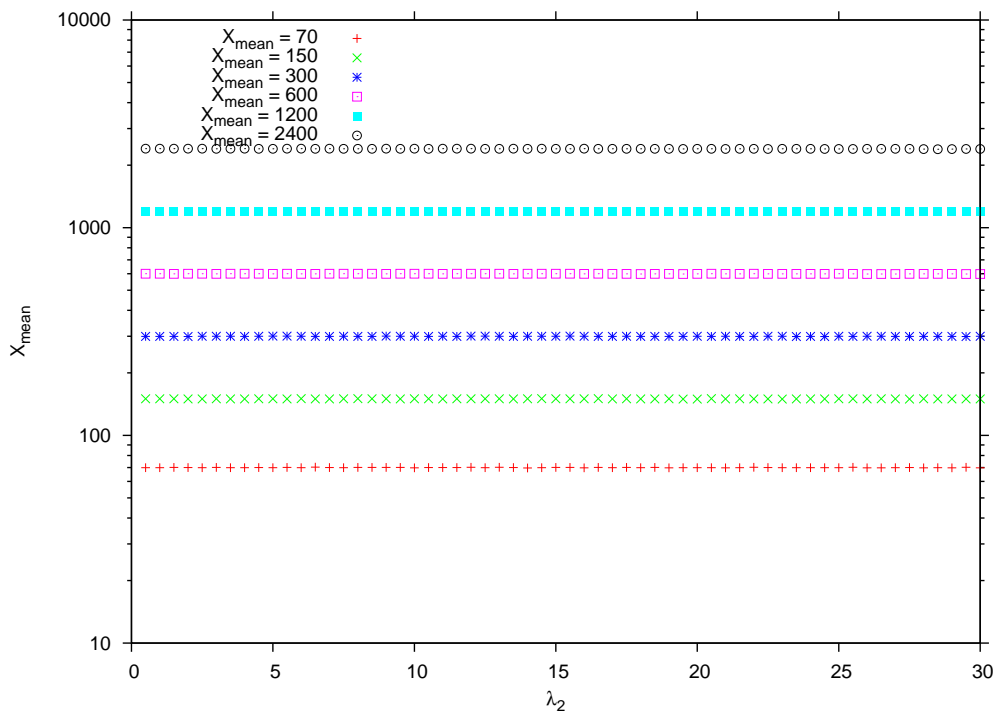
Figure 6.10: X_{mean} vs. λ_2
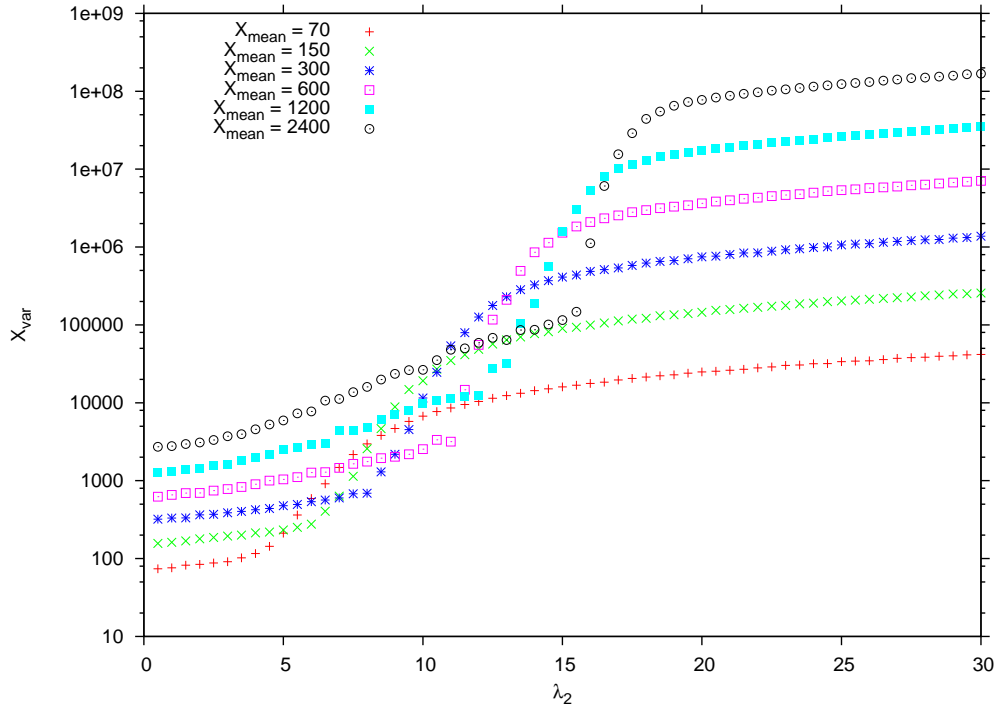
Figure 6.11: X_{var} vs. λ_2
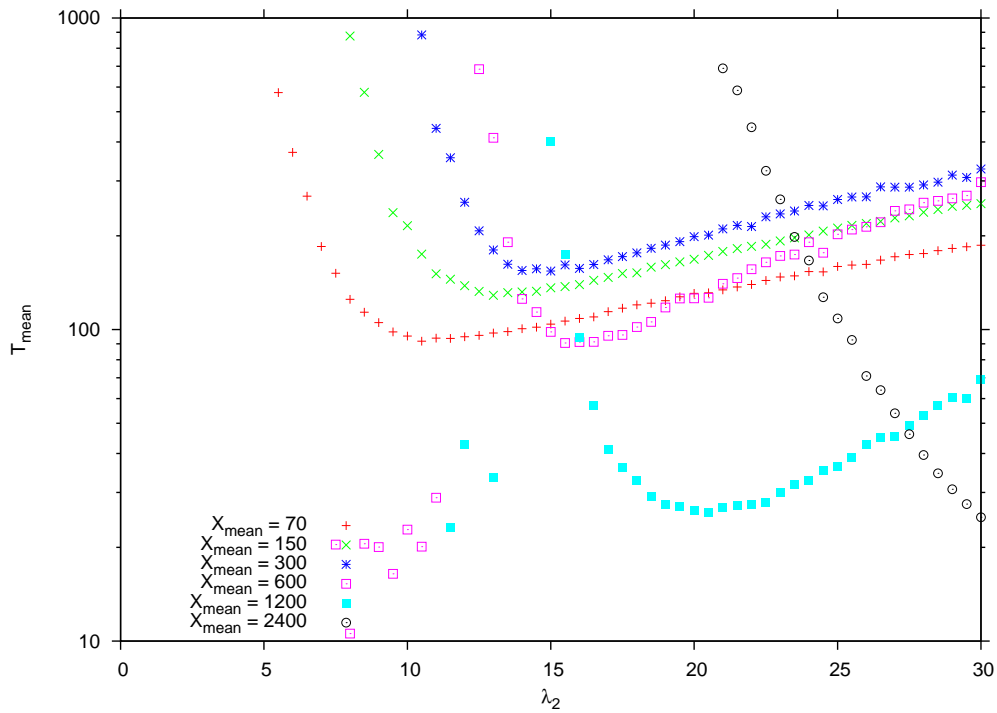
Figure 6.12: T_{mean} vs. λ_2
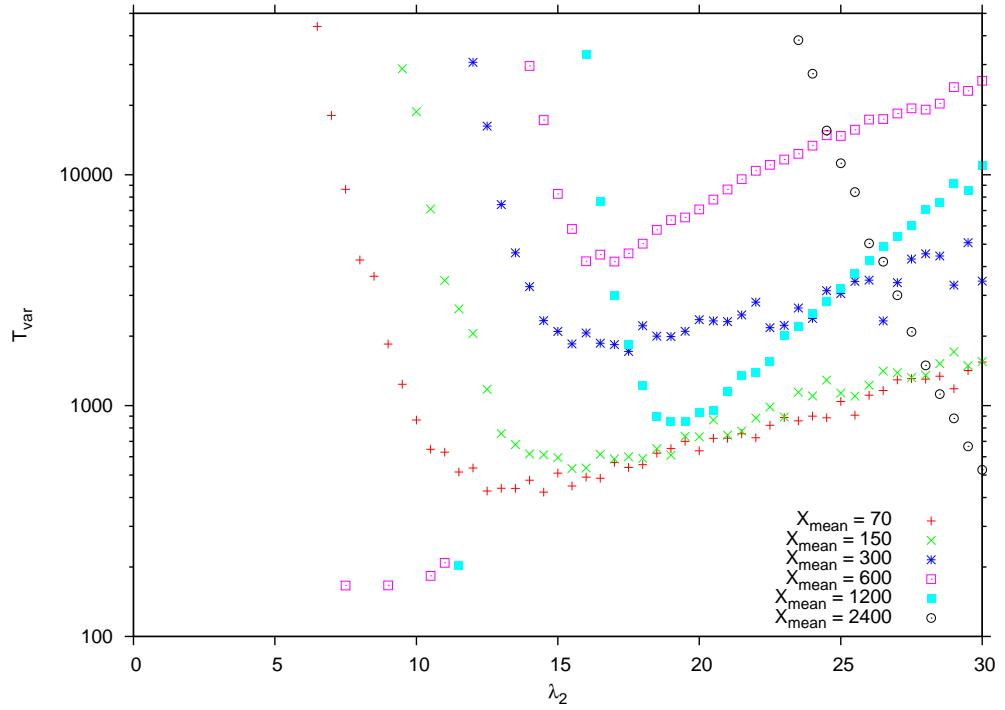
Figure 6.13: T_{var} vs. λ_2
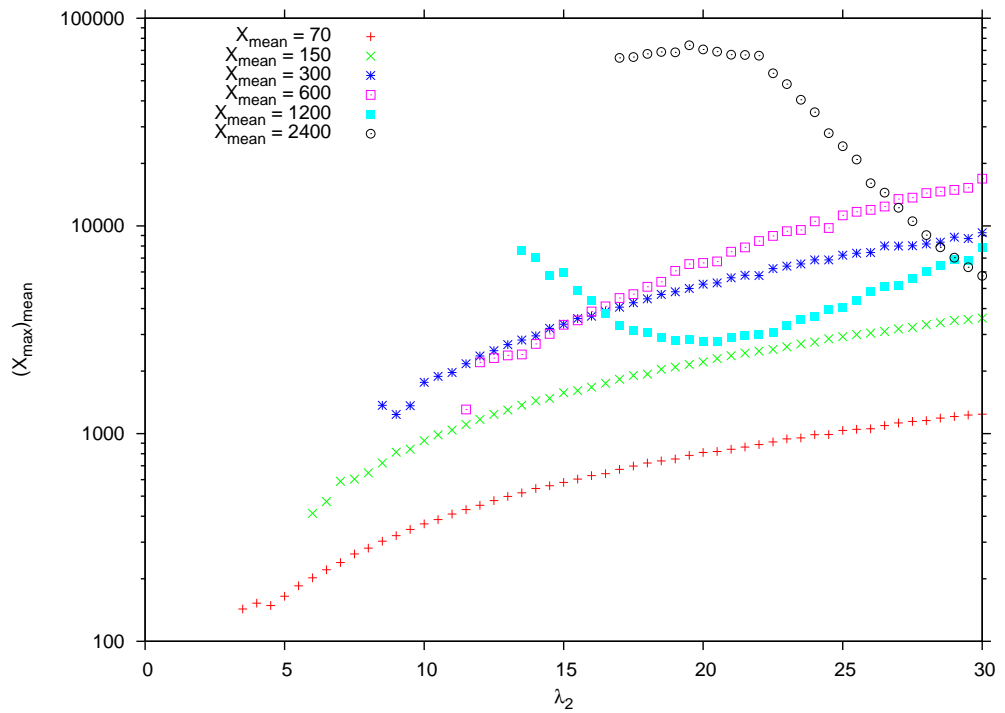
Figure 6.14: $(X_{max})_{mean}$ vs. λ_2
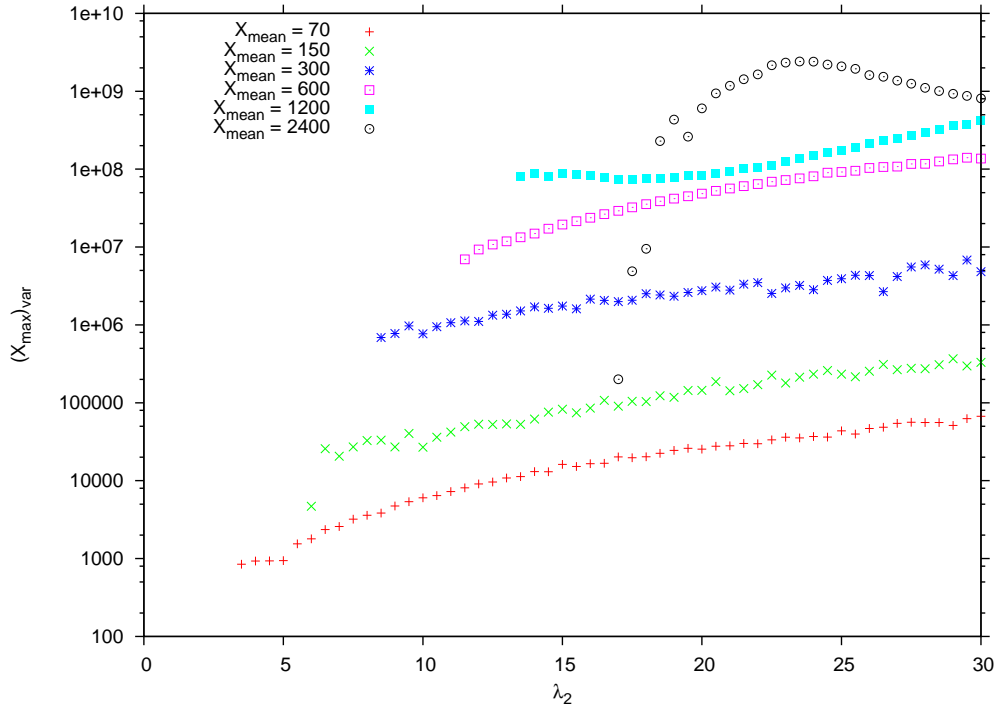
Figure 6.15: $(X_{max})_{var}$ vs. λ_2
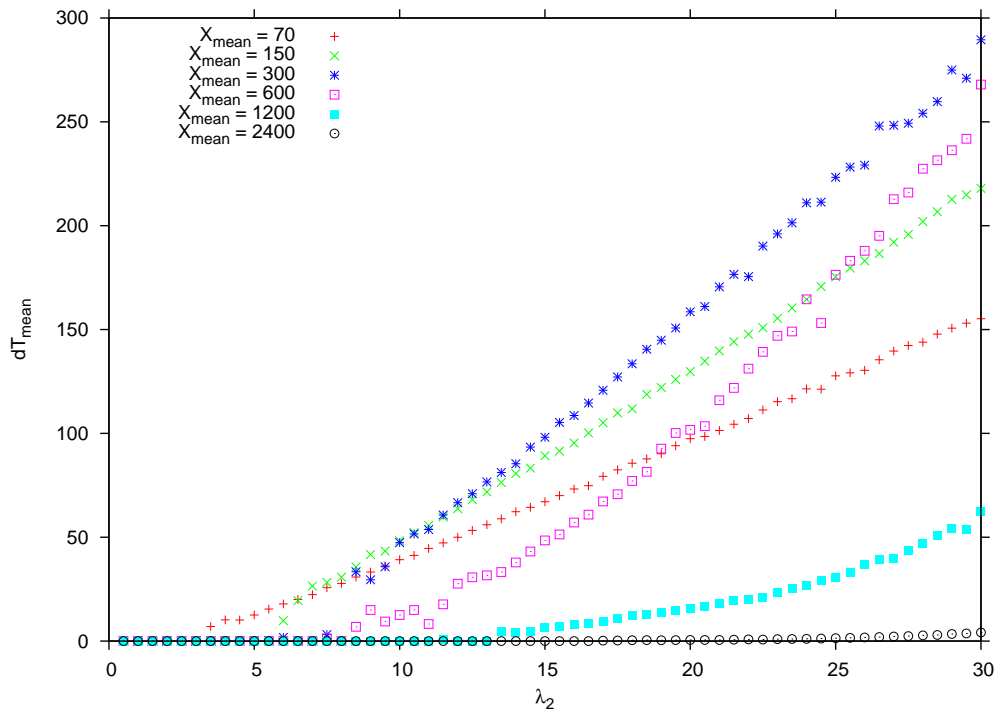
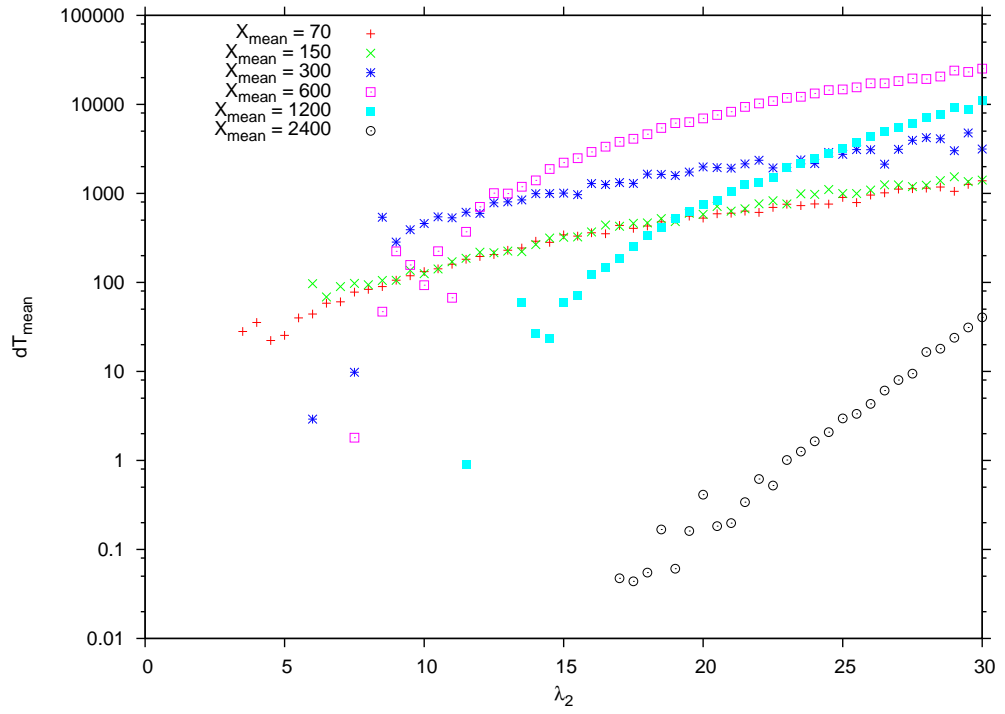Figure 6.16: dT_{mean} vs. λ_2

Figure 6.17: dT_{var} vs. λ_2

Chapter 7

Conclusions and Future Directions

7.1 Conclusions

- Mean field explains fixed point and periodic oscillations but is deterministic and cannot explain other rich behaviour observed.

- The second quantized formalism for the brusselator systems is developed, and effective hamiltonian and effective action for the system are derived.

- It is not possible to derive the differential equation for the field by integration, for the brusselator system.

- Unlike mean-field case, the transition from fixed point to limit cycle is through intermittent behaviour.

7.2 Future Directions

Further studies for a correct description of the phase transition in the brusselator model is a possible direction. Simulations of spatially extended system should be done and compared to the mean-field equations. It is expected to have a very rich behaviour.

Similar study for another model, namely Oregonator should be done because it is made from careful analysis of experiments. Brusselator on the other hand is a minimal mathematical model.

Study of non-linearities in chemical systems has been an active area of research and continues to be so. Under them, starting from the microscopic description remains to be an important goal of non-equilibrium statistical mechanics.

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