SOME EFFECTS OF SPATIAL NONUNIFORMITIES IN CHEMICALLY REACTING MIXTURES

Thesis by

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In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California

1980

(Submitted August 14, 1979)

ACKNOWLEDGMENT

I wish to thank my advisor, Donald S. Cohen, both for suggesting the topics in this work and offering encouragement during it's progress, and for teaching me many of the things I know from the very beginning of my student life as an undergraduate. I am indebted to Professor Gerald B. Whitham for valuable comments which led to some improvements in Chapters 1 and 3. I am also thankful to Dr. Bernardo A. Huberman for a conversation that gave me insight in the physics of Chapter 4 and for communicating to me some of his current work. My sincere thanks go to Vivian Davies for her excellent and very fast work in typing this thesis.

Financial support during my stay at Caltech was provided by Graduate Research Assistantships, Graduate Teaching Assistantships, and a Caltech Fellowship.

ABSTRACT

In Part I, a method is developed for treating reacting-diffusing systems whose kinetics lead to a limit cycle behavior with frequency varying slowly with position. This is accomplished by including the effects of the spatial variation in a phase variable that is introduced to parametrize the limit cycles at each point. The normalization of this phase variable is chosen such that the limit cycles at each point have the same frequency with respect to this variable. The method is motivated by treating the weakly coupled behavior of two oscillators that, unlike previous works, are not nearly identical. The analogy between discrete oscillator systems and continuous chemically reacting mixtures is explored by treating a chain of coupled limit cycle oscillators and considering various limits as the number of oscillators tends to infinity.

In Part II a different effect of spatial nonuniformities is studied: the modification of the simple diffusion approximation to treat situations of large deviations from equilibrium distributions in a mixture or proximity to some critical temperature. A technique for treating bifurcation from the continuous spectrum by introducing a slow space scale is developed. Using this, the onset of a spatially nonuniform state in a model chemically reacting system is studied, occurring when some reaction rate crosses the values at which linearized theory predicts destabilization of the uniform steady state solutions admitted by the system. Subscritical bifurcation is also found possible.

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GENERAL INTRODUCTION

In this work we shall study some effects of spatial nonuniformities in the evolution of chemically reacting mixtures of fluids.

We shall limit ourselves to the study of the change of the mixture composition at each point due only to the chemical reactions and to the diffusion flux induced by the nonuniformity of the composition. The fluid will be assumed at rest, pressure gradients will be ignored, and the temperature will be assumed initially uniform. Thus, bulk motion of the fluid can only be caused indirectly by the nonuniformity in composition leading, for example, to nonuniform reaction rates that can create temperature or pressure gradients, etc. The composition gradients will be assumed small, so all bulk motion effects can be ignored, as of 2nd order in these gradients.

So, in our case, the Navier-Stokes equations describing the mixture will reduce to a system of coupled continuity equations for the various components, of the form

$$\frac{\partial n_i}{\partial t} = G_i(\vec{n}) - \vec{\nabla} \cdot \vec{J}_i$$

where n_i, G_i and $\vec{J}_i$ are respectively the concentration, source term and diffusion flux density for the i-th component of the mixture.

The diffusion flux density will in general be a function of the gradients of the thermodynamic quantities describing the mixture, like the chemical potential μ, pressure p, and temperature T. Since we assume all gradients to be small and ignore $\vec{\nabla}$ T and $\vec{\nabla}$p, we can assume $\vec{J}_i$ to be approximately equal to

$$\vec{J}_i = -\alpha \vec{\nabla} \mu_i$$

where increase of the total entropy of the mixture with time dictates that α be a positive constant [1].

Our equations are purely phenomenological in that we assume certain functional forms for the thermodynamic potential μ, that then lead to predictions for the behavior of our system. These in turn, contrasted to experimental results, will determine the numerical values of the various phenomenological coefficients introduced and the domain of applicability of the model.

In Part 1 we work with "Fickian" systems where, sufficiently far from critical temperatures at which the qualitative behavior of the system undergoes sharp transitions, we assume that μ is proportional to the concentration. This is the well-charted realm of Reaction-Diffusion equations. Our work is on two component systems whose kinetics is such that, in the absence of diffusion, it would lead to temporal oscillations at each point. The form of these oscillations is allowed to vary continuously with position, while the frequency varies also with position but only slowly. We develop a method for treating this problem, by introducing a new phase variable with respect to which uncoupled frequencies at each point are normalized to the same value.

In Chapter 1 we motivate this method by treating two weakly coupled limit cycle oscillators. Then, by utilizing similar ideas for the treatment of a continuous system in Chapter 2, we are led to a

Burgers'-type equation for the new phase variable that includes a forcing term due to the small nonuniformity in intrinsic frequencies. This equation can be linearized by the Cole-Hopf transformation, allowing an exact solution for the behavior of the phase of the oscillations to 0th order, in terms of the eigenfunctions of some Sturm-Liouville operator. We find that systems of this type exhibit sustained traveling waves, as opposed to the uniform kinetics situation [2]. In Chapter 3 we apply these ideas to examine some phenomena encountered in chains of cellular electrical oscillators. We find that for the discrete model of these systems under consideration here, the diffusive continuous limit is too drastic. It conceals the threshold phenomena that are observed in these systems and which we are able to demonstrate using an alternative treatment: by postponing the passage to a continuous limit until after we have obtained the secular equations for the phase of each oscillator in the chain, we use a WKB-type approximation to obtain a first order quasi-linear evolution equation that can lead to sharp shocks in the phase, while it has Burgers' equation as a large wavelength limit.

In Part 2 we consider the effects of a nonlocal approximation to the chemical potential in chemically reacting mixtures far from equilibrium.

For simplicity, we treat the variation of only one of the components of the mixture, the others assumed to be kept constant throughout the process. It is well known that mixtures are characterized by the existence of a critical temperature T_c: below T_c the components form pure phases, separated by a rather sharp interphase in which there is some mixing. On the contrary, above T_c the substances mix freely in any proportion.

We assume that reactions and mixing occur at constant temperature and pressure, and that p and T are initially uniform, so that they will not change throughout the process. Then, in equilibrium, the Gibbs free energy F must attain a minimum value. Following the approach adopted in a recent paper by B. Huberman [3] we write F in a Landau functional form [4] including nonlocal effects due to intermolecular forces. This leads to an approximation for the chemical potential valid in the neighborhood of T_c that we then utilize in our continuity equations.

In Chapter 4 we treat a simple model autocatalytic chemical reaction, where only one component is allowed to vary. We find that close to the critical point we can be led to behavior of surprising complexity, including stable striations in the concentration of the considered chemical. Our system undergoes some interesting "phase transitions" and, as expected, the behavior in the neighborhood of the "triple point" is considerably more complex.

In treating the problem in Part 2, we had to develop a technique to analyze bifurcation from the continuous spectrum of an operator. The idea was basically to introduce a slow space scale to describe effects due to the interaction of solutions of the linearized problem with wave numbers in a neighborhood of a critical ("most unstable") wave number. The nonvanishing of this critical wave number is essential for our method.

The long time (relaxed) behavior of the system is analyzed here, by introducing a slow time scale, coupled to and dictated by the slow space scale. Self-consistency of the perturbation scheme we use leads to evolution equations for the amplitude of the $O(\epsilon)$ solution that are of the Ginzburg-Landau type and whose analysis shows us the form of the possible final states that the system can attain.

This technique, developed here independently, has also been used by other workers in various contexts [5], [6]. It appears that it was first developed by Newell and Whitehead in their treatment of the Bernard instability in fluids [7].

We conclude Part 2 with a discussion of other problems from physics where similar ideas can be applied as well as possible directions in which this work can be extended.

PART I

1. TWO WEAKLY COUPLED OSCILLATORS

1.1 Introduction

In order to motivate the method used in the next chapter for treating continuous systems of oscillatory chemical reactions with spatially nonuniform kinetics, we consider two weakly coupled limit cycle (l.c.) oscillators. We make no assumptions about their shapes or intrinsic frequencies.

The method we use to study their (weakly) coupled behavior assumes that both oscillators have relaxed near their limit cycles. We normalize the angular variable θ_i parametrizing the i-th limit cycle in such a way that the period of the i-th oscillator with respect to θ_i is 1.

In this way we include in the angle variables θ_i all effects due to intrinsic period differences and avoid all problems that might arise when averaging over time.

Previous investigations were limited to the treatment of the weak coupling of nearly identical oscillators. Here we are able to treat l.c. oscillators of arbitrary uncoupled periods and shapes, and derive conditions for their entrainment. In Section 1.3, in particular, we derive the entrainment condition when the periods are nearly equal. In Section 1.4, we demonstrate the behavior of the solution to 0th order by an example, in which we exactly solve the secular equation for the phase shift between the two oscillators.

The case where the oscillators have periods near some integral ratio $m:n \neq 1$, can also lead to entrainment. Apart from the fact that we would have to carry the analysis to a sufficiently high order, our method goes through with no added complications. We discuss this in Section 1.4 for m : n = 2.

1.2 The General Case

We consider the system

$$\left\{ \begin{aligned} \dot{u}_i &= F_i(u_i, v_i) + \epsilon k f_i(u_i, u_j, v_i, v_j) \\ \dot{v}_i &= G_i(u_i, v_i) + \epsilon k g_i(u_i, u_j, v_i, v_j) \end{aligned} \right. \tag{1}$$

$$i, j = 1, 2, \quad i \neq j$$

and assume that for k = 0 (uncoupled case) both pairs of equations possess a l.c. solution of period T_i :

$$\left\{ \begin{aligned} \dot{U}_i &= F_i(U_i, V_i) \\ \dot{V}_i &= G_i(U_i, V_i) \end{aligned} \right.$$

$$i = 1, 2$$

with

$$\left\{ \begin{aligned} U_i(t) &= U_i(t + T_i) \\ V_i(t) &= V_i(t + T_i) \end{aligned} \right.$$

We want to parametrize each limit cycle by an angular variable θ_i, so that each has period 1 with respect to θ_i, i.e.,

$$\begin{cases} U_i(t) \equiv \hat{U}_i\big(\theta_i(t)\big) = \hat{U}_i(\theta_i + 1) \\ V_i(t) \equiv \hat{V}_i\big(\theta_i(t)\big) = \hat{V}_i(\theta_i + 1) \end{cases}$$

In the new variables we have

$$\begin{cases} \hat{U}_i' = T_i F_i(\hat{U}_i, \hat{V}_i) \\ \hat{V}_i' = T_i G_i(\hat{U}_i, \hat{V}_i) \end{cases}$$

Having parametrized the limit cycles, we now introduce [2] the local coordinate system (Fig. 1):

$$\begin{cases} u_i(t) = \hat{U}_i(\theta_i) + \epsilon A_i \hat{V}_i'(\theta_i) \\ v_i(t) = \hat{V}_i(\theta_i) - \epsilon A_i \hat{U}_i'(\theta_i) \end{cases}$$

or

$$\begin{cases} u_i(t) = \hat{U}_i(\theta_i) + \epsilon T_i A_i G_i(\hat{U}_i, \hat{V}_i) \\ v_i(t) = \hat{V}_i(\theta_i) - \epsilon T_i A_i F_i(\hat{U}_i, \hat{V}_i) \end{cases}$$

$$i = 1, 2$$

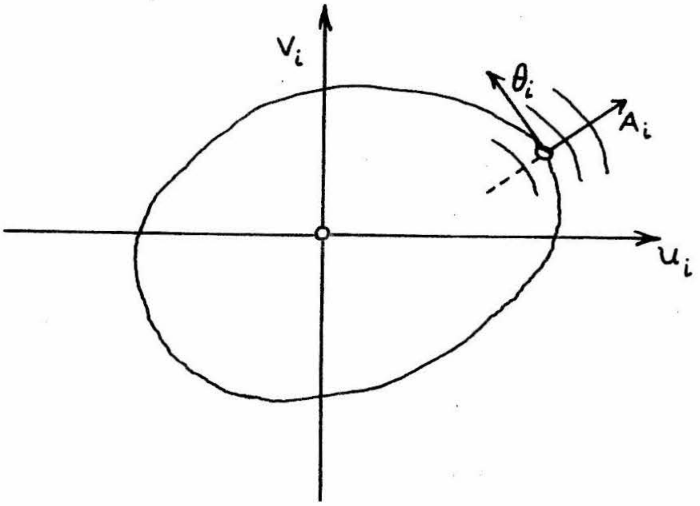

Fig. 1

We shall assume that the A_i and θ_i possess asymptotic expansions in powers of ϵ of the form:

$$A_i \simeq A_i^0 + \epsilon A_i^1 + O(\epsilon^2)$$

$$\theta_i \simeq \theta_i^0 + \epsilon\,\theta_i^1 + O(\epsilon^2)$$

and the T_i can be also expanded as $T_i \simeq T_i^0 + \epsilon T_i^1 + O(\epsilon^2)$.

Before rewriting system (1) in the new variables, it is convenient to derive asymptotic expansions in powers of ϵ of all the expressions involved. We have (within $O(\epsilon^2)$) :

$$\left\{\begin{aligned} \hat{U}_i(\theta_i) &\simeq U_i^0 + \epsilon F_i^0\, \theta_i^1\, T_i^0 \\ \hat{V}_i(\theta_i) &\simeq V_i^0 + \epsilon\, G_i^0\, \theta_i^1\, T_i^0 \end{aligned}\right. ,$$

$$\left\{\begin{aligned} F_i(\hat{U}_i, \hat{V}_i) &\simeq F_i^0 + \epsilon\, \theta_i^1\, (F_i^0)'\, T_i^0 \\ G_i(\hat{U}_i, \hat{V}_i) &\simeq G_i^0 + \epsilon\, \theta_i^1\, (G_i^0)'\, T_i^0 \end{aligned}\right. ,$$

$$\left\{\begin{aligned} u_i &\simeq U_i^0 + \epsilon T_i^0 \left\{F_i^0\, \theta_i^1 + A_i^0 G_i^0\right\} \\ v_i &\simeq V_i^0 + \epsilon T_i^0 \left\{G_i^0\, \theta_i^1 - A_i^0 F_i^0\right\} \end{aligned}\right.$$

$$\left\{\begin{aligned} F_i(u_i, v_i) &\simeq F_i^0 + \epsilon T_i^0 \left\{\theta_i^1 (F_i^0)' + A_i^0 \left(F_{i,1}^0 G_i^0 - F_{i,2}^0 F_i^0\right)\right\} \\ G_i(u_i, v_i) &\simeq G_i^0 + \epsilon T_i^0 \left\{\theta_i^1 (G_i^0)' + A_i^0 \left(G_{i,1}^0 G_i^0 - G_{i,2}^0 F_i^0\right)\right\} \end{aligned}\right.$$

and

$$\left\{\begin{aligned} \epsilon k f_i \left(u_i, u_j, v_i, v_j\right) &\simeq \epsilon k f_i^0 \\ \epsilon k g_i \left(u_i, u_j, v_i, v_j\right) &\simeq \epsilon k g_i^0 \end{aligned}\right.$$

where

$$U_i^0 \equiv \widehat{U}_i(\theta_i^0), \quad F_i^0 \equiv F_i\left(U_i^0, V_i^0\right), \quad \text{etc.,}$$

in the obvious convention.

Assuming also that the coupling introduces a slow time behavior in the problem, we introduce the slow time variable

$$\tau \equiv \epsilon t$$

so that

$$\frac{d}{dt} \equiv \frac{\partial}{\partial t} + \epsilon \frac{\partial}{\partial t}$$

Then, if we expand time derivatives in a power series in ϵ we get

$$\begin{aligned} \dot{U}_i \simeq {} & T_i^0 F_i^0 \theta_{it}^0 + \epsilon T_i^0 \left\{ F_i^0 \left(\theta_{it}^1 + \theta_{i\tau}^0\right) + G_i^0 A_{it}^0 + \right. \\ & \left. + T_i^0 \theta_{it}^0 \left[(G_i^0)' A_i^0 + (F_i^0)' \theta_i^1 \right] \right\} + \epsilon T_i^1 F_i^0 \theta_{it}^0 \end{aligned}$$

$$\begin{aligned} \dot{V}_i \simeq {} & T_i^0 G_i^0 \theta_{it}^0 + \epsilon T_i^0 \left\{ G_i^0 \left(\theta_{it}^1 + \theta_{i\tau}^0\right) - F_i^0 A_{it}^0 + \right. \\ & \left. + T_i^0 \theta_{it}^0 \left[(G_i^0)' \theta_i^1 - (F_i^0)' A_i^0 \right] \right\} + \epsilon T_i^1 G_i^0 \theta_{it}^0 \end{aligned}$$

Substituting now the above expressions into system (1) and equating coefficients of same powers of ϵ we get the hierarchy:

$$O(1):\ \begin{cases} T_i^0\, F_i^0\, \theta_{it}^0 = F_i^0 \\ \\ T_i^0\, G_i^0\, \theta_{it}^0 = G_i^0 \end{cases}$$

$$O(\epsilon)\ \begin{cases} T_i^0 \left\{F_i^0\left(\theta_{it}^1 + \theta_{i\tau}^0\right) + G_i^0 A_{it}^0 + T_i^0\, \theta_{it}^0 A_i^0\, (G_i^0)'\right\} + T_i^1 F_i^0 \theta_{it}^0 = \\ \qquad = +T_i^0\, A_i^0\left(F_{i,1}^0 G_i^0 - F_{i,2}^0\, F_i^0\right) + k\, f_i^0 \\ \\ T_i^0 \left\{G_i^0\left(\theta_{it}^1 + \theta_{i\tau}^0\right) - F_i^0 A_{it}^0 - T_i^0\, \theta_{it} A_i^0\, (F_i^0)'\right\} + T_i^1 G_i^0 \theta_{it}^0 = \\ \qquad = T_i^0 A_i^0\left(G_{i,1}^0 G_i^0 - G_{i,2}^0\, F_i^0\right) + k\, g_i^0 \end{cases}$$

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Solving the O(1) equations we find

$$\theta_i^0 = \frac{t}{T_i^0} + \psi_i(\tau).$$

Using this in the $O(\epsilon)$ system we have, after some manipulation

$$A_{it}^0 + A_i^0 \left\{\frac{1}{2}\left(\ell n\left[(F_i^0)^2 + (G_i^0)^2\right]\right)' - T_i^0\left[\frac{F_{i,1}(G_i^0)^2 + G_{i,2}^0 (F_i^0)^2 - F_i^0 G_i^0 (F_{i,2} + G_{i,1}^0)}{(F_i^0)^2 + (G_i^0)^2}\right]\right\} =$$

$$= k\left(\frac{f_i^0 G_i^0 - g_i^0 F_i^0}{(F_i^0)^2 + (G_i^0)^2}\right)$$

and

$$\theta^1_{it} = -\left(\psi_{i\tau} + \frac{T^1_i}{(T^0_i)^2}\right) + A^0_i \left\{ \frac{\left(F^0_{i,1} - G^0_{i,2}\right) F^0_i G^0_i - F^0_{i,2}(F^0_i)^2 + G^0_{i,1}(G^0_i)^2}{(F^0_i)^2 + (G^0_i)^2} \right\} +$$

$$+ k \left(\frac{f^0_i F^0_i + g^0_i G^0_i}{(F^0_i)^2 + (G^0_i)^2} \right)$$

or

$$\left\{ \begin{aligned} & A^0_{it} + A^0_i M_{i1}\left(\frac{t}{T^0_i} + \psi_i(\tau)\right) = k M_{i2}\left(\frac{t}{T^0_i} + \psi_i(\tau), \frac{t}{T^0_j} + \psi_j(\tau)\right) \\ & \theta^1_{it} = -\left(\psi_{i\tau} + \frac{T^1_i}{(T^0_i)^2}\right) + A^0_i N_{i1}\left(\frac{t}{T^0_i} + \psi_i(\tau)\right) + \frac{k}{T^0_i} N_{i2}\left(\frac{t}{T^0_i} + \psi_{i1} \frac{t}{T^0_j} + \psi_j\right) \end{aligned} \right. \qquad (2)$$

where, according to our convention, the functions N_{ik}, M_{ik} have period 1 w.r.t. their arguments.

These equations can be solved in the standard way: firstly, the equations for A^0_i will yield a bounded solution as a consequence of the fact that the two uncoupled systems possess stable limit cycle solutions. Then, substituting the known forms for the A^0_i in the equations for θ^1_i and requiring that the θ^1_i are bounded in t (necessary for the validity of the asymptotic expansion for θ_i) we shall get two coupled equations for the $\psi_i(\tau)$. The process can be carried to any order, to determine the behavior of the solution at all times. In general, the full solution will not be periodic in t.

The details of the calculations depend, among other things, on the T_i^0, and in the next section we carry them out for the special case

$$T_1^0 = T_2^0 = 1 .$$

This case, namely having nearly equal intrinsic periods for the two oscillators, is particularly interesting, as it can lead to the phenomenon of entrainment and rhythm splitting. Similar phenomena can be observed also when $T_1^0 : T_2^0$ is close to some other integral ratio $m : n \neq 1$, but since the calculations in this case become forbiddingly complicated (we must go beyond the first order in ϵ to pick the effect) without adding any more insight, we shall not pursue that further.

In Section 1.4 the theory is applied to a simple "λ-ω" system. In the 1:1 case, we shall see that entrainment is possible, while the special symmetry of this problem precludes secondary entrainment for other integral ratios.

Our analysis differs from previous works [2] in that we show that entrainment is possible not just between two nearly identical oscillators, but between oscillators of any shape, provided their intrinsic frequencies are sufficiently close.

1.3 The Case of Nearly Equal Periods: Entrainment

We assume now that

$$T_i^0 = 1, \quad i = 1, 2$$

System (2) then becomes

$$\begin{cases} A^0_{it} + A^0_i\, M_{i1}(t+\psi_i) = k\, M_{i2}\,(t+\psi_i,\, t+\psi_i) \\[2ex] \theta^1_{it} = -\left(\psi_{i\tau} + T^1_i\right) + A^0_i\, N_{i1}(t+\psi_i) + k\, N_{i2}\left(t+\psi_i,\, t+\psi_j\right) \end{cases}$$

or

$$\begin{cases} A^0_{it} + A^0_i\, \hat{M}_{i1}(t) = k\, \hat{M}_{i2}(t, \psi) \\[2ex] \theta^1_{it} = -\left(\psi_{i\tau} + T^1_i\right) + A^0_i\, \hat{N}_{i1}(t) + k\, \hat{N}_{i2}(t, \psi) \end{cases}$$

with $\psi = \psi_2 - \psi_1$, since change in both ψ_1 and ψ_2 can be incorporated in t as a phase shift. All the above functions have period 1 in t and ψ. Now, we solve the equations for the A^0_i. We have

$$\left[A^0_i \exp\left\{ \int_0^t \hat{M}_{i1}(\zeta)\, d\zeta \right\}\right]_t = k\, \hat{M}_{i2}(t, \psi) \exp\left\{ \int_0^t \hat{M}_{i1}(\zeta)\, d\zeta \right\}$$

$$\Longrightarrow A^0_i = \exp\left\{ -\int_0^t \hat{M}_{i1}(\zeta) d\zeta \right\} \left[C + k \int_0^t \hat{M}_{i2}(\zeta, \psi) \exp\left\{ \int_0^\zeta \hat{M}_{i1}(\zeta) d\zeta \right\} d\zeta \right]$$

Since for k = 0 (uncoupled systems) both limit cycles are stable, A^0_i must decay to zero for k = 0, so that

$$\int_t^{t+1} M_{i1}(\zeta) d\zeta \equiv \int_0^1 \hat{M}_{i1}(\zeta) d\zeta > 0$$

as a condition for stability.

It is easy to show that for $k \neq 0$, A_i^0 tends to a periodic function. To see this, let

$$\lambda = \int_0^1 \hat{M}_{i1} d\zeta > 0 \text{ (by stability.)}$$

Then

$$\exp\left\{ -\int_0^t \hat{M}_{i1} d\zeta \right\} = \exp\left\{ -\int_0^{[t]+(t-[t])} \hat{M}_{i1} d\zeta \right\} =$$

$$= e^{-\lambda[t]} \exp\left\{ -\int_0^{t-[t]} \hat{M}_{i1} d\zeta \right\}$$

Also

$$\int_0^t \hat{M}_{i2}(\zeta, \psi) \exp\left\{ \cdot \int_0^\zeta \hat{M}_{i1}(\xi) d\xi \right\} d\zeta =$$

$$= \sum_{n=1}^{[t]} \int_{n-1}^n \hat{M}_{i2} \exp\left\{ \int_0^\zeta \hat{M}_{i1} d\zeta \right\} d\zeta + \int_{[t]}^t \hat{M}_{i2} \exp\left\{ \int_0^\zeta M_{i1} d\xi \right\} d\zeta$$

But

$$\int_{n-1}^n \hat{M}_{i2} \exp\left\{ \int_0^\zeta \hat{M}_{i2} d\xi \right\} d\zeta = \int_0^1 \hat{M}_{i2}\Big(\zeta + (n-1), \psi\Big) \exp\left\{ \int_0^{\zeta+(n-1)} \hat{M}_{i1} d\zeta \right\} d\zeta =$$

$$= \int_0^1 \hat{M}_{i2}(\zeta, \psi) \exp\left\{ \int_0^\zeta \hat{M}_{i1} d\xi \right\} \exp\left\{ \int_\zeta^{\zeta+(n-1)} \hat{M}_{il} d\xi \right\} d\zeta =$$

$$= e^{\lambda(n-1)} \int_0^1 \hat{M}_{i2} \exp\left\{ \int_0^\zeta \hat{M}_{i1} d\xi \right\} d\zeta$$

So,

$$\int_0^t \hat{M}_{i2} \exp\left\{ \int_0^\zeta \hat{M}_{i1} d\xi \right\} d\zeta =$$

$$= \left(\sum_{n=1}^{[t]} e^{\lambda(n-1)} \right) \int_0^1 \hat{M}_{i2} \exp\left\{ -\int_0^\zeta \hat{M}_{i2} d\xi \right\} d\zeta +$$

$$+ \int_0^{t-[t]} \hat{M}_{i2} \exp\left\{ -\int_0^\zeta \hat{M}_i \, d\xi \right\} d\zeta$$

and, finally, A_i^0 can be written as

$$A_i^0 = [\text{decaying part}] + k\,Y(t, \Psi)$$

with $Y(t, \Psi)$, the periodic part (with period 1 in both t and ψ), found after some algebra to be

$$Y(t, \psi) = \exp\left\{ -\int_0^{t-[t]} \hat{M}_{i1}(\zeta) d\zeta \right\} \left(\left(\frac{1}{1-e^{-\lambda}} \right) \int_0^1 \hat{M}_{i2} \exp\left(\int_0^\zeta \hat{M}_{i1} d\xi \right) d\zeta + \right.$$

$$\left. + \int_0^{t-[t]} \hat{M}_{i2} \exp\left(\int_0 \hat{M}_{i1} d\xi \right) d\zeta \right) .$$

We now return to the equations for the θ_i^1. The boundedness requirement for θ_i^1 is

$$\psi_{iT} + T_i^1 = k \int_0^1 \left\{ Y_i(t, \psi) \hat{N}_{i1}(t) + \hat{N}_{i2}(t, \psi) \right\} dt$$

(In the general case, when there is no single period, the time averages will be integrals of the form: $\lim_{t \to \infty} \frac{1}{t} \int_0^t (\quad)$, assumed to exist). We note that with no coupling present ($k = 0$), the ψ_i will drift apart. In the coupled case, though eventually we will have to solve for each ψ_i separately, we only need to solve for the difference $\psi = \psi_2 - \psi_1$ in order to investigate entrainment. A necessary condition for entrainment is that ψ is bounded in τ.

In this general case, the entrainment can be broken by higher order effects.

We demonstrate the behavior of the phase shift ψ for an example in the next section.

1.4 Example: A λ-w System

To demonstrate the above ideas, consider the system

$$\left\{ \begin{aligned} u_i^0 &= u_i \lambda_i(r_i) - v_i w_i(r_i) + \epsilon k (u_j - u_i) \\ v_i^0 &= u_i w_i(r_i) + v_i \lambda_i(r_i) + \epsilon k (v_j - v_i) \end{aligned} \right.$$

$$i, j = 1, 2, \quad i \neq j$$

with $r_i^2 = u_i^2 + v_i^2$ and $\lambda_i = R_i^2 - r_i^2$, $w_i = \nu_i + \lambda_i$. For $k = 0$, this system has the stable circular limit cycle solution:

$$\left\{ \begin{aligned} U_i(t) &= R_i \cos \nu_i t \\ V_i(t) &= R_i \sin \nu_i t \end{aligned} \right. \qquad i = 1, 2$$

Introducing the variables θ_i we define

$$\begin{cases} \hat{U}_i(\theta_i) = R_i \cos\theta_i \\ \hat{V}_i(\theta_i) = R_i \sin\theta_i \end{cases}$$

Here we work with the frequencies ν_i and assume

$$\nu_i \simeq \nu_i^0 + \epsilon \nu_i^1 + \epsilon^2 \nu_i^2 + O(\epsilon^3)$$

Substituting into the expressions derived in Section 1.2, we get, after some manipulations:

$$O(1) \quad \begin{cases} V_i^0 \theta_{it}^0 = \nu_i^0 V_i^0 \\ U_i^0 \theta_{it}^0 = \nu_i^0 U_i^0 \end{cases} \quad \Longrightarrow \theta_i = \nu_i^0 t + \Psi_i(t)$$

$$O(\epsilon) \quad \begin{cases} A_{it}^0 + 2R_i^2 A_i^0 = k\left\{\left(\frac{R_j}{R_i}\right)\cos\left[(\nu_j^0 - \nu_i^0)t + (\psi_j - \psi_i)\right] - 1\right\} \\ \theta_{it}^1 = -\left(\psi_{i\tau} - \nu_i^1\right) - 2A_i^0 R_i^2 + k\left(\frac{R_j}{R_i}\right)\sin\left[(\nu_j^0 - \nu_i^0)t + \psi_j - \psi_i\right] \end{cases}$$

To solve this we note that there are two cases that need separate attention, namely $\nu_1^0 \neq \nu_2^0$ and $\nu_1^0 = \nu_2^0$.

We treat the case $\nu_1^0 \neq \nu_2^0$ first. The equation for A_i^0 yields

$$A_i^0 = C\,e^{-2R_i^2 t} - \frac{k}{2R_i^2} + \frac{k(R_j/R_i)}{4R_i^4 + (\nu_j^0 - \nu_i^0)^2} \left\{ 2R_i^2 \cos\left[(\nu_j^0 - \nu_i^0)t + \psi_j - \psi_i\right] + \right.$$

$$\left. + (\nu_j^0 - \nu_i^0)\sin\left[(\nu_j^0 - \nu_i^0)t + \psi_j - \psi_i\right]\right\}$$

For simplicity we ignore the decaying part, setting C = 0. The equation for θ_i^1 then gives

$$\theta_i^1 = - \frac{k(R_j/R_i)}{(\nu_j^0 - \nu_i^0)\left[4R_i^4 + (\nu_j^0 - \nu_i^0)^2\right]} \left\{ \left(2R_i^2 + (\nu_i^0 - \nu_j^0)\right)^2 \cos\left[(\nu_j^0 - \nu_i^0)t + (\nu_j^1 - \nu_i^1)\tau + \gamma\right] + \right.$$

$$\left. + 4\,R_i^4 \sin\left[(\nu_j^0 - \nu_i^0)t + (\nu_j^1 - \nu_i^1)\,\tau + \gamma\right]\right\} + \phi_i(\tau)$$

where, for θ_i^1 to be bounded in t, we required

$$\psi_i(\tau) = (v_i^1 + k)\,\tau + \text{const.}$$

We can continue in this way and find the solution to all orders, but it is easy to see that nothing new will emerge out of this process. This is due to the linearity of the coupling and the special properties of the trigonometric functions: as can be seen easily, the only combination of the frequencies that can appear is $(\nu_j^0 - \nu_i^0) + \epsilon(\nu_j^1 - \nu_i^1)$, so terms of all orders will have essentially the same behavior.

In particular, in the case $\nu_1^0 : \nu_2^0 = m : n\ (\neq 1)$ we see that "secondary entrainment" (i.e., locking to oscillations whose frequencies are exact multiples) is impossible if $n\nu_1^k \neq m\,\nu_2^k$ for some $k \neq 0$.

Incidentally, we note that an alternative treatment could introduce infinitely many time scales

$$\tau_k \equiv \epsilon^k t \ , \qquad k = 1, 2, \cdots$$

so that

$$\psi_i \equiv \psi_i(\tau_k)$$

and demand the θ_i^j, $j > 0$ to be bounded in all the τ_k, thus including all unbounded behavior in θ_i^0. We think this is a meaningful approach (more so if resonance is present) as it is not trying to approximate a nonperiodic phenomenon by periodic function; but we shall not expound on this further.

We return now to the case $\nu_1^0 = \nu_2^0$ and take $\nu_i^0 = 1$ for simplicity. We find

$$A_i^0 = C\, e^{-2R_i^2 t} - \frac{k}{2R_i^2}\left\{1 - \left(\frac{R_j}{R_i}\right)\cos(\psi_j - \psi_i)\right\}$$

and $\theta_i^1 \equiv \phi_i(\tau)$ + (decaying term) with the ψ_i satisfying

$$\psi_{i\tau} = \nu_i^1 + k\left\{1 + \left(\frac{R_j}{R_i}\right)\left\langle \sin(\psi_j - \psi_i) - \cos(\psi_j - \psi_i)\right\rangle\right\}$$

$$i = 1, 2 \ .$$

It is of interest now to ask whether the phases of the two oscillators will lock. To determine this, we must examine their difference, say, $\psi \equiv \psi_2 - \psi_1$. We have $\left(\text{let } \nu = \nu_2^1 - \nu_1^1\right)$

$$\Psi_\tau = \nu + k\left(\frac{R_2^2 - R_1^2}{R_1 R_2}\right)\cos\Psi - k\left(\frac{R_1^2 + R_2^2}{R_1 R_2}\right)\sin\Psi$$

or

$$\psi_\tau = \nu + \mu \sin(\Psi + \sigma)$$

with

$$\mu = \frac{k\sqrt{2(R_1^4 + R_2^4)}}{R_1 R_2}, \quad \sigma = \tan^{-1}\left(\frac{R_1^2 - R_2^2}{R_1^2 + R_2^2}\right)$$

which is easily integrated to give

$$\psi(\tau) + \sigma =$$

$$= \left\{\begin{array}{ll} 2\tan^{-1}\left[\frac{\sqrt{\nu^2-\mu^2}}{\nu}\tan\left(\frac{(\tau+c)}{2}\sqrt{\nu^2-\mu^2}\right) - \frac{\mu}{\nu}\right], \quad \nu^2 > \mu^2 & \\ \qquad\qquad\qquad \text{or} & \\ \left.\begin{array}{l} 2\tan^{-1}\left[\frac{\sqrt{\mu^2-\nu^2}}{\nu}\coth\left(-\frac{(\tau+c)}{2}\sqrt{\mu^2-\nu^2}\right) - \frac{\mu}{\nu}\right], \text{ if } \left|\nu\tan\left(\frac{\psi(0)+\sigma}{2}\right) + \mu\right| > \sqrt{\mu^2-\nu^2} \\ 2\tan^{-1}\left[\frac{\sqrt{\mu^2-\nu^2}}{\nu}\tanh\left(-\frac{(\tau+c)}{2}\sqrt{\mu^2-\nu^2}\right) - \frac{\mu}{\nu}\right], \text{ if } \left|\nu\tan\left(\frac{\psi(0)+\sigma}{2}\right) + \mu\right| < \sqrt{\mu^2-\nu^2} \end{array}\right\} \mu^2 > \nu^2 & \end{array}\right.$$

Obviously, if $|\nu| > \frac{k}{R_1 R_2}\sqrt{2(R_1^4 + R_2^4)}$, $\psi(\tau)$, (which must be continuous) is unbounded and the two phases pull apart in the slow time scale, while otherwise the two phases lock to a phase shift constant in τ and independent of the initial conditions as shown in Fig. 2.

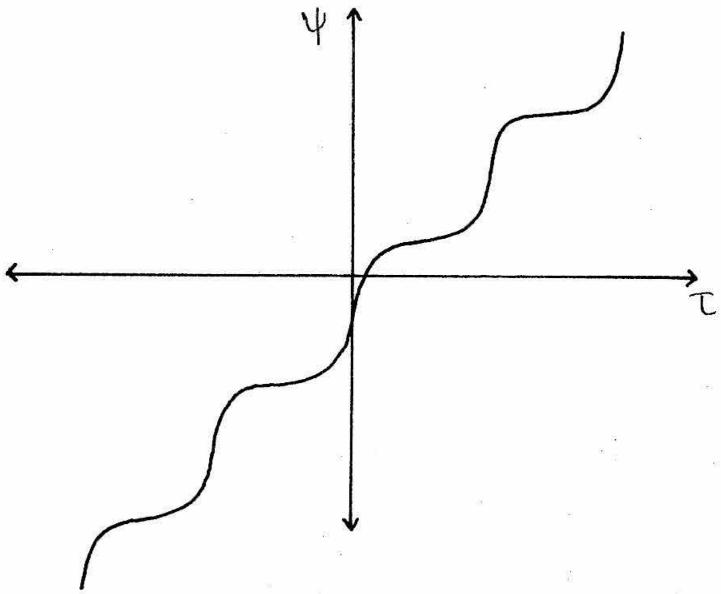


Fig. 2a. $(\nu^2 > \mu^2)$

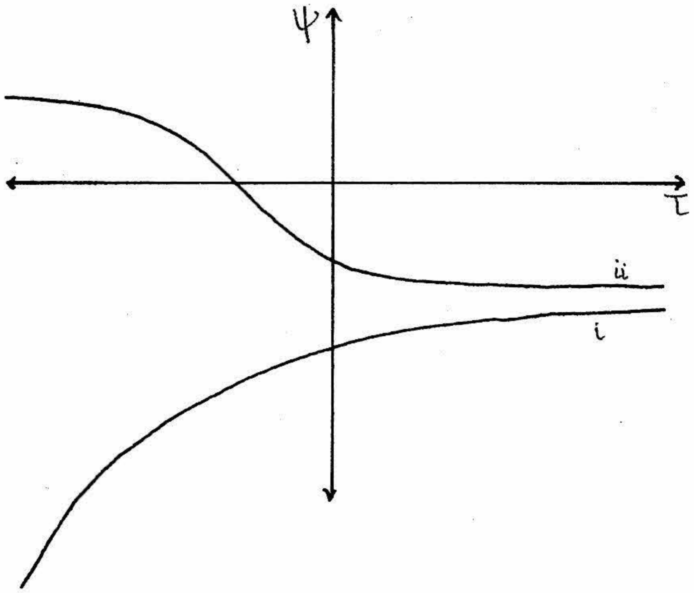


Fig. 2b. $(\mu^2 > \nu^2)$

2. REACTING-DIFFUSING SYSTEMS EXHIBITING TEMPORAL OSCILLATIONS WITH SPATIALLY DEPENDENT FREQUENCY

2.1 Introduction

Most work done on reacting-diffusing systems is concerned with coupled diffusion equations with nonlinear terms due to the creation-annihilation of chemicals by reactions taking place in the mixture. It is usually assumed that the various properties of these systems are uniform, i.e., reaction rates and diffusion coefficients do not have explicit spatial dependence.

There are systems of very important application where the spatial dependence of the reaction rates cannot be ignored. In some reactions the intrinsic rates depend proportionally on some external parameter. For instance, in photography, the rate of alteration of the photographic film's composition during exposure is proportional to the incident light. Likewise, in predator-prey systems, the terrain can affect predator ability to hunt or prey ability to hide, etc.

We shall concern ourselves here with chemical reactions in one space dimension that, in the absence of diffusion, exhibit temporal oscillations whose frequency varies slowly with position. We shall neglect all purely fluid dynamical effects (no bulk motion, etc.), so the Navier-Stokes equations for the mixture under consideration will reduce to coupled continuity equations including creation-annihilation terms and diffusion flux terms for the various components. For this work we shall assume that diffusion and all gradients are small and that we are far enough from critical temperatures that Fick's law holds.

(That is, the chemical potential for a component is proportional to its concentration at each point).

The conclusion will be that the phase of the oscillations at each point, coupled through diffusion, obeys to 1st order in ϵ (the small parameter in the problem determining smallness of diffusion and gradients), a Burgers'-type equation including a forcing term. This can be solved exactly and it leads to sustained traveling waves of chemical concentration, unlike the uniform case in which traveling waves are transient.

2.2 The Model

We consider the system

$$\begin{cases} \dot{u} = F(u,v,x) + \epsilon u_{xx} \\ \dot{v} = G(u,v,x) + \epsilon v_{xx} \end{cases}$$

with appropriate conditions specified on an interval.

We assume that, in the absence of diffusion, the above system possesses, at each point, a stable limit cycle solution $U(t,x)$, $V(t,x)$ such that

$$\begin{cases} \dot{U}(t,x) = F(U,V,x) \\ \dot{V}(t,x) = G(U,V,x) \end{cases}$$

Now, these functions will in general have different frequencies and different form at each point. We assume that variation with x is small. We rewrite the above functions in terms of a new variable $\theta \equiv \theta(t,x)$, defined so that their frequency with respect to θ is the same everywhere.

$$U(t,x) \equiv \hat{U}(\theta,x)$$

$$V(t,x) \equiv \hat{V}(\theta,x)$$

$$\theta = \theta(t,x)$$

Then

$$\hat{U}_\theta \cdot w(x) = F(\hat{U},\hat{V},x)$$

$$\hat{V}_\theta \cdot w(x) = G(\hat{U},\hat{V},x)$$

where w(x) is the frequency of the limit cycle (no diffusion) at x.

Without diffusion, θ is just

$$\theta(t,x) = w(x)t + c(x) \text{ (arbitrary, not necessarily continuous)}$$

when diffusion is present the phases θ are coupled through C. Away from an initial layer where rough initial conditions are smoothed out (for which our long-time analysis is not valid) C becomes a smooth function of x and a slow time variable which we shall have to introduce into the problem.

We transform to the usual local coordinate system in the neighborhood of the limit cycle at each point

$$u = \hat{U}(\theta, x) + \epsilon A \hat{V}_\theta(\theta, x)$$

$$v = \hat{V}(\theta, x) - \epsilon A \hat{U}_\theta(\theta, x)$$

All relevant quantities transform accordingly (analysis is similar in all details to that in Section 1.2, so we shall omit it here—only here we work with frequencies instead of periods).

The frequency w(x) is assumed to have an asymptotic expansion

$$w(x) \simeq 1 + \epsilon f(x) + \theta(\epsilon^2)$$

Substitution into the system yields the 0th order equations

$$\left\{ \begin{array}{l} F_t^0 \, \theta_t^0 = F^0 \\ F_t^0 \, \theta_t^0 = G^0 \end{array} \right.$$

$$\Longrightarrow \theta_t^0 = t + \psi(x, \tau).$$

To get the 1st order system, the only new terms we have to compute are the derivatives u_{xx} and v_{xx}, and these only to 0th order. We have

$$u_{xx} = U^0(\theta^0, x)\Big|_{xx} =$$

$$= \frac{\partial}{\partial x}\left[\psi_x U_1^0(\theta^0, x) + u_2^0(\theta^0, x)\right]$$

$$= \psi_{xx} U_1^0 + \psi_x^2 U_{11}^0 + 2\psi_x U_{12}^0 + U_{22}^0$$

now $$U_1^0 \equiv U_\theta^0 = \frac{1}{w(x)} F^0 \approx F^0$$

$$U_{11}^0 = F_\theta^0$$

while, since we assume small x dependence of F and G, it follows that the terms U_{12}^0 and U_{22}^0 are of higher order and will not appear in our analysis for ψ, and that we can write

$$U^0 = U^0(\theta) \quad \text{(no x-dependence to this order)}$$

So, the 1st order system will be

$$\left\{\begin{aligned} & F^0\left(f(x) + \theta_t^1 + \psi_\tau\right) + G_\theta^0 A^0 + G^0 A_t^0 = \\ & \qquad = \left(F_1^0 G^0 - F_2^0 F^0\right) A^0 + \psi_{xx} F^0 + \psi_x^2 F_\theta^0 \\ & G^0\left(f(x) + \theta_t^1 + \psi_\tau\right) - F_\theta^0 A^0 - F^0 A_t^0 = \\ & \qquad = \left(G_1^0 G^0 - G_2^0 F^0\right) A^0 + \psi_{xx} G^0 + \psi_x^2 G_\theta^0 . \end{aligned}\right.$$

This is easily transformed to

$$\left\{\begin{aligned}
&A_t^0 + A^0\left\{\frac{1}{2}\left(\ln\left[(G^0)^2 + (F^0)^2\right]\right)_\theta + \frac{\left(F_2^0 + G_1^0\right)G^0F^0 - F_1^0(G^0)^2 - G_2^0(F^0)^2}{(F^0)^2 + (G^0)^2}\right\} = \\
&\qquad = \psi_x^2\left(G^0F_\theta^0 - F^0G_\theta^0\right) \\
&\theta_t^1 = -(f(x) + \psi_\tau) + \left[\frac{F^0G^0\left(F_1^0 - G_2^0\right) - (F^0)^2F_2^0 + (G^0)^2G_1^0}{(F^0)^2 + (G^0)^2}\right]A^0 + \\
&\qquad + \psi_{xx} + \frac{1}{2}\psi_x^2\left(\ln\left[(F^0)^2 + (G^0)^2\right]\right)_\theta
\end{aligned}\right.$$

The equation for A^0 can be written as

$$A_t^0 + M(t + \psi)A^0 = N(t + \psi)\,\psi_x^2$$

where, since the functions M and N are periodic with respect to their arguments, their average over a period will be a constant, independent of the phase shift ψ, i.e., independent of x and τ, and the same is true for all other functions involved here.

Solving we find

$$A^0 = C\exp\left(-\int_0^t M(\zeta + \psi)d\zeta\right) + \psi_x^2\int_0^t N(\zeta+\psi)\exp\left(-\int_\zeta^t M(\xi+\psi)d\xi\right)d\zeta$$

$$= \psi_x^2 P(t+\psi) + (\text{exponentially dying part})^*,$$

---

*This follows from the stability of the l.c. at each point.

where $P(t+\psi)$ is given by an expression similar to that derived in p. 10, and is periodic of frequency 1. Using this in the equation for θ^1 we get

$$\theta_t^1 = -\left(f(x) + \psi_\tau\right) + A^0 R(t+\psi) + \psi_{xx} + \frac{1}{2}\psi_x^2 \left[\ell n\left((F^0)^2 + (G^0)^2\right)\right]_\theta$$

$$= -\left(f(x) + \psi_\tau\right) + \psi_x^2\, \tilde{P}(t+\psi) + \psi_{xx} + \text{(exponentially dying term)}$$

with $\tilde{P}(t+\psi)$ a periodic function of frequency 1. We demand that θ^1, found from the above equation, be bounded in t in order for our asymptotic expansion for θ to be valid, so that

$$\int_0^1 (\text{R.H.S.}) = 0 \Rightarrow$$

$$\Rightarrow \psi_\tau = -f(x) + \psi_{xx} + \psi_x^2 \int_0^1 \tilde{P}(t+\psi)\, dt$$

We let

$$\int_0^1 \tilde{P}(t+\psi)\, dt = k$$

a constant by the reasoning given before. Then

$$\psi_\tau = -f(x) + \psi_{xx} + k\psi_x^2$$

which is Burgers' equation with a nonhomogeneous term.

Letting $\psi = k^{-1}\ell n\,\phi$ (the Cole-Hopf transformation) we get

$$K^{-1}\,\phi_T/\phi = -f(x) + k^{-1}\left(\phi_{xx}/\phi - \phi_x^2/\phi^2\right) + k^{-1}\phi_x^2/\phi^2$$

$$\Longrightarrow \phi_{xx} - \phi_T = kf(x)\phi$$

which can now be solved using standard methods.

Note: In a more general case, where the shape of the limit cycles at each point varies to order 1 with x (but w still behaves the same) we would get an evolution equation for the phase containing a term proportional to ψ_x and coefficients dependent on x, which would not be linearizeable by the above Cole-Hopf transformation. So, in principle, the method would go through but it would lead us to a non-linear equation that cannot be solved exactly.

The equation that we found for ϕ is a parabolic equation. Application of the appropriate maximum principle ensures us that if ϕ is initially nonnegative, it will always stay nonnegative, so that the transformation is always invertible.

3. A CHAIN OF WEAKLY COUPLED OSCILLATORS

3.1 Introduction

Oscillatory phenomena of the relaxation type play a very important role in the self-regulation of biological systems. Transmission of information and control in populations of cells and coordination of their function is usually accomplished by some controlling agent through modulation of the phase of an oscillation in which all the cells are locked. This gets transmitted through the population via some medium carrying chemical or ionic messengers—this medium being also responsible for the coupling of the cellular oscillators [8].

The characteristics of cellular oscillations can be coupled to concentrations of certain substances in the medium surrounding the cells. For instance, in the case of neuronal oscillators, modification of the composition of the membrane of the sending cell at the synapse causes certain chemicals to be transmitted to the receiver cell, modifying its state (exciting or inhibiting some functions, etc.).

Populations of cells can exhibit many types of oscillations, either individually, with member cells oscillating regardless of the existence of an external periodic forcing, or as network oscillations, where certain subsystems form oscillating circuits, with an excitation going around the circuit, "passed" from one cell to the next.

Invariably, the detailed chemical mechanisms responsible for these phenomena involve extremely intricate combinations of reactions taking place simultaneously. In the vast majority of cases we know very little about the actual mechanisms, number of participating chemicals, ways by which cells transmit information or how they change when they receive it—the individual cell already being too complicated an entity for the present state of our knowledge.

But even though at this point we can say very little, if anything, about the exact nature of the phenomena involved, we can still draw some very general conclusions about how these populations can act collectively, provided they conform to some simple conditions. So, of necessity, we can only build "naive" models of biological systems at this stage. These must be complicated enough so that they can mimic some properties of real biological systems, but yet simple enough to be solvable by our techniques.

The usefulness of these models is twofold: solving them we might be able to combine seemingly unrelated phenomena, by attributing them to some common underlying feature of the model/system. And, predictions made based on these models might suggest new fruitful experimental directions. That is, building and solving models, provides us with a way of organizing what we already know and helps to show what we can expect from a self-consistent image of biological phenomena based on our present knowledge.

In this chapter we study a finite linear chain of weakly coupled λ-ω limit cycle oscillators.

In Section 3.2 we attempt an exact perturbative analysis in the strength of the mutual coupling (assumed small). We arrive at a system of equations that can be easily analyzed numerically (we do not attempt this here), to demonstrate the behavior of the phase in a slow time scale. Analyzing numerically these equations instead of the full system has the advantage of yielding results that are easier to interpret.

In Section 3.3, in order to gain more insight in these systems, we consider the limit when the number of oscillators in the chain becomes large. We employ two different limiting procedures. The first yields a forced Burgers' equation, the analogy with the result in Chapter 2 being apparent. The second procedure yields, to lowest order, a first order hyperbolic equation which we discuss. Based on previous results, we conjecture that similar equations will be obtained in the large population limit for more general models.

We conclude the topic with a discussion in Section 3.4.

3.2 The Model

We consider a chain of λ-ω limit cycle oscillators coupled weakly via diffusive coupling with free ends. It is described by the following system of pairs of 1st order ODE's:

$$\left\{\begin{aligned} \dot{u}_i &= u_i\left(1-r_i^2\right) - v_i\left(\nu_i + 1 - r_i^2\right) + \epsilon k\left\{u_{i-1} + u_{i+1} - 2u_i\right\} \\ \dot{v}_i &= u_i\left(\nu_i + 1 - r_i^2\right) + v_i\left(1 - r_i^2\right) + \epsilon k\left\{v_{i-1} + v_{i+1} - 2v_i\right\} \end{aligned}\right. \qquad i = 2,\ N-1$$

where $r_i^2 = u_i^2 + v_i^2$ and $\nu_i = \omega + \epsilon\alpha_i$.

At the two ends ($i = 1, N$) we have

$$u_1 = u_1 (1 - r_1^2 \quad - v_1 (\nu_1 + 1 - r_1^2 \quad + \epsilon \{ u_2 - u_1 \} \text{ etc.,}$$

the equations for V_1, U_N, V_N being similar. This system describes a chain of N oscillators that, in the absence of coupling ($k = 0$), would each relax to a circular limit cycle in their corresponding phase planes, with radius 1 and frequency ν_i. For $N = 2$ this reduces to the case studied in Section 1.4 for equal radii and nearly equal frequencies.

We introduce polar coordinates by the transformation

$$u_i = r_i \cos\theta_i$$

$$v_i = r_i \sin\theta_i$$

under which the system becomes

$$\left\{ \begin{aligned} \dot{r}_i &= r_i \left(1 - r_i^2 \right) - \epsilon k \left[2r_i - r_{i+1} \cos\left(\theta_{i+1} - \theta_i\right) - r_{i-1} \cos\left(\theta_{i-1} - \theta_i\right) \right] \\ \dot{\theta}_i &= \left[(\omega + \epsilon\alpha_i) + 1 - r_i^2 \right] + \epsilon k \left[\left(\frac{r_{i+1}}{r_i} \right) \sin\left(\theta_{i+1} - \theta_i\right) + \left(\frac{r_{i-1}}{r_i} \right) \sin\left(\theta_{i-1} - \theta_i\right) \right] \end{aligned} \right. \qquad i = 2, N-1 \qquad (1)$$

with end equations

$$\begin{cases} \dot{r}_1 = r_1\left(1-r_1^2\right) - \epsilon k\left[r_1 - r_2\cos\left(\theta_2-\theta_1\right)\right] \\ \\ \dot{\theta}_1 = \left(\omega+\epsilon\alpha_1\right) + 1-r_1^2 + \epsilon k\left(\frac{r_2}{r_1}\right)\sin\left(\theta_2-\theta_1\right) \end{cases}$$

and a similar pair for $i = N$.

We introduce the slow time scale $\tau = \epsilon t$, so that

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \epsilon\frac{\partial}{\partial\tau}$$

and assume that the r_i, θ_i have asymptotic expansions of the form

$$\begin{cases} r_i = 1 + \epsilon R_i(t,\tau) + O(\epsilon^2) \\ \\ \theta_i = \omega t + \psi_i(\tau) + \epsilon\phi_i(t,\tau) + O(\epsilon^2) \end{cases} \qquad i = 1, \cdots, N$$

The form of the O-th order terms is found by arguments similar to those used in the previous chapters.

Substituting the above expressions in system (1) and retaining terms up to $O(\epsilon)$ ($O(1)$ terms cancel since their assumed forms satisfy the $O(1)$ equations of the hierarchy) we find that the R_i and ϕ_i satisfy

$$\begin{cases} R_{it} = -2R_i - 2k + k\cos\left(\psi_{i+1}-\psi_i\right) + k\cos\left(\psi_{i-1}-\psi_i\right) \\ \\ \phi_{it} = -\psi_{i\tau} + \alpha_i - 2R_i + k\sin\left(\psi_{i+1}-\psi_i\right) + k\sin\left(\psi_{i-1}-\psi_i\right) \end{cases} \qquad i = 2, N-1$$

modified appropriately at i = 1 and i = N.

Solving the equation for R_i we get

$$R_i = C_i e^{-2t} + k\left\{-1 + \frac{1}{2}\cos\left(\psi_{i+1}-\psi_i\right) + \frac{1}{2}\cos\left(\psi_{i-1}-\psi_i\right)\right\}$$

For simplicity, set $C_i = 0$ (ignore transients) and substitute this in the equation for ϕ_i to find

$$\phi_{it} = -\psi_{i\tau} + \alpha_i + k\Big\{2-\cos\left(\psi_{i+1}-\psi_i\right) - \cos\left(\psi_{i-1}-\psi_i\right) + \sin\left(\psi_{i+1}-\psi_i\right) + \\ + \sin\left(\psi_{i-1}-\psi_i\right)\Big\}$$

Since the RHS of this equation is a constant in t, ϕ_i would be a linear function of t so our assumed asymptotic expansion for θ_i cannot be uniformly valid for large times unless the RHS vanishes. That is, in order to have a consistent scheme we demand that the ψ_i satisfy the system:

$$\left\{\begin{array}{ll} \psi_{1\tau} = \alpha_1 + k\left\{1-\cos\left(\psi_2-\psi_1\right) + \sin\left(\psi_2-\psi_1\right)\right\} & \\ \psi_{i\tau} = \alpha_i + k\left\{2-\cos\left(\psi_{i+1}-\psi_i\right) -\cos\left(\psi_{i-1}-\psi_i\right) + \sin\left(\psi_{i+1}-\psi_i\right) + \sin\left(\psi_{i-1}-\psi_i\right)\right\} & i=2,N-1 \\ \psi_{N\tau} = \alpha_N + k\left\{1-\cos\left(\psi_{N-1}-\psi_N\right) + \sin\left(\psi_{N-1}-\psi_N\right)\right\} & \end{array}\right. \qquad (2)$$

At this point we have reduced the problem, to O-th order in ϵ, to that of solving N 1st order coupled quasi-linear ODE's. One could now proceed numerically and study the behavior of this system for various values of the α_i and the coupling k. In Section 3.4 we discuss some situations in which this model can be useful. For the purposes of this work we shall not pursue a numerical attack on this problem, but will try to extract some more information from the exact perturbation equations (2) using simple ideas before we analyze, in Section 3.3, some properties of the phase shift ψ_i in the limit of large N.

We note that if we introduce the N-1 variables

$$\chi_i = \psi_{i+1} - \psi_i - \frac{\pi}{4}, \quad i = 1, \cdots, N-1$$

we find that they satisfy the system of N-1 equations

$$\chi_{i\tau} = p_i + k\sqrt{2}\left\{\left(\sin\chi_{i+1} - \cos\chi_i\right) - \left(\sin\chi_i - \cos\chi_{i-1}\right)\right\}, \quad i = 1, \cdots, N-1 \quad (3)$$

where we set

$$\chi_0 = \chi_N = -\frac{\pi}{4}$$

A question that is of interest in these systems is whether all the oscillators in the chain can become "locked," i.e., oscillate with the same (average) frequency, so that the phase shift between successive oscillators stays bounded. In this spirit we look for solutions of the system (3) of the form

$$\chi_i = C_i , \quad \text{(some constants)} \quad i = 1, \cdots, N-1$$

The constants c_i must satisfy the algebraic system

$$b_i + k\sqrt{2}\left\{\left(\sin c_{i+1} - \cos c_i\right) - \left(\sin c_i - \cos c_{i-1}\right)\right\} = 0 \quad i = 1, \cdots, N-1$$

with

$$c_0 \equiv c_N \equiv -\frac{\pi}{4}$$

or, setting $\sin c_i \equiv \sigma_i$, $\cos c_i = \sqrt{1-\sigma_i^2}$,

$$b_i + k\sqrt{2}\left\{\left(\sigma_{i+1} - \sqrt{1-\sigma_i^2}\right) - \left(\sigma_i - \sqrt{1-\sigma_{i-1}^2}\right)\right\} = 0 \qquad i = 1, \cdots, N-1$$

$$\sigma_0 = \sigma_N = -\frac{1}{\sqrt{2}}$$

This last system is recursive and one can trivially solve for the σ_i , but there is no guarantee that some $|\sigma_i|$ will not be greater than 1, or that they will be real. It is clear that this will depend on the numbers b_i/k. We can see this clearly in the simplest case, N = 3, that can be done explicitly and leads to a 4th order equation in σ_1, or σ_2. We will not do that here.*

In the following Section 3.3 we consider the case for large N.

---

* Note: The only case that N = 3 will not lead to a quartic is when $b_1+b_2 = 0$. It is easy to see that in this case the phase plane of χ_1 and χ_2 will not contain spiral points, which one can show to exist if $b_1+b_2 \neq 0$. In the latter case we conjecture that there must exist curves in the b_1-b_2 plane such that when they are crossed, the stability of some spiral point changes. In some neighborhood of these curves

3.3 Approximations for Large N

In the previous section we derived a system of algebraic equations that the constant phase shifts between successive oscillators in our chain must satisfy if their frequencies are locked (in the narrow sense). This answers the locking problem in principle, but the nature of the answer is not clear a priori and for more than three oscillators we cannot get explicit expressions for the solutions (for N oscillators we need to solve a polynomial of degree 2(N-1) in general). So, a numerical approach to the exact equations is necessary.

When the number of oscillators in the chain is large, we can study their behavior by the use of appropriate asymptotic methods. The large N limit is not unrealistic, since in most biological systems of interest we deal with large numbers of cells.

Here we shall consider two different limit processes. The first

---

(Note: (continued))

(on the instability side) we expect, by Hopf's theorem, the existence of a stable limit cycle in the phase plane of χ_1 and χ_2. This case, even though it does not fall within the narrow definition of frequency locking we used (constant phase shifts), must be characterized as phase locking in a broader sense (phase shifts have constant averages in the slow time). This phenomenon of oscillating phase shifts obviously cannot be observed in the N = 2 case. The algebraic complications for $b_1 + b_2 \neq 0$ did not allow us to give an explicit example of this interesting phenomenon.

will lead to the forced Burgers' equation we derived in the last chapter. The second will lead to a nonlinear PDE that can be reduced to a 1st order quasi-linear PDE solvable by the method of characteristics.

For the first limit process we define K by

$$k = K \cdot \frac{N^2}{L^2} ,$$

so that system (2) is written

$$\psi_{i\tau} = \alpha_i + \frac{K}{L^2} N^2 \{\cdots\} \quad , \quad i = 1, \cdots, N \tag{2'}$$

The number L is the "length" of the chain. We introduce a space coordinate x and we let the position of the i-th oscillator be

$$x_i \equiv i \cdot \Delta x$$

with Δx the (uniform) "distance" between successive oscillators. The length of the chain is then

$$L = N \cdot \Delta x$$

Finally, define a continuous variable ψ by

$$\psi(x_i) \equiv \psi_i$$

and assume it is sufficiently differentiable so that we can expand in

Taylor series:

$$\psi(x_i \pm \Delta x) = \psi(x_i) \pm \Delta x \, \psi_x(x_i) + O(\Delta x^2).$$

Then as N → ∞ with $N \cdot \Delta x = L$, fixed, system (2′) becomes

$$\psi_\tau = \lim_{\substack{\Delta x \to 0 \\ N \cdot \Delta x = L}} \left\{ \alpha(x) + \frac{KN^2}{L^2} \left[2 - 2\cos\left(\Delta x \cdot \psi_x + O(\Delta x^{2})\right) + \right.\right.$$

$$\left.\left. + \sin\left(+\Delta x \cdot \psi_x + \frac{(\Delta x)^2}{2} \psi_{xx} + O(\Delta x^3)\right) + \sin\left(-\Delta x \cdot \psi_x + \frac{(\Delta x)^2}{2} \psi_{xx} + O(\Delta x)^3\right) \right] \right\}$$

$$\simeq \alpha(x) + k \cdot \frac{1}{(\Delta x)^2} \left\{ 2 - 2\left(1 - \frac{(\Delta x)^2}{2} \psi_x^2 + O(\Delta x^3)\right) + \left((\Delta x)^2 \psi_{xx} + O(\Delta x^3)\right) \right\} \Longrightarrow$$

$$\Longrightarrow \psi_\tau \simeq \alpha(x) + k\left(\psi_x^2 + \psi_{xx}\right) + O(\Delta x). \quad \text{(forced Burgers' eqn.)} \tag{4}$$

The free ends condition becomes $\psi_x(0) = \psi_x(L) = 0$.

To examine whether entrainment is possible in this limit, we seek solution of the form

$$\psi = \omega \tau + \sigma(x) .$$

Equation (4) becomes

$$\sigma_x^2 + \sigma_{xx} + \left(\frac{\alpha(x) - \omega}{K}\right) = 0$$

leading, under the transformation $\sigma = \ell n \phi$, to

$$\phi_{xx} + \left(\frac{\alpha(x) - \omega}{K} \right) \phi = 0$$

$$\text{with } \phi_x(0) = \phi_x(L) = 0$$

and so, in this limit, the problem of entrainment is reduced to that of finding the eigenvalues corresponding to positive eigenfunctions of the above Sturm-Liouville problem (we need positivity so that the transformation can be inverted—see comment at the end of Chapter 2).

We consider now a different limiting procedure:

Define a new variable Ψ (continuous as before) by

$$\psi_i = \frac{N}{L} \Psi(x_i)$$

and change the time scale to

$$T = \frac{L}{N} \tau$$

In terms of these variables, system (2) gets rewritten as

$$\Psi(x_i)_T = \alpha(x) + k\left\{2 - \cos\left[\frac{N}{L}\left(\Psi(x_i + \Delta x) - \Psi(x_i)\right)\right] + \cdots \text{ etc.} \right\} \tag{5}$$

Now assume that all functions defined thus are sufficiently differentiable so that we can write:

$$\alpha(x_i + \Delta x) = \alpha(x_i) + \Delta x \cdot \alpha_x(x_i) + O(\Delta x^2)$$

and similarly for Ψ. Substituting these in (5) and taking the limit

$$N \rightarrow \infty \ , \quad N \cdot \Delta x = L \ ,$$

we have

$$\Psi_T = \alpha(x) + k \lim_{\substack{N \Delta x = L \\ N \to \infty}} \Big\{ 2 - \cos \Big[\frac{N}{L} \Big(\Psi_x \cdot \Delta x + \frac{\Psi_{xx} (\Delta x)^2}{2} + O(\Delta x^3) \Big) \Big] -$$

$$- \cos \Big[\frac{N}{L} \Big(- \Psi_x \cdot \Delta x + \Psi_{xx} \frac{(\Delta x)^2}{2} + O(\Delta x^3) \Big] + \sin \Big[\frac{N}{L} \Big(\Psi_x \cdot \Delta x + \Psi_{xx} \frac{(\Delta x)^2}{2} + O(\Delta x^3) \Big) \Big] +$$

$$+ \sin \Big[\frac{N}{L} \Big(- \Psi_x \Delta x + \Psi_{xx} \frac{(\Delta x)^2}{2} + O(\Delta x^3) \Big] \Longrightarrow$$

$$\Longrightarrow \Psi_T = \alpha(x) + k \lim_{\substack{\Delta x \to 0 \\ N \Delta x = L}} \Big\{ 2 - \cos \Big(\Psi_x + \frac{\Psi_{xx} \Delta x}{2} + O(\Delta x^2) \Big) - \cos \Big(- \Psi_x + \frac{\Psi_{xx} \Delta x}{2} + O(\Delta x^2) \Big) +$$

$$+ \sin \Big(\Psi_x + \Psi_{xx} \frac{\Delta x}{2} + O(\Delta x^2) \Big) + \sin \Big(\Psi_x + \frac{\Psi_{xx} \Delta x}{2} + O(\Delta^2 x)^2 \Big) \Big\} =$$

$$= \alpha(x) + k \lim_{\substack{N \to \infty \\ N \Delta x = L}} \Big\{ 2 \Big(1 - \cos \Psi_x \Big) + O(\Delta x^2) + (\Delta x) \cdot \cos \Psi_x \Psi_{xx} + O(\Delta x^2) \Big\}$$

$$\Longrightarrow \Psi_T = \alpha(x) + k \Big\{ 2 \Big(1 - \cos \Psi_x \Big) \Big\} + \Big(\frac{L}{N} \Big) \cos \Psi_x \Psi_{xx} + O\Big(\frac{1}{N^2} \Big) \tag{6}$$

Neglecting the $O\left(\frac{1}{N}\right)$ term, we have

$$\Psi_T = \alpha(x) + 2 \ k \Big(1 - \cos \Psi_x \Big) \tag{7}$$

Differentiating eqn. (7) by x and setting $\Psi_x \equiv \Phi$, we get

$$\Phi_T = \alpha_x + 2k(\sin\Phi)\Phi_x \tag{8}$$

a quasi-linear 1st order PDE solvable by the method of characteristics. This equation gives us a description for the phase $\Psi(x, \tau)$ in the limit of large slow time τ.

We note that equations (4) and (7) give us two different pictures for the evolution of the phase variable $\Psi(x, \tau)$. The first is a picture for intermediate (slow) times in which the spatial distribution of the phase is more or less smooth. The second is a large (slow) times picture, after the system has gone through many cycles (Ψ large). At this limit, the subcharacteristics of the 1st order part carry the information and sharp shocks in the phase can develop (smoothed out by the O(1/N) term we wrote in Eq. (6), which for very sharp shocks becomes important).

We observe a close analogy between the limiting procedures employed here, and similar results that we get when rescaling a reaction-diffusion equation with oscillatory kinetics.

The first limit is obviously the analogue of the method used in Chapter 2. By similarity we expect that this limit process, applied to more general chains, would still lead to the forced Burgers' equation.

The second procedure is the analogue of using a WKB-type approximation for the same reaction-diffusion equation. (Introduce phase variable Θ with assumed asymptotic expansion

$$\Theta \simeq \frac{\Theta_0}{\epsilon} + \Theta_1 + O(\epsilon)$$

while rescaling time and space variables—here we only had to rescale the time variable, since the space scale was defined on the basis of all other scales we assumed). This scaling leads to a first order equation of the form

$$\sigma_T + H(\sigma_x) = f(x)$$

in general, (with σ a properly defined variable), solvable by general Hamilton-Jacobi theory. Similar scaling has being used [9] by Howard and Kopell.

3.4 Discussion

In this chapter we showed that even though the exact equations for the phase in a linear chain of weakly coupled oscillators are too complicated to handle analytically (though not numerically), in the case of large populations we can get, in some limits, exactly solvable evolution equations.

We considered a very simple model here, to not cloud the concepts unnecessarily. In light of the results in Chapter 2 though, we feel justified to conjecture that the limiting processes we used would lead, applied to more general models, to similar evolution equations for the phase, as the ones derived here.

This work is part of our attempt to understand certain phenomena encountered by various workers [10] studying a network of electrical cellular oscillators that is thought to be responsible for peristalsis in the small intestine of mammals.

PART II

CHAPTER 4

4. ANALYSIS OF NONLOCAL EFFECTS IN THE DIFFUSION FLUX FOR A CHEMICALLY REACTING MIXTURE

4.1 Introduction - Physical Background

As is well known, intermixing among the different components of a mixture is greatly affected by temperature. More specifically, there exists a definite temperature value above which the components mix freely, while below it they form separate phases. This is called the critical temperature T_c of the mixture.

If no heat is released because of the mixing and volumes do not change, the equilibrium state of the system will be such as to minimize the total (Gibbs) free energy F. Let us consider a solution in which the mole fraction n of one of the components present at each point is nonuniform. Due to intermolecular forces, we expect the free energy at each point to depend not only on the composition at that point, but also on that of the surroundings.

Following Cahn and Hilliard [11], we assume $||\nabla n||$ to be small with respect to the inverse intermolecular distances and f, the free energy per molecule per unit volume, to be a continuous function of n and its derivatives. Then, at each point, f can be expanded in a Taylor series about f_0, the free energy per molecule of a solution of uniform composition. That is

$$f\left(n, \nabla n, \nabla^2 n, \cdots\right) = f_0(n) + \sum_i L_i \frac{\partial n}{\partial x_i} + \sum_{ij} k_{ij}^{(1)} \frac{\partial^2 n}{\partial x_i \partial x_j} + $$

$$+ \frac{1}{2} \sum_{ij} k_{ij}^{(2)} \left(\frac{\partial n}{\partial x_i}\right) \left(\frac{\partial n}{\partial x_j}\right) + \cdots$$

where

$$L_i = \partial f / \partial \left(\frac{\partial n}{\partial x_i}\right) \bigg|_0 \quad , \quad k_{ij}^{(1)} = \partial f / \partial \left(\frac{\partial^2 n}{\partial x_i \partial x_j}\right) \bigg|_0 \quad ,$$

and

$$k_{ij}^{(2)} = \partial^2 f / \partial \left(\frac{\partial n}{\partial x_i}\right) \partial \left(\frac{\partial n}{\partial x_j}\right) \bigg|_0 \quad \text{etc.}$$

For isotropic solutions (that will be our concern here), f must be invariant under rotation-reflections ($x_i \rightarrow x_j$ and $x_i \rightarrow -x_i$), so that

$$L_i = 0$$

$$k_{ij}^{(1)} = k_1 \delta_{ij} = \left[\partial f / \partial (\nabla^2 n) \Big|_0 \right] \delta_{ij}$$

$$k_{ij}^{(2)} = k_2 \delta_{ij} = \left[\partial^2 f / (\partial |\nabla n|)^2 \right]_0 \delta_{ij}$$

i.e., for the isotropic solutions under study

$$f\left(n, \nabla n, \nabla^2 n, \cdots\right) \simeq f_0(n) + k_1 \nabla^2 n + k_2 (\nabla n)^2 + \cdots$$

The total free energy in a volume is then

$$F = N_v \int_V f\,dV = N_v \int_V \left(f_0(n) + k\nabla^2 n + k_2(\nabla n)^2 + \cdots\right) dV$$

with N_v the number of molecules per unit volume. But

$$\int_V k_1 \nabla^2 n\, dV = -\int_V \frac{dk_1}{dn} (\nabla n)^2\, dV + \int_S \left(k_1 \nabla n \cdot \vec{N}\right) dS$$

where S is the boundary surface and N a unit normal vector. Since we are not concerned with effects at the external surface, we can pick it so as to make the surface integral vanish, so that we have for the free energy

$$F = N_v \int_V \left[f_0(n) + k(\nabla n)^2 + \cdots\right] dV$$

with

$$k = \left(dk_1/dn\right) + k_2 = -\left[\partial^2 f/\partial n \partial(\nabla^2 n)\right]_0 + \left[\partial^2 f/(\partial\,|\nabla n|)^2\right]_0$$

The effect of nonuniform composition on the diffusion flux for chemically reacting mixtures was first discussed by Huberman [3]. He argued that equilibrium for a mixture reacting chemically is not identical to chemical equilibrium. The mixture must minimize its total free energy both with respect to the chemical reaction taking place and with respect to the mixing. Hence when we describe the evolution of such systems away from equilibrium, we must use an approximation to the free energy of the above nonlocal form.

Our generalized continuity equation include a diffusion flux current $\vec{J}$, that is, in general, a function of the gradients of all the thermodynamic variables describing our system, namely

$$\vec{J} \equiv \vec{J}\left(\vec{\nabla}\mu, \vec{\nabla}T, \vec{\nabla}p\right) .$$

Here we ignore temperature and pressure gradients and we assume gradients in composition to be sufficiently small, so that we can approximate J by the first term in its Taylor series, i.e.,

$$\vec{J} = -M\vec{\nabla}\mu$$

where M, the interdiffusion motility, is shown by entropy increase arguments [1] to be always positive. Now, the chemical potential is given by

$$\mu(\vec{r}) = \delta F[n]/\delta n(\vec{r})$$

and since

$$\delta F[n] = \int_v \left[\frac{\partial f_0}{\partial n} - 2k\nabla^2 n\right] \delta n \, d\vec{r}$$

(v is a small volume in which $\delta n \neq 0$ in the usual fashion) it follows that μ for such systems can be approximated by

$$\mu(\vec{r}) = \frac{\partial f_0}{\partial n} - 2k\nabla^2 n$$

In the neighborhool of the critical point we assume, with Huberman, that $f_0(n)$ can be approximated by

$$f_0(n) = \frac{1}{2}\, a_0(T-T_c)n^2 + \frac{1}{4} bn^4 \equiv \frac{1}{2}\, an^2 + \frac{1}{4}\, bn^4$$

where a_0, $b > 0$ to ensure proper behavior for f (it must have a minimum). Then, in this approximation, the chemical potential will be

$$\mu(\vec{r}) = an + bn^3 - 2k\nabla^2 n\,,$$

a form in which temperature enters as a parameter. In a more complete model, where temperature is not uniform, we would have to include a heat flux current and augment our generalized continuity equations by a rate equation for heat production, etc.

The nature of this approximation to some quantum mechanical systems, as it is related to the Ginzburg-Landau theory for the behavior near critical points, is better understood than in classical chemical systems, due to the lack of experiments in this direction in the latter. It is hoped that the results of this analysis will point out some experimental possibilities in a way of verifying the theory and also some predictions about the behavior of reacting mixtures near the critical point.

In Section 4.2 we describe a model chemical reaction and write a generalized continuity equation in 1-dimension, involving the concentration of one component (the only one that is allowed to vary). We find the stable uniform steady states and show that for some interval of a free parameter (here a production rate) they lose their stability to some nonuniform state. As we vary the parameter the change of state of the system can be either smooth or discontinuous, depending on other parameters of the problem and simulating either a "2nd" or a "1st order phase transition," as our nonlinear stability analysis in Section 4.4 will show. (Section 4.3 contains a linearized analysis, which determines the parameter values of interest).

As it will be seen, linearized analysis of this model does not give the full stability picture. A steady state can become unstable to finite perturbations before it loses its linearized stability. In Section 4.5 we analyze the possible final states for the "2nd order transition" case, and in Section 4.6 we give some quantum mechanical examples where similar theory is applicable. We conclude with a discussion of some research questions opened by this work.

4.2 A Model Autocatalytic Reaction

We shall describe in this section a model autocatalytic chemical reaction proposed by Huberman [3]. This is

$$A + X \xrightarrow{k_A} 2X$$

$$X + B \xrightarrow{k_B} C$$

The concentrations n_A and n_B of A and B respectively are assumed to be held constant and we are only concerned with changes in the concentration n of X.

The generalized continuity equation for n will be of the form

$$\frac{\partial n}{\partial t} = k[n] - \vec{\nabla} \cdot \vec{J} \qquad (*)$$

where k[n] is a source term found as usual to be

$$k[n] = \left(k_A n_A - k_B n_B\right) n - k_A n^2 \equiv k_1 n - k_A n^2$$

and $\vec{J}$ is the diffusion flux current, which for small gradients is approximately equal to

$$\vec{J} = -M\vec{\nabla}\mu$$

Assuming that μ can be expressed by the approximation found in the previous section, equation (*) becomes (considering only one space dimension)

$$\partial_t n = k_1 n - k_A n^2 + M\,\partial_{xx}\left[an + bn^3 - 2k\,\partial_{xx} n\right]$$

For easy reference, we list here the various constants involved in the model

$k_1 = k_A n_A - k_B n_B$,	is the rate (per mole of X) at which X is produced in the 1st reaction and destroyed in the second. It can have either sign and is a free parameter that we can adjust to study the system. It will serve as our bifurcation parameter

k_A	reaction rate for 1st reaction assumed positive
M	interdiffusion motility, positive always by 2nd law of thermodynamics
$a = a_0\left(T-T_c\right) = \left(\partial\mu/\partial n\right)_{T,\,n=0}$	with a_0 positive
b	positive, so that f will have a minimum
k	a positive constant, related to the product of the energy of intermolecular interactions (here assumed attractive) and the square of the range of these interactions.

We proceed now with the linearized analysis of this model, finding the possible stable solutions for the various ranges of the parameters involved.

4.3 Linearized Analysis

We consider the equation

$$\partial_t n = k_1 n - k_A n^2 + M\partial_{xx}\left(an + bn^3 - 2k\partial_{xx} n\right)$$

with bounded solutions in $(-\infty, \infty)$.

The uniform steady states are

$$n_0 = 0 \text{ and } n_0 = k_1/k_A$$

Linearizing about them and assuming solutions of the linearized equation of the form

$$U = e^{\alpha t} \cos qx$$

we find after standard analysis, that there are two distinct cases depending on the sign of $a = a_0(T-T_c)$.

For $T > T_c$ $(a > 0)$, when fully mixed states are energetically favorable, we find that

i) if $k_1 > 0$, only $n_0 = k_1/k_A$ is stable

ii) if $k_1 < 0$, only $n_0 = 0$ is stable.

For $T < T_c$ $(a < 0)$, we find the following dispersion relation

$$\left(\frac{\alpha}{M}\right) = -\frac{|k_1|}{M} - \left(a + 3bn_0^2\right) q^2 - 2kq^4$$

We are interested in neutral stability points, i.e., values of q such that $\alpha = 0$. These are

$$q^2 = \frac{-\left(a + 3bn_0^2\right) \pm \sqrt{\left(a + 3bn_0^2\right)^2 - \frac{k|k_1|}{M}}}{4k}$$

where $n_0 = 0$ for $k_1 < 0$, $n_0 = k_1/k_A$ for $k_1 > 0$.

The dispersion relation for $a < 0$ is shown in Fig. 1)

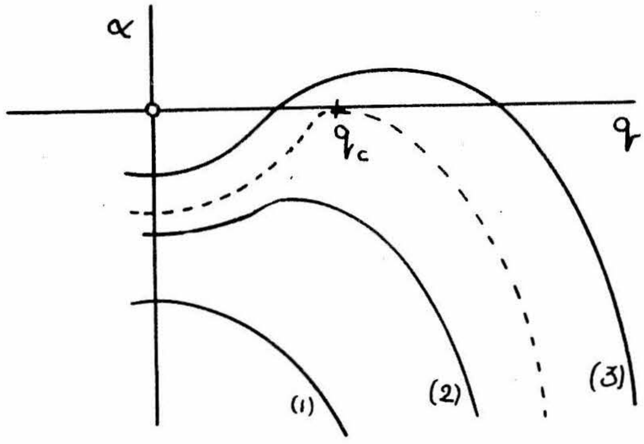


Fig. 1

(1) $|a| < 3\,bn_0^2$

(2) $|a| > 3\,bn_0^2$, $|a + 3\,bn_0^2| < \sqrt{\frac{8k|k_1|}{M}}$

(3) $|a| > 3\,bn_0^2$, $|a + 3\,bn_0^2| > \sqrt{\frac{8k|k_1|}{M}}$

Curves (1) → (3) shown for decreasing $|k_1|$. Shaded curve makes 2nd order contact with q axis at $q_c = \sqrt{8k|k_1|/M}$

—·—

We observe that as k_1 increases from large negative values, the curve moves up and at the value

$$a = -\sqrt{\frac{-8kk_1}{M}}$$

it makes second order contact with the q axis at the point

$$q_c = \pm\sqrt{\frac{-8kk_1}{M}}$$

Until this value of k_1 the solution of the linearized equation would decay to 0 but as k_1 grows past the above value, the linearized solution becomes unstable for a range of wave numbers in the neighborhood of q_c. As k_1 grows further to positive values, it reaches a value satisfying

$$a = -\left[3b\left(\frac{k_1}{k_0}\right)^2 + \sqrt{\frac{8kk_1}{M}}\right]$$

when the curve makes again second order contact with the q-axis. Then the second uniform steady state, i.e.,

$$n_0 = k_1/k_A$$

becomes stable.

These are shown in Fig. 2. This is all the information that one can get from a linearized analysis. Stability shown is not global but only with respect to small perturbations. For a more complete picture we have to include nonlinear effects. We do this in the next section.

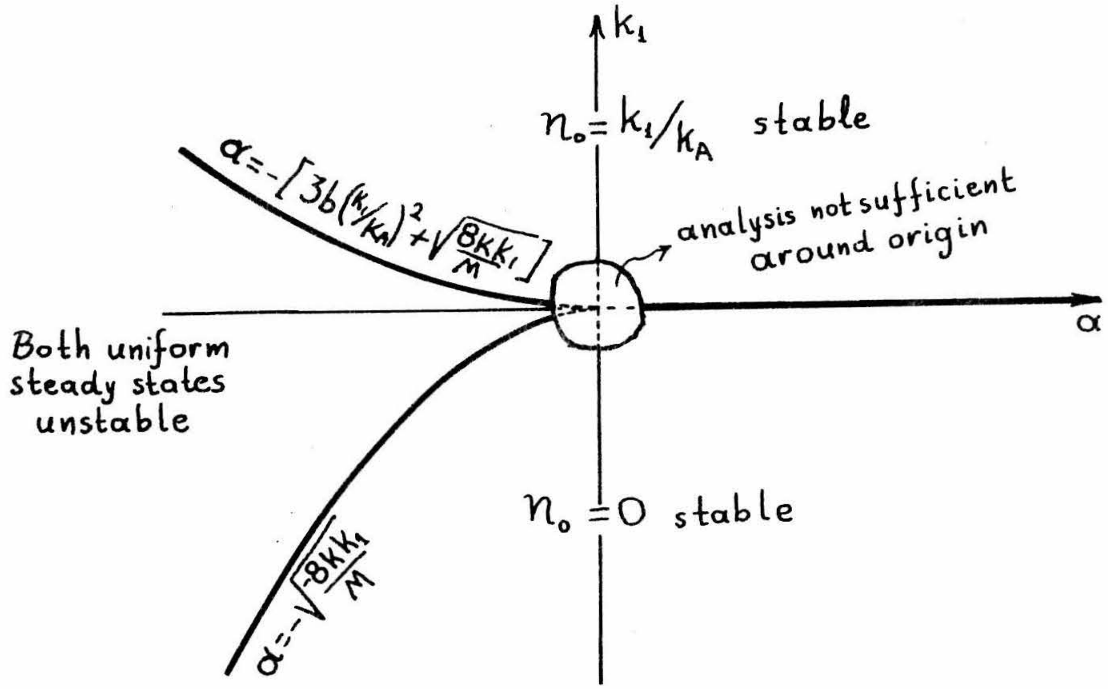
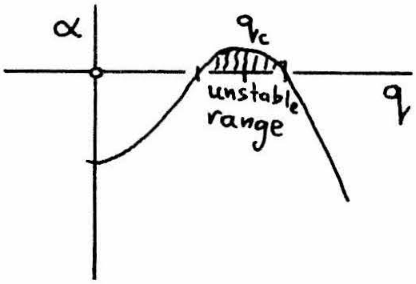
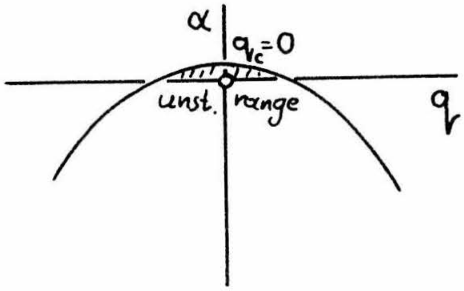


Fig. 2

*Notes on Fig. 2. i) Our analysis will not be sufficient in a neighborhood of the origin (triple point) of size ~ ϵ^{γ} (γ some positive power). Need a different scaling there. ii) For a < 0, crossing of the shaded curves implies a dispersion relation of the form



while for a < 0, when we linearize about the uniform state that loses stability, crossing implies:



4.4 Nonlinear Stability Analysis - Bifurcation from the Continuous Spectrum

The present problem differs from standard bifurcation problems in that a whole neighborhood of wave numbers becomes unstable when the parameter k_1 crosses some critical value. So, standard techniques assuming a 0th order operator with a discrete set of eigenfunctions and writing the lowest order solution as a series in these eigenfunctions with slowly varying coefficients would have to be modified here accordingly.

The technique that we develop here is based on q_c, the first wave number to become unstable being different from zero. It treats the behavior of the solution for large times, and it basically entails the introduction of a stretched space variable that expresses the effect of the interaction of neighboring unstable modes.

The analysis (similar for both the bifurcation points of our problem) is as follows:

Let k_1 be close to the critical value $\overline{k}_1$, i.e.,

$$k_1 = \overline{k}_1 + \epsilon^2 \delta \quad , \quad \epsilon << q_c$$

and assume that n has an asymptotic expansion

$$n \simeq u_0 + \epsilon n_1 + \epsilon^2 n_2 + \epsilon^3 n_3 + \cdots$$

We introduce the stretched variables

$$\tau \equiv \epsilon^2 t \quad \text{and} \quad \xi \equiv \epsilon x \; {}^{*}$$

Expanding all expressions in powers of ϵ we have

$$\bar{k}_1 n - k_A n^2 \simeq \epsilon\left(-|\bar{k}_1| n_1\right) + \epsilon^2\left(-|\bar{k}_1| n_2 + \delta\, n_0 - k_A n_1^2\right) + \epsilon^3\left(-|\bar{k}_1| n_3 + \delta n_1 - 2k_A n_1 n_2\right) + \cdots$$

$$\begin{aligned} aM\partial_{xx} n + bM\partial_{xx} n^3 \simeq {} & \epsilon\left[\frac{-2|\bar{k}_1|}{q_c^2}\partial_{xx} u_1\right] + \epsilon^2\left[\frac{-2|\bar{k}_1|}{q_c^2}\left(\partial_{xx} n_2 + 2\partial_{x\xi} n_1\right) + \right. \\ & \left. + 3 n_0 Mb\partial_{xx} n_1^2\right] + \epsilon^3\left[\frac{-2|\bar{k}_1|}{q_c^2}\left(\partial_{xx} u_3 + 2\partial_{x\xi} n_2 + \partial_{\xi\xi} n_1\right) + \right. \\ & \left. + Mb\partial_{xx} n_1^3 + 6Mbn_0\partial_{xx} n_1 n_2 + 6\,Mbn_0\partial_{x\xi}\, n_1^2\right] + \cdots \end{aligned}$$

$$\begin{aligned} -2kM\partial_{xxxx} n = {} & -\epsilon\left(\frac{|\bar{k}_1|}{q_c^4}\partial_{xxxx} n_1\right) - \epsilon^2\frac{|\bar{k}_1|}{q_c^4}\left(\partial_{xxxx} n_2 + 4\partial_{xxx\xi} n_2\right) - \\ & -\epsilon^3\frac{|\bar{k}_1|}{q_c^4}\left(\partial_{xxxx} n_3 + 4\partial_{xxx\xi} n_2 + 6\partial_{xx\xi\xi} n_1\right) + \cdots \end{aligned}$$

where we used that

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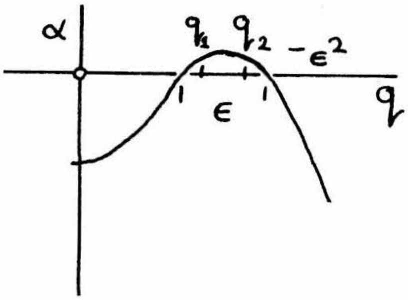
[*] Note: This scaling for x is suggested by the geometry of the problem, as seen in the figure. Combining two cosines, say, with wave numbers in a neighborhood of size ϵ, we have



$$\cos q_1 x \cos q_2 x = \frac{1}{2}\left[\cos(q_1+q_2)x + \cos(q_1-q_2)x\right] \simeq$$

$$\simeq \frac{1}{2}\left[\cos 2q_c x + \cos\epsilon x\right] \text{ etc.}$$

$$q_c^2 = \sqrt{\frac{|\overline{k}_1|}{2_k M}}\ , \quad M\left(a + 3bn_0^2\right) = -\ \frac{2|\overline{k}_1|}{q_c^2}$$

and $n_0 = 0$, for $k_1 < 0$ and $n_0 = k_1/k_A$ for $k_1 > 0$.

Substituting these in the equation and setting the coefficients of successive powers of ϵ equal to zero, we get the hierarchy:

$$O(1) \qquad n_0 = 0, \quad \overline{k}_1 < 0$$

$$n_0 = \overline{k}_1/k_A\, , \ \overline{k}_1 > 0$$

$$O(\epsilon) \qquad \partial_t n_1 = |\overline{k}_1|\left(\frac{1}{q_c^4}\,\partial_{xxxx} n_1 + \frac{2}{q_c^2}\,\partial_{xx} n_1 + u_1\right) \Rightarrow$$

$$\Rightarrow n_1 = \int_{-\infty}^{\infty}\left\{\hat{A}(\xi,\tau,q)\cos qx + \hat{B}(\xi,\tau,q)\sin qx\right\}\exp\left[\alpha(q)t\right]dq$$

This is the full solution, valid for short times as well, but it leads to expressions of unmanageable complexity. The picture simplifies somewhat if we ask about the behavior for large times t. Then, since $\alpha(q)$ has a maximum of q_c $(a(q_c) = 0)$, we can approximate the integral by Laplace's method to get

$$n_1 \simeq A(\xi\tau)\cos q_c x + B(\xi, \tau)\sin q_c x$$

So, from now on, we ignore t-dependence and tacitly assume that our analysis is valid for large times. The next order gives

$$O(\epsilon^2) : |\bar{k}_1| \left\{ \frac{1}{q_c^4} \partial_{xxxx} + \frac{2}{q_c^2} \partial_{xx} + 1 \right\} n_2 =$$

$$= \frac{4|\bar{k}_1|}{q_c^2} \partial_{x\xi} \left\{ \frac{1}{q_c^2} \partial_{xx} + 1 \right\} + \delta n_0 + \left(3n_0 Mb\partial_{xx} - k_A \right) n_1^2 =$$

$$= \left[\delta n_0 - k_A \left(\frac{A^2+B^2}{2} \right) \right] - \left[3Mbn_0 q_c^2 + K_A \right] \left\{ \left(\frac{A^2-B^2}{2} \right) \cos q_c x + AB \sin q_c x \right\}$$

$$\Longrightarrow n_2 = \frac{1}{|\bar{k}_1|} \Big[\delta n_0 - k_A \left(\frac{A^2+B^2}{2} \right) \quad \frac{1}{9|\bar{k}_1|} \left[3Mbn_0 q_c^2 + k_A \right] \left\{ \left(\frac{A^2-B^2}{2} \right) \cos q_c x + AB \sin q_c x \right\}$$

+ (Homogeneous soln.) (unimportant for our analysis).

We see that the special properties of the trigonometric functions made it impossible to determine A and B, that were arbitrary functions in n_1. So, we have to go to the next order:

$$O(\epsilon^2) |\bar{k}_1| \{\cdots\} n_3 = -\partial_\tau n_1 + \delta n_1 + \frac{4|\bar{k}_1|}{q_c^2} \partial_{\xi\xi} n_1 - 2\left(k_A - 3Mbn_0 \partial_{xx} \right) n_1 n_2 +$$

$$+ Mb\partial_{xx} n_1^3 + \left\{ 6Mbn_0 \partial_{x\xi} n_1^2 - \frac{4|\bar{k}_1|}{q_c^2} \partial_{x\xi} \left\{ \frac{1}{q_c^2} \partial_{xx} + 1 \right\} n_2 \right\}$$

$$= \Big[-\delta_\tau + \delta + \frac{4|\bar{k}_1|}{q_c^2} \partial_{\xi\xi} - \frac{2}{|\bar{k}_1|} \left\{ \delta n_0 - \frac{\left(19k_A + 3Mbn_0 q_c^2 \right)}{36} \left(A^2+B^2 \right) \right\}$$

$$\cdot \left(k_A + 3bMn_0 q_v^2 \right) - \frac{3}{4} Mbq_c^2 \left(A^2+B^2 \right) \Big] n_1 +$$

+ (higher harmonics).

To suppress secular terms, demand

$$\partial_\tau n_1 = \delta\left\{1 - \frac{2n_0}{|\overline{k}_1|}\left(k_A + 3bMn_0 q_c^2\right)\right\}n_1 - \left\{\frac{3}{4}Mbq_c^2 - \frac{\left(k_A + 3bMnq_c^2\right)\left(19k_A + 3bMn_0 q_c^2\right)}{18|\overline{k}_1|}\right\}(A^2 + B^2)n_1 + $$

$$+ \frac{4|\overline{k}_1|}{q_c^2}\partial_{\xi\xi} n_1$$

(a short way of writing the two identical equations satisfied by A and B). At $n_0 = 0$, this becomes $\left(k_1 < 0,\ \overline{k}_1 = -\frac{Ma^2}{8k},\ q_c^2 = \frac{|a|}{4k}\right.$

$$\partial_\tau n_1 = \delta n_1 - \left\{\frac{Mb|a|}{4k} - \frac{76kk_A^2}{9Ma^2}\right\}\left(A^2 + B^2\right)n_1 + 2M|a|\,\partial_{\xi\xi} n_1$$

whose behavior is summarized in the following table

	$\frac{Mb\|a\|}{4k} - \frac{76kk_A^2}{9Ma^2} < 0$	$\frac{Mb\|a\|}{4k} - \frac{76kk_A^2}{9Ma^2} > 0$
$\delta < 0$	n_1 blows up, unless it is small enough initially in which case it decays to 0	n_1 decays to 0
$\delta > 0$	n_1 blows up	n_1 evolves to some bounded steady state

At $n_0 = \overline{k}_1/k_A$ we have $\left(k_1 > 0,\ k_1\right.$ satisfying

$$a = -\left[3b\left(\overline{k}_1/k_A\right)^2 + \sqrt{\frac{8k\overline{k}_1}{M}}\right] \text{ with } q_c^2 = \sqrt{\frac{\overline{k}_1}{3kM}}\,\Bigg)$$

$$\partial_\tau n_1 = -\delta\left\{1 + \frac{6b}{k_A^2}\left(\frac{M\bar{k}_1^3}{2k}\right)^{1/2}\right\} n_1 - \left\{\frac{3}{4}\, b\left(\frac{M\bar{k}_1}{2k}\right)^{1/2} - \right.$$

$$\left. - \frac{k_A^2}{18\bar{k}_1}\left(1 + 3\,\frac{b}{k_A^2}\left(\frac{M\bar{k}_1^3}{2k}\right)^{1/2}\right)\left(19 + \frac{3b}{k_A^2}\left(\frac{M\bar{k}_1^3}{2k}\right)^{1/2}\right)\right\}$$

$$\cdot\left(A^2 + B^2\right) n_1 + 4\sqrt{2kM\bar{k}_1}\;\partial_{\xi\xi}\, n_1$$

(we wrote this in terms of $\bar{k}_1$ as it is a better parameter in this case) and can get a similar table as for the previous case.

So if we plot some norm $||n||$ of the solution $n(x, \xi, \tau)$ versus the parameter k_1, we get the following bifurcation diagrams (note that our analysis yields only the part of the bifurcated curve close to the bifurcation values $\bar{k}_1^-$, $\bar{k}_1^+$, the rest being conjectured at this point).

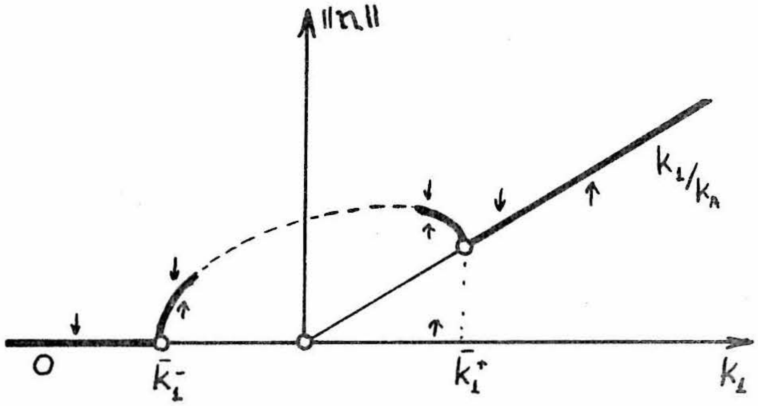


Fig. 3. 1. Bifurcation diagram for case

$$\frac{3}{4}\,Mbq_+^2 > \frac{19\,k_A^2}{18k_+}\left(1 + 3bMq_+^2\,\frac{k_+}{k_A^2}\right)\left(1 - 3bMq_+^2\,\frac{k_+}{19k_A^2}\right),\quad \frac{3}{4}\,Mbq_-^2 > -\frac{19k_A^2}{18k_-}$$

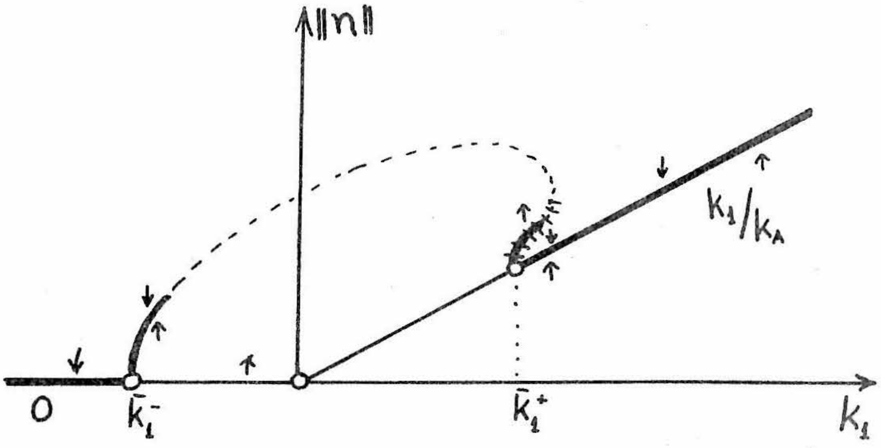


Fig. 3.2. Bifurcation diagram for

$$\frac{3}{4} Mbq_+^2 < \frac{19k_A^2}{18k_+}\left(1 + 3bMq_c^2 \frac{k_+}{k_A^2}\right)\left(1 + 4bMq_c^2 \frac{k_+}{19k_A^2}\right)$$

$$\frac{3}{4} Mbq_-^2 > - \frac{19k_A^2}{18k_-}$$

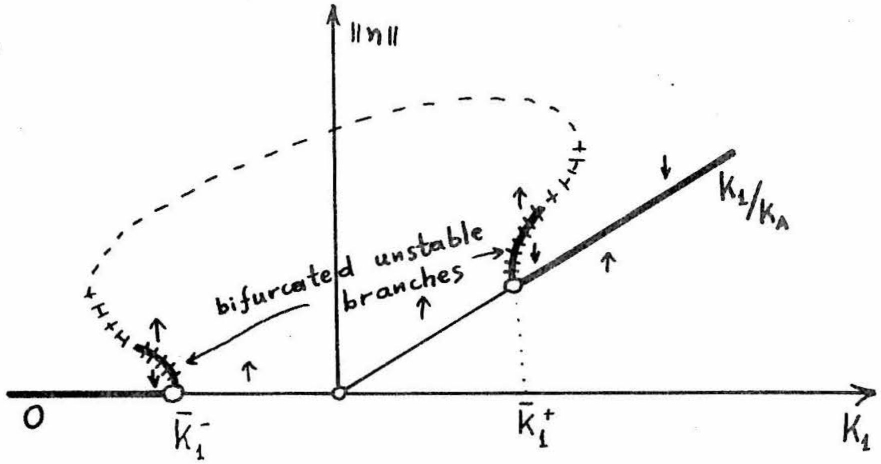


Fig. 3.3. Bifurcation diagram for the case

$$\frac{3}{4}\, bMq_+^2 < \frac{19k_A^2}{18k_+}\left(1 + 3bMq_+^2\, \frac{k_+}{k_A^2}\right)\left(1 + 3bMq_+^2\, \frac{k_+}{19k_A^2}\right)$$

$$\frac{3}{4}\, bMq_-^2 < - \frac{19k_A^2}{18k_-}$$

etc.

We observe that in the cases with turnaround, Fig.3.3, uniform states that are linearly stable can in reality be stable only with respect to small perturbations, while they are unstable for larger ones. The $\partial_{\xi\xi}$ term will not modify this picture much, except by introducing a whole class of possible stable solutions instead of just a uniform one. We analyze the smooth transition case depicted in Fig. 3.1 in the next section.

4.5 Analysis of the smooth transition case

For smooth transitions (case depicted in Fig. 3.1) the evolution equations for A and B are of the form

$$A_\tau - A_{\xi\xi} = A\left[1 - (A^2 + B^2)\right]$$

$$B_\tau - B_{\xi\xi} = B\left[1 - (A^2 + B^2)\right]$$

(all constants can be scaled out). Introduce transformation

$$A = R\cos\phi$$

$$B = R\sin\phi$$

Equations for R and ϕ are

$$R_{\tau} = R\left(1 - R^2\right) + \left(R_{\xi\xi} - R\phi_{\xi}^2\right)$$

$$\phi_{\tau} = \frac{1}{R^2}\left(R^2\phi_{\xi}\right)_{\xi}$$

These possess the following 1-parameter family:

$$\phi = C\,\xi \quad \text{(+ arbitrary constant)}$$

$$R = R(\tau; c)$$

which for $\tau \rightarrow \infty$, evolve to

$$\phi = c\xi$$

$$R = (1 - c^2)^{1/2} \equiv R_0\left(|c| < 1\right)$$

After some trivial analysis, we find that these are stable for

$$|c| < \frac{1}{\sqrt{3}}$$

and unstable otherwise (linearized stability).

So, the possible stable steady state solutions of the original problem, in the smooth transition case, will be of the form

$$n \simeq n_0 + \epsilon(1-c^2)^{1/2} \operatorname{Re} e^{ix(q_c+\epsilon c)} + \cdots$$

$$|c| < 1/\sqrt{3}$$

(within some scaling constants).

The R-ϕ equations have another family of exact solutions, namely

$$\phi = c$$

$$R = R(\xi)$$

For this class, R has the form of a Jacobian elliptic function. It is easy to see that the equation for R, when linearized about a periodic function leads to a PDE whose spatial part is a Hill's operator, so that there always exist positive eigenvalues leading to growing exponentials in time, so that all these periodic in R solutions are unstable.

4.6 Discussion - Applications

We described a theory that, by including nonlocal effects in the diffusion flux term of a reaction-diffusion equation, can deal with chemical phenomena far from equilibrium and in some neighborhood of the critical temperature.

Similar approximations can be used in the quantum mechanical many-body problem near phase transition points. As an example, we mention the model of the transition from a Peierls insulator to metallic conductor that under external dynamic excitation exhibits a passage to an intermediate metal-insulator phase proposed by Berggren and Huberman [12]. The equation describing the number Δn of excess quasi-particles in the upper band of the insulating phase is

$$\frac{\partial \Delta n}{\partial t} = I - \frac{\Delta n}{\tau} + \left(\frac{2DA}{\Delta_0}\right)\left(\Delta n_c - \Delta n\right)\nabla^2\left(\Delta n\right) - \frac{1}{2} D\xi_0^2 \nabla^4\left(\Delta n\right)$$

where I is a forcing term. We can show, in the same fashion as in Sections 4.2 - 4.5 that for some critical value of the forcing term the uniform state becomes unstable, and we are led to some nonuniform state that is modulated similarly to this found in the chemical problem. We can show that the transition in this case is always smooth (2nd order), regardless of parameter values.

Similar theory can be applied to explain the appearance of a mixed state in the superconductor-normal 2nd order phase transition of the BCS state in thin films [13], and the appearance of layered structures in whisker crystals [14].

The reason we needed to treat these problems in the infinite interval, and thus be led to bifurcation from the continuous spectrum, lies in the fact that the critical wavelengths that characterize them are of the order of either the range of intermolecular forces (in the chemical case), or the BCS coherence length (superconductor case), etc., that is much smaller than the usual macroscopic sample sizes that we deal with experimentally.

The rescaling that we used, developed here independently, has also been used by other workers, [5], [6] in treating instabilities of fluid flows. It is implicit in all our work that $q_c \neq 0$, i.e., the quartic dispersion relation has a minimum of $q = 0$. We can use perturbed bifurcation theory methods to treat the singular limit where $q_c \rightarrow 0$ like some positive power of ϵ; a priori we expect that a different scaling will be necessary in this limit. Another point of importance is the case when the coefficient of the cubic term in our modulation equations vanishes. Then, higher order analysis is necessary to determine the behavior of the bifurcated branch.

Finally, it is necessary to comment on our analysis of the bifurcation from the state $n_0 = 0$. Clearly, it is not physically correct (although accurate mathematically), since the bifurcated state becomes negative, which a chemical concentration cannot do! The analysis has to be modified to allow for the fact that only nonnegative initial conditions are possible, but since this would not change the qualitative behavior significantly, we did not pursue this direction further.

It seems that in order to treat the case $n = 0$ correctly, the physics itself will have to be modified. It is not clear at this point that our nonuniform concentrations approximation holds when the mixture becomes too dilute. It seems that when the mean distances between the solute molecules are larger than the range of the intermolecular forces, their effect can be ignored and we can treat the solute using a weak solution approximation that basically reinstates ordinary diffusion as a way of smearing out nonuniformities, by treating the solute as a perfect gas.

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