SMALL FLUCTUATIONS AT THE UNSTABLE

STEADY STATE

Ъy

Marc Mangel

B.S., University of Illinois, 1971M.S., University of Illinois, 1972

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

in the Institute of Applied Mathematics

and

Statistics

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

November, 1977



In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Mathematics Department of

The University of British Columbia 2075 Wesbrook Place Vancouver, Canada V6T 1W5

Date Nor 8, 1977

Small Fluctuations at the Unstable Steady State

Abstract

The effects of small random fluctuations on deterministic systems are studied. The deterministic systems of interest have multiple steady states. As parameters vary, two or three of the steady states coalesce. This work is concerned with the long time behavior of the system, when the system starts near an unstable steady state. The deterministic separatrix is surrounded by a tube that contains up to two stable steady states. The quantity of basic interest is the probability of first exit from the tube through a specified boundary, conditioned on initial position. In the diffusion approximation this probability satisfies a backward diffusion equation. Formal asymptotic solutions of the backward equation are constructed. The solutions are obtained by a generalized "ray method" and are given in terms of various incomplete special functions. As an example, the effects of fluctuations on a substrate inhibited reaction in an open vessel are analyzed. The theory is compared with exact solutions, for a one dimensional model; and Monte Carlo experiments, for a two dimensional model.

Table of Contents

Section	Title	Pages
	Introduction and Summary of Results	. 1
Chapter 1	Stochastic Macrovariables with Coalescing Steady States	. 10
1	Fluctuations and Systems with Multiple Steady States	. 10
2	Spontaneous Generation of Optical Activity: The Importance of Fluctuations at the Unstable Steady State	. 15
3	Birth and Death Approach to Chemical Kinetics	. 19
. 4	Stochastic Kinetic Equations, Backward Equation and First Exit Problem	. 22
5 5.1 5.2 5.3	Three Canonical Integrals	 27 28 30 32
Chapter 2	Asymptotic Solution of the First Exit Problem in the Normal Case	. 35
6	Normal Type Dynamical Systems	. 35
7	The Asymptotic Solution	. 36
8 8.1 8.2 8.3 9	Determination of ψ and g^0 : Contours of Probability	 . 37 . 37 . 40 . 42 . 42
Chapter 3	Asymptotic Solution of the First Exit Problem in the Marginal Case	. 44
10	Marginal Type Dynamical Systems	. 44
$\begin{array}{c} 11\\ 11.1\\ 11.2 \end{array}$	The Asymptotic Solution Breakdown of the Error Approximation Uniform Solution in Terms of the Airy Integral	. 46 . 46 . 46
12	Evaluation of the parameter $\alpha_0 \cdots \cdots \cdots \cdots \cdots$. 48
13	Determination of ψ and g ⁰ : Contours of Probabili	ty 50
14	Completion of the First Term	. 51

Chapter 4	Asymptotic Solution of the First Exit Problemin the Critical Case	53
15	Critical Type Dynamical Systems	53
16 16.1 16.2	The Asymptotic Solution	55 55 56
17	Determination of the Parameters	58
18	Determination of ψ and g ⁰ : Contours of Probability.	59
19	Completion of the First Term	60
20	Two Complex Steady States	62
Chapter 5	Fluctuation Effects on Substrate Inhibited Reactions \cdot	64
21 21.1 21.2	Multiple Steady States in an Enzyme ReactionDeterministic Kinetic Equations	64 64 67
. 22	Exact and Asymptotic Solutions • • • • • • • • • • • •	71
23	Comparison of the theory with Monte Carlo Experiments \cdot	81
Bibliography		96
Appendices		101
А	Solution of the Initial Value Problem for h^0	101
В	Regularity of Higher Order Terms in the Expansion	104
С	Asymptotic Solution of the Expected Time Equation	107
D	Regularity at the Marginal Bifurcation •••••••	113
Е	Regularity at the Critical Bifurcation \ldots	118
F	Existence of Solutions of the General Eikonal Equation	123

List of Tables

Number	Title	Pa	ige
I	Exact and Asymptotic Solutions in the Normal Case \cdot	•	74
II	Exact and Asymptotic Solutions in the Marginal Case	•	75
III	Exact and Asymptotic Solutions in the Critical Case	•	77
IV	Exact and Asymptotic Solutions in the Critical Bifurcation ••••••••••••••••••••••••••••••••••••	•	78
V	Exact and Asymptotic Solutions in the Case of Two Complex Steady States ••••••••••••••••••••••••••••••••••••		80
VI	Comparison of the theory and experiment in the Normal Case ••••••••••••••••••••••••••••••••••••	•	83
VII	Comparison of the theory and experiment in the Marginal Case ••••••••••••••••••••••••••••••••••••	•	86
VIII	Comparison of the theory and experiment in the Marginal Bifurcation ••••••••••••••••••••••••••••••••••••	•	89
IX	Comparison of the theory and experiment in the Critical Case ••••••••••••••••••••••••••••••••••••	•	92
Х	Comparison of the theory and experiment in the Critical Bifurcation ••••••••••••••••••••••••••••••••••••	•	95

List of Figures

Number	Title	Page
1	Normal Case	4
2	Marginal Case and Bifurcation	6
3	Critical Case and Bifurcation •••••••••	8
4	The First Exit Problem ••••••••••••••••••••••••••••••••••••	14
5	Binaphthyl Model ••••••••••••••••••••••••••••••••••••	18
6	Normal Type Dynamical System ••••••••••••••••••••••••••••••••••••	35
7	Marginal Type Dynamical System •••••••••••	45
8	Critical Type Dynamical System ••••••••••	54
9	Deterministic Phase Portrait and First Exit Boundaries in the Normal Case ••••••••••••	82
10	Deterministic Phase Portrait and First Exit Boundaries in the Marginal Case •••••••••••	85
11	Deterministic Phase Portrait and First Exit Boundaries in the Marginal Bifurcation ••••••	88
12	Deterministic Phase Portrait and First Exit Boundaries in the Critical Case •••••••••	91
13	Deterministic Phase Portrait and First Exit Boundaries in the Critical Bifurcation ••••••	94

Acknowledgements

I have been very fortunate to work with Professor Donald Ludwig, whose knowledge, advice and encouragement were a great help to me. Professor Neil Fenichel helped me understand the dynamical systems studied in this work. For other useful discussions, I thank Professors Robert Burgess (deceased), Robert Snider and Mr. Davis Cope.

This thesis is dedicated to Susan Mangel.

=12

Introduction and Summary of Results

In this section we formulate the problem of small fluctuations at the unstable steady state. Examples of natural systems which fit into this framework are given. Finally, we summarize the results obtained in the rest of the work. This section can be read independent of the remaining sections.

The evolution of natural systems is often described by a deterministic differential equation:

$$\dot{x}^{i} = b^{i}(x,\eta,\delta) \qquad x^{i}(0) = x_{0}^{i} \qquad i = 1,...,n$$
 (1)

In equation (1), η and δ are parameters. A steady state is characterized by $b^{i}(x,\eta,\delta) = 0$, i = 1,...,n. If $b(x,\eta,\delta)$ is nonlinear, the system may possess multiple steady states. As the parameters η and δ vary, it is possible that the steady states coalesce and annihilate each other, or exchange stability.

Equation (1) provides only an approximate description of the evolution of the system. In particular, it ignores fluctuations that are inherent to all natural systems. If the system has multiple stable steady states (P_0, P_2) , fluctuations may drive the system against the deterministic flow so that $P_0(P_2)$ is reached from an initial point which deterministically is attracted to $P_2(P_0)$. In this case, the quantity of basic interest is the probability of a specified outcome, conditioned on the initial data. In this work, the behavior of the conditional probability is determined by solving the diffusion equation that it satisfies, for the case of noise of

small intensity.

Many physical, chemical and biological systems fit into the framework of fluctuations superposed on a deterministic differential equation. Examples are: 1) Lasers, in which fluctuations are caused by the quantum nature of radiation (Graham, 1974). 2) Tunnel diode circuits may exhibit multiple steady states. Fluctuations are caused by the random motion of electrons (Landauer and Woo, 1972). 3) The mean field ferromagnet exhibits multiple steady states below the critical temperature (Griffiths et. al., 1967, Goldstein and Scully, 1973). 4) Isomerization, autocatalytic, chain and substrate inhibited reactions in open vessels may exhibit multiple steady states (Perlmutter, 1972; Higgins, 1967). Fluctuations are caused by the random motion of the molecules, which may lead to a birth and death description of the reaction process. 5) Membranes may exhibit states of high and low conductivity, separated by a threshold (e.g. Lecar and Nossal, 1971a,b). 6) The equations used in theoretical ecology may exhibit multiple steady states (Bazekin, 1975). Fluctuations are caused by the elementary birth and death processes. The theory developed in this work is applicable to all of the above systems. As examples, we discuss autocatalytic reactions (§2) and substrate inhibited reactions (§21). The discussion uses chemical terminology, but the results are equally applicable to physics and biology.

This work is concerned with the effects of fluctuations on systems initially in the vicinity of an unstable steady state. We assume that the unstable steady state is a saddle point, so that a deterministic separatrix exists. The separatrix divides the phase plane into two domains of attraction of the stable steady states. In Chapter 1, we show how the deterministic equation (1) is modified to include fluctuations. Experiments on the spontaneous resolution of optical activity are discussed, as an example of the effects of fluctuations on systems with multiple steady states (§2). In order to include fluctuations, the kinetic equation is reinterpreted in terms of a birth and death process (§3). This leads to a stochastic kinetic equation for the random variable $\tilde{x}_{\alpha}(t)$:

$$\frac{d\tilde{x}^{i}}{dt} = b^{i}(\tilde{x}_{\alpha}) + \frac{\sqrt{\varepsilon} f^{i}_{j}(\tilde{x}_{\alpha})}{\alpha} \tilde{Y}^{j}(t/\alpha^{2}), \qquad (2)$$

where Y(s) is a stationary, mixing process, α is a parameter and $\sqrt{\epsilon}$ f can be interpreted in terms of averages of increments of \tilde{x}_{α} (§4). The parameter ϵ , assumed to be small, is related to the size of the system (§1, 21). Equation (2) is treated by using the diffusion approximation. As $\alpha \to 0$, $\tilde{x}_{\alpha} \to \tilde{x}$, where $\tilde{x}(t)$ is a diffusion process. If $u(t,x) = E\{u_0(\tilde{x}(t)) | \tilde{x}(0) = x\}$, then u satisfies the backward equation (§4)

$$u_{t} = \frac{\varepsilon a^{ij}}{2} u_{ij} + b^{i} u_{i} + \varepsilon c^{i} u_{i}$$
(3)

In equation (3), subscripts indicate differentiation and repeated indices are summed from 1 to n. Equation (3) must be supplemented with boundary conditions. The separatrix is surrounded by a tube, with boundaries I, II. If u = 0 on I and u = 1 on II (Fig. 1), then the time invariant solution of (3) is the probability that the process \tilde{x} first exits from the tube around the separatrix through boundary II, given that $\tilde{x}(0) = x$. Asymptotic solutions of (3) are constructed. The method of solution is a generalization of the ray method of Luneberg (1948) and Keller (1958). The ray method uses a formal asymptotic technique to convert the second order boundary value problem for u(x) to a first order initial value problem for a function $\psi(x)$. The first order problem can be treated by the method of characteristics (§5).

The form of the asymptotic solution depends upon the deterministic system (§5). In the normal case, the three steady states are well separated and only the unstable steady state is contained by the separatrix tube (Fig. 1).



Fig. 1 Normal Case

The asymptotic solution of the time invariant backward equation is:

$$u(\mathbf{x}) = \sum_{n=0}^{\infty} \varepsilon^{n} g^{n}(\mathbf{x}) E(\psi(\mathbf{x})/\sqrt{\varepsilon}) + \varepsilon^{n+\frac{1}{2}} h^{n}(\mathbf{x}) E'(\psi(\mathbf{x})/\sqrt{\varepsilon}) , \qquad (4)$$

where E is the error function: E''(z) = -zE'(z). The functions $\psi(x)$, $g^{n}(x)$ and $h^{n}(x)$ are to be determined (§7). The form of (4) is suggested by the asymptotic expansion of a simpler problem (§5). The function $\psi(x)$ must satisfy

$$b^{i}\psi_{i} - \frac{a^{ij}}{2} \psi_{i}\psi_{j}\psi = 0 .$$
 (5)

By using Hamilton-Jacobi theory, we show that $\psi(\mathbf{x})$ is constant on the deterministic separatrix (§8). The derivatives of ψ are calculated on the separatrix. Thus, in a vicinity of the separatrix $\psi(\mathbf{x})$ can be calculated by a Taylor expansion. We show that g^0 is a constant (§8). The value of g^0 is chosen so that the boundary conditions are satisfied. Once ψ and g^0 are known, the leading part of the asymptotic solution,

$$u(\mathbf{x}) \sim g^{0} E(\psi(\mathbf{x})/\sqrt{\varepsilon}) + O(\sqrt{\varepsilon})$$
(6)

can be used to generate contours of equal probability in the plane (§8.3). The function $h^{0}(x)$ can be evaluated everywhere in the phase plane (§9 and Appendix A). Higher order terms are treated in an analogous fashion (Appendix B).

In the marginal case (§10), two steady states are contained by the separatrix tube (Fig. 2a). As one parameter varies, the two



Fig. 2 Marginal Case (a) and Bifurcation (b)

steady states coalesce and annihilate each other. The detailed properties of such a deterministic system are given in §10. The uniform asymptotic solution of the time independent backward equation is (§11)

$$u(x) = \sum \varepsilon^{n} A(\psi/\varepsilon^{1/3}, \alpha/\varepsilon^{2/3}) g^{n}(x) + \varepsilon^{n+2/3} A'(\psi/\varepsilon^{1/3}, \alpha/\varepsilon^{2/3}) h^{n}(x)$$
(7)

where A is the incomplete Airy integral: $A''(z,\beta) = -(z^2-\beta)A'$,

6

and $\alpha = \sum \alpha_k \varepsilon^k$. The form of (7) is suggested by the asymptotic analysis of a simpler problem (§5). The function $\psi(x)$ and parameter α_0 must be determined to satisfy:

$$b^{i}\psi_{i} - \frac{a^{ij}}{2}\psi_{i}\psi_{j} (\psi^{2} - \alpha_{0}) = 0 .$$
 (8)

Using Hamilton-Jacobi theory, we show that ψ is constant on the separatrix (§12). The parameter α_0 is determined by using the method of characteristics (§12). The function ψ and constant g^0 are evaluated as in the previous case (§13). Once ψ , α_0 and g^0 are known, the leading part of the asymptotic expansion:

$$u(x) \sim g^{0}A(\psi(x)/\epsilon^{1/3}, \alpha_{0}/\epsilon^{2/3}) + O(\epsilon^{2/3})$$
 (9)

can be used to generate contours of equal probability (§13). The function h^0 can be calculated everywhere in the phase plane (§14 and Appendix A). Higher order terms are treated in an analogous fashion (Appendix B).

In Appendix D, we show that all of the constructions are regular at the marginal bifurcation. At the bifurcation point, of more interest than u(x) is

$$T(x) = E\{\text{time for } \tilde{x}(t) \text{ to hit II} | \tilde{x}(0) = x, \tilde{x}(t) \text{ hits II} \}$$
(10)

In §4, we show that

$$\frac{\varepsilon a^{ij}}{2} T_{ij} + b^{i}T_{i} + \varepsilon c^{i}T_{i} = -1 \qquad (11)$$

The asymptotic solution of (11) is constructed in Appendix C. The

solution involves a special function similar to $A(z,\alpha)$, but satisfying an inhomogeneous differential equation.

In the critical case, three steady states are contained by the separatrix tube (Fig.3). As n, δ vary the steady states coalesce into one stable steady state.



Fig.3. Critical Case (a) and Critical Bifurcation (b)

The detailed properties of a critical type dynamical system are given in §15. The asymptotic solution of the time independent backward equation is

$$u(\mathbf{x}) = \sum \varepsilon^{n} g^{n}(\mathbf{x}) P(\psi/\varepsilon^{1/4}, \alpha/\varepsilon^{1/2}, \beta/\varepsilon^{3/4})$$

$$+ \varepsilon^{n+3/4} h^{n}(\mathbf{x}) P'(\psi/\varepsilon^{1/4}, \alpha/\varepsilon^{1/2}, \beta/\varepsilon^{3/4})$$
(12)

where P is the Pearcey integral: $P''(z,\alpha,\beta) = (z^3 - \alpha z - \beta)P'(z,\alpha,\beta)$, $\alpha = \sum \alpha_k \varepsilon^k$ and $\beta = \sum \beta_k \varepsilon^k$ (§16). The function $\psi(x)$ and parameters α_0 , β_0 must be determined so that

$$b^{i}\psi_{i} + (\psi^{3} - \alpha_{0}\psi - \beta_{0}) \frac{a^{ij}}{2} \psi_{i}\psi_{j} = 0 .$$
 (13)

The parameters α_0 , β_0 and functions ψ , g^0 are evaluated in a manner analogous to the previous cases (§17, 18). Once α_0 , β_0 , ψ and g^0 are known, contours of equal probability can be generated (§18). The function $h^0(x)$ can be evaluated everywhere in the plane (§19 and Appendix A). Higher order terms are treated in an analogous fashion (Appendix B). In Appendix E, we show that all constructions are regular at the bifurcation point and determine power series for α_0 , β_0 in terms of η , δ . These power series are useful if the deterministic system has two complex steady states with small imaginary part (§20).

An application of the above theory is presented in the final chapter. A model of Degn's experiments on NADH oxidation is presented in §21.1. The stochastic version is derived in §21.2. By assuming perfect control of one of the variables, the model becomes one dimensional. The asymptotic theory can then be compared with an exact solution (§22). The asymptotic results are accurate. The two dimensional asymptotic theory is compared with Monte Carlo experiments in §23.

Chapter 1: Stochastic Macrovariables with Coalescing Steady States

1. Fluctuations and Systems with Multiple Steady States

The classical method of describing the evolution of chemical reactions is by the use a deterministic differential equation

$$\dot{\mathbf{x}} = \mathbf{b}(\mathbf{x}) \qquad \mathbf{x} \in \mathbf{R}^{\Pi} \quad . \tag{1.1}$$

In (1.1), x is a macroscopic variable that represents concentrations of reactants or products. The macrovariable describes the average state of a large system and is obtained by averaging over many independent subunits. The form of b(x) is determined by the reaction mechanism.

Steady states are characterized by b(x) = 0. If b(x) is nonlinear, then the system may have multiple steady states. The eigenvalues of $B = (b^{i},)$ can be used to characterize the type of steady state. If all eigenvalues have non zero real part, the steady state is of the normal type. Following Kubo et. al. (1973) we distinguish two kinds of non-normal steady states: 1) the marginal type, in which the local dynamics are $\dot{x} \sim x^{2}$; 2) the critical type, in which the local dynamics are $\dot{x} \sim x^{3}$. A steady state is stable if all eigenvalues have negative real part. Otherwise is is unstable. The deterministic approach can be improved if statistical fluctuations are included. The concentrations, represented by a random variable $\ddot{x}(t)$, will fluctuate for two reasons (Keizer, 1975). First, due to experimental limitations, it is impossible to specify concentrations exactly. Second, even if the concentrations were known at some time t, the exact concentrations at a later time $t + \Delta t$ would not be known unless all of the microscopic variables were known at time t. The specification of all the microscopic variables is, presently, not possible. With this viewpoint, equation (1.1) describes the average behavior of a large number of statistical variables. A more exact description of the system would specify the volume V of the reaction vessel and an integer valued random variable $\tilde{X}(t)$ that represents the number of molecules in V at time t. The mean of $\tilde{x}(t) = \tilde{X}(t)/V$ will correspond to the deterministic concentration. The variance of $\tilde{x}(t)$ provides a measure of statistical fluctuations (McQuarrie, 1967).

In chemical systems the intensity of fluctuations is proportional to 1/V (Keizer, 1975; Van Kampen, 1976). In macroscopic systems, V is large so that the fluctuations are of small intensity. When the fluctuations are of small intensity, equation (1.1) usually provides an adequate description of the evolution of the system. There are, however, exceptions, some of which have been studied. When reactions occur in relatively small volumes (e.g. biological cells) or involve small numbers of molecules, fluctuations can have a profound effect on the evolution of the system (Delbruck, 1940; McQuarrie, 1967). Initial fluctuations will be amplified in autocatalytic or chain reactions (Singer, 1940). In the sequel, we set $\varepsilon \propto 1/V$ (see § 21).

Many authors have studied the effects of fluctuations on systems in the vicinity of the stable steady state (Lax 1960, 1966; Nitzan et al., 1974). In this work, we investigate the effects of fluctuations on systems initially in a vicinity of a kinetic saddle point. There are a number of reasons for studying chemical systems in the vicinity of an unstable steady state. In the first place, one would like to verify that the unstable steady state exists (Chang and Schmitz, 1975). Due to fluctuations, it is not possible to observe the unstable steady state. In later chapters, we will show that the unstable steady state has a certain probabilistic description. Secondly, in many reactions the stable steady states represent \sim 0 or 100% completion of the reaction. The most significant kinetic information is obtained from rate data in a vicinity of the unstable steady state. Chang and Schmitz (1975) point out that often it is desirable to start a chemical reactor near the unstable steady state, but that one stable steady state is preferred. In this case, one wishes to estimate the probability that the less desirable stable state is reached. The gating mechanisms of nerve membranes involve reactions with multiple steady states (Armstrong, 1975). The study of fluctuations at the unstable steady state (threshold) may lead to information about conductivity mechanisms (Lecar and Nossal, 1971a, b).

In practice, it is very difficult to prepare a system in an unstable steady state. However, many systems exhibit behavior in which a stable steady state becomes unstable as a parameter is varied (Degn, 1968, Pincock et. al. 1971, Lavenda, 1975). When a parameter α is less than a critical value α_c , the system has only one steady state, P_1 , which is stable. When α is increased, so that $\alpha > \alpha_c$, P_1 becomes unstable and two stable steady states P_0 , P_2 are created. We call this the critical bifurcation. The mean-field ferromagnet 12

exhibits such behavior. Many chemical systems also exhibit the critical bifurcation (§2, §21). A second type of bifurcation is possible as α increases. The steady state P_1 remains stable when $\alpha > \alpha_c$ and two new steady states Q_1 , which is unstable, and Q_0 , which is stable, appear. We call this the marginal bifurcation. The marginal bifurcation has not received adequate attention in the chemical literature because there is a feeling among chemists and physicists that one can not observe it. In §22-23 we shall demonstrate that substrate inhibited reactions may exhibit the marginal bifurcation.

If P_1 is unstable when $\alpha > \alpha_c$, the system will always leave a neighborhood of P_1 and approach P_0 or P_2 . Even if the system were initially at P_1 , any minute fluctuation will cause it to leave the neighborhood of P_1 . In the vicinity of an unstable steady state, fluctuations can never be ignored. According to the deterministic theory, the separatrix (Fig. 4) S divides the phase plane into two domains of attraction. All phase points initially on one side of S approach P_0 ; phase points on the other side approach P_2 . Points initially on S approach the saddle point P_1 .

When a more exact, stochastic description is used, the deterministic picture must be modified. No phase points will reach P_1 and remain there. Due to fluctuations, all phase points reach a vicinity of P_0 or P_2 . More importantly, phase points which deterministically would approach P_0 might approach P_2 (and vice versa). Namely, fluctuations may drive the system against the

13

deterministic flow. Ideally, one would like to calculate the probability that a specified steady state is reached first. This problem is generally too difficult to solve. Instead, we surround the separatrix by a tube with boundaries I, II (Fig. 4).



Fig. 4. First Exit Problem

We will calculate the probability, u(x), that the process $\tilde{x}(t)$ first exits from this tube through boundary II, given that $\tilde{x}(0) = x$. In the diffusion approximation, this probability satisfies a diffusion equation. We shall construct formal asymptotic solutions of the diffusion equation. Our technique will convert the second order boundary value problem for u to a first order initial value problem for a new function ψ . Although we will give an existence proof for $\psi(\mathbf{x})$ (Appendix F), we do not prove that our solution is asymptotic to the true solution.

Spontaneous Generation of Optical Activity: The Importance of Fluctuations at the Unstable Steady State

The experimental work of Pincock et. al. (1971) provides an example of a chemical system in which a stable steady state becomes unstable as a parameter varies. The experiments also indicate the importance of fluctuations in determining the evolution of a system initially in the vicinity of an unstable steady state.

1,1' Binaphthyl has enantiomers which are interconverted by a bond rotation. At room temperature, the rotation is sufficiently slow so that a molecule is "fixed" in one conformation. Above 160°C, the interconversion rate has a half life of 0.5 seconds, so that all mixtures are racemic above 160°C. The experiments involved heating samples of binaphthyl above 160°C and then rapidly crystallizing the melt. The optical activity of the resulting crystal was determined. The distribution of specific rotation in 200 experiments was -218° to 206°, with mean 0.14°. The distribution of the data was similar to the distribution of "heads" if a fair coin were flipped 8 times. A, complex nucleation process is involved in these experiments. The following simple model illustrates the phenomenon of interest here. Assume that each sample contains a large number of microregions, which act independently. Above 160°C, the racemic statesis stable and all microregions are racemic. Below 160°C, the two resolved states are stable. In each microregion, "a fair coin is flipped" to decide the final optical activity of the region. Although some samples remained in a supercooled racemic state for a few hours, no sample remained in the racemic state indefinitely. The resolution of optical activity was completely determined by random fluctuations.

The probability of achieving a given resolved state was modified by the addition of certain optically active substances. For example, when 2.5 weight % D(-) mandelic acid was added to the racemic mixture, 21 samples with negative rotation and 7 samples with positive rotation were obtained. The probability of observing such a result with a "fair coin" is \sim .004. When the concentration of mandelic acid was doubled, 27 (-) samples and 0 (+) samples were obtained. The probability of observing this result with a fair coin is $\sim 1.5 \times 10^{-8}$. Thus, the addition of mandelic acid at low concentrations (12-24 binaphthyl molecules/mandelic acid molecule) affected the evolution of the system.

In order to understand these experiments, we consider the following simple mathematical model. Let x^1 , x^2 denote the concentrations of (+), (-) enantiomers respectively. Following Frank (1953) we assume that each enantiomer is the catalyst for its own production and the anticatalyst for the other enantiomer. Let R denote the racemic melt, which is treated as a constant source of molecules. The reaction scheme is: 16

$$\begin{array}{l} x^{1} + R \xrightarrow{1+\alpha} 2x^{1} \\ x^{2} + R \xrightarrow{1+\alpha} 2x^{2} \end{array} \right\} \quad \text{autocatalytic step} \\ x^{1} + x^{2} \xrightarrow{\alpha} 2R \\ x^{1} + x^{1} \xrightarrow{1} \text{ inert} \\ x^{2} + x^{2} \xrightarrow{1} \text{ inert} \end{array}$$

$$(2.1)$$

The last two steps were added to insure that all concentrations remain bounded. They might correspond to molecules which are no longer on the surface and hence are inert to catalysis. The kinetic equations (with $R \equiv 1$) are

$$\dot{x}^{1} = (1+\alpha)x^{1} - \alpha x^{1}x^{2} - (x^{1})^{2}$$
(2.2)

$$\dot{x}^{2} = (1+\alpha)x^{2} - \alpha x^{1}x^{2} - (x^{2})^{2}. \qquad (2.3)$$

The rate parameter α is assumed to be a function of temperature such that $\alpha>1$ if T < 160°C and $\alpha<1$ if T > 160°C .

When $T > 160^{\circ}C$, $\alpha < 1$, the only steady state is (1,1), which is stable (Fig. 5a). When $\alpha > 1$, $T < 160^{\circ}C$, the racemic state is unstable. Two stable steady states appear on the x^{1} and x^{2} axes (Fig. 5b). The racemic state in this special model is the entire separatrix $S: x^{1} = x^{2}$. When $\alpha > 1$, if the sample is initially in the racemic state, any small fluctuation will cause the sample to evolve towards one of the resolved states.

The experiments with mandelic acid can be explained using this model. For example, point A in Fig. 5b might represent an experiment in which 2.5% mandelic acid was added. An experiment starting at point A is more likely to approach 0_1 than an experiment starting



Fig. 5. Binaphthyl Model

at 0. The result of an experiment starting at point B will probably not be affected by fluctuations of small intensity.

In this model, the multiple steady states arise in a natural fashion due to the nonlinearity of the kinetic equations. Fluctuations can be included by treating the reactions (2.1) as a birth and death process (§3).

The theory developed in Chapter 2 can be used to treat the above model of the binaphthyl experiments when fluctuations are included.

The model=in=this section is, of course, an oversimplification of the physical nucleation process. However, the model illustrates how fluctuations may affect systems with multiple steady states.

3. Birth and Death Approach to Chemical Kinetics

The birth and death approach provides a method for giving a statistical interpretation to macroscopic chemical kinetics (Bartholomay, 1957; McQuarrie, 1967). For the purposes of illustration, consider the following reactions which appear in the work of Harrison (1974) and Glansdorff and Prigogine(1971):

$$A + 2B \xrightarrow{k_1} 3B \tag{3.1}$$

$$B \xrightarrow{k_2} C \tag{3.2}$$

Let $k = k_1[A]$, x = [B] and assume that [A] is a constant. The kinetic equation for x is

$$\dot{x} = kx^2 - k_2 x$$
 (3.3)

Equation (3.3) has steady states x = 0 (stable) and $x = \frac{k_2}{k} \equiv \frac{x_u}{u}$ (unstable). We assume that other reactions insure that x does not become unbounded, but x may tattain a stable steady state x_s , with $x_s > x_u$.

If $x(0) = x_0$, the deterministic description of the reaction is as follows. If $x_0 < x_u$, then $x(t) \rightarrow 0$ as t increases. If $x_0 = x_u$, then $x(t) \equiv x_u$ for all t. If $x_0 > x_u$, then $x(t) \rightarrow x_s$ as t increases.

In the stochastic approach, reaction (3.1) is treated as a birth of a molecule of B; reaction (3.2) is a death of a molecule of B. Let $\tilde{X}(t)$ be a random variable that represents the number of molecules of B in the reaction vessel, of volume V, at time t. We assume that the following transition probabilities exist:

$$\Pr\{\tilde{X}(t+\Delta t) - \tilde{X}(t) = 1 | \tilde{X}(t) = X\} = \alpha X^2 \Delta t + o(\Delta t) \quad (3.4)$$

$$\Pr\{X(t+\Delta t) - X(t) = -1 | X(t) = X\} = \beta X \Delta t + \delta(\Delta t)$$
 (3.5)

$$Pr\{all higher transitions\} = o(\Delta t)$$
. (3.6)

By using forward differences in equations (3.4 - 3.6), we are making an implicit assumption about the stochastic process. Different approaches (e.g. centered differences) are also possible. The choice of forward differences agrees with McQuarrie (1967) and Bartholomay (1957). The constants α , β are determined by requiring that $E(\tilde{X}(t))$ satisfy the law of mass action (3.3).

Let $\Delta X = X(t+\Delta t) - X(t)$. Using equations (3.3 - 3.6):

$$E(\Delta \tilde{X} | \tilde{X}(t) = X) = (\alpha X^{2} - \beta X) \Delta t + o(\Delta t) \quad . \tag{3.7}$$

We define

$$\dot{X}(t) \equiv \lim_{\Delta t \to 0} \frac{1}{\Delta t} E(\Delta \tilde{X} | \tilde{X}(t) = X)$$
$$= \alpha X^{2} - \beta X . \qquad (3.8)$$

We require that (3.8) and (3.3) agree, when (3.8) is rewritten in terms of the concentration variable x = X/NV, where N is Avogadro's number and $\tilde{X} = \tilde{E(X)}$. Equation (3.8) becomes

$$\dot{\mathbf{x}} = \alpha N V \mathbf{x}^2 - \beta \mathbf{x}, \qquad (3.9)$$

which will agree with (3.3) if

$$\alpha = k/NV$$
 and $\beta = k_2$. (3.10)

A measure of inherent fluctuations about the mean is provided by the infinitesimal variance (Feller, 1971):

$$a(X) \equiv \lim_{\Delta t \to 0} \frac{1}{\Delta t} E\{(\tilde{\Delta X})^2 | \tilde{X}(t) = X\}.$$
(3.11)

Using the transition probabilities (3.4 - 3.6), we find

$$a(X) = \alpha X^2 + \beta X . \qquad (3.12)$$

In general, many different reaction mechanisms can produce the same rate law. The stochastic approach provides a more accurate description of the system, since the chemical mechanism figures prominently in the calculation of b(X) and a(X).

McQuarrie (1967) presents an extensive discussion in which mean motion and fluctuation effects are compared. We note the following points:

1) McQuarrie did not allow b(X) to vanish, i.e. that the system has a steady state. At an unstable steady state, fluctuations greatly influence the behavior of the system.

Experimental techniques are available for the direct measurement of fluctuation effects in chemical reactions (Feher and Weissman, 1973, Vereen and De Felice, 1974).

3) Experimentalists working with chemical reactors are concerned with fluctuation effects (Chang and Schmitz, 1975). Chang and Schmitz do not estimate the intensity of the fluctuations, but it is clear from their discussion that the fluctuations are of concern.

4. <u>Stochastic Kinetic Equations</u>, <u>Backward Equation and First</u> Exit Problem

The macrovariable x(t) represents the average concentrations of reactants at time t and evolves according to the kinetic equation

$$\dot{x}^{i} = b^{i}(x) \qquad x^{i}(0) = x_{0}^{i} \qquad i = 1, 2$$
 (4.1)

According to the statistical theory of chemical kinetics, x(t) is the mean value of a random variable $\hat{x}(t)$, which will satisfy a stochastic kinetic equation. It is not yet possible to derive the stochastic kinetic equation from basic principles. Ideally, one would start with the Liouville equation and reduce it to a stochastic kinetic equation. This reduction has been performed only on the simplest system (Sinai, 1970). Instead, we shall use a Langevin method (Lax, 1966) and add a stochastic term to the right hand side of (4.1). The source of the stochastic term is the random motion of the solvent and solute molecules, which occurs on a time scale τ , small compared to the macroscopic time scale t, on which measurements are made.

The increments in τ and t are related by a parameter α :

$$\Delta \tau = \Delta t \cdot \alpha^2, \qquad (4.2)$$

where α^2 will characterize the fast time scale. The random process generated by the microscopic motions is assumed to be a mixing process $\tilde{Y}(\tau)$. In most of the physical literature (e.g. Mori, 1965; Ma, 1976) it is assumed that

$$E[\tilde{Y}^{k}(s)\tilde{Y}^{\ell}(0)] = \delta^{k\ell}(s)$$
(4.3)

where $\delta^{k\ell}(s) = 0$ unless $k = \ell$ and s = 0. We shall not make this assumption and define

$$\gamma^{k\ell} = \int_{0}^{\infty} E[\tilde{Y}^{k}(s)\tilde{Y}^{\ell}(0)]ds . \qquad (4.4)$$

In the case that (4.3) holds, $Y(\tau)$ is the "white noise" process. We assume that the stochastic variable $\tilde{x}(t;\alpha)$ satisfies

$$\frac{d\tilde{x}^{i}(t;\alpha)}{dt} = b^{i}(\tilde{x}) + \sqrt{\varepsilon} \frac{\sigma_{j}^{i}(\tilde{x})}{\alpha} \tilde{Y}^{j}(t/\alpha^{2}) \quad i = 1,...,n . \quad (4.5)$$

Langevin was the first to use a kinetic equation of the form (4.5) (Lax, 1966). Such equations have been used in the last fifty years by almost all physical scientists working in this field. The use of (4.5) represents an approximate, somewhat ad hoc, way of treating stochastic effects in macroscopic systems. Equation (4.5) is the stochastic kinetic equation that will be used in the rest of this work.

The functions $b^{i}(x)$ appearing in (4.5) are the same functions appearing in the macroscopic equation (4.1). They determine the average or macroscopic evolution of x(t). For example, for the model of binaphthyl experiments

$$b^{1}(x) = (1+\alpha)x^{1} - \alpha x^{1}x^{2} - (x^{1})^{2}$$
 (4.6a)

$$b^{2}(x) = (1+\alpha)x^{2} - \alpha x^{1}x^{2} - (x^{2})^{2}$$
. (4.6b)

The function Y(s) is a zero mean process, satisfying the mixing hypothesis of Papanicolaou and Kohler (1974). The field $\sigma_j^i(x)$ is assumed to be known. It characterizes the x dependence of the fluctuations. Since (4.5) is not derived from first principles, we need to provide a prescription for the calculation of $\sigma(x)$. In §21, we discuss how $\sigma(x)$ can be calculated. We assume that $\tilde{x}(0;\alpha) = x_0$ remains a deterministic condition.

As $\alpha \to 0$, $\tilde{x}(t;\alpha)$ converges to a diffusion process $\tilde{x}(t)$ (Papanicolaou and Kohler, 1974). Let $u_0(x)$ be integrable and

$$u(t,x) = E\{u_0(\tilde{x}(t)) | \tilde{x}(0) = x\}.$$
(4.7)

Then u(t,x) satisfies the backward equation

$$u_{t} = \frac{\varepsilon a^{ij}}{2} u_{ij} + b^{i} u_{i} + \varepsilon c^{i} u_{i}$$
(4.8)

where

$$a^{ij}(x) = \sigma_k^i(x)\sigma_\ell^j(x)(\gamma^{k\ell} + \gamma^{\ell k})$$
(4.8a)

$$c^{i}(x) = \gamma^{k\ell} \sigma^{j}_{k} \frac{\partial}{\partial x^{j}} (\sigma^{i}_{\ell})$$
(4.8b)

If $\tilde{Y}(\tau)$ were white noise, the resulting diffusion equation would be

$$u_{t} = \frac{\varepsilon a^{ij}}{2} u_{ij} + b^{i} u_{i} . \qquad (4.9)$$

If a^{ij} is independent of x, then equations (4.8) and (4.9) are identical. In §22, we present a numerical comparison of solutions of equations (4.8) and (4.9). Our results indicate that (4.9) is an

excellent approximation to (4.8) if the boundaries are non-singular.

The fundamental equation derived above is (4.8) or its time independent version

$$0 = \frac{\varepsilon a^{ij}}{2} u_{ij} + b^{i}u_{i} + \varepsilon c^{i}u_{i} . \qquad (4.10)$$

Equation (4.10) must be supplemented by boundary conditions if the problem is to be properly posed. We surround the separatrix by a tube with boundaries I, II. If u = 0 on I, u = 1 on II, then u(x) is the probability that $\tilde{x}(t)$ first exits from the tube around the separatrix through boundary II. Let the boundaries be determined by $f_{I}(x)=0$, $f_{II}(x)=0$. Let $H_{I}(t)=0$ if $f_{I}(\tilde{x}(s))=0$ for some s, $0 \le s \le t$ and 1 otherwise. The $u_{0}(\tilde{x}(t))$ in (4.7) is $\delta(f_{II}(\tilde{x}(t)))H_{T}(t)$.

We distinguish three cases of increasing complexity.

1) The Normal Case: in which the separatrix tube contains only the unstable steady state.

2) The Marginal Gase: in which the separatrix tube contains the unstable steady state and one stable steady state. As one parameter varies, the two steady states coalesce and annihilate each other (the marginal bifurcation). After the bifurcation, only one stable steady state remains. This steady state is not in the separatrix tube, so that the deterministic flow is always across the tube in the same direction (Fig. 2, pg. 6).

The first exit problem as formulated is of little interest. A more interesting question involves the expected time to reach boundary II, given that $\tilde{x}(0) = x$, T(x). Let d(x) denote the distance from the point x to II. Let

$$T(x) \equiv \int_{0}^{\infty} tu_{t}(x,t) dt \qquad (4.11)$$

where u(x,t) satisfies (4.8) with boundary conditions u(x,t) = 1on II, $u_i \rightarrow 0$ as $d \rightarrow \infty$, u(x,0) = 0 unless $x \in II$. Then u(x,t) is the probability that $\tilde{x}(t)$ has reached II by time t, given that $\tilde{x}(0) = x$. Let u(x)+be the limit of u(x,t), as $t \rightarrow \infty\infty$.

T(x) satisfies (Gihman and Skorohod, 1972)

$$\frac{\varepsilon a^{ij}}{2} T_{ij} + b^{i} T_{i} + \varepsilon c^{i} T_{i} = -u(x)$$
(4.12)

where u(x) is the probability of eventually reaching II, given that $\tilde{x}(0) = x$. T(x) satisfies the boundary conditions

$$T(x) = 0$$
, $x \in II$; $T_i \rightarrow 0$ as $d \rightarrow \infty$. (4.13)

3) The Critical Case: in which the separatrix tube contains the unstable steady state and both stable steady states. As two parameters vary the three steady states move together and coalesce (the critical bifurcation). The remaining steady state is assumed to be stable.

Recently, Matkowsky and Schuss (1977), Schuss (1977) and Williams (1977) have studied stochastic exit problems. They were interested in the exit distribution and mean exit time from a domain containing a simple, stable steady state. There is little overlap between their work and this one.

5. Three Canonical Integrals

Equations (4.10) and (4.12) are singularly perturbed elliptic equations. The equations are further complicated by the fact that b(x) vanishes at one or more points in the separatrix tube. We seek approximate solutions of the equations. We will use asymptotic methods for the calculation of the first exit probability. Similar methods apply to the first exit time (Appendix C). The form of the asymptotic solutions will be suggested by the analysis of a one dimensional version of (4.10):

$$0 = \frac{\varepsilon a(x)}{2} u_{xx} + b(x,\eta,\delta) u_{x} + \varepsilon c u_{x} . \qquad (5.1)$$

The analysis of (5.1) will lead to three canonical integrals which will be used in the solution of (4.10).

The reduced ($\varepsilon \equiv 0$) deterministic system is

$$\dot{\mathbf{x}} = \mathbf{b}(\mathbf{x}, \mathbf{\eta}, \delta) = \mathbf{b}(\mathbf{x}) \tag{5.2}$$

which may have three steady states, x_0 , x_1 and x_2 (lst case). As n, δ vary, two steady states coalesce (2nd case) or all three coalesce (3rd case). The 2nd case is the marginal type steady state, x_m , characterized by (Kubo et. al., 1973)

$$b(x_{m}) = 0$$
; $b'(x_{m}) = 0$, $b''(x_{m}) \neq 0$
 $\eta = \eta_{m} \quad \delta = \delta_{m}$. (5.3)

The third case is the critical type steady state, x_c , characterized by $(n = n_c, \delta = \delta_c)$

$$b(x_c) = b'(x_c) = b''(x_c) = 0, \quad b'''(x_c) \neq 0.$$
 (5.4)

Equation (5.1) must be supplemented by boundary conditions. We choose ℓ_1 , ℓ_2 so that $x_1 \in [\ell_1, \ell_2]$, where x_1 is the unstable steady state. If $u(\ell_1) = 0$, $u(\ell_2) = 1$, then u(x) is the probability that the process first exits from $[\ell_1, \ell_2]$ through the right hand boundary. The solution of (5.1) is

$$u(x) = \frac{\int_{\ell_1}^{x} \exp\left[-\int_{\ell_1}^{x'} \frac{2(b(s) + \varepsilon c(s))}{\varepsilon a(s)} ds\right] dx'}{\int_{\ell_1}^{\ell_2} \exp\left[-\int_{\ell_1}^{x'} \frac{2(b(s) + \varepsilon c(s))}{\varepsilon a(s)} ds\right] dx'}$$
(5.5)

When ε is small, the behavior of (5.5) will be determined by the 2b/ ε a term. Thus, we shall consider the simpler integral

$$\mathbf{v}(\mathbf{x}) = \int_{\ell_1}^{\mathbf{x}} \exp\left[-\int_{\ell_1}^{\mathbf{x}'} \frac{2\mathbf{b}(\mathbf{s})}{\mathbf{\epsilon}\mathbf{a}(\mathbf{s})} \, d\mathbf{s}\right] d\mathbf{x}' \quad . \tag{5.6}$$

By using (5.6) rather than (5.5), the algebraic details of the analysis are simplified, but the main points remain unchanged. The two results will differ by terms $O(\varepsilon)$ or less. Our analysis will be based upon Laplace's method (Olver, 1974; Bleistein and Handelsman, 1975).

5.1. Normal Case: The Error Integral

In the normal case, only one steady state is contained in $[\ell_1, \ell_2]$. The main contribution to (5.6) will come from the minimum of

$$\phi(x') = \int_{-\infty}^{x'} \frac{2b(s)}{a(s)} \, ds \quad . \tag{5.7}$$
Since $\phi'(x_1) = 0$ and $\phi''(x_1) = 2b'(x_1)/a(x_1) > 0$, the minimum of $\phi(x')$ is at $x' = x_1$. Using a Taylor expansion of ϕ about x_1 in (5.6) yields

$$\mathbf{v}(\mathbf{x}) \sim \mathbf{k} \int_{\ell_1}^{\mathbf{x}} \exp\left[-\frac{\mathbf{b}'(\mathbf{x}_1)}{\varepsilon \mathbf{a}(\mathbf{x}_1)} (\mathbf{x}' - \mathbf{x}_1)^2\right] d\mathbf{x}' + \mathbf{0}(\sqrt{\varepsilon}), \qquad (5.8)$$

where k is constant. Differentiation of (5.8) gives

$$v_{x}(x) \sim k \exp\left[-\frac{b'}{\epsilon a}(x-x_{1})^{2}\right]$$
 (5.9)

For small ε , v_x is very small, except in a region around x_1 . Hence, we obtain an internal boundary layer about x_1 of width $O((\varepsilon a(x_1)/b'(x_1))^{\frac{1}{2}})$. A change of variables converts (5.8) to

$$v(x) \sim k \int_{-\infty}^{\tilde{x}(x)} \exp(-s^2/2\varepsilon) ds + 0(\sqrt{\varepsilon})$$
 (5.10)

The integral in (5.10) is the Error integral

$$E(z) = \int_{z_0}^{z} e^{-s^2/2} ds . \qquad (5.11)$$

The function E(z) satisfies the following equation

$$\frac{d^2 E}{dz^2} = -z \frac{dE}{dz}, \qquad z_0 \le z \le z_1.$$
(5.12)

The error integral is closely related to the normal distribution function (Abramowitz and Stegun, 1965).

5.2. Marginal Case: The Airy Integral

In §5.1 we assumed that $b'(x_1)$ does not vanish. This asumption is not valid at a marginal or critical type steady state. Thus, the Error integral no longer adequately represents the asymptotic behavior of the probability. The cause of the breakdown is clear: the Error integral corresponds to linear dynamics, but the dynamics at the marginal and critical steady states are totally nonlinear. In order to obtain an expansion at a marginal type steady state, a more complicated special function is needed. We use a third term in the Taylor expansion of ϕ :

$$\phi(\mathbf{x}) = \phi(\mathbf{x}_1) + \frac{b'(\mathbf{x}_1)}{a(\mathbf{x}_1)}(\mathbf{x} - \mathbf{x}_1)^2 + \frac{b''(\mathbf{x}_1)}{3a(\mathbf{x}_1)}(\mathbf{x} - \mathbf{x}_1)^3 + O((\mathbf{x} - \mathbf{x}_1)^4) \quad . \tag{5.13}$$

A change of variables converts (5.13) to

$$\phi = \frac{b''(x_1)}{a(x_1)} \left[\frac{1}{3} y^3 - \tilde{\alpha}y + \beta \right] + 0(y^4)$$
(5.14)

where y is a regular function of x and $\tilde{\alpha}$, β are functions of b'(x₁), b"(x₁) and a(x₁); $\tilde{\alpha}$ vanishes when b' vanishes. Another change of variables converts (5.6) to the form

$$\mathbf{v}(\mathbf{x}) \sim \mathbf{c} \int^{\tilde{\mathbf{x}}(\mathbf{x})} \exp\left[-\frac{1}{\varepsilon}(\frac{1}{3}\mathbf{r}^3 - \alpha \mathbf{r})\right] d\mathbf{r} + \mathbf{0}(\varepsilon^{2/3})$$
(5.15)

where c is a constant and $\alpha = (b''/a)^{1/3}\tilde{\alpha}$. The integral (5.15) can be obtained by applying Levinson's result directly to (5.6) (Levinson, 1961). Differentiation of (5.15) gives

$$v_{\tilde{x}} \sim \exp\left[-\frac{1}{\varepsilon}\left(\frac{1}{3}\tilde{x}^3 - \alpha \tilde{x}\right)\right]$$
 (5.16)

Hence, for small ε , $v_{\tilde{x}}$ will be very small except in a region around the origin where $\frac{1}{3}\tilde{x}^3 - \alpha \tilde{x}$ is $O(\varepsilon)$. Thus we obtain an internal boundary layer of width $O(\varepsilon^{1/3})$.

The integral in (5.15) is an incomplete Airy integral

$$A(z,\alpha) = \int_{z_0}^{z} \exp((-\frac{1}{3}s^3 + \alpha s)) ds . \qquad (5.17)$$

The function $A(z, \alpha)$ satisfies the differential equation

$$\frac{\mathrm{d}^{2}A(z,\alpha)}{\mathrm{d}z^{2}} = -(z^{2} - \alpha) \frac{\mathrm{d}A(z,\alpha)}{\mathrm{d}z} \qquad z_{0} \leq z \leq z_{1} \quad (5.18)$$

Equation (5.17) is analogous to the incomplete Airy function, which arises in diffraction problems (Levey and Felsen, 1969). The asymptotic properties of $A(z,\alpha)$, for large α , can be determined by Laplace's method and repeated integration by parts (Olver, 1974). We obtain

$$A(z,\alpha) \sim \frac{k(\alpha)}{2\sqrt{\alpha}} E(\tilde{z}) + O(1/\alpha)$$
(5.19)

where \tilde{z} is a regular function of z and $k(\alpha)$ is a function of α :

$$k(\alpha) = \exp[(2/3)\alpha^{3/2}]$$
 (5.20)

The result (5.19) ignores endpoint contributions, and is obtained by assuming that $-\sqrt{3\alpha} < z_0$. The condition on z_0 can be further weakened, but it will not be necessary to do so in this work.

5.3. Critical Case: The Pearcey Integral

The analysis in §5.2 is not valid at a critical type steady state, since $b''(x_c, n_c, \delta_c) \equiv 0$. Thus the Airy integral does not provide an adequate asymptotic representation. In order to obtain the expansion of (5.6), another term must be used in the Taylor expansion of $\phi(x')$. If a Taylor expansion of ϕ up to $(x-x_1)^4$ and two changes of variable are used, then (5.6) can be put into the form

$$v(x) \sim c \int^{\tilde{x}(x)} \exp\left[+\frac{1}{\varepsilon}(\frac{1}{4}y^4 - \frac{\alpha y^2}{2} - \beta y)\right] dy + 0(\varepsilon^{3/4})$$
 (5.21)

where c is a constant, $\tilde{x}(x)$ is a regular function of x. The parameters α , β are functions of $b'(x_1)$, $b''(x_1)$, $b'''(x_1)$ and $a(x_1)$, and vanish at the critical bifurcation. In this case, the boundary layer around x_1 clearly has width $O(\epsilon^{1/4})$.

The integral in (5.21) is the incomplete Pearcey integral

$$P(z,\alpha,\beta) = \int_{z_0}^{z} \exp\left[\left(\frac{1}{4}s^4 - \frac{\alpha s^2}{2} - \beta s\right)\right] ds$$
 (5.22)

and satisfies

$$\frac{d^2 P}{dz^2} = (z^3 - \alpha z - \beta) \frac{dP}{dz} \qquad z_0 \le z \le z_1 .$$
 (5.23)

An integral analogous to (5.22) was discovered by Pearcey (1946) during his investigation of the electromagnetic field at a cusped caustic. The asymptotic properties of $P(z,\alpha,\beta)$, for large α , β can be determined by Laplace's method. Let \tilde{s} be the middle root

$$s^{3} - \alpha s - \beta = 0 \qquad (5.24)$$

and

of

$$\tilde{\gamma} \stackrel{s}{\equiv} \frac{\tilde{s}^4}{4} - \alpha \frac{\tilde{s}^2}{2} - \beta \tilde{s} . \qquad (5.25)$$

Then we find that

$$P(z,\alpha,\beta) \sim \begin{cases} \frac{e^{\tilde{\gamma}}}{\sqrt{\alpha}} E(\tilde{z}_{1}) & \alpha \text{ large, } |\beta| \text{ small, i.e., } |\beta^{2}|/\alpha^{3} << 1 \\ (5.26) \\ e^{\tilde{\gamma}}k(\alpha,\beta)A(z_{1}',\eta) & \alpha \text{ large, } |\beta| \text{ large, i.e.,} \\ \beta^{2} = O(\alpha^{3}). \end{cases}$$

In (5.26),

$$k(\alpha,\beta) = \frac{1}{(3|\tilde{s}|)^{1/3}} \exp \left[-\frac{2}{3}(\frac{3\tilde{s}^2-\alpha}{2})^3 \frac{1}{9\tilde{s}^2}\right]$$
(5.27)

The parameter η is given in terms of α and β . The functions \tilde{z}_1 and z'_1 are regular functions of z and α or α and β . The results given in (5.26) are obtained by ignoring end point contributions to the integrals, so that we assume $r_0 < z_0$ and $z_1 < r_4$, where r_0 is the minimum and r_4 is the maximum root of

$$\frac{s^4}{4} - \alpha \frac{s^2}{2} - \beta s = 0.$$
 (5.28)

When α is small and $|\beta|$ is large (i.e., $\alpha^3/\beta^2 << 1$), the main contribution to (5.22) comes from the end points z_0 and z_1 , so that simple exponential estimates are obtained (Olver, 1974, page 80).

Asymptotic analysis of the exact solution of a one dimensional version of (4.12) leads to special functions that satisfy inhomogeneous

versions of (5.12), (5.18) and (5.23). The results given above indicate that it may be possible to solve the two dimensional problems (4.10), (4.12) by an asymptotic method. The separatrix would be surrounded by a boundary layer. Outside of the boundary layer u(x) is approximately constant and inside the boundary layer, u(x) changes rapidly. The width of the boundary layer will depend upon the type of deterministic dynamics. Consequently, we shall construct formal asymptotic solutions of the backward equation in the normal, marginal and critical cases. Although the solutions will be formal, the numerical results presented in Chapter 5 indicate that they are satisfactory.

The results obtained in this section could also have been obtained by the use of the method of matched asymptotic expansions (Nayfeh, 1973).

Chapter 2. Asymptotic Solution of the First Exit Problem in the Normal Case

6. Normal Type Dynamical Systems

The reduced ($\epsilon = 0$) deterministic system corresponding to equation (4.10),

$$\dot{x}^{i} = b^{i}(x),$$
 (6.1)

is assumed to have three steady states, P_0 , P_1 , and P_2 . Let $B_k = (b^i, j)$ denote the matrix obtained by linearizing b(x) and evaluating the result at P_k . We assume that B_0 and B_2 have two negative real eigenvalues and that P_0 and P_2 are bounded away from the separatrix tube. The matrix B_1 has one real positive and one real negative eigenvalue. The eigenvector corresponding to the negative eigenvalue has positive slope. A deterministic system satisfying the above postulates will be structurally similar to the one sketched in Fig. 6.



Fig. 6. The Normal Type Dynamical System

It is assumed that a(x) is bounded above and is positive definite on the deterministic separatrix.

7. The Asymptotic Solution

The analysis of the one dimensional problem in §5 indicates that a possible formal solution of the backward equation is

$$u(x) = \sum \varepsilon^{n} g^{n}(x) E(\psi(x)/\sqrt{\varepsilon}) + \varepsilon^{n+\frac{1}{2}} h^{n}(x) E'(\psi/\sqrt{\varepsilon}) . \qquad (7.1)$$

In (7.1), E(z) is the Error integral:

$$E''(z) = -zE'(z)$$
 $z_0 \le z \le z_1$. (7.2)

The limits z_0 , z_1 are chosen so that (7.1) will satisfy the boundary conditions to within asymptotically small correction terms. The ansatz (7.1) was used by Mangel and Ludwig (1977). The theory of that paper is a special case of the theory presented in this chapter.

When derivatives of u(x) are evaluated, equation (7.2) is used to replace E" and E'" by products of E' and $\psi'/\sqrt{\epsilon}$. After derivatives are evaluated and substituted into (4.10) terms are collected according to powers of ϵ . We obtain

$$0 = \sum_{n=0}^{\infty} e^{n-\frac{L}{2}} (g^{n}-\psi h^{n}) (b^{i}\psi_{i} - \frac{a^{ij}}{2}\psi_{i}\psi_{j}\psi)E'(\psi/\sqrt{\epsilon}) + e^{n} (b^{i}g_{i}^{n} + \frac{a^{ij}}{2}g_{ij}^{n-1} + c^{i}g_{i}^{n-1})E(\psi/\sqrt{\epsilon}) +E'(\psi/\sqrt{\epsilon})e^{n+\frac{L}{2}} (b^{i}h_{i}^{n} + a^{ij}g_{i}^{n}\psi_{j} + \frac{a^{ij}}{2}g^{n}\psi_{ij} + g^{n}c^{i}\psi_{i}$$
(7.3)
$$- c^{i}h^{n}\psi_{i}\psi + c^{i}h_{i}^{n-1} - \psi a^{ij}h_{i}^{n}\psi_{j} + \frac{a^{ij}}{2}h_{ij}^{n-1} - \frac{a^{ij}}{2}h^{n}((\psi\psi_{i}),_{j}))$$

In equation (7.3), if the superscript of g^n or h^n is less than zero, that term is set equal to zero. The leading term, n = 0, is composed of three parts and vanishes if

$$b^{i}\psi_{i} - \frac{a^{ij}}{2}\psi_{i}\psi_{j}\psi = 0$$
 (7.4)

$$b^{i}g^{0}_{i} = 0$$
 (7.5)

$$b^{i}h_{i}^{0} + \frac{a^{i}j}{2}g^{0}\psi_{ij} + a^{ij}g_{i}^{0}\psi_{j} - h_{i}^{0}a^{ij}\psi_{j}$$

+ $g^{0}c^{i}\psi_{i} - c^{i}h^{0}\psi\psi_{i} - \frac{a^{ij}}{2}h^{0}((\psi\psi_{i})_{j}) = 0$. (7.6)

Equation (7.4) is analogous to the eikonal equation of optics (see §8). It is obtained independently of $g^{n}(x)$ and $h^{n}(x)$. Since $b^{i} = dx^{i}/dt$, equation (7.5) indicates that

$$\frac{\mathrm{dg}^{0}}{\mathrm{dt}} = 0 \quad . \tag{7.7}$$

Thus g^0 is constant on trajectories. In §8, we show that the constant is the same on all trajectories. Once ψ and g^0 are known, h^0 can be calculated from equation (7.6). In §8,9 we explicitly treat equations 7.4 - 7.6. Higher order terms are treated in an analogous fashion (Appendix B).

8. Determination of ψ and g^0 : Contours of Probability

8.1. Determination of $\psi(x)$

The transformation $\phi = -\frac{1}{2}\psi^2$ converts equation (7.4) to

$$b^{i}\phi_{i} + \frac{a^{ij}}{2}\phi_{i}\phi_{j} = 0.$$
(8.1)

Equation (8.1) is the Hamilton-Jacobi equation or eikonal equation (see also Cohen and Lewis, 1967; Ventcel and Freidlin, 1970). It corresponds to a Hamiltonian

$$H(x,p) = \frac{1}{2} a^{ij} p_{i} p_{j} + b^{i} p_{i}, \qquad (8.2)$$

and Lagrangian

$$L(x,\dot{x}) = \frac{1}{2} a_{ij} (\dot{x}^{i} - b^{i}) (\dot{x}^{j} - b^{j}), \qquad (8.3)$$

where $(a_{ij}) = (a^{ij})^{-1}$ and

$$\dot{x}^{i} = \frac{\partial H}{\partial p_{i}} . \qquad (8.4)$$

According to Hamilton-Jacobi theory, $\phi(\mathbf{x})$ is the minimum value of the integral of the Lagrangian taken over all paths joining \mathbf{x}_0 and \mathbf{x} . If \mathbf{x}_0 is the saddle point, then $\phi \equiv 0$ on the separatrix, since $\mathbf{L}(\mathbf{x},\dot{\mathbf{x}}) \equiv 0$ if $\dot{\mathbf{x}}^{i} = \mathbf{b}^{i}$. Thus $\phi = \psi = 0$ on the separatrix.

Since equation (8.1) is nonlinear, it may have solutions in which $\phi(x)$ is non-zero on the separatrix. Consequently, by setting $\phi = \psi = 0$ on S, we are imposing an extra condition on $\psi(x)$. This condition can not be determined directly from equation (7.4) or (8.1). If ψ is non-zero on S, then the first derivatives of ψ must vanish on S. In this case, it is not possible to construct a solution of (4.10) that approaches zero on one side of the separatrix and one on the other side.

Equations (7.4) and (8.1) with initial data on S represent

singular characteristic initial value problems. We will show that the singularity (the saddle point) allows the unique determination of $\psi(\mathbf{x})$. In Appendix F, we give an existence proof for this type of initial value problem.

The most interesting experiments begin in the vicinity of the separatrix. Consequently, we will now determine $\psi(x)$ by a Taylor expansion, for points near S. In Appendix F we show how $\psi(x)$ can be calculated in the entire plane by the method of characteristics.

When equation (7.4) is differentiated and evaluated on S, we obtain

$$\frac{d\psi_k}{dt} + b^i, \quad \psi_i - \frac{a^{ij}}{2} \psi_i \psi_j \psi_k = 0, \quad k = 1, 2$$
(8.5)

where $d\psi_k/dt = b^i \psi_{ik}$. Since ψ is constant on *S*, the tangential derivative of ψ vanishes. Then equation (8.5) can be used to derive an equation for the normal derivative of ψ :

$$\frac{\mathrm{d}\psi_n}{\mathrm{d}t} + \hat{b}\psi_n - \frac{\hat{a}\psi_n^3}{2} = 0 \quad \text{on } S. \qquad (8.6)$$

In equation (8.6)

$$\hat{b}(t) = [(b^2)^2 b^1, -b^1 b^2 (b^2, +b^1, 2) + (b^1)^2 b^2, 2] / ((b^1)^2 + (b^2)^2)$$
(8.7)

$$\frac{a}{2} = [a^{11}((b^{2})^{4} + (b^{1})^{2}(b^{2})^{2}) - 2a^{12}((b^{1})^{3}b^{2} + b^{1}(b^{2})^{3}) + a^{22}((b^{1})^{2}(b^{2})^{2} + (b^{1})^{4}]/(((b^{1})^{2} + (b^{2})^{2})^{2}).$$
(8.8)

Equation (8.6) is a version of Abel's equation (Davis, 1962, pg. 75) and is solved by introducing z(t) defined by

$$\psi_{n} = [B(t)z(t)]^{-1},$$
(8.9)

where $B'(t) = \hat{b}B$. The solution of (8.6) is

$$\psi_{n}(t) = \left\{ \int_{t}^{\infty} \hat{a}(s) \exp\left[-2 \int_{t}^{s} \hat{b}(s') ds'\right] ds \right\}^{-\frac{1}{2}}.$$
 (8.10)

Equation (8.10) satisfies the condition

$$\psi_{n}(\infty) = \sqrt{\frac{2\hat{b}(\infty)}{\hat{a}(\infty)}},$$
(8.11)

which is consistent with (8.6) at the saddle point (where $t = \infty$ and $d\psi_n/dt = 0$ }. The higher derivatives of ψ , up to order r can be calculated in an analogous fashion, if deterministic equations are C^r in x.

8.2. Determination of z_0, z_1 and g^0

We first suppose that the boundaries I and II are level curves of $\psi(\mathbf{x})$, say $\psi = \psi_{I}$ on I and $\psi = \psi_{II}$ on II. We set $z_{0} = \psi_{I}$ and $z_{1} = \psi_{II}$ in equation (7.2). To leading order u = 0on boundary I, and u = 1 on boundary II if

$$g_0 = \frac{1}{E(\psi_{TT}/\sqrt{\epsilon})} \quad . \tag{8.12}$$

In light of (7.7), $g^0 = 1/E(\psi_{II}/\sqrt{\epsilon})$ on all trajectories that intersect boundary II. Since all trajectories in the lower half plane intersect at P_2 , $g^0 = 1/E(\psi_{II}/\sqrt{\epsilon})$ on all those trajectories. In particular, g^0 has the above value on the trajectory from P_1 to P_2 . Thus, g_0 has the above value on the trajectory from P_1 to P_0 . If this were not so, equation (7.7) would be violated when t is replaced by -t. Since all trajectories in the upper half plane intersect at P_0 , $g^0 = 1/E(\psi_{II}/\sqrt{\epsilon})$ on all of these trajectories. Thus, g^0 is constant in the entire phase plane.

If $\psi(\mathbf{x})$ is not constant on I and II, then $u(\mathbf{x})$ will not be 0 or 1 on the boundaries, but will be close to 0 or 1. Let $\psi_{\mathbf{I}}^{0}$, $\psi_{\mathbf{I}}^{1}$ be the minimum and maximum values of ψ on I. We set $z^{0} = \psi_{\mathbf{I}}^{0}$. Then on I, $u(\mathbf{x})$ is not zero, but

$$u(x) \leq g^{0}E(\psi_{1}^{1}/\sqrt{\varepsilon}) = g^{0} \int_{\psi_{1}^{0}/\sqrt{\varepsilon}}^{\psi_{1}^{1}/\sqrt{\varepsilon}} e^{-s/2} ds . \qquad (8.13)$$

An integration by parts yields

$$u(\mathbf{x}) \leq \sqrt{\varepsilon} \left[\frac{e^{-((\psi_{I}^{0})^{2}/\varepsilon)}}{\psi_{I}^{0}} - \frac{e^{-((\psi_{I}^{1})^{2}/\varepsilon)}}{\psi_{I}^{1}} \right] g^{0}$$
(8.14)
+ $0(\varepsilon^{3/2})$.

Thus, if ψ_{I}^{0} and ψ_{I}^{1} are bounded away from 0, u(x) will be exponentially small on boundary I. This restriction is an implicit assumption about the boundaries.

If ψ_{II}^1 is the maximum value of ψ on II, we set

$$g^{0} = \frac{1}{E(\psi_{II}^{1/2}/\sqrt{\epsilon})} \quad . \tag{8.15}$$

An argument similar to the one above shows that on boundary II:

$$|1-u(x)| \leq \sqrt{\varepsilon} \left[\frac{e^{-(\psi_{II}^{0})^{2}/\varepsilon}}{\psi_{II}^{0}} - \frac{e^{-(\psi_{II}^{1})^{2}/\varepsilon}}{\psi_{II}^{1}} \right] g^{0}$$
(8.16)
+ $0(\varepsilon^{3/2}),$

where ψ_{II}^0 is the minimum value of $\psi(x)$ on boundary II .

With the above choices of z_0 , z_1 and g^0 , the ansatz (7.1) will satisfy the boundary conditions to within exponentially small correction terms.

8.3. Contours of Probability

Once ψ and g^0 are known, the leading term in the expansion of u(x) is

$$u(x) \sim g^{0} E(\psi(x)/\sqrt{\varepsilon}) + O(\varepsilon^{\frac{1}{2}}) . \qquad (8.17)$$

Since $\psi_{\scriptscriptstyle +}$ vanishes on the separatrix, in a vicinity of the separatrix

$$\psi(x) = \psi_n(x_s) \delta n + O(\delta n^2)$$
 (8.18)

where x is a point on the separatrix and $\,\delta n\,$ is the distance from x to x .

Contours of equal probability are obtained when $\psi(x)$ is a constant. Thus, to leading order, we obtain contours at distances $\delta n = 1/\psi_n$ from the separatrix.

9. Completion of the first term: Evaluation of h^0

Since $\psi = 0$ on the separatrix, equation (7.6) becomes

$$\frac{dh^{0}}{dt} - \frac{a^{ij}}{2}h^{0}\psi_{i}\psi_{j} = -\frac{a^{ij}}{2}\psi_{ij}g^{0} - g^{0}c^{i}\psi_{i} . \qquad (9.1)$$

At the saddle point, dh^0/dt vanishes. Equation (9.1) can then be solved for $h^0(P_1)$:

$$h^{0}(P_{1}) = \frac{a^{ij}\psi_{ij}g^{0} + 2g^{0}c^{i}\psi_{i}}{a^{ij}\psi_{i}\psi_{j}} \Big|_{P_{1}} \equiv K .$$
(9.2)

The solution of (9.1) which satisfies (9.2) is

$$h^{0}(t) = \frac{\int_{t}^{\infty} p(s) [\frac{a_{ij}}{2} \psi_{ij} + c^{i} \psi_{i}] g^{0} ds + K}{p(t)}, \qquad (9.3)$$

where

$$p(s) = \exp\left[\int_{s}^{\infty} \frac{a^{ij}}{2} \psi_{i}\psi_{j}dt'\right]$$
(9.4)

and K is given by equation (9.2).

Once $h^{0}(t)$ is known on *S*, equation (7.6) can be used to calculate h^{0} in the plane. Since the separatrix is a characteristic curve of (7.6), the problem as posed is a characteristic initial value problem. In Appendix A, we show how the above problem can be converted to a noncharacteristic initial value problem and h^{0} calculated everywhere in the plane. The existence proof for solutions of (7.6), with initial data on the separatrix is analogous to the existence proof given in Appendix F.

Chapter 3. <u>Asymptotic Solution of the First Exit Problem in</u> the Marginal Case

10. Marginal Type Dynamical Systems

The deterministic evolution of the macrovariables is governed by

$$\dot{x} = b(x,\eta)$$
 (10.1)

where $n \in \mathbb{R}^1$ is a parameter. Equation (10.1) may have three steady states, $Q_0(n)$, $Q_1(n)$ and P_2 . Let B_k be the matrix (b^i, j) evaluated at Q_0 , Q_1 or P_2 (k = 0,1,2). We assume that:

1) For all values of n, B_2 has two real negative eigenvalues. Although P_2 may depend upon n, P_2 is always bounded away from the separatrix tube.

2) As $n \neq 0$, the distance between $Q_0(n)$ and $Q_1(n)$ decreases. When n = 0, Q_0 and Q_1 coalesce and annihilate each other (i.e. when n < 0, (10.1) has one real and two complex steady states).

3) When $\eta > 0$, B_0 has two real negative eigenvalues and B_1 has one real positive and one real negative eigenvalue. When $\eta = 0$, $B_0 = B_1$ has one zero and one real negative eigenvalue. The eigenvector corresponding to the negative eigenvalue has positive slope. The double point $Q_0(0)/Q_1(0)$ is called a saddle node (Andronov et. al., 1973).

A deterministic system satisfying the above assumptions will be structurally similar to the system sketched in Fig. 7.



Fig. 7. Marginal Type Dynamical System

The above conditions can be reformulated by a change of coordinates. Define the y^1 axis in the direction of the eigenvector of the non-negative eigenvalue of B_1 . The y^2 axis is in the direction of the eigenvector of the negative eigenvalue of B_1 , with the origin at Q_1 . Then

$$\dot{y} = \tilde{b}(y,\eta) \tag{10.2}$$

is the deterministic system in the new coordinates. The system is of the marginal type if:

1)
$$\det(b^{1}, (Q_{1}, 0)) = 0$$

2) $\tilde{b}^{1}, (Q_{1}, 0) = \tilde{b}^{2}, (Q_{1}, 0) = 0$ (10.3)

3)
$$\tilde{b}^{2}, {}_{2}(Q_{1}, 0) \neq 0$$

4) $\tilde{b}^{1}, {}_{11}(Q_{1}, 0) - \tilde{b}^{2}, {}_{11}(Q_{1}, 0) \neq 0$.

11. The Asymptotic Solution

11.1. Breakdown of the Error Approximation

If one wishes to use the theory of §8 to solve the backward equation, then $\psi(\mathbf{x})$, the argument of the Error integral, must satisfy

$$b^{i}\psi_{i} - \frac{a^{ij}\psi_{i}\psi_{j}}{2}\psi = 0. \qquad (11.1)$$

In the marginal case, b(x) vanishes at two points Q_0 and Q_1 . In §7, we showed that $\psi(Q_1) = 0$. It is clear that $\psi(Q_0)$ must be less than $\psi(Q_1)$. Thus, at Q_0 , the ψ_1 must vanish or be infinite and $\psi(x)$ is no longer a regular function. If $\psi(x)$ is to be regular, the Error integral must be replaced by a more complicated special function.

11.2. Uniform Solution in Terms of the Airy Integral

The analysis presented in §5 indicates that the uniform solution of the backward equation in the marginal case can be given in terms of the Airy integral and its derivative. In analogy to §7, we seek a formal solution of (4.10) of the form

$$u(\mathbf{x}) = \sum \varepsilon^{n} g^{n}(\mathbf{x}) A(\psi/\varepsilon^{1/3}, \alpha/\varepsilon^{2/3}) + \varepsilon^{n+2/3} h^{n}(\mathbf{x}) A'(\psi/\varepsilon^{1/3}, \alpha/\varepsilon^{2/3}) .$$
(11.2)

In equation (11.2), the parameter α and functions $\psi(x)$, $g^n(x)$ and $h^n(x)$ are to be determined. The function $A(z,\beta)$ is the Airy integral and satisfies

$$\frac{\mathrm{d}^{2}A}{\mathrm{d}z^{2}} = -(z^{2}-\beta) \frac{\mathrm{d}A(z,\beta)}{\mathrm{d}z} \qquad z_{0} \leq z \leq z_{1} \qquad (11.3)$$

When the derivatives of u(x) are evaluated, equation (11.3) is used to replace A" by products of A' and $(\psi^2 - \alpha)/\epsilon^{2/3}$. Following Lynn and Keller (1970) we assume that

$$\alpha = \sum_{k} \alpha_{k} \varepsilon^{k} . \qquad (11.4)$$

After derivatives are evaluated and substituted into the backward equation (4.10), terms are collected according to powers of ϵ . We obtain:

$$0 = \sum_{n=0}^{\infty} e^{n-1/3} A' (g^{n} - (\psi^{2} - \alpha_{0})h^{n}) (b^{i}\psi_{i} - (\psi^{2} - \alpha_{0})\frac{a^{ij}}{2}\psi_{i}\psi_{j}) + \sum_{n=0}^{\infty} e^{n-1/3} A' (b^{i}g_{i}^{n} + \frac{a^{ij}}{2}g_{ij}^{n-1} + c^{i}g_{i}^{n-1}) + \sum_{n=0}^{\infty} e^{n+2/3} A' (b^{i}h_{i}^{n} + c^{i}g^{n}\psi_{i} - c^{i}\psi_{i}(\psi^{2} - \alpha_{0})h^{n} + c^{i}h_{i}^{n-1} + \frac{a^{ij}}{2}g^{n}\psi_{ij} + a^{ij}g_{i}^{n}\psi_{j} + \frac{a^{ij}}{2}h_{ij}^{n-1} - (\psi^{2} - \alpha_{0})a^{ij}h_{i}^{n}\psi_{j} - h^{n}\frac{a^{ij}}{2}(\psi_{i}(\psi^{2} - \alpha_{0}))_{j}$$
(11.5)
$$+ \sum_{k=1}^{n+1} \alpha_{k} \{h^{n+1-k}(b^{i}\psi_{i} - (\psi^{2} - \alpha_{0})\frac{a^{ij}}{2}\psi_{i}\psi_{j}\} + \frac{a^{ij}}{2}\psi_{i}\psi_{j}(g^{n+1-k} - (\psi^{2} - \alpha_{0})h^{n+1-k})\} + \sum_{k=1}^{n} \alpha_{k}(c^{i}\psi_{i}h^{n-k} + \frac{a^{ij}}{2}(2h_{i}^{n-k}\psi_{j} + h^{n-k}\psi_{ij})) + \sum_{k=2}^{n+1} \frac{a^{ij}}{2}\psi_{i}\psi_{j}h^{n-k+1}(\sum_{j=1}^{k-1} \alpha_{j}\alpha_{k-j})) .$$

In equation (11.5), if a superscript is less than zero, that term is set equal to zero.

The leading term (n=0) is composed of three parts and will vanish if

$$b^{i}\psi_{i} - \frac{a^{ij}}{2}\psi_{i}\psi_{j}(\psi^{2}-\alpha_{0}) = 0 \qquad (11.6)$$

$$b^{i}g^{0}_{i} = 0$$
 (11.7)

$$b^{i}h_{i}^{0} - h^{0} \frac{a^{ij}}{2} ((\psi_{i}(\psi^{2} - \alpha_{0}))_{j}) - (\psi^{2} - \alpha_{0})a^{ij}h_{j}^{0}\psi_{i}$$

- $\alpha_{1} \frac{a^{ij}}{2} \psi_{i}\psi_{j}(g^{0} - (\psi^{2} - \alpha_{0})h^{0}) + \frac{a^{ij}}{2} g^{0}\psi_{ij}$ (11.8)
+ $c^{i}\psi_{i}g^{0} + c^{i}\psi_{i}h^{0}(\psi^{2} - \alpha_{0}) = 0$.

Equations (11.6, 7) were used in obtaining (11.8).

From equation (11.6), we see that $\psi(x)$ will be a regular function of x. The field b(x) vanishes at two points Q_0, Q_1 . We require that $\psi^2 = \alpha_0$ at these two points. Since $\psi(Q_1) > \psi(Q_0)$ for the problem as formulated, we set $\psi(Q_0) = -\sqrt{\alpha_0}$ and $\psi(Q_1) = \sqrt{\alpha_0}$.

In §12-14, we explicitly treat (11.6 - 11.8). Higher order terms can be treated in an analogous fashion (Appendix B).

12. Evaluation of the Parameter α_0

The substitution $\phi = -\frac{1}{3}\psi^3 + \alpha_0\psi - \frac{2}{3}\alpha_0^{3/2}$ converts equation (11.6) to the eikonal equation (8.1). An argument analogous to the one in §8 shows that $\psi = \sqrt{\alpha_0}$ on the entire separatrix S. The

parameter α_0 must be determined so that (11.6) is satisfied with initial data $\psi = \sqrt{\alpha_0}$ on the separatrix and the additional condition that $\psi = -\sqrt{\alpha_0}$ at Q_0 . The one additional condition allows the unique determination of α_0 .

The following iterative procedure can be used to determine α_0 . An initial choice of α_0 , $\alpha_0^{(0)}$ is made. We set $\psi = -\sqrt{\alpha_0^{(0)}}$ at Q_0 . Equation (11.6) is then solved by the method of characteristics (Courant, 1962). When the method of characteristics is used, the phase plane is covered by a family of trajectories called rays. The rays are generated from the system of ordinary differential equations

$$\frac{dx^{i}}{ds} = b^{i} - \frac{a^{ij}}{2} p_{j}(\psi^{2} - \alpha_{0})$$
(12.1)

$$\frac{d\psi}{ds} = \frac{dx^{i}}{ds} \cdot p_{i}$$
(12.2)

$$\frac{d p_k}{ds} = -b^i, \quad p_i + 2a^{ij} \psi p_j p_i p_k + \frac{a^{ij}}{2} p_i p_j (\psi^2 - \alpha_0), \quad (12.3)$$

where $p_i = \psi_i$. Some of the rays emanating from Q_0 will hit the separatrix S. If $\psi \neq \sqrt{\alpha_0^{(0)}}$ on S, then $\alpha_0^{(0)}$ must be replaced by an improved estimate of α_0 , $\alpha_0^{(1)}$. The method of false position (Dennis and More, 1977) can be used to calculate increments in α_0 . The above procedure can be repeated until α_0 is determined to any desired accuracy. As the estimates $\alpha_0^{(n)}$ approach the true value α_0 , the rays will begin to bend and run parallel to the separatrix, which is itself a ray. An indication that a ray is approaching the separatrix is that $b^i \psi_i = \psi_t \rightarrow 0$. This criterion can be used in numerical determination of α_0 .

An equivalent procedure would follow rays that emanate from the saddle Q_1 and approach Q_0 . If ψ does not approach $-\sqrt{\alpha_0^{(0)}}$ as the ray approaches Q_0 , the estimate of α_0 must be modified. A priori it is not clear which technique is preferable. The decision must be made on the basis of practicality. The calculations described in Chapter 5 used the first technique.

13. Determination of ψ and g^0 : Contours of Probability

A procedure analogous to the one in §8 yields the following equation for $\psi_n(t)$ on S:

$$\frac{\mathrm{d}\psi_{\mathrm{n}}}{\mathrm{d}t} + \hat{\mathrm{b}}\psi_{\mathrm{n}} - \sqrt{\alpha_{0}} \hat{\mathrm{a}}\psi_{\mathrm{n}}^{3} = 0 . \qquad (13.1)$$

When $\alpha_0 > 0$, i.e. the two points have not coalesced, equation (13.1) can be treated exactly as (8.6) was. In Appendix D we show that the constructions given here and in §14 are regular at the marginal bifurcation.

Similarly, the values of z_0 , z_1 and g_0 can be determined as in §8.2, except that the Error integral is replaced by the incomplete Airy integral. When g^0 is evaluated, the expansion of the Airy integral (5.19) can be used to simplify the evaluation of g_0^0 .

Once ψ and g^0 are known, the leading part of the formal expansion for the first exit probability is

$$u(x) \sim g^{0} A(\psi(x)/\epsilon^{1/3}, \alpha_{0}/\epsilon^{2/3}) + O(\epsilon^{2/3})$$
 (13.2)

Equation (13.2) can be used to generate contours of equal probability.

14. Completion of the First Term: Calculation of
$$h^0$$
 and α_1

The function $h^0(x)$ must satisfy equation (11.8). Since $\psi^2 = \alpha_0$ on the separatrix, on S the equation for h^0 is

$$\frac{dh^{0}}{dt} - h^{0} a^{ij} \left[\sqrt{\alpha_{0}} \psi_{i} \psi_{j} \right] = (\alpha_{1} \frac{a^{ij}}{2} \psi_{i} \psi_{j} - \frac{a^{ij}}{2} \psi_{ij} - c^{i} \psi_{i}) g^{0}. \quad (14.1)$$

We assume that $\alpha_0 > 0$, i.e. that Q_0 and Q_1 are distinct. In Appendix D, we show how to calculate h^0 when $\alpha_0 = 0$.

Since $d/dt = b^i \partial/\partial x^i$, at the saddle point equation (14.1) becomes an algebraic equation, with solution

$$h^{0}(Q_{1}) = \frac{(\alpha_{1}a^{ij}\psi_{i}\psi_{j} - a^{ij}\psi_{ij} - 2c^{i}\psi_{i})}{-2\sqrt{\alpha_{0}}a^{ij}\psi_{i}\psi_{j}}g^{0}\Big|_{Q_{1}}.$$
 (14.2)

If p(t) is defined by

$$p(t) = \int_{t}^{\infty} a^{ij} \psi_{i} \psi_{j} \sqrt{\alpha_{0}} ds, \qquad (14.3)$$

then the solution of (14.1) satisfying (14.2) is

$$h^{0}(t) = \frac{-\int_{t}^{\infty} \exp(p(s))g^{0}[\alpha_{1}\frac{a^{ij}\psi_{i}\psi_{j}}{2} - \frac{a^{ij}\psi_{ij}}{2} - c^{i}\psi_{i}]ds + h^{0}(Q_{1}).$$

$$\exp(p(t)) \qquad (14.4)$$

Once $h^{0}(t)$ is known on the separatrix, it can be determined everywhere in the plane by the method of characteristics, as described in Appendix A.

The parameter α_1 is still undetermined. It can be approximately calculated as follows. The field b(x) vanishes at Q_0 , where $\psi = -\sqrt{\alpha_0}$. At Q_0 , equation (14.1) becomes

$$h^{0}(Q_{0}) = \frac{(\alpha_{1}a^{ij}\psi_{i}\psi_{j} - a^{ij}\psi_{ij} - 2c^{i}\psi_{i})}{2\sqrt{\alpha_{0}}a^{ij}\psi_{i}\psi_{j}}g^{0}\Big|_{Q_{0}}$$
(14.5)

When Q_0 and Q_1 are close together, we determine h^0 at Q_0 by a Taylor expansion

$$h^{0}(Q_{0}) \simeq h^{0}(Q_{1}) + v_{i}\delta x^{i},$$
 (14.6)

where $v_i = \partial h^0 / \partial x^i |_{Q_1}$. The parameter α_1 is chosen so that equations (14.5) and (14.6) agree.

A more exact determination of α_1 uses the method of characteristics, as the calculation of α_0 did. As described in Appendix A, a manifold S' can be determined on which (14.1) is not a characteristic initial value problem. Then, equation (14.1) can be solved by the method of characteristics, starting at Q_1 . When a ray reaches Q_0 , h^0 should have the value given in (14.5). If the value of h^0 at Q_0 , when calculated by the method of characteristics, is not the same as the value given in (14.5), then the estimate of α_1 must be modified. The method of false position can be used to calculate the iterates of α_1 .

Chapter 4: Asymptotic Solution of the First Exit Problem in the Critical Case

15. Critical Type Dynamical Systems

The macrovariables evolve according to a deterministic kinetic equation

$$\dot{\mathbf{x}} = \mathbf{b}(\mathbf{x}, \mathbf{\eta}, \delta) \tag{15.1}$$

where η , δ are one dimensional parameters. The entire bifurcation set of equation (15.1) is still unknown (Arnold, 1972). The physical systems of interest here motivate the following assumptions:

1) For some values of η , δ , (15.1) has three steady states $P_0(\eta, \delta)$, $P_1(\eta, \delta)$ and $P_2(\eta, \delta)$. All three steady states are contained in the separatrix tube. If $B_k = (b^i, j)$ evaluated at P_k , then when the three steady states are distinct, B_0 and B_2 have real negative eigenvalues. B_1 has one real negative and one real positive eigenvalue. The eigenvector corresponding to the negative eigenvalue has positive slope.

2) As η , δ vary, two of the steady states may coalesce and annihilate each other. This behavior is analogous to the marginal bifurcation.

3) As n, δ vary, all three steady states may move together and coalesce when $\eta = \delta = 0$. At the critical bifurcation, $B_1 = (b_{,j}^i)$ has a zero eigenvalue. We assume that the steady state remaining after the critical bifurcation is a stable steady state. A deterministic system satisfying the above postulates will be structurally similar to the one sketched in Fig. 8.



Fig. 8. Bifurcations of a Critical Type Dynamical System

The above properties can be restated in terms of a new coordinate system as follows. The y^1 axis is in the direction of the eigenvector of the non negative eigenvalue of B_1 . The y^2 axis is in the direction of the eigenvector of the negative eigenvalue, with the origin at P_1 . The deterministic evolution is then

$$\dot{y} = \dot{b}(y,\eta,\delta)$$
 (15.2)

A dynamical system is a critical type system if:

1)
$$\det(b^{i}, {}_{j}(P_{1}, 0, 0)) = 0$$

2) $\tilde{b}^{1}, {}_{1}(P_{1}, 0, 0) = \tilde{b}^{2}, {}_{1}(P_{1}, 0, 0)$
 $= \tilde{b}^{1}, {}_{11}(P_{1}, 0, 0) = \tilde{b}^{2}, {}_{11}(P_{1}, 0, 0) = 0$ (15.3)
3) $\tilde{b}^{2}, {}_{2}(P_{1}, 0, 0) \neq 0$
4) $\tilde{b}^{1}, {}_{111} - \tilde{b}^{2}, {}_{111} \neq 0.$

16. The Asymptotic Solution

16.1. Breakdown of Solutions Using the Airy Integral

If the theory of Chapter 3 were used in the critical case, the argument of the Airy integral would have to satisfy

$$b^{i}\psi_{i} - \frac{a^{ij}}{2}\psi_{i}\psi_{j}(\psi^{2}-\alpha_{0}) = 0. \qquad (16.1)$$

Since the deterministic field now vanishes at three points in the separatrix tube, expression (16.1) indicates that $\psi(x)$ will not be regular at the third steady state. If we wish to construct a solution in which $\psi(x)$ is regular, the Airy integral must be

replaced by a more complicated special function.

16.2. Uniform Solution in terms of the Pearcey Integral

The analysis in §5 and results in Chapters 2, 3 indicate that a possible formal solution of the backward equation in the critical case is

$$u(x) = \sum \varepsilon^{n} g^{n}(x) P(\psi(x)/\varepsilon^{1/4}, \alpha/\varepsilon^{1/2}, \beta/\varepsilon^{3/4})$$

$$+ \varepsilon^{n+3/4} h^{n}(x) P'(\psi(x)/\varepsilon^{1/4}, \alpha/\varepsilon^{1/2}, \beta/\varepsilon^{3/4})$$
(16.2)

where the parameters α , β and functions $\psi(x)$, $h^n(x)$ and $g^n(x)$ are to be determined. The function $P(z,\alpha,\beta)$ is the Pearcey integral, satisfying

$$\frac{\mathrm{d}^2 P}{\mathrm{d}z^2}(z,\alpha,\beta) = (z^3 - \alpha z - \beta) \frac{\mathrm{d} P(z,\alpha,\beta)}{\mathrm{d} z} \qquad z_0 \leq z \leq z_1 \quad . \tag{16.3}$$

When the derivatives of u(x) are evaluated, equation (16.3) is used to replace P" by products of P' and $(\psi^3 - \alpha \psi - \beta)/\epsilon^{3/4}$. We assume that α and β have asymptotic expansions of the form

$$\alpha = \sum \varepsilon^{k} \alpha_{k} \qquad \beta = \sum \beta_{k} \varepsilon^{k} \qquad (16.4)$$

After derivatives of u(x) are evaluated and substituted into the backward equation (4.10), terms are collected according to powers of ε . We obtain

$$0 = \sum_{n=0}^{\infty} e^{n-1/4} P'(g^{n}+h^{n}(\psi^{3}-\alpha_{0}\psi-\beta_{0}))(b^{i}\psi_{i}+\frac{a^{ij}}{2}\psi_{i}\psi_{j}(\psi^{3}-\alpha_{0}\psi-\beta_{0})) + \sum_{n=0}^{\infty} e^{n}P(b^{i}g^{n}_{i}+\frac{a^{ij}}{2}g^{n-1}_{ij}+c^{i}g^{n-1}_{i}) + \sum_{n=0}^{\infty} e^{n+3/4}P'(b^{i}h^{n}_{i}+c^{i}g^{n}_{i}+c^{i}h^{n-1}_{i}+h^{n}c^{i}\psi_{i}(\psi^{3}-\alpha_{0}\psi-\beta_{0}) + a^{ij}g^{n}_{i}\psi_{j}+\frac{a^{ij}}{2}h^{n-1}_{ij}+\frac{a^{ij}}{2}g^{n}\psi_{ij}+(\psi^{3}-\alpha_{0}\psi-\beta_{0})a^{ij}h^{n}_{i}\psi_{j} + \frac{a^{ij}}{2}h^{n}(\psi_{i}(\psi^{3}-\alpha_{0}\psi-\beta_{0}))_{j} - \sum_{k=1}^{n+1}^{n+1}(\psi_{k}\alpha_{k}+\beta_{k})\{\frac{a^{ij}}{2}\psi_{i}\psi_{j}(\varphi^{n+1-k}+h^{n+1-k}(\psi^{3}-\alpha_{0}\psi-\beta_{0})+h^{n+1-k}(b^{i}\psi_{i}+\frac{a^{ij}}{2}\psi_{i}\psi_{j}(\psi^{3}-\alpha_{0}\psi-\beta_{0})\}$$
(16.5)
$$+ \sum_{k=2}^{n+1}\frac{a^{ij}}{2}\psi_{i}\psi_{j}h^{n-k+1}(\sum_{j=1}^{k-1}(\psi\alpha_{j}+\beta_{j})(\psi\alpha_{k-j}+\beta_{k-j})) + \sum_{k=1}^{n}(\psi\alpha_{k}+\beta_{k})(c^{i}\psi_{i}h^{n-k} - \frac{a^{ij}}{2}(2h^{n-k}_{i}\psi_{j}+h^{n-k}\psi_{ij})) + \sum_{k=1}^{n}\alpha_{k}\frac{a^{ij}}{2}\psi_{i}\psi_{j}h^{n-k}\}$$

In equation (16.5), if a superscript is less than zero, that term is set equal to zero.

The first term in (16.5) is composed of three parts and will vanish if

$$b^{i}\psi_{i} + \frac{a^{ij}}{2}\psi_{i}\psi_{j}(\psi^{3} - \alpha_{0}\psi - \beta_{0}) = 0$$
 (16.6)

÷,

$$b_{g_{i}}^{i} = 0$$
 (16.7)

$$b^{i}h_{i}^{0} + \frac{a^{ij}}{2} g^{0}\psi_{ij} + (\psi^{3} - \alpha_{0}\psi - \beta_{0})a^{ij}h_{i}^{0}\psi_{j}$$

$$+ \frac{a^{ij}}{2} h^{0}\psi_{ij}(\psi^{3} - \alpha_{0}\psi - \beta_{0}) + h^{0}\frac{a^{ij}}{2}\psi_{i}\psi_{j}(3\psi^{2} - \alpha_{0}) \qquad (16.8)$$

$$- (\psi\alpha_{1} + \beta_{1})f^{0}(\psi, 1) + g^{0}c^{i}\psi_{i} + c^{i}\psi_{i}h^{0}(\psi^{3} - \alpha_{0}\psi - \beta_{0}) = 0 ,$$

where we have denoted

$$f^{n}(\psi, k) = \sum_{k=1}^{n+1} \frac{a^{ij}}{2} \psi_{i} \psi_{j} (g^{n+1-k} + h^{n+1-k} (\psi^{3} - \alpha_{0} \psi - \beta_{0})) + h^{n+1-k} (b^{i} \psi_{i} + \frac{a^{ij}}{2} \psi_{i} \psi_{j} (\psi^{3} - \alpha_{0} \psi - \beta_{0})) .$$
(16.9)

The field b(x) vanishes at P_0 , P_1 and P_2 . The function $\psi(x)$ will remain regular if $\psi^3 - \alpha_0 \psi - \beta_0$ vanishes at the points where b(x) vanishes. Let $\tilde{\psi}_0 \leq \tilde{\psi}_1 \leq \tilde{\psi}_2$ denote the ordered roots of

$$\psi^3 - \alpha_0 \psi - \beta_0 = 0 . \qquad (16.10)$$

We then set $\psi(P_0) = \tilde{\psi}_0$, $\psi(P_1) = \tilde{\psi}_1$ and $\psi(P_2) = \tilde{\psi}_2$.

In §18-19 we treat equations (16.6 - 8) explicitly. Higher order terms are discussed in Appendix B.

17. Determination of the Parameters α_0 and β_0

The transformation $\phi = \frac{1}{4} \psi^4 - \alpha_0 \psi^2 / 2 - \beta_0 \psi - \frac{1}{4} \tilde{\psi}_1^4 + \alpha_0 \tilde{\psi}_1^2 / 2 + \beta_0 \tilde{\psi}_1$ converts equation (16.6) to the eikonal equation (8.1). An argument using Hamilton-Jacobi theory, as in §8, shows that $\psi = \tilde{\psi}_1$ on the entire separatrix.

Equation (16.6) must be solved with initial data on the separatrix and the two extra conditions $\psi(P_0) = \tilde{\psi}_0$ and $\psi(P_2) = \tilde{\psi}_2$. The two extra conditions allow the unique determination of α_0 and β_0 . As in §12, an iterative procedure is used to determine α_0 and β_0 .

Initial estimates, $\alpha_0^{(0)}$ and $\beta_0^{(0)}$, are used in (16.6). Equation (16.6) is solved by the method of characteristics, starting close to the saddle point where $\psi = \tilde{\psi}_1$ and $\tilde{\psi}_1$ is the middle root of

$$\psi^{3} - \alpha_{0}^{(0)}\psi - \beta_{0}^{(0)} = 0 . \qquad (17.1)$$

Some rays emanating from P_1 will approach P_0 , others will approach P_2 . As P_0 is approached, ψ should approach $\tilde{\psi}_0$; as P_2 is approached ψ should approach $\tilde{\psi}_2$. If $\psi(P_0)$, $\psi(P_2)$ are not $\tilde{\psi}_0$, $\tilde{\psi}_2$, then the values of the parameters must be modified. The method of false position can be used to calculate iterates of α_0 and β_0 . This procedure can be repeated until α_0 and β_0 are determined to any order of accuracy.

18. Determination of ψ and g⁰: Contours of Probability

Using the procedure outlined in §8, the following equation can be derived for $\psi_n(t)$ on the separatrix

$$\frac{d\psi_n}{dt} + \hat{b}\psi_n + \hat{a}_2 \psi_n^3 (3\tilde{\psi}_1^2 - \alpha_0) = 0 . \qquad (18.1)$$

We assume that the three points have not coalesced, so that ψ_1 and α_0 are not both zero. In Appendix E we show that the constructions in §17-19 are regular at the critical bifurcation. Equation (18.1) can be treated exactly as (8.6) was treated.

Similarly, z_0 , z_1 and g^0 can be calculated as in §8.2, except that the error integral is replaced by the incomplete Pearcey integral. When g^0 is evaluated, the expansions (5.26) can be used to simplify numerical calculation. Once $\alpha_0,\,\beta_0,\,\psi$ and g^0 are known, the leading term in the formal expansion of u is

$$u(x) \sim g^{0} P(\psi/\epsilon^{1/4}, \alpha_{0}/\epsilon^{1/2}, \beta_{0}/\epsilon^{3/4}) + O(\epsilon^{3/4})$$
 (18.2)

Equation (18.2) can be used to generate contours of equal probability.

19. Completion of the first term: Calculation of h^0 , α_1 and β_1

The function h^0 must be determined from equation (16.8). On the separatrix, where $\psi = \tilde{\psi}_1$ and $\psi^3 - \alpha_0 \psi - \beta_0$ vanishes, (16.8) becomes

$$\frac{dh^{0}}{dt} + h^{0} \frac{a^{ij}}{2} \psi_{i}\psi_{j}(\tilde{3\psi_{1}^{2}} - \alpha_{0}) = (\tilde{\psi}_{1}\alpha_{1} + \beta_{1}) \frac{a^{ij}}{2} g^{0}\psi_{i}\psi_{j} - g^{0}c^{i}\psi_{i} - \frac{a^{ij}}{2} g^{0}\psi_{ij} \cdot (19.1)$$

Since $d/dt = b^i \partial/\partial x^i$, at the saddle point P₁ equation (19.1) becomes

$$h^{0}(P_{1}) = \frac{(\tilde{\psi}_{1}\alpha_{1} + \beta_{1})a^{ij}\psi_{i}\psi_{j} - 2c^{i}\psi_{i} - a^{ij}\psi_{ij})}{(3\tilde{\psi}_{1}^{2} - \alpha_{0})a^{ij}\psi_{i}\psi_{j}}g_{0}^{0}\Big|_{P_{1}}.$$
 (19.2)

If p(t) is defined by

$$p(t) = \int_{t}^{\infty} (3\tilde{\psi}_{1}^{2} - \alpha_{0}) \frac{a^{ij}}{2} \psi_{i}\psi_{j} ds, \qquad (19.3)$$

and

$$f(t) = (-(\tilde{\psi}_{1}\alpha_{1}+\beta_{1})\frac{a^{ij}}{2}\psi_{i}\psi_{j} + c^{i}\psi_{i} + \frac{a^{ij}\psi_{ij}}{2})g^{0}, \qquad (19.4)$$

the solution of (19.1) satisfying (19.2) is

$$h^{0}(t) = \frac{\int_{t}^{\infty} f(s)e^{-p(s)}ds + h^{0}(P_{1})}{\exp[-p(t)]} . \qquad (19.5)$$

Once $h^{0}(t)$ is known on the separatrix, it can be determined everywhere in the plane, by the method of characteristics, as described in Appendix A.

The parameters α_1 and β_1 are still undetermined. They can be determined by using the method of characteristics, in a manner analogous to the calculation of α_0 and β_0 . As described in Appendix A, a new manifold S' can be constructed, with h^0 known on S', so that (16.8) is not a characteristic initial value problem. Then (16.8) can be solved by the method of characteristics. Some rays emanating from S' will approach P_0 or P_2 , where h^0 must have the value

$$h^{0}(P_{k}) = \frac{(\tilde{\psi}_{k}\alpha_{1}+\beta_{1})a^{ij}\psi_{i}\psi_{j} - 2c^{i}\psi_{i} - a^{ij}\psi_{ij})g^{0}}{(3\tilde{\psi}_{k}^{2}-\alpha_{0})a^{ij}\psi_{i}\psi_{j}} \Big|_{P_{k}}, k=1,2. \quad (19.6)$$

If the value of h^0 at P_k , when calculated by the method of characteristics, is not the same as the value determined from (19.6), then the estimates of α_1 and β_1 must be improved. The method of false position can be used to calculate iterates of α_1 and β_1 .

20. Two Complex Steady States with Small Imaginary Parts

When $\eta < 0$ (marginal case) or $\eta < 0$, $\delta < 0$ (critical case) only one real steady state exists. There will be two complex steady states. If the imaginary parts of the complex steady states are small, then the linear part of the deterministic equations about the real steady state will be small. Consequently, the dynamics at the steady state are almost completely nonlinear. We thus expect that the Error integral, which corresponds to nonvanishing linear dynamics, will not provide an adequate asymptotic solution of the first exit problem. The Pearcey integral, however, can be used to provide an adequate asymptotic solution.

When the ansatz (16.2) is used, the function $\psi(x)$ must satisfy (16.6). In order to determine α_0 and β_0 by the method of characteristics, complex rays would be needed. An easier, although less accurate, technique uses power series for α_0 , β_0 . In Appendix E, we derive power series of the form

$$\alpha_0 = \sum_{i,j}^{r} A_{ij} \eta^i \delta^j$$
(20.1)

$$\beta_0 = \sum_{i,j}^r B_{ij} \eta^i \delta^j . \qquad (20.2)$$

The power series extend up to order r, in η and δ , if the deterministic equations are C^{r} in η and δ . Since we are using power series, the results given in this section are valid only in a neighborhood of the origin in (η, δ) space.

62

The value of ψ on the separatrix is $\psi_r, \ \mbox{where} \ \ \psi_r$ is the real root of

$$\psi^3 - \alpha_0 \psi - \beta_0 = 0 . \qquad (20.3)$$

Using the technique in §18, we can calculate the value of ψ in a neighborhood of the separatrix by a Taylor expansion. The value of g^0 can be determined as described in § 8.2. Thus, the leading term of the first exit probability is

$$u(x) \sim g^{0} P(\psi(x)/\epsilon^{1/4}, \alpha_{0}/\epsilon^{1/2}, \beta_{0}/\epsilon^{3/4})$$
 (20.4)

Our solution is approximate in the following sense. Since α_0 , β_0 are only given as power series, equation (16.6) is not satisfied identically, but must be replaced by

$$b^{i}\psi_{i} + \frac{a^{i}\psi_{i}\psi_{j}}{2}(\psi^{3} - \alpha_{0}\psi - \beta_{0}) = 0(\eta^{r+1} + \delta^{r+1}).$$

Let L indicate the backward operator. Then, our formal result will satisfy the backward operator to an order of $\epsilon n \delta$:

$$Lu = 0(\varepsilon^{-1/4}(\eta^{r+1} + \delta^{r+1})).$$
 (20.5)

The estimate (20.5) indicates how close n, δ must be to the origin for our ansatz to be valid. Unlike all previous results, which were independent of ε , the validity of the extension presented in this section is dependent upon ε .

Chpater 5. Fluctuation Effects on Substrate Inhibited Reactions

21. Multiple Steady States in Enzyme Reactions

The experiments of H. Degn (1968) conclusively demonstrated that multiple stable steady states actually can be observed. In his experiments, Degn was concerned with observing the multiple steady states and not with fluctuation effects. It is clear, however, that his techniques could be used to study fluctuation effects at the unstable steady state. In this chapter, we study fluctuation effects on a substrate inhibited reaction. Our choice of model was motivated by Degn's experiments, but is not meant to correspond to the experiments exactly.

21.1. Deterministic Kinetic Equations

In this section, we develop a model of Degn's experiments. The model has the following features.

1) A reaction vessel of volume V can exchange substrate '1' with an external reservoir of volume V'.

2) Substrate '1' is converted into product by a substrate inhibited enzyme. The concentration of substrate '1' in the reservoir is \tilde{x}_r^1 ; or x_r^1 molecules. An example of this reaction is the oxidation (x^1 being $[0_2]$) of NADH catalyzed by horse radish peroxidase.

3) Substrate '2' is continually fed into the reaction vessel, at rate $\tilde{\alpha}$, and reacts with substrate '1'. The reaction is catalyzed by an enzyme that obeys the usual Michaelis-Menten

64
mechanism (White et. al., 1969). An example of this reaction is the oxidation of glucose, catalyzed by glucose oxidase.

The elementary steps involved in these reactions are

a)
$$x^{1} + E^{1} \xrightarrow{k_{1}} (x^{1}E^{1})$$

b) $(x^{1}E^{1}) + E^{1} \xrightarrow{k_{3}} (x^{1}E^{1})$
c) $x^{1}E^{1} \xrightarrow{k_{2}} E^{1} + P^{1}$
d) $x^{1} + x^{2} + E^{2} \xrightarrow{\ell_{1}} (x^{1}x^{2}E^{2})$
e) $(x^{1}x^{2}E^{2}) \xrightarrow{\ell_{2}} E^{2} + P^{2}$
f) $x^{1} \xrightarrow{k} x^{1}_{R}$
(21.1)

In order to derive the kinetic equations for the concentrations of x^1 and x^2 , we use the Michaelis-Menten assumption (White et. al., 1969). Nondimensional concentration variables are

$$x^{i}(t) = \frac{[\text{concentration of species i at time t}]}{[\text{concentration of species i at 0}]} .$$
(21.2)

Then the kinetic equations for x^1 and x^2 are (Degn, 1968, Higgins, 1967)

$$\dot{x}^{1} = \frac{-x^{1}(k_{2}/k_{1}x^{10})}{\frac{k_{2}}{k_{1}x^{10}} + \frac{k_{-1}}{k_{1}x^{10}} + x^{1} + \frac{k_{3}x^{10}(x^{1})^{2}}{k_{-3}} + k(x_{r}^{1} - x^{1})}$$

$$\frac{-x^{2}x^{1}(\ell_{2}/x^{10}x^{20}\ell_{1})}{\frac{(\ell_{-1}+\ell_{2})}{x^{10}x^{20}\ell_{1}} + x^{2}x^{1}}$$

$$\dot{x}^{2} = \alpha - \frac{\frac{x^{2}x^{1}(\ell_{2}/x^{10}x^{20}\ell_{1})}{\frac{(\ell_{-1}+\ell_{2})}{x^{10}x^{20}\ell_{1}} + x^{2}x^{1}}.$$
(21.4)

In the above equations, x^{i0} is the initial concentration of species i. We choose the following values of the parameters: $\alpha = .09$, $x^{10} = x^{20} = 10^{-7}$ M, $k_1 = 1.2 \times 10^7 \ell$ /M-sec, $k_{-1} = .12 \text{ sec}^{-1}$, $k_2 = 1.68 \text{ sec}^{-1}$, $k_3 = 1.3 \times 10^6 \text{ M}^{-2} \text{ sec}^{-1}$, $k_{-3} = .01 \text{ sec}^{-1}$, $\ell_{-1} = 0 \text{ sec}^{-1}$, $\ell_2/\ell_1 x^{10} x^{20} = .1$. The values of x^{i0} and k_i roughly correspond to Chance's (1951) experimental data. The ℓ_i were chosen as "reasonable" estimates, since no data were available. With these choices, we obtain

$$\dot{\mathbf{x}}^{1} = \frac{-1.4\mathbf{x}^{1}}{1.5 + \mathbf{x}^{1} + 13(\mathbf{x}^{1})^{2}} + \mathbf{k}(\mathbf{x}_{r}^{1} - \mathbf{x}^{1}) - \frac{\mathbf{x}_{r}^{1}}{1 + 10\mathbf{x}_{r}^{1}}$$
(21.5)

$$\dot{x}^2 = .09 - \frac{x^1 x^2}{1 + 10 x^1 x^2}$$
 (21.6)

We assume that ε =100 and the 'volume' V=1/ ε . Equations.

Ś

(21.5,6) are model equations that exhibit the marginal and critical bifurcations. They are not meant to simulate a particular set of experiments. Since the rate constants of enzyme preparations vary widely, this appears to be a reasonable approach. We will refer to (x^1, x^2) as concentration variables. We will treat V as a non-dimensional quantity and treat $X^i = Vx^i$ as a variable corresponding to the number of "molecules".

21.2. Stochastic Model of the Enzyme Reactions

In the stochastic approach, the natural random variables are the numbers of molecules of species 1 and 2 in the reaction vessel at time t, \tilde{x}^1 and \tilde{x}^2 . The concentrations are then $\tilde{x}^i = \tilde{x}^i/V$. From the reaction mechanism (21.1), transition probabilities can be constructed. These are probabilities in a 5 dimensional space $(x^{1}, x^{2}, E^{1}, E^{2}, (x^{1}E^{1}))$. In order to be consistent, we must apply the Michaelis-Menten assumption to these probabilities; we replace E^{1}, E^{2} and $(X^{1}E^{1})$ by their steady state values. Once this replacement is performed, the transition probabilities will be given solely in terms of X^{2} and X^{2} . By using the Michaelis-Menten assumption, we are treating the enzyme concentrations as parameters rather than variables. Thus, we are assuming that fluctuations in enzyme concentration can be ignored in comparison to fluctuations in substrate concentration. This assumption is consistent with the work of Heyde and Heyde (1971). They found that the steady state fluctuations in enzyme concentration were $10^{+6} - 10^{+8}$ times smaller than the

fluctuations in substrate concentration.

When the Michaelis-Menten assumption is used, the transition probabilities for $\Delta \tilde{X}^{i} = \tilde{X}^{i}(t+\Delta t) - \tilde{X}^{i}(t)$ are

$$\Pr\{\Delta \tilde{x}^{1}=1, \Delta x^{2}=0 | \tilde{x}^{i}(t)=x^{i}\} = \frac{kx_{R}^{1}}{v'} \Delta t + o(\Delta t)$$
(21.7)

$$\Pr\{\Delta \tilde{x}^{1} = -1, \ \Delta \tilde{x}^{2} = 0 \ | \ \tilde{x}^{i}(t) = x^{i} \} = \left(\frac{1.4x^{1}}{1.5v + x^{1} + 13(x^{1})^{2}} + \frac{kx^{1}}{v} + \frac{x^{1}x^{2}}{v^{2} + 10^{1}x^{1}x^{2}} \right) \Delta t$$

$$+ o(\Delta t)$$
 (21.8)

$$\Pr\{\Delta \tilde{x}^{2} = -1, \ \Delta \tilde{x}^{1} = 0 | \tilde{x}^{i}(t) = x^{i} \} = \frac{x^{1} x^{2} \Delta t}{v^{2} + 10 x^{1} x^{2}} + o(\Delta t)$$
(21.9)

$$\Pr\{\Delta \tilde{X}^{2}=1, \ \Delta \tilde{X}^{1}=0 | \tilde{X}^{i}(t)=X^{i}\} = .09V\Delta t + o(\Delta t) . \qquad (21.10)$$

In Chapter 1, we introduced the infinitesimal covariance $\epsilon(a^{ij})$ and pointed out that since the stochastic kinetic equation was not derived from first principles, we need to provide a prescription for the calculation of $\epsilon(a^{ij})$. We shall now provide one such prescription by using the birth and death approach to chemical kinetics. One can obtain a result identical to ours by using Keizer's technique, (Keizer, 1975), which does not use the birth and death approach. Since none of the boundaries are singular, a change in the method used to calculate $\epsilon(a^{ij})$ will change some quantitative details, but will leave the qualitative results unchanged.

Instead of the kinetic equation (4.5), consider the kinetic equation

$$d\tilde{x}^{i} = b^{i}(\tilde{x})dt + \sqrt{\varepsilon a^{ij}} d\tilde{W}_{j} . \qquad (21.11)$$

In (21.11), $\tilde{W}(t)$ is the Wiener process. The functions b^{i} and ϵa^{ij} have the simple interpretation (Feller, 1971):

$$b^{i} = \lim_{\Delta t \to 0} \frac{1}{\Delta t} E\{ (\tilde{x}^{i}(t + \Delta t) - \tilde{x}^{i}(t)) | \tilde{x}^{k}(t) = x \quad k = 1, ..., n \}$$
(21.12)

$$\varepsilon a^{\mathbf{i}\mathbf{j}} = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \mathbb{E}\{ (\tilde{\mathbf{x}}^{\mathbf{i}}(t+\Delta t) - \tilde{\mathbf{x}}^{\mathbf{i}}(t)) (\tilde{\mathbf{x}}^{\mathbf{j}}(t+\Delta t) - \tilde{\mathbf{x}}^{\mathbf{j}}(t)) | \tilde{\mathbf{x}}^{\mathbf{k}}(t) = \mathbf{x} \quad \mathbf{k} = 1, \dots, n \}.$$
(21.13)

Equations (21.12,13) are the Ito interpretation of equation (21.11) (Nelson (1967), Arnold (1974)). Using the transition probabilities (21.7-10) we can easily calculate the covariance $\varepsilon(a^{ij})$. This procedure yields a result analogous to that obtained by the use of Keizer's fluctuation-dissipation postulates (Keizer, 1975). McQuarrie (1967) would calculate the covariance $\varepsilon(a^{ij})$ in a manner identical to the one described above. Kubo [et. al., (1973) and Matsuo (1977) also use similar procedures.

A white noise equation such as (21.11) can never really represent a physical process. However, such equations are used almost uniformly by physical scientists (e.g. Landau and Lifshitz (1959), (1968), Ma (1976)), based on the idea that $\tilde{Y}(s)$ has a negligible correlation time. We realize that (21.11) is an idealization of equation (4.5). Following Wong and Zakai (1965), we will give a white noise interpretation to (4.5). Consider a sequence of mixing processes $\tilde{Y}^{n}(\tau)$, which converge to $\tilde{W}(\tau)$ as $n \to \infty$. If the stochastic variable is $\tilde{x}^{n}(t;\tau)$, then as $n \to \infty$, $\tilde{x}^{n} \to \tilde{x}$ where \tilde{x} satisfies the Ito equation (Wong and Zakai (1965))

$$d\tilde{x}^{i} = (b^{i}(\tilde{x}) + \frac{1}{4} \frac{\partial}{\partial x^{j}} \epsilon a^{ij})dt + \sqrt{\epsilon a^{ij}} d\tilde{W}_{j} . \qquad (21.14)$$

We shall use (21.14) as an approximation to (4.5). The backward equation corresponding to (21.14) is

$$u_{t}^{ST} = \frac{\varepsilon a^{ij}}{2} u_{ij} + (b^{i} + \varepsilon c^{i}) u_{i}, \qquad (21.15)$$

where $c^{i} = \frac{1}{4} a^{ij}$, The backward equation corresponding to (21.11) is

$$u_{t}^{WN} = \frac{\varepsilon a^{ij}}{2} u_{ij} + b^{i} u_{i} . \qquad (21,16)$$

In §22, one dimensional versions of (22.15,16) are compared. The results of §22 indicate that for the problems of interest here, the choice of stochastic calculus is not important. Consequently, equation (21.14) is a useful approximation to (4.5).

The deterministic kinetic equations are given in terms of the "concentration" variable $x^{i}(t)$. When the transition probabilities are rewritten in terms of the concentration variables, the infinitesimal covariance is

$$\varepsilon a(\mathbf{x}) = \frac{1}{(100)^2} \begin{bmatrix} (\lambda_1 + \mu_1) \mathbf{x}^1 & 0 \\ 0 & (\lambda_2 + \mu_2) \mathbf{x}^2 \end{bmatrix}$$
(21.17)

where

$$\lambda_1 x^1 = k x_r^1$$
 (21.18a)

$$\mu_{1}x^{1} = \frac{1.4x^{1}}{1.5 + x^{1} + 13(x^{1})^{2}} + kx^{1} + \frac{x^{1}x^{2}}{1 + 10x^{1}x^{2}}$$
(21.18b)

$$\lambda_2 x^2 = .09$$
 (21.19a)

$$\mu_2 x^2 = \frac{x^1 x^2}{1 + 10x^1 x^2} \quad . \tag{21.19b}$$

When the transition probabilities are used to calculate the infinitesimal drift $b^{i}(x)$, we find

$$b^{1}(x) = \frac{1}{100} (\lambda_{1} - \mu_{1}) x^{\frac{1}{2}}$$
 (21.20)

$$b^{2}(x) = \frac{1}{100} (\lambda_{2} - \mu_{2})x^{2}$$
 (21.21)

A rescaling of time then yields $\dot{x}^{i} = b^{i}(x)$, so that the mean stochastic motion and the law of mass action agree.

The covariance (21.17) and drift (21.20,21) were used in all of the calculations reported in this chapter.

22. Exact and Asymptotic Solutions of the Backward Equation

In this section, we assume that the concentration of species 2 is subject to perfect control, so that x^2 is always at its steady value. When $\dot{x}^2 = 0$, equation (21.5) becomes

$$\dot{x}^{1} = \frac{-1.4x^{1}}{1.5 + x^{1} + 13(x^{1})^{2}} - kx^{1} + (kx^{1}_{r} - .09) = b(x^{1}, n, \delta) . \quad (22.1)$$

In the sequel, we drop the superscript 1 on x^1 . When k = .0968493and $kx_r - .09 = .182033$, equation (22.1) exhibits the critical bifurcation (b = b' = b" = 0 at the steady state).

The backward equation, if the non-white process is used, is

$$\frac{\varepsilon a(x)}{2}u_{xx} + bu_{x} + \varepsilon cu_{x} = 0, \qquad (22.2)$$

where b(x) is given by (22.1), $c = \frac{1}{4} a_x$, $\varepsilon = 10^{-2}$ and

$$a(x) = \frac{1.4x}{1.5 + x + 13x^2} + kx + kx_r + .09 . \qquad (22.3)$$

We denote the solution of (22.2) by $u^{ST}(x)$. When a white noise approximation is used, (22.2) is replaced by an equation in which $c \equiv 0$. We denote the solution of that equation by u^{WN} .

The unstable steady state is denoted by x_u . The boundary conditions for (22.2) are $u(x_u - .4) = 0$ and $u(x_u + .4) = 1$. When b(x) has only one steady state, x_s , the boundary conditions are $u(x_s - .4) = 0$ and $u(x_s + .4) = 1$.

All the exact solutions were calculated by a fourth order Runge Kutta routine. The function $\psi(x)$, the argument of the special function, will satisfy

$$b\psi_{x} - \frac{a}{2} f(\psi)\psi_{x}^{2} = 0,$$
 (22.4)

where $f(\psi) = \psi$, $\psi^2 - \alpha_0$ or $-\psi^3 + \alpha_0 \psi + \beta_0$, in normal, marginal or critical case respectively. At the unstable steady state, $\psi = \psi_s$, where $f(\psi_s) = 0$. Solving (22.4) yields

$$\psi_{\rm x} = \left(\frac{2b'}{af'}\right)^{1/2}$$
 except at the bifurcations, (22.5)

$$\psi_{\rm x} = \left(\frac{2{\rm b}''}{{\rm af}''}\right)^{1/3}$$
 marginal bifurcation (22.6)

$$\psi_{\rm x} = \left(\frac{2b^{\prime\prime\prime}}{af^{\prime\prime\prime}}\right)^{1/4}$$
 critical bifurcation. (22.7)

Equations (22.5-7) were used in the calculation of $\psi(x)$.

A) The Normal Case

Values of parameters corresponding to the normal case are k = .038, $kx_r = .2225$. The flow corresponding to (22.1) is sketched below:



In Table I, we compare the exact, white noise and 'mixing' solutions of (22.2) with the asymptotic solution of (22.2), using the theory developed in Chapter 2. The agreement between the exact and asymptotic solutions is excellent. This is to be expected, since the asymptotic ansatz was based on the expansion of a one dimensional problem.

B) The Marginal Case

Values of parameters corresponding to the marginal case are k = .0533, $kx_r = .24898$. The flow of (22.1) is sketched below:



In Table II, we compare the exact solutions with the asymptotic solutions using the theory developed in Chapters 2 (u^{Error}) and $3(u^{\text{Airy}})$. The results clearly indicate the breakdown of the Error integral, but the success of the theory that uses the Airy integral.

<u>Table I</u>

Exact and Asymptotic Solutions in the Normal Case

x	EXACT			ASYMPTOTIC			
	, WN u	u ST	% diff*	. WN u	% diff	ST u	% diff **
.878	.47262	.47097	0.3	.47304	0.1	.47101	0.1
.978	.68808	.68675	0.2	.68732	0.1	.68458	0.3
1.078	.84730	.84650	0.1	.84510	0.3	.84333	0.4
.778	.26257	.26112	0.6	.26218	0.2	.25910	0.8
.678	.10814	.10729	0.8	.10782	0.3	.10606	1.1

* % diff =
$$\frac{|u^{WN} - u^{ST}|}{u^{ST}} \times 100$$

-

** % diff =
$$\frac{|u^{\text{exact}} - u^{\text{asymptotic}}|}{u^{\text{asymptotic}}} \times 100$$

These definitions are used in Tables I - V.

<u>Table II</u>

Exact and Asymptotic Solutions in the Marginal Case

x	EXACT			ASYMPTOTIC					
				ERRO	R	-	AIRY		
	uWN	uST	% diff	WN u	% diff	WN u	% diff	ST u	% diff
.5266	.71003	.71185	.2	.50000	42	.71298	.4	.71426	0.3
.6266	.83243	.83048	.2	.69140	20	.82215	1.3	.83500	0.5
.7266	.92219	.92133	.1	.84134	9.6	.92833	.7	.92949	0.7
.4266	.58959	.59536	1.0	.30860	91	.59708	1.3	.59492	0.1
.3266	.48614	.48872	.5	.15866	206	.49105	1.1	.49394	1.1

C) The Critical Case

Values of parameters corresponding to the critical case are k = .08125 and $kx_r = .261199$. The flow of (22.1) is sketched below:



In Table III, the exact solutions are compared with the asymptotic solution using the theory of Chapter 4.

The widening of the boundary layer around the unstable steady state as the type of deterministic system changes is apparent in Tables I-III. For instance, in the interval $[x_u - .1, x_u + .1]$, u(x)increases by .42551 in the normal case, but only by .27620 in the critical case.

D) The Critical Bifurcation

Values of parameters corresponding to the critical bifurcation are k = .0968493, $kx_r = .2720033$. The flow of (22.1) is



The steady state is weakly attracting. In Table IV, we compare the exact solution with the asymptotic solution, using the theory of Chapter 4.

Table III

.

Exact and Asymptotic Solutions in the Critical Case

x	,	EXACT			ASYMPTOTIC			
	u ^{WN}	uST	% diff	.WN u	% diff	.ST u	% diff	
.7024	.47157	.47142	.03	.47319	.3	.47178	0.1	
.8024	.61193	.61185	.01	.61693	.8	.61269	0.1	
.9024	.74255	.74255	0.0	.73248	1.4	.74344	0.1	
.6024	.33573	.33557	0.5	.33300	.8	.33505	0.2	
.5024	.21003	.20996	.03	.21342	1.6	.20960	0.2	

Table IV

Exact and Asymptotic Solutions at the Critical Bifurcation

x	EXACT ASYMPTOTIC				۹.		
	uWN	ST u	%diff	UWN	% diff	. ST u	% diff
.60077	.57340	.57504	.3	.57472	.2	.57777	.4
.70077	.67425	.67557	.2	.67108	.5	.67349	.3
.80077	.77315	.77413	.1	.77001	.4	.77103	.4
.50077	.47573	.47765	.4	.47920	.7	.48334	1.1
 .40077	.37610	.37826	.6	.38046	1.1	.38422	1.6

E) Two Complex Steady States

When k = .11 and $kx_r = .2799039$, the real steady state is $x_s = .600773$; the complex steady states are $x_{\pm} = .6899153 \pm .2426429i$. The real steady state is attracting. As noted in §20, the Pearcey function is needed to provide an adequate asymptotic solution of the backward equation. In Table V, we compare the exact solutions with the leading part (g^0P or g^0E) of the asymptotic solution of Chapters 2 and 4. The parameters α_0 and β_0 were calculated using the first terms in the power series derived in Appendix E.

The Error integral did not provide an adequate asymptotic solution, but the Pearcey integral did.

The results presented in this section indicate that for one dimensional problems the asymptotic theory is very accurate. This was expected, since the asymptotic forms were obtained by an analysis of an exact one dimensional problem.

<u>Table V</u>

Exact and Asymptotic Solutions in the Case of One Real

x		EXACT		. E	PEARCEY	ASYMP	TOTIC	ERROR	
	uWN	u ST	% diff	u	%d u ^{WN}	%d u ST	u	%d u ^{WN}	%d u ST
.60077	.58657	.58907	0.4	.58509	0.3	0.6	.5000	17.3	18.3
.70077	.66667	.66883	0.3	.68920	3.2	2.9	.6031	10.5	11.1
.80077	.75110	.75287	0.2	.77304	2.8	2.6	.71386	5.2	5.7
.50077	.50918	.51196	0.5	.50423	1.0	1.5	.3969	28.3	50.5
.40077	.42479	.42778	0.6	.41289	2.9	3.6	.28613	48.4	50.5

and Two Complex Steady States

23. Comparison of the theory with Monte Carlo Experiments

No exact solution of the two dimensional backward equation (4.10), with b^{i} given by (21.20,21) and ϵa^{ij} given by (21.17), could be found. Thus the asymptotic results will be compared with Monte Carlo experiments. The experiments were performed by using the transition probabilities (21.7-10) or by working with the Ito equation

$$d\tilde{x} = b(\tilde{x})dt + \sqrt{\epsilon a(\tilde{x})} dW$$
, (23.1)

where W(t) is a standard Brownian motion process (Ito and McKean, 1965). The two techniques lead to equivalent first exit probabilities.

A) The Normal Case

When k = .038 and $kx_r^1 = .2225$ in (21.5), the corresponding deterministic system is the normal type. The first exit probability was calculated using the theory of Chapter 2. The integration of the equation for ψ_n used a fourth order Runge-Kutta routine. In Fig. 9 the deterministic phase portrait and the u = .3contour of first exit probability are plotted. In Table VI the probability calculated using the theory is compared with the probability observed in Monte Carlo simulations.

The function $\psi(\mathbf{x})$ was calculated in a vicinity of S by a Taylor expansion. The contours were calculated by using the leading part of the expansion of $u(\mathbf{x})$ (eqn. 8.17).



Figure 9 Deterministic Phase Portrait and First Exit Boundaries in the Normal Case. (Also shown is the u = 0.3 contour.)

Table VI

Comparison of the Theory with Monte Carlo Experiments

in the Normal Case

Test Point	Theory	<pre>Experiment (# trials)</pre>
(.878, 1.025)	.50	.51 (2000)
(.49, .058)	.50	.49 (1700)
(.75, .75)	.40	.39 (1750)
(.54, .55)	.22	.23 (1500)
(.40, 1.24)	.03	.02 (2000)
(.65, 1.125)	.17	.15 (2000)
(.475, 1.20)	.05	.04 (2000)
(.73, .72)	.41	.39 (1700)

B) The Marginal Case

When k = .0533 and $kx_r^1 = .24898$ and the boundaries I, II are as shown in Fig. 10, the theory of Chapter 3 will apply.

The parameter α_0 in the Airy integral was calculated by the method of characteristics, as described in §12. A double precision Runge Kutta routine was used. When a ray hit the separatrix, $\psi_t = b^i \psi_i = 0$. The intersection of the ray and the separatrix was noted by calculating ψ_t along the ray. Similar results were obtained when a routine with error control was used (UBC DDIFSY). The method of false position was used to calculate iterates of α . The value of ψ on boundary I was calculated by a Taylor expansion about the node Q_0 , where $\psi = -\sqrt{\alpha_0}$.

In Table VII, we compare the theory with Monte Carlo experiments for a number of test points. Also shown are some theoretical results in which the Error integral was used. Using the leading part of the asymptotic expansion, contours of first exit probability could be calculated. The 0.30 contour is shown in Fig. 10. The theory using the Error integral did not yield satisfactory results, but the theory using the Airy integral did.

The Monte Carlo results are very sensitive to the location of boundary I. Since the attractor Q₀ is within the separatrix tube, it is possible to choose boundary I so that the process will not hit I before II with probability close to 1. Thus, the Monte Carlo study of marginal (and critical) type systems is time



Figure 10 Deterministic Phase Portrait and First Exit Boundaries in the Marginal Case. (Also shown is the u = 0.3 contour.)

Table VII

Comparison of the Theory with Computer Experiments

in the Marginal Case

Test Point	u ^{theory} (Airy)	u ^{MC} (#trials)	u ^{theory} (Error)
(.2, 1.2)	.29	.24 (1650)	.12
(.3, 1.0)	.63	.67 (1040)	.78
(.5, 2.2)	.38	.41 (1710)	.23
(.32, 2.8)	.17	.14 (1150)	.001
(.53, 1.71)	.57	.55 (1100)	.50
(6, 1.8)	.62	.65 (1430)	.77

.

consuming. On the other hand, the asymptotic calculations, although sensitive to the location of the boundary, are not any more difficult than in the normal case. In this sense, the Monte Carlo and asymptotic techniques are complementary.

C) Marginal Bifurcation

0

When k = .069979 and $kx_r^1 = .25901$, the deterministic system exhibits the marginal bifurcation (§10). In this case, the first exit probability is of little interest (Fig. 11). The expected time that it takes the process to hit a specified curve R given that $\tilde{x}(0) = x$, is of more interest. The function T(x) satisfies equation (4.12). In Appendix C, we calculate the first term of the asymptotic solution of (4.12). The solution is very similar to the ansatz (11.2).

In Table VIII we compare the theoretical results with Monte Carlo experiments. The theoretical results correspond to the leading part of the asymptotic solution. Since the expected time represents a first moment, the difference between the asymptotic and Monte Carlo results for the expected time was larger than for the probabilities.



Figure 11 Deterministic Phase Portrait at the Marginal Bifurcation. The Boundary R was used in the calculation of the mean first exit time.

Table VIII

Comparison of the Theory and Monte Carlo Experiments

in the Marginal Bifurcation

Test Point	<u>T(x)</u> Theory	<u>T(x) Experiment (# Trials</u>)
(.42, 2.06)	60.3	56.4 (950)
(.38, 2.36)	104.1	91.2 (400)
(.20, 2.0)	66.1	62.4 (2000)
(.3, 1.8)	37.7	35.0 (1550)
(.16, 2.4)	119.6	103.5 (400)
(.7, 2.2)	36.1	31.4 (1750)
(.6, 2.4)	74.9	68.2 (800)

D) The Critical Case

When k= .08125 and kx_r^1 .261199, and the boundaries I and II are as shown in Fig. 12, the theory of Chapter 4 will be applicable. The parameters α,β were calculated using the method of characteristics, as described in §17. A double precision Runge-Kutta routine was used to calculate the rays. More sophisticated routines, with error control, gave similar results. Iterates of α_0 and β_0 were calculated using the method of false position. The values of ψ on the boundaries I, II were determined by Taylor expanding around the nodes and then following rays that hit the boundary. A similar technique was used in the marginal case and at the critical bifurcation. The value of ψ in a vicinity of the separatrix was calculated by a Taylor expansion. The derivative of ψ on S was calculated by integrating equation (18.1). A fourth order Runge Kutta routine was used. In Table IX, we compare the Monte Carlo experiments and the theoretical results.

The Monte Carlo results were very sensitive to the location of the boundary. Since both attractors P₀ and P₁ are contained by the separatrix tube, it is possible to choose I and II so that the probability of hitting either boundary is very small. The problem of excessive machine time places a restriction on the choice of boundaries IĮ,II; when the tube contains a stable steady state.



.

Figure 12 Deterministic Phase Portrait and First Exit Boundaries in the Critical Case. (Also shown is the u = 0.6 contour).

,

Table IX

Comparison of Theory and Monte Carlo Experiments

in the Critical Case

Test Point	u theory	u ^{MC} (# trials)
(.7, 1.28)	.67	.71 (2040)
(.5, 1.2)	.63	.68 (980)
(.9, 2.0)	.54	.50 (980)
(.6, 1.0)	.76	.76 (1060)
(.5, .82)	.78	.77 (1060)
(.9, 1.8)	.59	.61 (980)

E) Critical Bifurcation

When k = .0968493 and $kx_r^1 = .1820033$, the deterministic system exhibits the critical bifurcation. The theory of Chapter 4 and Appendix E applies. The calculation of ψ was performed as described in part D above.

In Table X we compare the theory of Chapter 4 with Monte Carlo experiments. The widening of the boundary layer around S as the type of deterministic system changes is clearly exhibited in Figs. 9 and 13. In the normal case, the 0.3 contour is 0.93 units from the saddle point. At the critical bifurcation, the 0.3 contour is .275 units from the steady state.



Figure 13 Deterministic Phase Portrait and First Exit Boundary at the Critical Bifurcation. (Also shown is the u = 0.3 contour.)

Table X

Comparison of the Theory with Monte Carlo Experiments at the Critical Bifurcation

Test Point	utheory	u ^{MC} (# trials)
(.4, 1.4)	.46	.50 (1900)
(.6, 1.4)	.54	.56 (1950)
(.6, 1.5)	.50	.46 (1970)
(.8, 1.0)	.87	.92 (2000)
(.3, 1.0)	.68	.72 (2000)
(.5, 1.8)	.29	.26 (2000)
(.2, 1.2)	.54	.58 (1970)
(.7, 1.7)	.44	.40 (2000)

,

Bibliography

- Abramowitz, M. and I. Stegun (1965). Handbook of Mathematical Functions, Dover Publications, N.Y., N.Y.
- Andronov, A.A., E.A. Leontovich, I.I. Gordon and A.G. Maier (1973). Qualitative Theory of Second Order Dynamic Systems. Halsted Press, N.Y.
- Armstrong, C. (1975). Ionic pores, gates and gating currents. Quart. Rev. Biophysics 7(2): 179-210.
- Arnold, L. (1974). Stochastic Differential Equations: Theory and Applications. Wiley-Interscience, N.Y.
- Arnold, V.I. (1972). Lectures on bifurcations in versal families. Russian Math. Surveys 27(5): 54-123.
- Barnett, V.D. (1962). The Monte Carlo solution of a competing species problem. Biometrics 18: 76-103.
- Bartholomay, A. (1957). Stochastic models for chemical reactions. Bulletin Math. Biophysics 20: 97-118.
- Bazekin, A.D. (1975). Structural and dynamic stability of model predator-prey systems. Institute of Animal Resource Ecology. Univ. of B.C., Vancouver.
- Bleistein, N. and Handelsman, R. (1975). Asymptotic Expansion of Integrals. Holt, Rinehart and Wilson, N.Y.
- Chang, M. and R.A. Schmitz (1975). Feedback control of unstable states in a laboratory reactor. Chemical Engineering Science 30: 837-846.
- Chance, B. (1951). Enzyme substrate compounds, Advances in Enzymol 12: 153-190.
- Cohen, D.S. (1972). Multiple solutions of nonlinear partial differential equations. Springer Notes in Math., Vol. 322: 15-77.
- Cohen, J.K. and R.M. Lewis (1967). A ray method for the asymptotic solution of the diffusion equation, J. Inst. Math. Appl. 3: 266-290.
- Courant, R. (1962). Methods of Mathematical Physics, Wiley Interscience, N.Y., N.Y.
- Davis, H.T. (1962). Introduction to Nonlinear Differential and Integral Equations. Dover, N.Y., N.Y.

- Degn, H. (1968). Bistability caused by substrate inhibition of peroxidase in an open reaction system. Nature 217: 1047-1050.
- Delbruck, M. (1940). Statistical fluctuations in an autocatalytic reaction. Jour. Chemical Physics 9: 120-124.
- Dennis, J.E. and J.J. More (1977). Quasi-Newton methods, motivation and theory. SIAM Rev. 19(1): 46-89.
- Feher, G. and M. Weissman (1973), Fluctuation spectroscopy. Proc. Nat. Acad. Sci. U.S.A. 70(3): 870-875.
- Feller, W. (1952). The parabolic differential equations and the associated semi-groups of transformations. Annals of Math. 55(3): 468-519.
- Feller, W. (1971). An Introduction to Probability Theory and Its Applications. Wiley Interscience, N.Y.
- Frank, F.C. (1953). On spontaneous asymmetric synthesis, Bioch. Bioph. Acta 11: 459-463.
- Gihman, I.I. and A.V. Skorohod (1972). Stochastic Differential Equations. Springer Verlag, New York.
- Glansdorff, P. and I. Prigogine (1971). Thermodynamic Theory of Stability, Structure and Fluctuations. Wiley-Interscience, 1971.
- Goldstein, J.C. and M.O. Scully (1973). Nonequilibrium properties of an Ising-model ferromagnet. Phys. Rev. B 7(3): 1084-1096.
- Graham, R. (1974). Statistical theory of instabilities in stationary nonequilibrium systems with applications to lasers and nonlinear optics. Springer Tracts in Modern Physics, Vol. 66, Springer, Berlin.
- Griffiths, R.B. C-Y Weng and J.S. Langer (1966). Relaxation times for metastable states in the mean-field model of a ferromagnet. Phys. Rev. 149: 301-305.
- Harrison, L. (1973). Evolution of biochemical systems with specific chiralities: a model involving territorial behavior. J. Theor. Biol. 39: 333-341.
- Hartman, P. (1973). Ordinary Differential Equations, Hartman, Baltimore, 612 pp.
- Heyde, C.C. and E. Heyde (1971). Stochastic fluctuations in a one substrate one product enzyme system: are they ever relevant? J. Theor. Biol. 30: 395-404.

- Higgins, J. (1967). Chemical oscillations. Indus. Eng. Chem. 59(5): 19-62.
- Ito, K. and H.P. McKean (1965). Diffusion Processes and Their Sample Paths. Springer Verlag, 321 pp.
- Keizer, J. (1975). Concentration fluctuations in chemical reactions. J. Chem. Phys. 63: 5037-5043.
- Keller, J.B. (1958). A Geometrical theory of diffraction. Proc. Symp. Appl. Math. 8: 27-52.
- Kubo, R., K. Matsuo and K. Kitahara, Fluctuation and relaxation of macrovariables, J. Stat. Phys. 9(1): 51-96.
- Landau, L. and E.M. Lifshitz (1968). Statistical Physics. Pergamon Press, New York, N.Y.
- Landau, L. and E.M. Lifschitz (1959). Fluid Mechanics. Addison-Wesley, Reading, Mass. 536 pp.
- Landauer, R. and J.W.F. Woo (1972). The steady state far from equilibrium: phase changes and entropy of fluctuations; in <u>Statistical Mechanics</u>, S.A. Rice et al., eds., Univ. of Chicago Press, Chicago, pg. 299-318.
- Lavenda, B. (1975). Dynamic phase transitions in nonequilibrium processes. Phys. Rev. A 11(6): 2066-2078.
- Lax, M. (1960). Fluctuations from the nonequilibrium steady state. Rev. Modern Phys. 32(1): 25-65.
- Lax, M. (1966). Classical noise IV: Langevin methods. Rev. Mod. Phys. 38: 541-566.
- Lecar, H. and R. Nossal (1971a). Theory of threshold fluctuations in nerves. I. Relationships between electrical noise and fluctuations in axon firing. Bioph. J. 11: 1048-1067.
- Lecar, H. and R. Nossal (1971b). Theory of threshold fluctuations in nerves. II. Analysis of various sources of membrane noise. Bioph. J. 1068-1084.
- Levinson, N. (1961). Transformation of an analytic function of several variables to a canonical form. Duke Math. J. 28: 345-353.
- Levey, L. and L.B. Felsen (1969). On incomplete Airy functions and their application to diffraction problems. Radio Science 4: 959-969.

- Ludwig, D. (1975). Persistence of dynamical systems under random perturbations. SIAM Rev. 17(4): 605-640.
- Luneberg, R.K. (1945). Propagation of Electromagnetic waves. New York University, N.Y.
- Lynn, R.Y.S. and J.B. Keller (1970). Uniform asymptotic solutions of second order linear ordinary differential equations with turning points. Comm. Pure. Appl. Math. 23: 379-408.
- Ma, S.K. (1976). Scale transformations in dynamic models. Springer Lecture Notes in Physics, Vol. 54: 44-79.
- Mangel, M. and D. Ludwig (1977). Probability of extinction in a stochastic competition. SIAM J. Appl. Math., 33:256-266
- McQuarrie, D. (1967). Stochastic Approach to Chemical Kinetics, J. Appl. Prob. 4: 473-478.
- Matkowsky, B. and Z. Schuss (1977). The exit problem for randomly perturbed dynamical systems, 33:365-382
- Matsuo, K. (1977). Relaxation mode analysis of nonlinear birth and death processes. J. Stat. Phys. 16(2): 169-195.
- Moore, W. (1962). Physical Chemistry, 3rd edition. Prentice Hall, New York, N.Y.
- Mori, H. (1965). Transport, collective motion and Brownian motion. Prog. Theor. Phys. 33(3): 423-455.
- Nayfeh, A.H. (1973). Perturbation Methods. Wiley Interscience, New York, N.Y.
- Nelson, E. (1967). Dynamical Theories of Brownian Motion. Princeton Univ. Press, Princeton N.Y.
- Nitzan, A., P. Ortoleva, J. Deutch and J. Ross (1974). Fluctuations and transitions at chemical instabilities: the analogy to phase transitions. J. Chem. Phys. 61(3): 1056-1074.
- Olver, F.J.W. (1974). Introduction to Asymptotics and Special Functions. Academic Press, N.Y.
- Papanicolaou, G.C. (1975). Asymptotic analysis of transport processes. Bull. Amer. Math. Soc. 81(2): 330-392.
- Papanicolaou, G.C. and W. Kohler (1974). Asymptotic theory of mixing stochastic ordinary differential equations. Comm. Pure Appl. Math. 27: 641-668.

- Pearcey, T. (1946). The structure of an electromagnetic field in the neighborhood of a cusp of a caustic. Phil. Mag. 37: 311-317.
- Perlmutter, D.D. (1972). Stability of Chemical Reactors. Prentice-Hall, Englewood Cliffs, N.Y.
- Pincock, R.E., R.R. Perkins, A.S. Ma and K.R. Wilson (1971). Probability distribution of enantiomorphous forms in spontaneous generation of optically active substances. Science 174: 1018-1020.
- Schuss, Z. (1977). Stochastic Differential Equations. Notes, University of Delaware.
- Sinai, Ya. G. (1970). Dynamical systems with elastic reflections. Russ. Math. Surveys 25: 137-189.
- Singer, K. (1953). Application of the theory of stochastic processes to the study of irreproducible chemical reactions and nucleation processes. J. Ray Stat. Soc. B 15: 92-106.
- Stein, W.D. (1967). The Movement of Molecules across Cell Membranes. Academic Press, New York.
- Van Kampen, N.G. (1976). The expansion of the master equation, Adv. Chem. Phys. 34: 245-309.
- Ventcel, A.D. and M.I. Freidlin (1970). On small random perturbations of dynamical systems. Russ. Math. Surveys 25: 1-55.
- Vereen, A.A. and L.J. DeFelice (1974). Membrane noise Prog. Bioph. Mol. Biol. 28: 191-265.
- White, A, P. Handler and E.L. Smith (1968). Principles of Biochemistry, 4th edition, McGraw Hill, N.Y.
- Williams, R.G. (1977). The Stochastic Exit Problem for Dynamical Systems. Thesis, California Institute of Technology.
- Wong, E. and M. Zakai (1965). On the relation between ordinary and stochastic differential equations. Int. J. Eng. Sci. 3: 213-229.
Appendices

With the exception of Appendix C, these appendices are concerned with the treatment of some fine points related to the asymptotic expansions given in the body of the paper. In Appendix C, we show how to construct the leading term in the solution of the equation for the mean exit time (4.12).

Appendix A: Solution of the Initial Value Problem for h

In Chapters 2-4, a characteristic initial value problem arises. The function h^0 satisfies

$$b^{i}h_{i}^{0} + \frac{h^{0}}{2} a^{ij}\psi_{i}\psi_{j}f'(\psi) - a^{ij}h_{i}^{0}\psi_{j}f(\psi) + c^{i}\psi_{i}h^{0}f(\psi) = F(x) .$$
(A.1)

In equation (A.1), F(x) is bounded, integrable and differentiable. The function $f(\psi) = -\psi$, $-(\psi^2 - \alpha_0)$, or $\psi^3 - \alpha_0 \psi - \beta_0$ in the normal, marginal and critical cases respectively. Except at the bifurcations $f(\psi)$ vanishes on the separatrix but $f'(\psi)$ does not. At the marginal bifurcation f and f' vanish on the separatrix, but f" does not vanish. At the critical bifurcation, f, f' and f" vanish, but f''' does not vanish. To avoid repetition, we shall not consider either of the bifurcations. On the separatrix, equation (A.1) becomes

$$\frac{dh}{dt}^{0} + h^{0} \frac{a^{ij}}{2} \psi_{i} \psi_{j} f'(\psi_{s}) = F(x(t)) , \qquad (A.2)$$

where ψ_s is the value of ψ on the separatrix. Since $d/dt = b^i \partial/\partial x^i$, at the saddle point, P_1 , dh^0/dt vanishes. Equation (A.2) is then solved for $h^0(P_1)$. Once h^0 is known at the saddle, equation (A.2) can be solved to obtain h^0 on the separatrix. We denote this solution by h_0^0 .

The initial value problem P: {solve (A.1) with $h = h_s^0$ on S} is a characteristic initial value problem (Courant, 1962) since the separatrix S corresponds to the direction of differentiation in (A.1). The problem P is not a typical characteristic initial value problem; it is more singular (see also Appendix F, where we give an existence proof for these types of equations). The presence of the singularity on the initial manifold allows the unique determination of $h^0(x)$. We construct a new manifold S', which will not be a characteristic manifold. Let $v_i = \frac{\partial h}{\partial x^i}$. If (A.1) is differentiated with respect to x^1 and evaluated on the separatrix, we obtain

$$\frac{dv_1}{dt} + \alpha^i v_i = \gamma_1, \qquad (A.3)$$

where

$$\alpha^{1} = b^{1}, + \frac{a^{ij}}{2} \psi_{i}\psi_{j}f'(\psi_{s}) - a^{1j}\psi_{j}\psi_{1}f'(\psi_{s})$$
(A.4)

$$\alpha^{2} = b^{2}, - a^{2j}\psi_{j}\psi_{1}f'(\psi_{s})$$
(A.5)

$$\gamma_{1} = F_{,1} - h^{0} [\frac{a^{ij}}{2} \psi_{i} \psi_{j} f'(\psi) + c^{i} \psi_{i} f(\psi)]_{,1} .$$
 (A.6)

Differentiation of (A.1) with respect to x^2 and evaluation on the separatrix yields:

$$\frac{dv_2}{dt} + \beta^i v_i = \gamma_2$$
 (A.7)

where

$$\beta^{1} = b^{1}, 2 - a^{1j}\psi_{j}\psi_{2}f'(\psi_{s})$$
(A.8)

$$\beta^{2} = b^{2}, + \frac{a^{ij}}{2} \psi_{i} \psi_{j} f'(\psi_{s}) - a^{2j} \psi_{j} \psi_{2} f'(\psi_{s})$$
(A.9)

$$\gamma_{2} = F_{2} - h^{0} \left[\frac{a^{ij}}{2} \psi_{i} \psi_{j} f'(\psi) + c^{i} \psi_{i} f(\psi) \right]_{2} .$$
 (A.10)

At the saddle point, P_1 , equations (A.3, 7) become

$$\alpha^{1}v_{1} + \alpha^{2}v_{2} = \gamma_{1}(P_{1})$$
 (A.11)

$$\beta^{1}v_{1} + \beta^{2}v_{2} = \gamma_{2}(P_{1})$$
 (A.12)

Equations (A.11, 12) determine the integration constants when (A.3, 7) are solved. Once $v_1(P_1)$ are known, v_1, v_2 can be determined along the entire separatrix.

The new manifold S' is determined by a Taylor expansion about S :

$$\hat{h}(x_{s}) = \hat{h}(x_{s}) + v_{i}(x_{s})(x_{s}^{i}, -x_{s}^{i}) + O((x_{s}, -x_{s})^{2}) . \quad (A.13).$$

The value of h^0 on S' is not arbitrary, but is specified by equation (A.13). In (A.13), x_s is a point on S; x_s , is a point on S'. We are free to choose the manifold in any form desired. In particular, S' can be chosen so that it is nowhere tangent to deterministic trajectories. The problem P': {Solve (A.1) with initial data $h^0 = h_S^0$, on S'} is a well posed problem that can be solved by the method of characteristics (Courant, 1962). In Appendix F, we give an existence proof for problems similar to the characteristic initial value problem treated here. Our proof justifies the treatment given in this Appendix.

Appendix B: Regularity of Higher Order Terms in the Expansions

In Chapters 2-4, we constructed the first term of the asymptotic expansion of u(x). The higher order terms are treated in an analogous fashion. In this appendix we indicate in more detail how the higher order terms are treated.

The terms order $\varepsilon^{n-1/2}$ (normal case), $\varepsilon^{n-1/3}$ (marginal case) and $\varepsilon^{n-1/4}$ (critical case) in the expansions (7.3), (11.5) and (16.5) will vanish identically, since

$$b^{i}\psi_{i} + f(\psi) \frac{a^{ij}}{2} \psi_{i}\psi_{j} = 0$$
 (B.1)

In equation (B.1) $f(\psi) = -\psi$ (normal case), $-(\psi^2 - \alpha_0)$ (marginal case), or $\psi^3 - \alpha_0 \psi - \beta_0$ (critical case).

In each expansion, the $O(\epsilon^n)$ term vanishes if

$$b^{i}g^{n}_{i} = -\frac{a^{ij}}{2}g^{n-1}_{ij} - c^{i}g^{n-1}_{i}$$
 (B.2)

Starting with g^0 , we recursively show that each g^n is constant on trajectories. An argument identical to the one in §8 shows that g^n has one value in the entire phase plane. The value of g^n will be chosen to insure regularity of h^n . When studying the h^n equation, each case must be treated separately.

1) Normal Case

The $O(\epsilon^{n+1/2})$ term in (7.3) vanishes if

$$b^{i}h_{i}^{n} - a^{ij}h_{i}^{n}\psi_{j}\psi - \frac{a^{ij}}{2}h^{n}\{(\psi\psi_{i})_{j}\} - c^{i}\psi_{i}h^{n}\psi$$

$$= -\frac{a^{ij}}{2}g^{n}\psi_{ij} - \frac{a^{ij}}{2}h_{ij}^{n-1} - g^{n}c^{i}\psi_{i} - c^{i}h_{i}^{n-1}.$$
(B.3)

The functions g^n , h^{n-1} are assumed to be known. On the separatrix (B.3) becomes

$$\frac{dh^{n}}{dt} - \frac{a^{ij}}{2}h^{n}\psi_{i}\psi_{j} = -\frac{a^{ij}}{2}g^{n}\psi_{ij} - \frac{a^{ij}}{2}h^{n-1}_{ij} - g^{n}c^{i}\psi_{i} - c^{i}h^{n-1}_{i}.$$
 (B.4)

In equation (B.4), $d/dt = b^i \partial/\partial x^i$ vanishes at the saddle point. We choose g^n so that h^n will vanish at the saddle point. Once g^n is known, equation (B.4) can be used to determine h^n on the separatrix. Once h^n is known on the separatrix, it can be calculated everywhere in the phase plane using the technique described in Appendix A.

2) <u>Marginal Case</u>

The $O(\epsilon^{n+2/3})$ term in (11.5) vanishes if

$$b^{i}h_{i}^{n} - h^{n} \frac{a^{ij}}{2} [\psi_{i}(\psi^{2}-\alpha_{0})]_{j} + a^{ij}g_{i}^{n}\psi_{j} + \frac{a^{ij}}{2}g^{n}\psi_{ij} + \frac{a^{ij}}{2}h_{ij}^{n-1} - (\psi^{2}-\alpha_{0})(a^{ij}h_{i}^{n}\psi_{j}) + c^{i}h_{i}^{n-1} + c^{i}g^{n}\psi_{i} - c^{i}\psi_{i}h^{n}(\psi^{2}-\alpha_{0}) + \sum_{k=1}^{n+1} \frac{a^{ij}}{2}\psi_{i}\psi_{j}(g^{n+1-k} - (\psi^{2}-\alpha_{0})h^{n+1-k})\alpha_{k} \quad (B.5)$$

$$+ \sum_{k=1}^{n+1} \alpha_{k}[h^{n+1-k}(b^{i}\psi_{i} - (\psi^{2}-\alpha_{0})\frac{a^{ij}}{2}\psi_{i}\psi_{j})] + \sum_{k=1}^{n} c^{i}\psi_{i}\alpha_{k}h^{n-k} + \frac{a^{ij}_{i}(\psi_{i}-\psi_{i})}{2}h^{n-k+1}(\sum_{j=1}^{k-1}\alpha_{j}\alpha_{k-j}) + \sum_{k=1}^{n}\alpha_{k}(2h_{i}^{n-k}\psi_{j} + h^{n-k}\psi_{ij})$$

105

= 0 .

In equation (B.5) h^n , g^n and α_{n+1} are to be determined, h^m , g^m and α_{m+1} for $m \le n - 1$ are assumed to be known.

The procedure used to determine the unknowns in (B.5) is the following. Equation (B.5) is first converted to an ordinary differential equation on the separatrix S, where $\psi^2 = \alpha_0$. Since $dh^n/dt = b^i h_i^n$, at the saddle point, Q_1 , dh^n/dt vanishes. The value of g^n is determined so that $h(Q_1) = 0$. Once g^n is known, h^n can be evaluated on the separatrix. Using the technique described in Appendix A, h^n can be calculated in the entire plane by the method of characteristics. The parameter α_{n+1} is determined by an iterative procedure identical to the one described in §12. Essentially, α_{n+1} must be chosen so that h^n , calculated by the method of characteristics at the node Q_0 , is equal to the value of $h^n(Q_0)$ determined from (B.5).

3) Critical Case

The $0(\varepsilon^{n+3/4})$ term in the expansion (16.5) satisfies an equation analogous to (B.5), with $\psi^2 - \alpha_0$ replaced by $-\psi^3 + \alpha_0 \psi + \beta_0$, and α_k replaced by $\psi \alpha_k + \beta_k$ (see (16.5)). In the critical case, the unknowns are h^n , g^n , α_{n+1} and β_{n+1} ; h^m , g^m , α_{m+1} , β_{m+1} are presumed known for $m \le n - 1$. The value of g^n is determined so that h^n vanishes at the saddle point. As above, h^n is calculated on the separatrix. Once known on the separatrix h^n can be calculated in the entire plane, as described in Appendix A. The parameters α_{n+1} and β_{n+1} can be calculated using the technique described in §19.

The above procedures insure that the higher order terms in the asymptotic solutions are regular and bounded.

Appendix C: Asymptotic Solution of the Expected Time Equation

Let T(x) be defined by

$$\Gamma(x) = E\{t: \tilde{x}(t) \in R, \tilde{x}(t') \notin R \ t' < t | \tilde{x}(0) = x, \tilde{x}(t) \text{ hits } R\}.$$
 (C.1)

Then T(x) is the expected amount of time it takes the process to hit R starting at x . In §4, we showed that T(x) satisfies the backward equation

$$\frac{\varepsilon a^{ij}}{2} T_{ij} + b^{i}T_{i} + \varepsilon c^{i}T_{i} = -u(x) . \qquad (C.2)$$

In (C.2), u(x) is the probability of eventually reaching \mathcal{R} , conditioned on $\tilde{x}(0) = x$. Equation (C.2) is an inhomogeneous backward equation. In this appendix, we give the asymptotic solution of (C.2). The solutions are closely related to the solutions in Chapters 2-4, so that only the first term will be considered. Equation (C.2) must be supplemented by boundary conditions. Let d be the distance from x to \mathcal{R} .

The first boundary condition is

$$T(x) \equiv 0 \qquad x \in \mathcal{R} \quad . \tag{C.3}$$

As a second boundary condition, we require that T(x) is bounded as $|d| \rightarrow \infty$. In Feller's terminology (Feller, 1952), we are requiring that ∞ is an "entrance boundary". Feller's theory applies to one dimensional systems and there is no analogous two dimensional theory. On the other hand, the second boundary condition is in accord with intuition for the systems of interest here.

C.1 Normal Case

The results presented in Chapter 2 and the asymptotic analysis of a one dimensional version of (C.2) indicate that a possible solution of (C.2) is

$$T(x) = \sum \varepsilon^{n} g^{n} F(\psi(x)/\sqrt{\varepsilon}) + \varepsilon^{n+1/2} h^{n}(x) F'(\psi(x)/\sqrt{\varepsilon}) + \varepsilon^{n} k^{n}(x) .$$
(C.4)

In (C.4), $g^{n}(x)$, $h^{n}(x)$, $k^{n}(x)$ and $\psi(x)$ are to be determined. The function F(z) satisfies

$$\frac{d^{2}F(z)}{dz^{2}} = -z \frac{dF}{dz} - 1 \qquad z_{0} \le z \le z_{1} .$$
 (C.5)

Equation (C.5) is an inhomogeneous version of the sequation that the Error integral satisfies.

When derivatives are evaluated, (C.5) is used to replace F" by $(-\psi F'/\sqrt{\epsilon} - 1)$. After substitution into equation (C.2), terms are collected according to powers of ϵ . The leading term (n=0) vanishes if the following equations are satisfied:

$$0(\mathbf{F}'/\sqrt{\varepsilon}): \mathbf{b}^{\mathbf{i}}\psi_{\mathbf{i}} - \frac{\mathbf{a}^{\mathbf{i}\mathbf{j}}}{2}\psi_{\mathbf{i}}\psi_{\mathbf{j}}\psi = 0$$
 (C.6)

$$0(F): b^{i}g^{0}_{i} = 0$$
 (C.7)

$$0(\epsilon^{0}): b^{i}k^{0}_{i} - \frac{a^{1}}{2} \psi_{i}\psi_{j}g^{0} = -u(x)$$
(C.8)

$$0(\epsilon^{\frac{1}{2}}F'): b^{i}h_{i}^{0} + \frac{a^{ij}}{2}g^{0}\psi_{ij} - h^{0}_{i}a^{ij}\psi_{j}\psi - h^{0}c^{i}\psi_{i}\psi + g^{0}c^{i}\psi_{i} - h^{0}\frac{a^{ij}}{2}[(\psi\psi_{i})_{j}] = 0.$$
(C.9)

Equations (C.6, C.7, C.9) are identical to equations (7.4-6). Thus, the constructions in §8, 9 for ψ and h^0 are applicable here. Equation (C.7) indicates that g^0 is constant on trajectories. The argument in §8 shows that g^0 has the same value on all trajectories.

At the saddle point P_1 , b(x) vanishes. Equation (C.8) becomes

$$\frac{-a^{ij}}{2}\psi_{i}\psi_{j}g^{0} = -u(P_{1}) . \qquad (C.10)$$

Thus, the value of g^0 is $g^0 = 2u(P_1)/a^{ij}\psi_i\psi_j$. Once g^0 is known, k^0 can be calculated by the method of characteristics if initial data are given. We assume that R is not a characteristic curve, and set $k^0 = 0$ on R. (If R is a characteristic curve, then the equation (C.8) must be treated by a procedure similar to the one described in Appendix A).

We also assume, without losing generality, that $\psi = \psi_0$ on R. Then, we set $z_0 = \psi_0/\sqrt{\epsilon}$ and $F(\psi_0/\sqrt{\epsilon}) = F'(\psi_0/\sqrt{\epsilon}) = 0$ in equation (C.4). With the above choices, $T(x) \equiv 0$ if $x \in R$. If R is not a level curve of ψ , then T(x) will not identically vanish if $x \in R$ but will be exponentially small (§8.2).

C.2. Marginal Case

The above solution for T(x) breaks down in the marginal case for the same reason that the solution for u(x) that used the Error integral broke down (§11.1). Based on the ansatz given in §11 and the expansion of a simpler problem, we seek a solution of (C.2) of the form

$$T(\mathbf{x}) = \sum \varepsilon^{n} g^{n}(\mathbf{x}) B(\psi/\varepsilon^{1/3}, \alpha/\varepsilon^{2/3}, 1/\varepsilon^{1/3}, \gamma) + \varepsilon^{n+2/3} h^{n}(\mathbf{x}) B'(\psi/\varepsilon^{1/3}, \alpha/\varepsilon^{2/3}, 1/\varepsilon^{1/3}, \gamma)$$
(C.11)
+ $\varepsilon^{n} k^{n}(\mathbf{x})$.

In (C.11), the function $B(z, \alpha, \gamma_1, \gamma_2)$ satisfies an inhomogeneous version of the equation that the Airy integral satisfies:

$$\frac{d^{2}B(z;\alpha,\gamma_{1}\gamma_{2})}{dz^{2}} = -(z^{2}-\alpha) \frac{dB}{dz} - \gamma_{1} + \gamma_{2}z \qquad z_{0} \le z \quad .$$
(C.12)

When derivatives of T(x) are calculated, (C.12) is used to replace B" by terms involving B', ψ , α and γ . We assume that

$$\alpha = \sum \alpha_k \varepsilon^k$$
 and $\gamma = \sum \gamma_k \varepsilon^k$. (C.13)

After derivatives of T(x) are calculated and substituted into equation (C.2), terms are collected according to powers of ε . The leading term (n=0) vanish if

$$0(\bar{\epsilon}^{1/3}B'): b^{i}\psi_{i} - \frac{a^{1j}}{2}\psi_{i}\psi_{j}(\psi^{2}-\alpha_{0}) = 0 \qquad (C.14)$$

$$0(\epsilon^{0}B): b^{i}g^{0}_{i} = 0$$
 (C.15)

$$0(\epsilon^{0}): b^{i}k^{0}_{i} + \frac{a^{ij}}{2} \psi_{i}\psi_{j}g^{0}(-1+\psi\gamma_{0}) = -u(x) . \qquad (C.16)$$

The $O(\epsilon^{2/3}B')$ term vanishes if h^0 satisfies equation (11.8).

Equation (C.14) is identical to (11.6). Thus, the constructions for ψ , α_0 and h^0 in §12-14 can be used here. Equation (C.15) indicates that g^0 is a constant on trajectories. The argument used in §8.2 shows that g^0 has the same value on all trajectories.

In the marginal case, the vector field b(x) vanishes at two points Q_0 , Q_1 within the domain of interest. At these two points, equation (C.16) becomes

$$\frac{a^{ij}\psi_{i}\psi_{j}}{2}g^{0}(-1+\psi\gamma_{0})\Big|_{Q_{k}} = -u(Q_{k}) \quad k = 1,2. \quad (C.17)$$

Equation (C.17) provides two equations for g^0 and γ_0 . At the marginal bifurcation, an application of 1'Hospital's rule shows that $\gamma_0 = 0$. Equation (C.17) still provides one equation (at the saddle-node Q) for g^0 :

$$\frac{-a^{ij}\psi_{i}\psi_{j}}{2}g^{0}\Big|_{Q} = -u(Q) . \qquad (C.18)$$

Once g^0 and γ_0 are known, k^0 can be calculated as described above,

We also assume that R is a level curve of ψ , say $\psi = \psi_0$ on R. Then, in (C.12) we set $z_0 = \psi_0/\epsilon^{1/3}$ and $B(z_0) = B'(z_0) = 0$. With these choices, $T(x) \equiv 0$ on R.

If R is a characteristic curve, or ψ is not constant on R, the remarks of the previous section apply.

111

C.3. Critical Case

9

The solution in the previous section will break down if the domain of interest contains three steady states or the deterministic system exhibits the critical bifurcation (§15, 16.1). Based on the results in §16.2 and the expansion of a simpler problem, we seek a solution of (C.2) of the form

$$T(\mathbf{x}) = \sum \varepsilon^{n} g^{n}(\mathbf{x}) Q(\psi/\varepsilon^{1/4}; \alpha/\varepsilon^{1/2}, \beta/\varepsilon^{3/4}, 1/\varepsilon^{1/2}, \gamma_{1}/\varepsilon^{1/4}, \gamma_{2}) + \varepsilon^{n+3/4} h^{n}(\mathbf{x}) Q'(\psi/\varepsilon^{1/4}; \alpha/\varepsilon^{1/2}, \beta/\varepsilon^{3/4}, 1/\varepsilon^{1/2}, \gamma_{1}/\varepsilon^{1/4}, \gamma_{2}) + \varepsilon^{n} k^{n}(\mathbf{x}).$$
(C.19)

In (C.19), the function $Q(z;\alpha,\beta,\gamma_1,\gamma_2,\gamma_3)$ satisfies

$$\frac{d^2 Q}{dz^2} = (z^3 - \alpha z - \beta) \frac{dQ}{dz} - \gamma_1 + \gamma_2 z + \gamma_3 z^2 \qquad z_0 \le z \quad . \tag{C.20}$$

When derivatives of T(x) are evaluated, (C.20) is used to replace Q" by terms involving Q', α, β, γ_1 and γ_2 . After derivatives are evaluated and substituted into (C.2), terms are collected according to powers of ε . We assume that

$$\alpha = \sum \alpha_{k} \varepsilon^{k} \qquad \beta = \sum \beta_{k} \varepsilon^{k}$$

$$\gamma_{1} = \sum \gamma_{1k} \varepsilon^{k} \qquad \gamma_{2} = \sum \gamma_{2k} \varepsilon^{k} \qquad (C.21)$$

The first term of the asymptotic solution vanishes if

$$0(e^{-1/4}Q'): b^{i}\psi_{i} + \frac{a^{ij}}{2}\psi_{i}\psi_{j}(\psi^{3}-\alpha_{0}\psi-\beta_{0}) = 0 \qquad (C.22)$$

$$0(\epsilon^{0}Q): b^{i}g^{0}_{i} = 0$$
 (C.23)

$$0(\varepsilon^{0}): b^{i}k^{0}_{i} + g^{0}(-1 + \gamma_{10}\psi + \gamma_{20}\psi^{2})\frac{a^{-3}\psi_{i}\psi_{j}}{2} = -u(x). \quad (C.24)$$

The $0(\epsilon^{3/4}Q')$ term vanishes if h^0 satisfies equation (16.8). Equation (C.22) is identical to (16.6). Thus, the constructions given in §16-19 for ψ , α_0 , β_0 and h^0 are applicable here.

At the nodes P_0 , P_2 and saddle point P_1 , b(x) vanishes. Equation (C.24) becomes

$$g^{0}(-1 + \gamma_{10}\psi(P_{k}) + \gamma_{20}\psi^{2}(P_{k}))\frac{a^{1}\psi_{i}\psi_{j}}{2} = -u(P_{k}) \quad k = 0, 1, 2 .$$
 (C.25)

The constants g^0 , γ_{10} and γ_{20} can be determined from (C.25). Once g^0 , γ_{10} and γ_{20} are known, k^0 can be determined as described in §C.1. At the critical bifurcation $\gamma_{10} = \gamma_{20} = 0$. We assume that R is a level curve of ψ , $\psi = \psi_0$ on R. Then, in C.20, we set $z_0 = \psi_0 / \epsilon^{1/4}$ and $Q(z_0) = Q'(z_0) = 0$. If $k^0 \equiv 0$ on R, then $T(x) \equiv 0$ on R.

Appendix D: Regularity at the Marginal Bifurcation

In Chapter 3, the asymptotic solution of the backward equation was constructed assuming that two steady states, Q_0 and Q_1 , were contained by the separatrix tube. As a deterministic parameter η varies, the two steady states move together and coalesce at $\eta = 0$. The marginal type dynamical system was defined by introducing new coordinates $y^1(\eta)$, $y^2(\eta)$, where $y^1(\eta)$ was defined in the direction of the eigenvector of the non-negative eigenvalue at Q_1 . The deterministic system is

$$\dot{y} = \tilde{b}(y,\eta) \quad . \tag{D.1}$$

The steady state Q is of the marginal type if

a)
$$\det(b_{j}^{1}(Q,0)) = 0$$

b) $\tilde{b}^{1},_{1} = \tilde{b}^{2},_{1}(Q,0) = 0$
c) $\tilde{b}^{2},_{2}(Q,0) \neq 0$ (D.2)
d) $\tilde{b}^{1},_{11} - \tilde{b}^{2},_{11} \neq 0.$

The conditions (D.2) were introduced in §11 and have the following interpretations. Condition a) indicates that $B = (b^{i}, {}_{j})$ has a zero eigenvalue when $\eta = 0$. Condition c) insures that the second eigenvalue of B is non-zero. Condition b) indicates that the linear dynamics in the y^{1} direction vanish and d) indicates that the dynamics in the y^{1} direction are quadratic. When $\eta = 0$, the double point Q_{0}/Q_{1} is called a saddle-node (Andronov et. al. (1973)). In this Appendix, we show that the constructions of Chapter 3 are regular at the marginal bifurcation. This demonstration consists of three parts: 1) First, we show that $\partial \alpha / \partial \eta \neq 0$ when $\eta = 0$. Our technique can be used to calculate a power series $\alpha = \sum A_{i} \eta^{i}$ for α in terms of the deterministic parameter. 2) Second, we show how to calculate the normal derivative of ψ on the separatrix, at the marginal bifurcation. 3) Third, we show that h^{0} can be calculated at the marginal bifurcation.

D.1. Regularity of α_0

In §11, we showed that

$$b^{i}\psi_{i} - \frac{a^{ij}}{2}\psi_{i}\psi_{j}(\psi^{2} - \alpha_{0}) = 0 . \qquad (D.3)$$

Also, $\psi(Q_0) = -\sqrt{\alpha_0}$ and $\psi(Q_1) = \sqrt{\alpha_0}$. When Q_0 and Q_1 coalesce, $\boldsymbol{\alpha}_{\bigcap}$ must vanish. When equation (D.3) is differentiated with respect to η and evaluated at Q_k (k=1,2), we obtain

$$\mathbf{b}^{\mathbf{i}}, \boldsymbol{\psi}_{\mathbf{i}} \Big|_{\mathbf{Q}_{\mathbf{k}}} - \frac{\mathbf{a}^{\mathbf{i}}\boldsymbol{\psi}_{\mathbf{i}}\boldsymbol{\psi}_{\mathbf{j}}}{2} \Big|_{\mathbf{Q}_{\mathbf{k}}} (2\boldsymbol{\psi}(\mathbf{Q}_{\mathbf{k}})\boldsymbol{\psi}_{\mathbf{\eta}} - \frac{\partial\alpha_{\mathbf{0}}}{\partial\mathbf{\eta}}) = 0 \quad . \tag{D.4}$$

When $\partial \psi / \partial \eta$ is eliminated from the two equations (D.4), and the limit $\tilde{\eta} \rightarrow 0$ is taken, we obtain

$$\frac{\partial \alpha_0}{\partial \eta} = \frac{-2b^{i}, \psi_{i}|_{Q}}{a^{ij}\psi_{i}\psi_{i}|_{Q}} \quad \text{at} \quad \eta = 0 \quad . \tag{D.5}$$

In order to explicitly calculate $\partial \alpha / \partial \eta$, the ψ_i must be known at the saddle node $\, {\tt Q}$. The derivatives of $\, \psi \,$ are calculated in §D.2. The higher derivatives of α with respect to η can be calculated in an identical fashion. Equation D.3 is differentiated twice with respect to η and evaluated at Q_0 and Q_1 :

$$b^{i},_{\eta\eta}\psi_{i}\Big|_{Q_{k}}^{+} 2b^{i},_{\eta}\psi_{i\eta}\Big|_{Q_{k}} - \frac{a^{ij}\psi_{i}\psi_{j}}{2}\Big|_{Q_{k}}(2\psi_{\eta}^{2} - 2\psi(Q_{k})\psi_{\eta\eta} - \frac{\partial^{2}\alpha}{\partial\eta^{2}}) = 0.$$
(D.6)

From (D.4) $\partial \psi/\partial \eta$ and $\partial \psi_i/\partial \eta$ can be expressed in terms of $\partial \alpha_0/\partial \eta$.

(D.6)

Thus, the $\psi_{\eta\eta}$ term can be eliminated from(D.6) and it is possible to calculate $\partial^2 \alpha_0 / \partial \eta^2$. This procedure can be repeated r times if the deterministic equations are C^r with respect to η . In this fashion, we can construct a truncated power series, of order r, for α_0 in terms of η . Such power series are useful when the deterministic equations have complex steady states (§20).

D.2. Calculation of the Normal Derivative of ψ

The easiest way to show that ψ_n can be calculated on the separatrix when $\eta = 0$ is to use the (y^1, y^2) coordinate system and the variational equations analogous to (8.6). These are, when $\eta = 0$

$$\frac{d\psi_k}{dt} + \tilde{b}^i, \quad \psi_i = 0 \quad \text{on} \quad S \quad k = 1, 2 .$$
 (D.7)

At the saddle node b(x) vanishes, so that (D.7) becomes

$$\tilde{b}^{i}, \psi_{i} = 0 \qquad k = 1, 2$$
 (D.8)

The condition for a nontrivial solution of (D.8) is that $det(\tilde{b}^i,_k) = 0$, condition (D.2a). If $\partial \psi / \partial y^1$ can be calculated, then the normal derivative of ψ can be evaluated. In the y variables, when $\eta = 0$, equation (11.6) is

$$\tilde{b}^{i} \frac{\partial \psi}{\partial y^{i}} - \frac{\tilde{a}^{ij}}{2} \frac{\partial \psi}{\partial y^{i}} \frac{\partial \psi}{\partial y^{j}} \psi^{2} = 0 .$$
 (D.9)

When equation (D.9) is differentiated with respect to y^1 and evaluated at the saddle-node, we obtain

$$\tilde{b}^{i}, \frac{\partial \psi}{\partial y^{i}} = 0,$$
 (D.10)

which is satisfied identically due to condition (D.2b). When (D.9) is differentiated twice with respect to y^1 and evaluated at the saddle-node, we obtain (using conditions(D.2))

$$\tilde{b}^{i},_{11} \frac{\partial \psi}{\partial y^{i}} - \tilde{a}^{ij} \frac{\partial \psi}{\partial y^{i}} \frac{\partial \psi}{\partial y^{j}} (\frac{\partial \psi}{\partial y^{l}})^{2} = 0$$
 (D.11)

Using the fact that the tangential derivative of ψ vanishes on the separatrix, $\partial \psi / \partial y^2$ can be expressed in terms of $\partial \psi / \partial y^1$. Then (D.11) becomes an algebraic equation for $\partial \psi / \partial y^1$. We obtain

$$\frac{\partial \psi}{\partial y^{1}} = \left[\frac{\tilde{b}^{1}, 1 - \tilde{b}^{2}, 1}{\tilde{a}^{11} - 2\tilde{a}^{12} + \tilde{a}^{22}}\right]^{\frac{1}{2}} \neq 0 \text{ at } \eta = 0.$$
 (D.12)

Since (\tilde{a}^{ij}) is positive definite on *S*, equation (D.12) is always meaningful.

Since the first derivatives of ψ can be calculated at the saddle-node, the derivatives can be calculated along the entire separatrix by solving (D.7). Hence, the normal derivative of ψ can be calculated along the entire separatrix.

D.3. Calculation of h^0 at the Bifurcation

When η and α_0 vanish, equation (11.8) becomes

$$b^{i}h_{i}^{0} - \frac{h^{0}}{2} a^{ij}((\psi_{i}\psi^{2})_{j}) - \psi^{2}a^{ij}h_{j}^{0}\psi_{i} + \alpha_{1}\frac{a^{ij}}{2}\psi_{i}\psi_{j}h^{0}\psi^{2} + \frac{a^{ij}\psi_{i}\psi_{j}}{2}g^{0} + c^{i}\psi_{i}h^{0}\psi^{2} - \alpha_{1}\frac{a^{ij}\psi_{i}\psi_{j}}{2}g^{0} = 0.$$
(D.13)

On the separatrix, where ψ = 0, equation (D.13) becomes

$$\frac{dh^{0}}{dt} = -(\frac{a^{ij}\psi_{ij} + 2c^{i}\psi_{i} - \alpha_{l}a^{ij}\psi_{i}\psi_{j}}{2})g^{0} \equiv H(x) . \qquad (D.14)$$

We choose α_1 so that the right hand side of (D.14) vanishes at the saddle-node. In order to calculate the value of h^0 at the saddle-node, we differentiate (D.13) with respect to x^k and evaluate the result at the saddle-node. We obtain

$$b^{i}, k^{0}_{i} - h^{0}a^{ij}[\psi_{i}\psi_{j}\psi_{k}] = \left(-\frac{a^{ij}\psi_{ij}}{2} - c^{i}\psi_{i} + \alpha_{1}\frac{a^{ij}\psi_{i}\psi_{j}}{2}\right), k^{0}g^{0}$$

$$k = 1, 2. \qquad (D.15)$$

Condition (D.2a) $(\det(b^i, k) = 0)$ allows the elimination of the derivatives of h^0 from (D.15). When the resulting expression is solved for h^0 , we obtain

$$h^{0}(Q) = \frac{-(b^{1}, 2 + b^{2}, 2)H_{1} + (b^{1}, 1 + b^{2}, 1)H_{2}}{a^{ij}\psi_{i}\psi_{j}[b^{1}, 2 + b^{2}, 2 - b^{1}, 1 - b^{2}, 1]\psi_{1}} \bigg|_{Q} \qquad (D.16)$$

In (D.16), H(x) is the right hand side of (D.14). On the separatrix,

$$h^{0}(t) = - \int_{t}^{\infty} H(x(s)) ds$$
 (D.17)

Once h^0 is known on the separatrix, the technique of Appendix A can be used to calculate h^0 everywhere in the plane.

Appendix E: Regularity at the Critical Bifurcation

In Chapter 4, the asymptotic solution of the backward equation was constructed assuming that three steady states P_0 , P_1 and P_2 were contained by the separatrix tube. As two parameters, η and δ , vary the steady states move together and coalesce at $\eta = \delta = 0$. The critical type dynamical system was defined by introducing new coordinates $y^{1}(\eta)$, $y^{2}(\eta)$, where $y^{1}(\eta)$ was defined in the direction of the nonnegative eigenvalue at P_{1} . The deterministic system becomes

$$\dot{y} = \tilde{b}(y,\eta,\delta)$$
 (E.1)

When $\eta = \delta = 0$, the steady state P is of the critical type if

a)
$$\det(b^{1}, j) = 0$$

b) $\tilde{b}^{1}, 1 = \tilde{b}^{2}, 1 = \tilde{b}^{1}, 11 = \tilde{b}^{2}, 11 = 0$
c) $\tilde{b}^{2}, 2 \neq 0$
d) $\tilde{b}^{1}, 111 - \tilde{b}^{2}, 111 \neq 0$.
(E.2)

The conditions (E.2) were introduced in §15 and have the following interpretation. Condition a) indicates that $B = (b^{i}, j)$ has a zero eigenvalue, while c) insures that the second eigenvalue is non-zero. Condition b) indicates that the linear and quadratic parts of the y^{1} dynamics vanish. Condition d) indicates that the y^{1} dynamics are cubic when $\eta = \delta = 0$. The triple point $P = P_{0}/P_{1}/P_{2}$ will be called a saddle-node (Andronov et. al. (1973)). In this appendix, we show that the constructions of Chapter 4 are regular at the critical bifurcation $(\eta = \delta = 0)$. First we show that α_{0} and β_{0} , the parameters in the Pearcey integral, are regular functions of η and δ . Second, we show that the normal

derivative of ψ can be calculated at the critical bifurcation. Third, we show that h^0 can be calculated at the critical bifurcation. Our arguments are analogous to those of Appendix D.

E.1. Regularity of α_0 and β_0

In §16 we showed that

$$b^{i}\psi_{i} + \frac{a^{ij}}{2}\psi_{i}\psi_{j}(\psi^{3}-\alpha_{0}\psi-\beta_{0}) = 0$$
 (E.3)

and that $\psi(P_k) = \tilde{\psi}_k$, k = 0, 1, 2, where $\tilde{\psi}_k$ are the ordered roots of

$$\psi^3 - \alpha_0 \psi - \beta_0 = 0 .$$

When P_0, P_1, P_2 coalesce, α_0 and β_0 must vanish and $\psi(P) = 0$. We shall calculate the derivatives of α_0 and β_0 with respect to n; the calculation of derivatives with respect to δ uses an identical procedure. The procedure used is a generalization of the procedure in §D.1.

When (E.3) is differentiated with respect to η and evaluated at $P_{\rm k},$ we obtain

$$\mathbf{b}^{\mathbf{i}}, \boldsymbol{\psi}_{\mathbf{i}} \Big|_{\mathbf{P}_{\mathbf{k}}} + \frac{\mathbf{a}^{\mathbf{i}\mathbf{j}}\boldsymbol{\psi}_{\mathbf{i}}\boldsymbol{\psi}_{\mathbf{j}}}{2} \Big|_{\mathbf{P}_{\mathbf{k}}} (+3\boldsymbol{\psi}_{\mathbf{k}}^{2}\boldsymbol{\psi}_{\mathbf{n}} - \boldsymbol{\alpha}_{0}\boldsymbol{\psi}_{\mathbf{n}} - \boldsymbol{\psi}_{\mathbf{n}} \frac{\partial\boldsymbol{\alpha}_{0}}{\partial\boldsymbol{\eta}} - \frac{\partial\boldsymbol{\beta}_{0}}{\partial\boldsymbol{\eta}}) = 0$$

$$\mathbf{k} = 0, 1, 2 . \qquad (E.4)$$

As in §D.1, ψ_{η} and $\partial \alpha_0 / \partial \eta$ are eliminated from the three equations generated by (E.4). The limit $\eta \rightarrow 0, \delta \rightarrow 0$ is taken to obtain

$$\frac{\partial \beta_0}{\partial \eta} = \frac{2b^i, \eta \psi_i}{a^{ij} \psi_i \psi_j} \Big|_P \qquad (E.5)$$

The values of ψ_i at the steady state P are needed to calculate $\partial \beta_0 / \partial \eta$. These derivatives are calculated in §E.2. The second and higher (up to order r if the deterministic equations are C^r in η) derivatives of β_0 can be calculated in an analogous fashion (§D.1).

In order to obtain a power series for α_0 in terms of η and δ , equation (E.3) is first differentiated with respect to x^k , then η . The resulting system of equations is solved for $\partial \alpha_0 / \partial \eta$. When the limit $\eta \rightarrow 0, \delta \rightarrow 0$ is taken we obtain

$$\frac{\partial \alpha_0}{\partial \eta} = \sum_{k} \frac{2b^i, k\eta \psi_i}{a^{ij} \psi_i \psi_j \psi_k} \bigg|_{P} . \qquad (E.6)$$

The higher derivatives of α_0 with respect to η can be calculated in a similar fashion.

By using these techniques, we can generate power series

$$\alpha_0 = \sum A_{ij} \eta^i \delta^j \qquad \beta_0 = \sum B_{ij} \eta^i \delta^j . \qquad (E.7)$$

These power series are useful when the deterministic system has two complex steady states with small imaginary part (§20).

E.2. Calculation of the Normal Derivative of ψ

At the critical bifurcation, the equation for the derivatives of ψ on the separatrix is

$$\frac{d\psi_k}{dt} + b^i, \quad \psi_i = 0 \qquad k = 1, 2.$$
 (E.8)

At the steady state P, (E.8) becomes

$$b^{i}, \psi_{i} = 0$$
 $k = 1, 2$. (E.9)

These equations will have a nontrivial solution (condition E.2a).

In the y variables, equation (E.3) is (at $\eta = \delta = 0$)

$$\tilde{b}^{i} \frac{\partial \psi}{\partial y^{i}} - \frac{\tilde{a}^{ij}}{2} \frac{\partial \psi}{\partial y^{i}} \frac{\partial \psi}{\partial y^{j}} (\psi^{3}) = 0 . \qquad (E.10)$$

When (E.10) is differentiated three times with respect to y^1 evaluated at P and simplified using (E.2a-d) we obtain:

$$\tilde{b}^{i},_{111} \frac{\partial \psi}{\partial y^{i}} + 3\tilde{a}^{ij} \frac{\partial \psi}{\partial y^{i}} \frac{\partial \psi}{\partial y^{j}} (\frac{\partial \psi}{\partial y^{l}})^{3} = 0$$
. (E.11)

An argument identical to the one in §D.2 leads to

$$\frac{\partial \psi}{\partial y^{1}} = \left[\frac{-(\tilde{b}^{1}, 111 - \tilde{b}^{2}, 111)}{(a^{11} - 2a^{12} + a^{22})} \right]^{1/4} .$$
(E.12)

Once the derivatives of ψ are known at P, they can be calculated along the entire separatrix using equation (E.8). Thus, the normal derivative of ψ can be calculated on the separatrix.

E.3. Calculation of h^0

The technique used to calculate h^0 is analogous to the one in §D.3. Equation (16.10) is first evaluated on the separatrix. The parameter α_1 vanishes and β_1 is chosen so that h^0 is regular at P. Equation (16.10) is differentiated twice and evaluated at

P, in order to calculate $h^{0}(P)$. Once $h^{0}(P)$ is known, h^{0} can be calculated along the entire separatrix. The technique of Appendix A can then be used to calculate h^{0} in the entire plane.

Appendix F: Existence of Solutions of the General Eikonal Equation

In this appendix, we prove the existence of solutions of the equation

$$F(x^{1}, x^{2}, \psi, \psi_{1}, \psi_{2}) = b^{i}\psi_{i} - \psi \frac{a^{ij}}{2}\psi_{i}\psi_{j} = 0$$
 (F.1)

with initial data $\psi = 0$ on the separatrix S. Equation (F.1) arises in the normal case. The marginal and critical cases are treated in a similar fashion, although some details are changed.

Associated with equation (F.1) is a system of ordinary differential equations (Courant, 1962). Let $p_i = \psi_i$. The characteristic or ray equations are

$$\frac{dx^{i}}{ds} = b^{i} - \psi a^{ij}p_{j}$$

$$\frac{d\psi}{ds} = p_{i} \frac{dx^{i}}{ds} \qquad (F.2)$$

$$\frac{dp_{k}}{ds} = -b^{i}, p_{i} + \frac{a^{ij}, p_{i}}{2} p_{i}p_{j}\psi + a^{ij}p_{i}p_{j}p_{k} \quad k = 1,2.$$

Integrating equations (F.2) is equivalent to solving (F.1). The initial value problem for (F.1) with initial data on the separatrix is a characteristic initial value problem. Namely, the initial data are given on a curve that is a solution of (F.2). In general, a characteristic initial value problem does not have a unique solution because it is not possible to calculate ψ_n on the initial manifold. In this problem, the initial manifold is more singular than usual, since it contains the saddle point. Also, F_{ψ_i} vanishes at the singularity. These singularities distinguish our problem from the usual characteristic initial value problem and allowed the calculation of ψ_n on the initial manifold. This calculation was given in Chapter 2. Since we are able to calculate ψ_n on the initial manifold, this characteristic initial value problem

Let N denote distance normal to the separatrix and Y measure distance along the separatrix, with the saddle point representing Y = 0. The separatrix corresponds to N = 0. When equations (F.2) are rewritten in terms of (N,Y) we obtain (using a Taylor expansion)

$$\frac{dN}{ds} = N - \psi a^{ij} p_{j} + 0(N^{2} + Y^{2})$$

$$\frac{dY}{ds} = -Y - \psi a^{ij} p_{j} + 0(N^{2} + Y^{2})$$

$$\frac{d\psi}{ds} = -\frac{1}{2} \psi a^{ij} p_{i} p_{j}$$

$$\frac{dp_{k}}{ds} = -b^{i}, _{k} p_{i} + \frac{a^{ij}}{2} p_{i} p_{j} \psi + a^{ij} p_{i} p_{j} p_{k} .$$
(F.3)

In (F.3), p_i refers to p_Y or p_N . We have assumed that the eigenvalues of $B = (b_{,j}^i)$, evaluated at the saddle point, are ± 1 . Since $\psi = 0$ on S, we obtain

$$\frac{\mathrm{dN}}{\mathrm{ds}}\Big|_{S} \equiv 0 \qquad \frac{\mathrm{d}\psi}{\mathrm{ds}}\Big|_{S} \equiv 0 \qquad (F.4)$$

Namely, it is not possible to move off the initial manifold S by integrating (F.3). Equation (F.4) is simply a restatement of the characteristic nature of S.

In Chapter 2, we showed that the normal derivative of ψ could be calculated on S. Instead of choosing the separatrix as the initial manifold, we choose a manifold S_{γ} , on which $\psi = \gamma$. The new manifold S_{γ} can be constructed by a Taylor expansion:

$$S_{\gamma} = \{ (N,Y): N = \gamma/\psi_N(Y) + O(\gamma^2) \}$$
 (F.5)

We will show that dN/ds and d ψ/ds are non-zero on S $_{\!\!\!\!\!\!\!\!\!\!}$.

In order to integrate (F.3), starting on S_{γ} , initial data must be given. We already have shown that $\psi(0;\gamma) = \gamma$ and $N(0;\gamma) = \gamma/\psi_N + 0(\gamma^2)$. Clearly $Y(0;\gamma) = Y$ and $P_Y(0;\gamma) = o(\gamma)$, since ψ is constant on S_{γ} . Finally, $P_N(0;\gamma) = P_N^0 + o(\gamma)$, where P_N^0 is the value of ψ_N on the separatrix.

Using this initial data and the first equation in (F.3), we obtain

$$\frac{\mathrm{dN}}{\mathrm{ds}}\Big|_{s=0} = \frac{\gamma}{\psi_{\mathrm{N}}} - \gamma [a^{\mathrm{NN}} P_{\mathrm{N}}^{0}] + o(\gamma^{2}) . \qquad (F.6)$$

We now introduce a new ray parameter σ , defined by

 $\sigma = \gamma s . (F.7)$

Then

$$\frac{\mathrm{dN}}{\mathrm{d\sigma}}\Big|_{\sigma=0} = \frac{1}{\psi_{\mathrm{N}}} - (a^{\mathrm{NN}} P_{\mathrm{N}}^{0}) + o(\gamma) . \qquad (F.8)$$

In a similar fashion, we can show that

$$\frac{d\psi}{d\sigma}\Big|_{\sigma=0} = -\frac{1}{2} a^{NN} (P_N^0)^2 + o(\gamma) . \qquad (F.9)$$

We now let $\gamma \to 0,$ so that the manifold S_γ collapses onto the separatrix. We obtain:

$$\lim_{\gamma \to 0} \left. \frac{dN}{d\sigma} \right|_{\sigma=0} = \frac{1}{\psi_{\rm N}} - a^{\rm NN} P_{\rm N}^{\rm O} \neq 0$$
 (F.10)

$$\lim_{\gamma \to 0} \left. \frac{\mathrm{d}\psi}{\mathrm{d}\sigma} \right|_{\sigma=0} = -\frac{1}{2} \left. \mathrm{a}^{\mathrm{NN}} \left(\mathrm{P}_{\mathrm{N}}^{0} \right)^{2} \neq 0 \right.$$
 (F.11)

Equations (F.10,11) indicate that it is possible to calculate N and ψ off the separatrix, so that equations (F.10,11) and the equations for Y and p_k on (F.3) can be used to calculate ψ in the phase plane.

An intuitive description of the effect of the reparametrization is the following. For each value of γ , $\gamma \neq 0$, equations (F.3) can be solved, so that we draw the rays emanating from S_{γ} . We denote this set of rays by $\{R_{\gamma}\}$. As $\gamma \rightarrow 0$, equations (F.10,11) indicate that the rays $\{R_{\gamma}\}$ converge to a set of rays $\{R_{0}\}$, rays that appear to emanate from the separatrix.

Our construction is valid if the linear dynamics for N and Y are replaced by nonlinear ones. At the marginal bifurcation, the appropriate reparametrization is $\sigma = \gamma^2 s$. At the critical bifurcation the appropriate reparametrization is $\sigma = \gamma^3 s$. The above analysis then applies with only slight modifications.

The method described above produces local solutions of (F.1). Global solutions can be obtained by piecing local solutions of (F.2) or (F.3) together (Hartman, 1973). •

Mangel, M.S., A treatment of complex ions in seawater, Marine Geology 11:M24-26, 1971

Jendrasiak, G.L. and M.S. Mangel, Ion pair movement across bilayer lipid membranes, Nature 234:89-91, 1971

Mangel, M., D.S. Berns and A. Ilani, The dependence of photosensitivity of bileaflet lipid membranes upon the chlorophyll and carotenoid content, J. Mem. Biol. 20:171-180, 1975

Mangel, M., The enhancement of photocurrents in bilayer lipid membranes by phycocyanin: pH and surface charge dependence, Bioch. Bioph. Res. Comm. 66:393-397, 1975

Berns, D.S., Ilani, A. and M.S. Mangel, Photosensitivity in bilayer lipid membranes, in Proc. of the International Conference on the Excited States of Biological Molecules (Lisbon, 1974), J. Birks (ed.), John Wiley and Sons, 277-287, 1976

Mangel, M. and G.L. Jendrasiak, The movement of ion pairs across bilayer lipid membranes, Chem. Phys. Lipids 16:167-180, 1976

Mangel, M., The relationship of the photosensitivity of bilayer lipid membranes and the aqueous acceptor: Studies using complex ions of amino acids, Bioch. Bioph. Acta 419:404-410, 1976

Mangel, M., Properties of liposomes that contain chloroplast pigments: photosensitivity and efficiency of energy conversion, Bioch. Bioph. Acta 430:459-466, 1976

Mangel, M. and D. Ludwig, Probability of extinction in a stochastic competition, SIAM J. Appl. Math 33:256-266, 1977