

Selected Topics from the Theory of Nonlinear Physico-Chemical Phenomena

P. Ortoleva

Department of Chemistry,
Indiana University, Bloomington, Indiana

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I. Introduction

One of the most significant advances of the macroscopic theory of continuum systems in recent years is the analysis of a variety of biological, geological, and other systems in terms of nonlinear physico-chemical phenomena. It is the purpose of this article to describe some of these developments and to set forth the framework in which several other phenomena may be studied in the future. I shall refer to existing reviews (Hess and Boiteaux, 1971; Chance *et al.*, 1973; Nicolis and Portnow, 1973; Noyes and Field, 1974; Ross, 1976; Hanusse *et al.*, 1978) when appropriate to avoid duplication and shall point out certain features not emphasized or covered by them. In many cases I shall draw on unpublished results or on work in progress so that the coverage is up to date. In addition, an attempt is made to point out possible directions of future development and in some cases to map out the methods that will most likely be useful in solving and formulating the mathematical problems associated with the physical phenomena.

The wealth of phenomena found in nonequilibrium physico-chemical systems seems almost endless. These systems are usually describable by nonlinear partial differential equations and in a certain sense one can say "anything can happen," as a well-known statistical mechanician once told me. Although this is probably somewhat alarming to those wishing to make simple statements delineating the kinds of phenomena that can occur, we should be thankful for this "principle" since its application by nature has apparently led to much of the beauty and variation of the universe.

Before proceeding with the main body of this article I would like to stress that I have not tried to write an "unbiased" review. The reader is referred to reviews (Hedges and Myers, 1926; Glansdorff and Prigogine, 1971; Hess and Boiteaux, 1971; Chance *et al.*, 1973; Nicolis and Portnow, 1973; Noyes and Field, 1974; Ross, 1976; Hanusse *et al.*, 1978) where other authors have made varying degrees of effort to be objective and complete in their coverage. It has been my hope that the present article would cover some topics not already covered in the reviews and to choose areas that I feel will lead to interesting new results in the near future. To the degree that the examples

have been chosen too heavily from my own present interests, I apologize to my fellow workers in the field.

A. MACROSCOPIC THEORY

We shall discuss a variety of physico-chemical systems within the framework of the continuity equations describing the temporal evolution of macroscopic variables such as concentrations, temperature, and local center of mass velocity (DeGroot and Mazur, 1962; Fitts, 1962; Glansdorff and Prigogine, 1971). The appropriate equations corresponding to these variables are, respectively, the equations of conservation of mass, energy, and fluid momentum. In addition, if the chemical species involved are charged, then we must also find the electric and magnetic fields. In this section we briefly discuss the general features of the macroscopic theory and the relationship between boundary condition and the maintenance of a system far from equilibrium.

We concentrate on processes that are slow compared to the time required for the passage of light through the system and to the dielectric relaxation times. Hence the electric field \mathbf{E} satisfies Poisson's equation. To provide a full macroscopic description of a system we need the form of the continuity equations, the dependence of the dielectric constant on composition, temperature and electric field, and finally the boundary and initial conditions for the descriptive variables.

We shall focus our attention mainly on systems that are isothermal, isobaric and at rest, and neglect magnetic effects. [Magnetic phenomena have been studied extensively in the magnetohydrodynamic (Chandrasekar, 1964) and plasma physics (Davidson, 1973) literature.] For this case the system is completely described by the concentration $C(\mathbf{r}, t)$ and the electric field $\mathbf{E}(\mathbf{r}, t)$ at all points \mathbf{r} and times t . To solve a specific problem we need to know these quantities at $t = 0$ and the boundary conditions.

B. BOUNDARY CONDITIONS AND CONSTRAINTS

The phenomena of interest in this article arise in systems maintained far from equilibrium (Glansdorff and Prigogine, 1971). This condition may be obtained by the application of either homogeneous or heterogeneous constraints. Heterogeneous constraints are those conditions applied to the system at boundary surfaces. Mathematically, they enter the macroscopic description through the boundary conditions. Homogeneous constraints are the ideal limit of heterogeneous constraints when certain species are so mobile that they are maintained constant throughout the system despite their consumption in chemical reactions within the system.

Let \mathbf{J}_i be the flux (moles/area-time) of species i in the system. Then, if G_i is

the rate of passage of i through the boundary surface S out of the system, we have

$$-\mathbf{n} \cdot \mathbf{J} = G. \quad (1.1)$$

In Eq. (1.1) we have denoted the unit normal vector to S pointing into the system by \mathbf{n} and have introduced the vector notation $C = \{C_1, C_2, \dots, C_N\}$, $\mathbf{J} = \{\mathbf{J}_1, \mathbf{J}_2, \dots, \mathbf{J}_N\}$, etc. convenient for the N species problem. For systems in which the boundary surface is mobile, the "free boundary problem," an additional term must be added to (1.1) as we shall discuss in Section VI.

If the system is bounded by a catalytic surface, then G_i has a contribution due to the rate of consumption of i in the heterogeneous reaction. Of course if i is produced, this contribution to G_i is negative. Also, as mentioned above, G_i may represent the rate of passage of i out of the system. For example, if the system is surrounded by a thin membrane and kept in contact with a well-stirred reservoir at constant composition C^0 , then for simple passive permeation we have

$$G_i = h_i(C_i - C_i^0) \quad (1.2)$$

where h_i is a permeability factor. For this case C_i^0 is a typical constraint parameter since its value controls the degree to which the system is maintained out of equilibrium. If Fick's law without cross-coupled transport is assumed valid for charge neutral species at low concentrations, we have

$$\mathbf{J}_i = -D_i \nabla C. \quad (1.3)$$

Hence combining (1.1) with (1.3) results in

$$\mathbf{n} \cdot D_i \nabla C_i = h_i(C - C^0). \quad (1.4)$$

Since $h_i \rightarrow \infty$ as the membrane becomes thinner, we see that this reduces to the case $C_i = C_i^0$ where the concentrations are fixed at the boundaries. To rigorously arrive at the connection between homogeneous constraints, $C_j = \text{constant}$ within the system for some j , we must invoke the time scale of the fastest reaction in which species j participates. Letting this time be τ_j the limit of homogeneous constraints arises when the diffusion length l_j [$\equiv (D_j \tau_j)^{1/2}$] is much longer than the maximum system dimension l ,

$$l/l_j \ll 1, \text{ homogeneous constraint.} \quad (1.5)$$

This is clearly a rather limiting restriction and probably not valid for most cases.

One notable exception is the situation of the maintenance of nonequilibrium conditions by the imposition of light. If the Beer's law length (the distance that the light intensity decreases by a factor e^{-1} due to absorption) is much greater than the dimensions of the system, we may consider the system to be under homogeneous photochemically driven constraint (Nitzan and Ross, 1973; Nitzan, *et al.*, 1974a; Creel and Ross, 1976; DelleDonne and Ortoleva, 1977).

Transient situations provide another approximation to homogeneous constraints. If within the system certain parts of the overall chemical kinetic network reach a steady state of production of certain species used as reactants for other parts of the scheme, then this provides a homogeneous source of these species and hence a homogeneous constraint may be established. Another approximation to this occurs if certain reactant species are in large excess and are only slowly consumed. These methods for keeping the system out of equilibrium are the basis for many known nonequilibrium chemical systems—the Belousov–Zhabotinsky–Zaikin (BZZ) reaction, oscillatory glycolysis, and the Bray reaction. (See appropriate chapter in this volume.) Homogeneous constraints have received a great deal of theoretical analysis both because of its experimental applicability and its mathematical simplicity.

In this article we shall discuss a variety of nonequilibrium phenomena arising in reaction–transport systems. To start our discussion (Section II) we consider some simple model systems that lend themselves to analytically tractable solutions. In doing so we introduce many of the concepts that we shall use throughout this article. In later sections we discuss a variety of phenomena and the theories that have been used to describe them.

II. Nonequilibrium Phenomena in Soluble Model Systems

Let us now study several simple soluble model systems that introduce some important concepts.

A. BRANCHING OF HOMOGENEOUS STEADY STATES

First consider examples of the simplest situation, steady states. We assume mass action kinetics to hold in all examples and that the systems are under homogeneous constraint. Finally, we take all rate coefficients to be unity unless stated otherwise.

1. Exchange of Stability

Consider the reaction scheme



The rate equation for X is

$$\begin{aligned} dX/dt &= B(\lambda - X)X \\ \lambda &\equiv (A - 1)/B. \end{aligned} \tag{2.2}$$

Clearly this system has steady states $X^* = 0, \lambda$. These are shown in Fig. 1 along with their stability as determined from linear stability analysis. Note

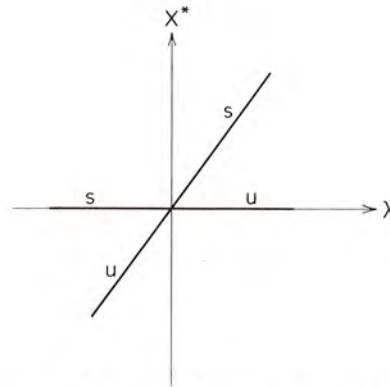


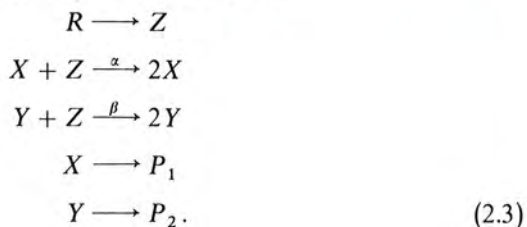
Fig. 1. Exchange of stability of steady states of mechanism (2.1). Labels *s* and *u* denote stable and unstable to small perturbations.

that the behavior of this system changes qualitatively if we add a small term ε to (2.2); the steady states are solutions of $X^2 - \lambda X - \varepsilon/B = 0$, i.e., $X_{\pm}^* = \frac{1}{2}[\lambda \pm (\lambda^2 + 4\varepsilon/B)^{1/2}]$. For $\varepsilon > 0$ the system only has one state, X_+^* , which is stable for all λ . The state X_-^* is negative for all λ and hence is unphysical.

As λ passes through zero the two branches of steady states intersect and an exchange of stability takes place. The point $\lambda = 0$ is the bifurcation point for this system—a new branch of states, $X^* = \lambda$, is said to bifurcate from the branch of states $X^* = 0$. This phenomenon is studied in more generality in Appendix A in the framework of bifurcation theory to illustrate the latter as a powerful tool in analyzing these problems. The bifurcation theory has been applied to a variety of reaction diffusion problems including static dissipative structures (Achmuty and Nicolis, 1975), chemical waves (Kopell and Howard, 1973; Ortoleva and Ross, 1974), and the problem of secondary branching, i.e., the bifurcation of secondary branches from new branches (Keener, 1976).

2. Exchange of Stability without Branch Intersection: Continua of States

Consider the three species system X, Y, Z evolving according to a mechanism of competitive preying by X and Y on Z :



The rate equations take the form

$$\begin{aligned} dX/dt &= (\alpha Z - 1)X \\ dY/dt &= (\beta Z - 1)Y \\ dZ/dt &= R - (\alpha X + \beta Y)Z \end{aligned} \tag{2.4}$$

where we have taken all rate coefficients equal to 1 (except α and β) for the second and third steps in (2.4). There are two steady states of the system,

$$\begin{aligned} (X_1^*, Y_1^*, Z_1^*) &= (R, 0, \alpha^{-1}) \\ (X_2^*, Y_2^*, Z_2^*) &= (0, R, \beta^{-1}), \end{aligned} \tag{2.5}$$

except for the special case $\alpha = \beta$ where we have a continuum of states connecting the branches,

$$(X_3^*, Y_3^*, Z_3^*) = (\mu R, (1 - \mu)R, \alpha^{-1}), \quad \alpha = \beta, 0 \leq \mu \leq 1. \tag{2.6}$$

Note that at $\alpha = \beta$ the stability of states 1 and 2 is exchanged without the intersection of these branches. We also see the possibility of a continuum of states. This model has a clear ecological interpretation in terms of mutants X and Y whose competition advantage for the prey Z exchanges at $\alpha = \beta$. At this point the system becomes degenerate because X and Y become indistinguishable, accounting for the continuum of states. The bifurcation diagram for this system is shown in Fig. 2.

3. Bifurcation of a Pair of Branches: Critical Index $\frac{1}{2}$

The mechanism

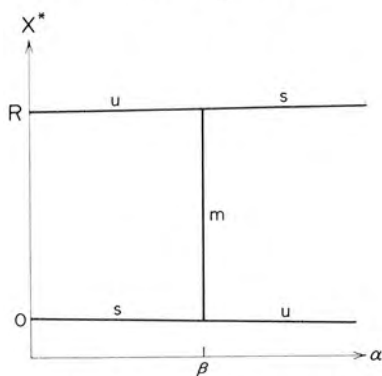


Fig. 2. Exchange of stability without branch crossing in mechanism (2.3). Note the continuum of marginally stable states (m) at $\alpha = \beta$.

leads to the kinetic equation

$$\begin{aligned} dX/dt &= \lambda X - X^3 \\ \lambda &= A - 1. \end{aligned} \quad (2.8)$$

It is clear that the pair of steady states

$$X_{\pm}^*(\lambda) = \pm\sqrt{\lambda} \quad (2.9a)$$

bifurcate from the branch

$$X_0^* = 0 \quad (2.9b)$$

at $\lambda = 0$ as shown in Fig. 3. The branch X_-^* is negative and is unphysical since concentrations are positive. A slight modification of (2.7) leads to a cubic with three positive roots as in the Edelstein mechanism (Glansdorff and Prigogine, 1971) and below. Note that here as in mechanism (2.1) the intersection of branches is accompanied by an exchange of stability.

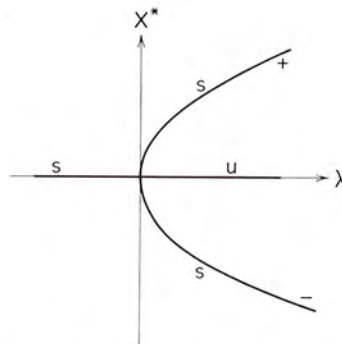


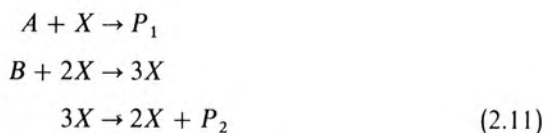
Fig. 3. Bifurcation of steady states for the mechanism (2.7) with critical index $\frac{1}{2}$.

4. Finite Amplitude Instability

The kinetic equation

$$dX/dt = -(X^2 - X + \frac{1}{4}\lambda)X \quad (2.10)$$

may be derived from the mechanism



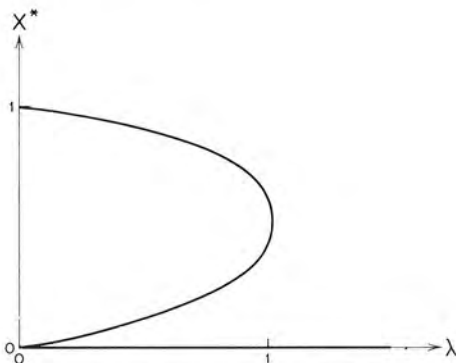


Fig. 4. Bifurcation of steady states at $\lambda = 1$ at finite amplitude.

where $B = 1$, $\lambda = 4A$. The system has steady states

$$X_0^* = 0, \quad X_{\pm}^* = \frac{1}{2}[1 \pm (1 - \lambda)^{1/2}]. \quad (2.12)$$

In Fig. 4 we see that as λ passes through the bifurcation point at $\lambda = 1$ the new states arise at finite distances away from the state $X_0^* = 0$. Thus the transition between the stable branches $X_+ \rightarrow X_0$ that occurs if we are on branch X_+^* and increase λ beyond 1 will be a "hard transition." This is unlike the "soft" transitions of mechanisms (2.1) and (2.7) where the system variable (X concentration) changes continuously as λ passes through the bifurcation point. The hard and soft transitions are analogous to first- and second-order equilibrium phase transitions (Nitzan *et al.*, 1974). Note that typically a hard transition is characterized by a region of multiple states where the system can reside in more than one state. However this multiplicity is not necessary as we have seen in the example of Section II,A,2 where a hard transition occurs without an overlapping region (and accompanying hysteresis).

For cases with regions of multiple stable steady states, the system has a finite amplitude instability as transitions between stable states can occur when perturbations of sufficient magnitude, suprathreshold perturbations (Nitzam, Ortoleva, and Ross, 1974b), are applied.

B. HOMOGENEOUS OSCILLATIONS

We now consider several soluble oscillatory systems introduced long ago in the study of nonlinear oscillations (Caesari, 1971). The model demonstrates several important properties of nonlinear oscillations. To my knowledge there has been no soluble model oscillation based on chemical kinetics, although the present model can be viewed as an approximate description of

a model in terms of deviations of chemical concentrations from their steady-state values.

Let X and Y be two variables evolving according to (Caesari, 1971; Kopell and Howard, 1973; Ortoleva and Ross, 1974; Dreitlein and Smoes, 1974).

$$\frac{d}{dt} \begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} B & -A \\ A & B \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix}$$

$$R^2 = X^2 + Y^2, \quad A = A(R), \quad B = B(R). \quad (2.13)$$

Transformation of variables according to the polar variables R and θ ,

$$X = R \cos \theta \quad Y = R \sin \theta, \quad (2.14)$$

yields

$$dR/dt = RB(R) \quad (2.15)$$

$$d\theta/dt = A(R). \quad (2.16)$$

From (2.15) we see that the simplification in this model is that R decouples from θ , the latter of which can be obtained from $R(t)$ through (2.16). Since R obeys a first-order ordinary differential equation, it can only asymptotically ($t \rightarrow \infty$) obtain either steady states R_0 ,

$$R_0 B(R_0) = 0 \quad (2.17)$$

or unbounded growth for which $|R| \rightarrow \infty$. Let us assume that the system is globally stable so that the last possibility is eliminated although we note that such "runaway states" are not without physical interest as has been shown recently (DelleDonne and Ortoleva, 1977).

The steady states R_0 correspond to oscillations about the point $X = Y = 0$ which, if $|B(R)| > 0$ as $R \rightarrow 0$, is a steady state of (2.13). In the subsections to follow we examine various cases of $A(R)$ and $B(R)$ to illustrate important oscillatory phenomena in nonequilibrium systems. Note that the oscillation at amplitude R_0 is stable if

$$[(d/dR)RB(R)]_{R_0} < 0, \text{ stable cycle.} \quad (2.18)$$

1. Bifurcation of a Cycle from a Steady State

Taking $B = \lambda - R^2$, we find the family of oscillatory states

$$R_0 = \lambda^{1/2}. \quad (2.19)$$

The oscillation bifurcates from the steady state $X = Y = 0$ for $\lambda > 0$. The steady state at the origin exchanges stability with the cycle at the bifurcation point. This type of bifurcation of a cycle with a critical index of $\frac{1}{2}$ was first studied by Hopf (1942) for a general system. [See the Appendix of Del-

leDonne and Ortoleva (1977) for a simple introduction to this theory.] It is interesting that the lowest order bifurcation analysis gives the exact result for this system. The bifurcation diagram is analogous to that of Fig. 3.

2. *Threshold Oscillation*

In the previous example the cycle surrounded an unstable steady state at the origin and hence the latter was not a physically obtainable state. However, for the example $B = 1 - \lambda - (R_1^2 - R^2)^2$, we obtain two distinct oscillatory states:

$$R_{0,\pm} = [R_1^2 \pm (1 - \lambda)^{1/2}]^{1/2}. \tag{2.20}$$

Note that in analogy to the steady-state example of Section II,A,4 a pair of oscillatory states bifurcates at finite amplitude at $\lambda = 1$ from the stable steady state $X = Y = 0$. Stability analysis shows that $R_{0,+}$ is stable while $R_{0,-}$ is not. This system demonstrates the common property of hard transition systems that in a given range of parameter values (λ, R_1) the system may reside in either of two (or more) stable states. This system demonstrates “threshold” or “finite amplitude instability” for although the states $R_{0,0} = 0$ and $R_{0,+}$ are stable to small perturbations they are not stable to perturbations of sufficient magnitude.

3. *Frequency and Continua of Steady States*

The frequency of the various models one constructs depends on a parameter λ through the relation

$$\omega(\lambda) = A(R_0(\lambda)) \tag{2.21}$$

as can be seen by integrating (2.16), noting that R_0 is constant in time. Since A is an arbitrary function of R , it is clear that a great variety of frequency variations with λ are possible.

In the above examples we have implicitly assumed that $\omega \neq 0$ in stating that the solutions of $B(R) = 0$ correspond to oscillations. If, however, there is an R_L such that

$$A(R_L) = B(R_L) = 0, \tag{2.22}$$

then there is a family of steady states at R_L (i.e., oscillations with zero frequency). If we vary λ through the value $\lambda_L(R(\lambda_L) = R_L)$, then the frequency vanishes and the system may reside in any of the continuum of marginally stable states $R = R_L, 0 \leq \theta \leq 2\pi$.

C. PROPAGATING STRUCTURES

Models with known spatio-temporal solutions have been studied and some of them are presented here.

1. Propagating Front

A front is a propagating transition between two states of a system. A solution of this type has been found for the following equation (Montrol, 1972; Nitzan, Ortoleva, and Ross, 1974b) for a one-dimensional system

$$\partial X/\partial t = D(\partial^2 X/\partial r^2) - q(X - X_1)(X - X_2)(X - X_3), \quad (2.23)$$

where X_1 , X_2 , and X_3 are homogeneous steady states for the infinite system. The solution given involves a propagating transition between the two stable states X_1 and X_3 for $X_3 > X_2 > X_1$. Letting ϕ be the spatial coordinate in a reference frame moving with the front, one finds the wave profile taking the form

$$X = X_1 + (X_3 - X_1)(1 + e^{\pm\beta\phi})^{-1} \quad (2.24)$$

where $\phi = r - vt$ is the wave coordinate and β is the inverse length of the transition layer

$$\beta = (q/2D)^{1/2}(X_3 - X_1) \quad (2.25)$$

and the velocity of propagation is given by

$$v = (\frac{1}{2}qD)^{1/2}(X_1 + X_3 - 2X_2). \quad (2.26)$$

Wave solutions of other equations closely related to the reaction diffusion equations have been also found (Montrol, 1972). Much work has been done on variants of (2.23) with different nonlinear terms and are reviewed in Aronson and Weinberger (1975) and Murray (1977).

2. Periodic Wave Trains

Periodic wave trains for the model of Section II,B have been given for various choices of the functions $A(R)$ and $B(R)$ (Kopell and Howard, 1973; Ortoleva and Ross, 1974; Dreitlein and Smoes, 1974). As was shown for the homogeneous oscillations in Section II,B, it was found that the wave solutions can demonstrate a number of nonlinear wave phenomena (as stressed in the Appendix of Ortoleva and Ross, 1974).

For the problem of periodic wave trains we seek solutions of the form

$$X = X(\rho), \quad Y = Y(\rho) \quad (2.27)$$

where

$$\rho = kr - \omega t = k\phi.$$

Here k is the wave vector (i.e., 2π divided by the wavelength) and ω is the wave frequency showing dispersion because of diffusion

$$\omega = \omega(k^2). \quad (2.28)$$

If we let $D_x = D_y = D$ for the diffusion coefficients of X and Y of the model of Section II,B and introduce the polar transformation of (2.14), we obtain

$$k^2 D[R'' - R\theta'^2] + \omega R' + RB(R) = 0 \quad (2.29)$$

$$k^2 D[\theta'' + 2R'\theta'/R] + \omega\theta' + A(R) = 0. \quad (2.30)$$

From this we see that there are wave solutions with $R = R_0(k^2)$ such that

$$B(R_0) - k^2 D\theta'^2 = 0 \quad (2.31)$$

$$k^2 D\theta'' + \omega\theta' + A(R_0) = 0. \quad (2.32)$$

Periodic solutions for X and Y are obtained with $\theta'' = 0$. Hence

$$B(R_0)\bar{\theta}k^2 D[A(R_0)/\omega]^2 = 0. \quad (2.33)$$

Integration of (2.32) with $\theta(\rho = 0) = \bar{\theta}$, $\theta'' = 0$, yields

$$\theta = \bar{\theta} - [A(R)/\omega]\rho. \quad (2.34)$$

Since X and Y are 2π periodic functions of ρ and since by definition of the polar coordinate transformation the solutions must be 2π periodic in θ , we have

$$\omega(k^2) = -A(R_0(k^2)) \quad (2.35)$$

giving the dispersion relation for the waves.

Using this model one can take various cases as in Section II,B and obtain examples of bifurcation of families of waves as a function of k^2 and of threshold wave phenomena. For these developments the parameter k^2 plays the role of λ in Section II,B. Details are found in Kopell and Howard (1973), Ortoleva and Ross (1974), and Dreitlein and Smoes (1974). These models verify the bifurcation (Kopell and Howard, 1973; Ortoleva and Ross, 1974) and limit-cycle (Kopell and Howard, 1973; Ortoleva and Ross, 1973a, 1974; Ortoleva, 1976) perturbation theories of chemical waves [see Hanusse *et al.* (1978) for a review of the theory of chemical waves].

D. STATIC PATTERNS

Here we consider three cases where time-independent spatial structures may be found in soluble model systems.

1. Coexistence Structure

For the special case $X_1 + X_3 = 2X_2$ of the multiple steady-state system studied in Section II,C,1 the velocity v is seen to vanish and the system has a static interface between the two states X_3 and X_1 . This state, as all non-equilibrium structures in an infinite system, is marginally stable to a

perturbation that uniformly translates the structure. The translation operator is d/dr and indeed this translation type perturbation is proportional to dX^*/dr where X^* is the static structure given by (2.24) for this special case.

2. Periodic Structures

For the case $A = 0$ of the model of Section II,C,2 we have static periodic structures. Thus the system

$$\frac{\partial}{\partial t} \begin{bmatrix} X \\ Y \end{bmatrix} = D \frac{\partial^2}{\partial r^2} \begin{bmatrix} X \\ Y \end{bmatrix} + B(R) \begin{bmatrix} X \\ Y \end{bmatrix}, \quad R^2 = X^2 + Y^2 \quad (2.36)$$

has static periodic structures in the form

$$\begin{bmatrix} X \\ Y \end{bmatrix}^* = R_0 \begin{bmatrix} \cos kr \\ \sin kr \end{bmatrix} \quad (2.37)$$

where R_0 is determined by the condition

$$B(R_0) - k^2 D = 0. \quad (2.38)$$

The stability and other properties of these solutions have not been studied. It is clear that by making appropriate choices for $B(R)$ one may construct a model with a cutoff wave vector k_c beyond which the system has no solution. For example, in the case $B = [Q^2 R^2 - M^2]/[R^2 + M^2]$, $k_c^2 = Q^2/D$. This system has a stable homogeneous steady state at $X = Y = 0$ and a continuum of homogeneous states at $R_0 = |M/Q|$. This continuum has a patterned extension that exists for k in the interval $0 < k < k_c$. The properties of this and other cases warrants further investigation.

3. Symmetry Breaking Instability in a Model Reaction

Using the mechanism

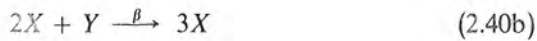


it has recently been found possible to determine many of the properties of the static dissipative structures analytically (Lefever *et al.*, 1977). We do not review the details here, but in short bifurcations of symmetry breaking states can be found. As the system length is changed the number of undulations that are possible takes on discrete (i.e., quantized) values.

E. RUNAWAY STATES

In a far from equilibrium system open to energy exchange with an external bath one might imagine that under certain conditions the temperature of the system would increase without bound (unless at elevated temperatures new kinetic processes become important). This phenomena has been termed the "runaway state" (DelleDonne and Ortoleva, 1977).

Consider a closed illuminated system with two species X and Y involved in the reactions



The last two steps are photochemically induced isomerizations and the first two are collision induced. The first reaction is taken to proceed with negligible activation energy barrier whereas the second involves an activation energy E_a such that

$$\beta = \beta_0 e^{-E_a/k_B T} \quad (2.41)$$

where β_0 is a constant, k_B is Boltzmann's constant, and T is the absolute temperature. The state X is taken to have the highest internal energy, $E_x > E_y$. The only exchange of energy between the system and the environment is via (2.40c,d).

It should be noted that as stated the model (2.40) violates microscopic reversibility. This inconsistency may be removed by reinterpreting the mechanism with intermediate photochemical steps (Noyes, DelleDonne, and Ortoleva, 1978). Furthermore, it should be pointed out that (2.40) represents a reduction of the model of Prigogine and Lefever (1968) (see DelleDonne and Ortoleva, 1977).

Letting x be the mole fractions of X and taking the system to be closed (so that the total number of particles X or Y is constant), we have, assuming simple mass action kinetics,

$$dx/dt = \eta - [\alpha + \mu + \eta]x + [\alpha + \beta(T)]x^2 - \beta(T)x^3. \quad (2.42)$$

Assume that the time scale of the reactions is long relative to that of attaining a Maxwellian velocity distribution, so that the average kinetic energy is given by $C'_v T$ where C'_v is a kinetic specific heat. With this one finds that for a gas the temperature obeys the equation

$$dT/dt = h[\eta - (\mu + \eta)x - (dx/dt)] \quad (2.43)$$

where $h = (E_x - E_y)/C'_v$.

The steady states of the system may be obtained from (2.41)–(2.43). Although the steady-state equations are transcendental, it is interesting that for this system they can be solved: one finds

$$x^* = \eta/(\mu + \eta) \quad (2.44)$$

$$T^* = -E_a/\ln[\alpha(\mu + \eta)/\beta_0 \eta]. \quad (2.45)$$

Note that for physical steady states T^* must be positive. This can only be obtained if

$$\alpha(\mu + \eta) > \beta_0 \eta. \quad (2.46)$$

It has been shown that in the domain of parameters (μ, η) where this is not satisfied the system temperature increases linearly in time and without bound.

Physically, the temperature will not increase without bound for even if the vessel in which the experiment was carried out was not destroyed, the integrity of the molecules X and Y would not be maintained. Thus new processes and chemical species would eventually arise and the runaway would be terminated. However the important point is that for some far from equilibrium systems runaway states may indeed be possible wherein the temperature increases over many order of magnitude.

F. REMARKS

An examination of soluble model systems serves as an introduction to a variety of nonequilibrium phenomena and, furthermore, allows for the detailed checking of various general approximation schemes such as bifurcation theory (Stakgold, 1971; Sattinger, 1973; Kopell and Howard, 1973; Ortoleva and Ross, 1974; Achmuty and Nicolis, 1975; Keener, 1976) and limit-cycle perturbation techniques (Kopell and Howard, 1973; Ortoleva and Ross, 1973a, 1974; Ortoleva, 1976) [see also the review in Hanusse *et al.* (1978)].

In addition to the phenomena introduced by these soluble model systems, there is the possibility of homogeneous (Rossler, 1976) or inhomogeneous (DelleDonne and Ortoleva, 1978) chaotic evolution of a reacting diffusing system. Also these systems may propagate single pulses of activity as has been shown experimentally (see A. T. Winfree, this volume) and theoretically via an analytical solution of a piecewise-linear kinetic system (Rinzel and Keller, 1973).

Let us now turn to the study of a number of physical systems and to general formulations and approximate descriptions of these systems.

III. Symmetry Breaking Transitions to Static Patterns

One of the most interesting possibilities that arises far from equilibrium is that of the instability of a homogeneous state to patterned perturbations and the subsequent development and sustaining of a patterned distribution of concentration of a lower symmetry. This idea for reaction diffusion systems was first introduced by Turing (1952) in his prophetic invocation of this

phenomena as a mechanism for biomorphogenesis. The idea has been extensively worked on by other authors (Prigogine and Lefever, 1968; Nitzan, Ortoleva, and Ross, 1974a; Auchmuty and Nicolis, 1975; Keener, 1976; Herskowitz-Kaufman, 1978). In this section we discuss several symmetry breaking instabilities that do not appear to have received a great deal of attention.

A. SPONTANEOUS PATTERN FORMATION IN PRECIPITATING SYSTEMS

1. The Patterning Phenomena

In the classic experiment of Liesegang (Liesegang, 1896; Hedges and Myers, 1926) a salt such as $\text{Pb}(\text{NO}_3)_2$ was mixed with a gel and allowed to set in a test tube. Upon placing a solution of KI over the gel solution, precipitation of PbI_2 occurs in the gel. The striking feature of this system is that the precipitation does not necessarily occur with monotonic decrease in intensity down the tube. It may vary in an undulatory way, with many bands of precipitate alternating with clear areas, under certain ranges of concentrations. The historical explanation of the phenomena was given by Ostwald (1925) and Prager (1956). Their theory depends on the presence of cross gradients of reactants and is based on the periodic attainment of the critical concentrations of Pb^{2+} and I^- for nucleation of precipitate with subsequent elimination of these ions in the vicinity of each successively forming band as the more mobile ion (I^- in the PbI_2 example) moves down the tube.

Flicker and Ross (FR) (1974) proposed describing this phenomena as a chemical instability leading to symmetry breaking in the Liesegang experiment. To test this idea I suggested that a homogeneous PbI_2 sol be prepared and allowed to age. If a symmetry breaking was indeed present, then the homogeneous experiment would be a clear cut demonstration of this fact since, unlike the classic Liesegang experiment, cross gradients were not present. In the experiments carried out by FR they found that yellow patterns of PbI_2 precipitate did indeed develop (Flicker and Ross, 1974).

In order to explore this phenomena further, some new experiments have been devised (Feinn *et al.*, 1978). In one experiment a solution of PbI_2 agar and water is heated until all solid is dissolved. Since PbI_2 is about three times more soluble at 100°C than it is at room temperature, this allows for the creation of a supersaturated PbI_2 solution that is free of irrelevant ions such as NO_3^- and K^+ as were present in the earlier experiment. It was found that after the precipitation occurred in a Petri dish one obtains speckled, mosaic, or wavy patterns at different initial concentrations of PbI_2 and conditions of cooling. The result of one experiment is shown in Fig. 5. Note the presence of spirallike phenomena that arise spontaneously under certain conditions. In a second experiment (Feinn *et al.*, 1978) three gel layers were

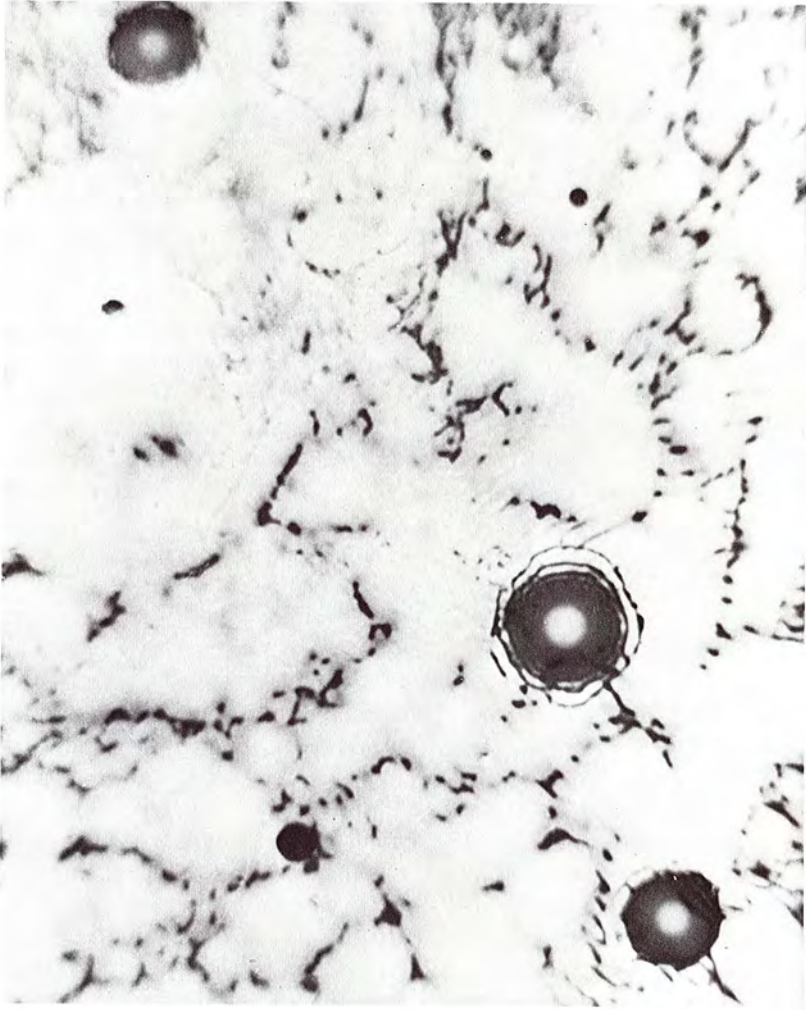


Fig. 5. Photograph of supercooling PbI_2 experiment for an agar solution [see Feinn *et al.* (1978) for experimental details].

prepared separately and stacked. They contained in sequence $\text{Pb}(\text{NO}_3)_2$, pure gel, and KI. When Pb^{2+} and I^- diffused into the "reaction layer" precipitation may be made to occur in a single band totally within the center gel layer by appropriate choice of layer thickness and concentrations. Since the gel was already set before the experiment started, convection could not be a factor in pattern formation. Furthermore, this second experiment provides much better controls since the supercooling experiment involves possible evaporation and temperature gradients as the poured gel cools.

The results of the second experiment is first the development of a uniform haze in a narrow band in the reactant layer. Within times of the order of 1–4 hours, depending on concentrations in the reactant layers, the uniform haze evolves to speckled or mosaic patterns of PbI_2 precipitate. The final result of one experiment is shown in Fig. 6.

2. Instability of the Particle Size Distribution Function

In order to explain this phenomena we must invoke a different mechanism than the Ostwald–Prager theory (Ostwald, 1925; Prager, 1956) since the

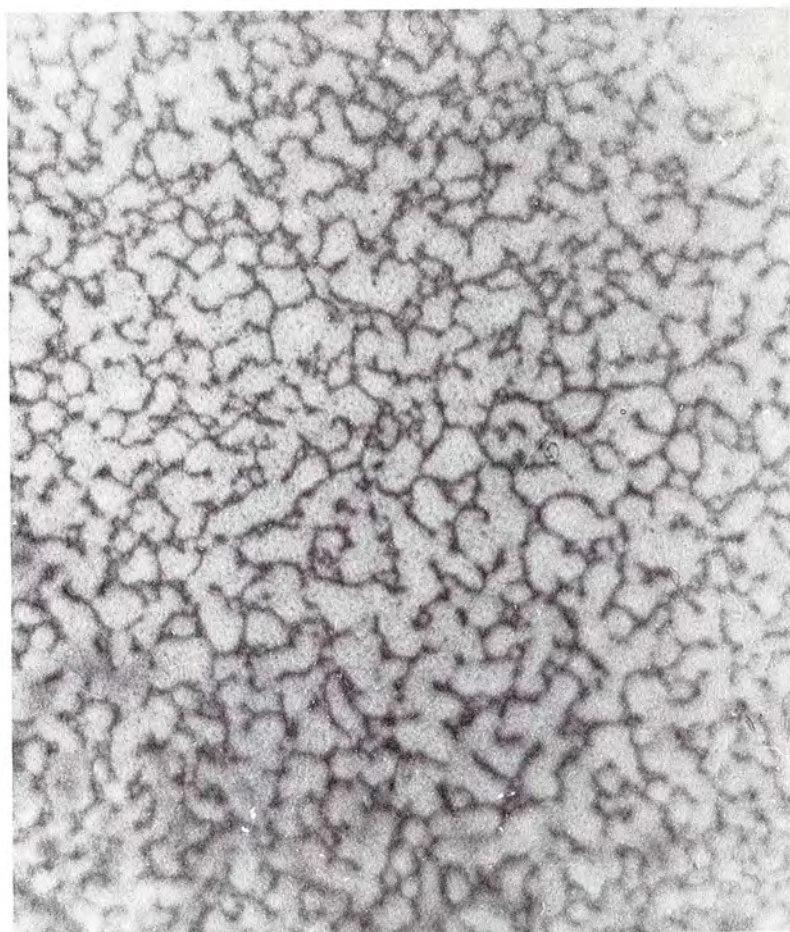


Fig. 6. Three-layer PbI_2 experiment of Section III.A showing precipitation patterning

latter requires the presence of cross gradients, clearly absent in the spontaneous pattern formation experiments described above.

Both the three layer and the supercooled PbI_2 systems develop a uniform yellow haze indicating particles of the order of microns, the wavelength of visible light, are initially essentially uniformly distributed throughout the system. Because of surface tension (Defay and Prigogine, 1956; Overbeek, 1971) a larger particle can exist in equilibrium with a PbI_2 solution of lower concentration than one of smaller radius. Thus in any small volume centered about a point \mathbf{r} , particles significantly smaller than the mean particle radius $R(\mathbf{r}, t)$ are rapidly consumed since the particle growth is a rapid process. However, the competition of neighboring volume elements is on a much slower time scale since the rate of exchange of material is the diffusion time associated with the length scale of the gradients involved. It is clear that if the average particle size at a point \mathbf{r} is bigger than that in its surroundings, then the particles at \mathbf{r} will grow at the expense of those in the vicinity of \mathbf{r} . This is a runaway effect since the more adjacent regions become separated in particle size the greater the difference in the equilibrium salt concentration becomes. The result of this situation is the creation of a dot of precipitate particles as found in Petri dish experiments of relatively low concentration. The mosaic pattern may be viewed as more complex initial conditions on $R(\mathbf{r}, t)$. Furthermore, as initial concentration increases it becomes less frequent to find regions where $R(\mathbf{r}, t)$ is sufficiently small after the initial burst of nucleation that the equilibrium concentration associated with them is appreciably sensitive to radius. (Note that as R increases the equilibrium concentration reaches its usual thermodynamic value obtained for a planar interface.)

To formulate these ideas mathematically one may study the local particle size distribution $f(\tilde{R}, \mathbf{r}, t)$ giving the density of particles of radius \tilde{R} at point \mathbf{r} and time t . For the purpose of illustrating the theory here we consider a simple approximation that appears to explain many features of interest. We assume that f is sufficiently narrowly peaked about $\tilde{R} = R$ as per our earlier discussion vis-a-vis particle competition in a small volume element. Thus we need only formulate an equation for $R(\mathbf{r}, t)$.

The rate of change of R is approximated by a simple rate law

$$\partial R / \partial t = q(C - C^{\text{eq}}) / \rho_s \quad (3.1)$$

where q is a positive quantity (which may depend on R and C in general) and ρ_s is the solid density. We have assumed a simple growth rate (moles/unit area-time) proportional to the difference between the salt concentration C at (\mathbf{r}, t) and C^{eq} , the equilibrium concentration for particles of radius R . We assume the particles to be immobilized so there is no flux term in (3.1). Let E represent the rate of increase in C due either to evaporation in the supercooling experiment or influx from the reactant layers in the three-

layer experiment. Then we have a continuity equation for C ,

$$\partial C / \partial t = D \nabla^2 C - 4\pi R^2 n q (C - C^{eq}) + E \quad (3.2)$$

where D is the diffusion coefficient of PbI_2 and n is the number of precipitate particles per unit volume. The factor $4\pi R^2$ arises because the consumption of salt is proportional to the surface area of the local particles.

Equations (3.1) and (3.2) provide a mathematical formulation of our picture. It is found that the state of initially homogeneous evolution where R and C are independent of \mathbf{r} at $t = 0$ becomes unstable to small spatial deviation in R or C , even under the assumption that n is constant.

Since q is typically very large, one can look at the limit of $q \rightarrow \infty$. In this limit one finds that $C = C^{eq}(R)$ and that R evolves according to

$$f(R) \frac{\partial R}{\partial t} = D \left\{ \left(\frac{\partial C^{eq}}{\partial R} \right) \nabla^2 R + \left(\frac{\partial^2 C^{eq}}{\partial R^2} \right) |\nabla R|^2 \right\} + E$$

$$f(R) = 4\pi n \rho R^2 + \frac{\partial C^{eq}}{\partial R}.$$

The factor f is found to be positive for physically realizable initial sols. Since $\partial C^{eq} / \partial R$ is negative for particle radii greater than the critical nucleation size, it is seen that the effective diffusion coefficient $f^{-1} D (\partial C^{eq} / \partial R)$ is negative and hence patterns are amplified. Finally we note that the theory presented here (based on the physical chemistry of the present problem) has a formal similarity to the theory of Glass (1973) on the random generation of pattern in the presence of expanding inhibitory fields.

B. PATTERN FORMATION IN SINGLE-CELL SYSTEMS

The most familiar electrochemical propagating phenomena in electrophysiology is that of axonal transmission. However, this is apparently not the only spatially patterned nonequilibrium structure to be found in cellular electrophysiological systems. For example, it has been shown that well in advance (and apparently independent of) mitotic processes there exists a transition from a state of spherically symmetric membrane potential to a polarized state in the spherical egg of *Fucus* (Jaffe *et al.*, 1974). This phenomenon has been termed self-electrophoresis and is believed to be the essential step in the development of the egg that leads to dramatically different daughter cells after the first mitosis. It appears that the *Fucus* system is an example of the chemical instability based biomorphogenesis theory of Turing (1952).

1. Two-Box Model

The idea of symmetry breaking instabilities leading to asymmetric mitosis was first considered using a two-box model (Ortoleva and Ross, 1973b,c).

Such two-box models had been used to demonstrate sustained stable patterns in reacting diffusing systems (Glansdorff and Prigogine, 1971). By representing the cell by two homogeneous compartments a tractable theory resulted. It was shown that the symmetric state (concentration in both boxes equal) could become unstable to a small asymmetric concentration perturbation if certain nonlinear membrane transport and reactions in the compartments took place. The theory was limited to neutral species and so self-electrophoresis, involving electrical fields and currents, was not demonstrated. It was shown, however, that the symmetric state of the cell dynamics could become unstable and that spontaneous asymmetric mitosis could result at the system, and not necessarily only at the genetic, level. Furthermore, this developed and sustained asymmetry could exist in a homogeneous environment, free of imposed gradients. This was an application of Turing's general hypothesis (Turing, 1952) that certain biomorphogenic events could be attributed to a pattern forming instability in the equations of reaction and transport.

2. *A Theory of Self-Electrophoresis*

Writing down equations for membrane and cytoplasmic transport and reaction, it has been shown (Ortoleva, 1978a) that the spherically symmetric state of membrane potential and cell composition may become unstable to small asymmetric perturbations leading to a polarized self-electrophoretic state of the cell with net transcellular ionic currents. It was further shown that the axis of the polarization was unstable to rotations in agreement with early behavior of the system. The later freezing in of the axis of the polarization was conjectured to be attributable to condensation phenomena associated with or driven by the symmetry breaking self-electrophoretic instability. Since the types of cell dynamical features that lead to such symmetry breaking instabilities are membrane transport nonlinearities, product activated catalytic reactions, cross catalysis, etc., and since these phenomena are common in cellular systems, it appears that self-electrophoretic and other symmetry breaking or wave and oscillatory electrophysiological phenomena should be found in a great variety of systems. Slow (minute) time-scale cellular oscillations are in fact common in cellular systems from heart, nerve, algal, and many other systems [see Hess and Boiteaux (1971) and Chance *et al.* (1973) for a review]. It is probable that many new developments should be forthcoming in this area in the near future.

C. LOCAL STEADY STATES IN SYSTEMS UNDER HOMOGENEOUS CONSTRAINT

Single propagating disturbances as for pulses along the axon or in Winfree's modification of the BZZ system (see Winfree, this volume) are now well-established phenomena. It has not been shown, however, that there can

exist inhomogeneous steady states that are localized in space in an infinite system under homogeneous constraint. In the mechanism of spontaneous pattern formation considered in Section III,A it can be shown that if initially the particle size R is at a value R_0 greater than the value R_h in the rest of the system, then eventually all the particles (except those in the central region) will be eliminated and those that started out at R_0 will grow indefinitely causing an intense localized dot. [This picture actually breaks down as the particles become a size of the order of the interparticle distance. This leads to a multicrystalline mass and, in fact, has been observed in gel precipitation experiments in our laboratory (Feinn *et al.*, 1978).] The question arises as to whether local states can be found in chemically reacting diffusing systems.

A suggestive model example of this comes from the following system. A species X has a diffusion coefficient $D(X)$ that is proportional to X . Defining length so that this proportionality factor is 1, consider the following system:

$$\partial X / \partial t = (\partial / \partial r) X (\partial / \partial r) X + F(X).$$

Taking $F(X) = 2X^2(1 + 4 \ln X)$, one may verify that

$$X^* = e^{-r^2}$$

is a steady-state solution for the system. It is an isolated disturbance in a system that has homogeneous steady states at $X_h^* = 0$, $e^{-1/4}$. (Note that this model is globally unstable since as $X \rightarrow \infty$, $F \rightarrow \infty$ although the state $X^* = 0$ is stable.) The question arises as to whether this phenomenon can arise in more physically interesting systems. It would be interesting to find stable localized structures in unbounded systems under homogeneous constraint.

The analogy of these localized self-sustaining regions of organized behavior to life is an attractive one to make. Indeed such an analogy of non-equilibrium structures to life is not new, but has been proposed by others in the field.

D. PATTERN FORMATION, SCALING, AND SPATIAL DIMENSIONALITY

Before concluding our discussion on spatial patterning, we will briefly discuss two general concepts regarding these phenomena.

1. Intrinsic and Extrinsic Length Scales

Consider a large system under homogeneous constraint. We assume that it has a homogeneous steady-state solution with descriptive variable ψ at the value ψ^* . Then perturbations from this state may be written as a linear combination of the eigen perturbations of the form $e^{i\mathbf{k} \cdot \mathbf{r}}$. We assume that there is one real branch of the stability eigenvalue spectrum $Z_u(\mathbf{k})$ that indicates instability by being positive for some range of wavevectors. We distinguish the following two cases (Nitzan, Ortoleva, and Ross, 1974a):

a. *Intrinsic Scaling*: Z_u is negative for k near 0, but is positive for an interval around some value k_c of k . Thus the pattern that arises has a wavelength of order of $2\pi/k_c$, the intrinsic length of the chemical kinetics and transport.

b. *Extrinsic Scaling*: Z_u is zero at $k = 0$ and as some constraint λ passes through a critical value λ_c , Z_u is positive for an interval $0 < k < k_m(\lambda)$ that increases for λ beyond λ_c . Thus the first mode that becomes unstable as λ increases beyond λ_c is that with a wavelength of order of the system size and hence the pattern length is not intrinsic to the reaction transport phenomenological relations, but is extrinsic to it, being fixed by the size of the particular system the reaction is being carried out in.

2. Space Dimensionality and Critical Bifurcation Exponent

A discussion of spatial patterning would hardly be complete without mentioning the relationship between the spatial dimensionality and the analytic behavior of bifurcating spatial patterns (Segel, 1965; Ponmarenkov, 1968). In one dimension only a single mode becomes unstable as a constraint λ passes through a critical value λ_c . However, in two and higher dimensions it is possible that because of rotational or other symmetries a number of modes may simultaneously become unstable at λ_c . It is this difference between one and higher dimensions and the fact that the critical modes may couple to each other in lower order nonlinear terms than the single mode case that leads to marked differences in the dependence of the amplitude A of the pattern on $(\lambda - \lambda_c)$. Thus near λ_c we have $A \sim (\lambda - \lambda_c)^\nu$ where the bifurcation exponent ν depends strongly on the dimensionality of the system. This point has been pursued in the Be'nard problem (Segel, 1965; Ponmarenkov, 1968), but apparently has not been discussed in detail for chemical instabilities.

IV. Chemical Waves

The theory of chemical waves has recently been reviewed (Hanusse *et al.*, 1978) and hence a summary of these results is not included here. Rather, we shall now discuss several theoretical aspects of chemical waves that have not received much attention until recently. First we discuss the electrochemical nature of chemical waves, then we pose the problem of a scattering theory for nonlinear reaction-diffusion waves, and finally study inhomogeneous evolution in systems with limit cycle kinetics.

A. ELECTROCHEMICAL WAVES AND WAVE-FIELD INTERACTIONS

In the most well-studied example (see Field and Winfree, this volume) of a system that can support chemical waves, most of the chemical species of

interest are ions, yet little attention has been paid to the electrochemical nature of wave propagation in an electrochemical system. In a recent study (Schmidt and Ortoleva, 1977) a new equation for plane waves valid for ionic media was derived. Furthermore, it is important to point out that a great number of instabilities in electrochemical systems are known to exist (de Levie, 1970), but these will not be reviewed here.

We now consider the derivation of a wave equation for ionic media. In one dimension (r) the equation of continuity takes the form

$$\partial C/\partial t = -\partial J/\partial r + \mathcal{R}[C] \quad (4.1a)$$

where $J = \{J_1, J_2, \dots, J_n\}$ is the flux. Assuming linear relations between the flux and the concentration gradient and electric field E , we have

$$J_i = -[D_i \partial C_i / \partial r - z_i u_i C_i E] \quad (4.2)$$

where D_i , z_i , and u_i are, respectively, the diffusion coefficient, valence, and mobility of species i (DeGroot and Mazur, 1962; Fitts, 1962). This is valid for sufficiently dilute solutions. To complete the theory, we have Poisson's equation relating E to the charge density $\sum_i z_i \mathcal{F} C_i \equiv \mathcal{F} zC$,

$$dE/dr = (4\pi/\epsilon) \mathcal{F} zC, \quad (4.1b)$$

where \mathcal{F} is Faraday's constant and ϵ is the dielectric constant of the system (assumed independent of C and E). Introducing a coordinate $\rho (= r - vt)$ moving along with a constant velocity (v) wave, we obtain coupled wave equations for E and C that can be combined (by integrating Poisson's equation with respect to ρ) into an integro-differential equation for C only.

By scaling the equation with typical mobilities and diffusion constants, reaction time scales and concentrations a smallness parameter α becomes manifest in this integro-differential equation:

$$\alpha = (l_D/l)^2 \quad (4.3)$$

where l is a typical reaction diffusion length (i.e., minimum length associated with the wave profile) and l_D is the Debye length. Since l_D is typically on the order of 10–1000 Å and l is of order of about a tenth of a millimeter (say for quasi-discontinuous waves), it is clear that $\alpha \ll 1$. Thus using α as an expansion parameter a new wave equation was derived. To lowest order the condition of charge neutrality resulted. In the next higher order the new wave equation was obtained:

$$(d/d\rho)[D_i(dC_i/d\rho) - \mathcal{E}u_i C_i] + v(dC_i/d\rho) + R_i[C] = 0 \quad (4.4a)$$

$$\mathcal{E} = \sum_{i=1}^N z_i D_i dC_i/d\rho \bigg/ \sum_{j=1}^N z_j^2 u_j C_j. \quad (4.4b)$$

The novel feature of this equation is that added to the transport term $D(d^2/d\rho^2)$ of the neutral species plane-wave equation is a term due to a Planck liquid junction type potential \mathcal{E} . The presence of the liquid junction term is in fact what coordinates the various ionic motions so that local charge neutrality is assured. With this it becomes clear that a compositional wave in an ionic system is associated with a propagating Planck liquid junction potential.

These electrochemical effects are not important in the presence of a large background electrolyte that does not take part in the chemistry of the wave propagation [because of the large denominator in (4.4b)]. Thus for the BZZ system under conditions studied to date, this effect may not be important except for the determination of the H^+ profile. Several possible changes in the composition of the BZZ reagent compatible with wave propagation, but which lowered or immobilized the background electrolyte, were suggested in Schmidt and Ortoleva (1977). It seems likely that interesting new propagating electrochemical phenomena will be discovered along these lines.

Another important feature of electrochemical systems is the possibility of studying the interaction of chemical waves with applied electrical fields. Indeed it is possible to stop, reverse, or destroy chemical waves by imposed electric fields (Schmidt and Ortoleva, 1977; 1978) and interesting effects even arise in the presence of a significant background electrolyte where the Planck term is not present.

Preliminary results (Heiney and Ortoleva, 1977) have been obtained using electric fields across the classic Liesegang band phenomena (Liesegang, 1896; Ostwald, 1925; Prager, 1956). A silver nitrate-potassium dichromate system was set up with the potassium dichromate in the gel. Voltages were applied making the silver nitrate solution above the gel positive. It was found that as the voltage increased the band spacing became strikingly regular as can be seen in Fig. 7. The spacing between bands also decreased and it was found that a critical voltage V_c exists such that for voltages beyond V_c the precipitation occurs as a single front of continuous precipitation propagating down the tube.

B. SCATTERING OF CHEMICAL WAVES

Although scattering theory is well developed in field theories such as quantum mechanics, optics, and acoustics, this has not been the case for nonlinear chemical waves (Ortoleva, 1978c). Consider, for example, the following scattering problem. Suppose that localized in the vicinity of a point \mathbf{r}_0 there is a disturbance of the chemical kinetics due to say a local hot spot or catalyst. The reaction diffusion equation for a dilute solution of neutral species then reads

$$\partial C/\partial t = D\nabla^2 C + \mathcal{R}(C) + \mathcal{S}(\mathbf{r}, C) \quad (4.5)$$

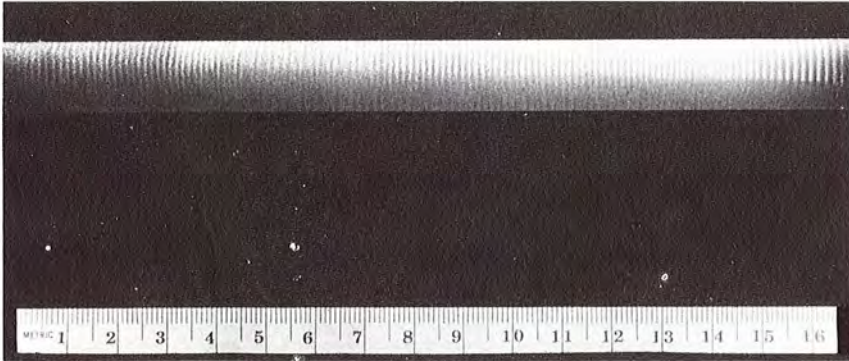


Fig. 7. Silver dichromate regularized patterns arising in a Liesegang-type experiment with an imposed voltage as described at the end of Section IV,A.

where the scattering source function $\mathcal{S}(\mathbf{r}, C)$ vanishes for large values of $|\mathbf{r} - \mathbf{r}_0|$. Let us assume that in the absence of \mathcal{S} the system propagates planar chemical waves and in particular a pulse. We induce such a planar pulse far from \mathbf{r}_0 so that it propagates towards \mathbf{r}_0 . The question arises as to what will be the resultant wave form long after the plane wave would have passed through \mathbf{r}_0 in the absence of the scattering center \mathcal{S} . Depending on the form and magnitude of \mathcal{S} , one might expect that either essentially no effect would occur, that a circularly radiating wave could be induced with \mathbf{r}_0 as the center, that a local oscillation could be induced at \mathbf{r}_0 , or any number of more complex phenomena such as the induction of a pair of counter rotating spiral waves as the wave passes around the center.

One method of studying scattering phenomena is the introduction of a smallness parameter into \mathcal{S} , i.e.,

$$\mathcal{S} = \sigma S, \quad (4.6)$$

and developing a theory in the limit of weak centers, $\sigma \rightarrow 0$, via appropriate expansion techniques. A second approach to the problem is in terms of matching solutions valid near the center and far from the center. Finally there is the nonlinear analog to the WKB theory where the characteristic length of the wave is much smaller than the length scale on which \mathcal{S} varies. These are developed in Ortoleva (1978c).

For one-dimensional systems the scattering problem stated above is somewhat simpler in the sense that if we limit ourselves to the question of what will be the behavior far from the center, there are only four possibilities: annihilation, reflection, transmission, or reflection and transmission. However even here the situation is rather complicated since, for example, it is possible that we could send a single pulse at the scattering center, have excitation of a local oscillation at the center, and subsequent emission of a

periodic wave train in the forward or reverse directions. Finally, a wave could be captured or pinned in the vicinity of the scatterer.

A second type of scattering situation is that which occurs when a wave collides with an impenetrable object. For example, it may be possible that if a plane wave impinges upon a wall of finite dimensions in the transverse direction, then a spiral wave can be the scattered wave.

Finally, if there are objects embedded in the medium with catalytic properties, then it is possible that, for example, planar chemical waves can be reflected from a catalytic wall. Clearly, nonlinear chemical waves have a rich scattering theory, although one might add, a difficult one.

C. INHOMOGENEOUS EVOLUTION IN SYSTEMS WITH LIMIT-CYCLE KINETICS

In this section we consider the inhomogeneous evolution of a system with chemical kinetics $\mathcal{R}[C]$ that supports a limit cycle in the absence of diffusion. When the frequency ω_c of the unperturbed limit cycle reflects a time scale short relative to other times in the phenomena of interest, it is reasonable to consider a multiple time scale development. In a sense the resulting theory should be in the spirit of the WKB approximation. In the latter the scale separation occurs between the wave length and the characteristic length over which the medium changes. This idea has been used to study acoustic instabilities in a reacting system where the acoustic period is much shorter than the chemical relaxation time (Toong, 1972; Gilbert *et al.*, 1973; Nitzan, Ortoleva, and Ross, 1974a).

We consider the reaction diffusion equation as introduced earlier,

$$\partial C/\partial t = \mathcal{D}\nabla^2 C + \mathcal{R}[C] + \mathcal{G}[\mathbf{r}, C] \quad (4.7)$$

where we envision \mathcal{G} to be an inhomogeneous perturbation on the kinetics due to a catalyst or hot spot. We assume the unperturbed system has a homogeneous cycle solution $\psi_c(\omega_c t)$

$$d\psi_c/dt = \mathcal{R}[\psi_c] \quad (4.8)$$

with frequency ω_c . Note that ψ_c is a 2π periodic function of its argument. We consider both autonomous cases, $\mathcal{G} = 0$, and cases with heterogeneous kinetics, $\mathcal{G} \neq 0$.

1. Introducing the Scaling Parameter

We introduce a scaling of terms via characteristic values as follows:

$$\begin{aligned} \mathcal{D} &= \bar{D}D \\ \mathcal{R} &= \omega_c R \\ \mathcal{G} &= \nu G \end{aligned} \quad (4.9)$$

where ν is a characteristic inverse time for \mathcal{G} . The time scale ν^{-1} introduces a length scale l given by

$$l^2 = \bar{D}\nu^{-1}. \tag{4.10}$$

We consider the case for which l is much longer than the cycle diffusion length l_c defined by

$$l_c^2 = \bar{D}\omega_c^{-1}. \tag{4.11}$$

The heterogeneous term \mathcal{G} will only introduce the length scale l into the problem when \mathcal{G} itself contains no shorter length scale variations; we limit our considerations here to this case. With this we define a dimensionless spatial coordinate $\boldsymbol{\rho}$,

$$\boldsymbol{\rho} = l^{-1}\mathbf{r}, \tag{4.12}$$

and assume that the explicit spatial variations in \mathcal{G} may be written as a function of $\boldsymbol{\rho}$, i.e., $\mathcal{G} = \nu G[\boldsymbol{\rho}, C]$. With this we divide (4.7) by ω_c and obtain

$$\partial C/\partial \tau = \varepsilon \bar{D}\nabla^2 C + R[C] + \varepsilon G[\boldsymbol{\rho}, C] \tag{4.13}$$

where

$$\tau = \omega_c t \quad \varepsilon = \nu/\omega_c \tag{4.14}$$

and we write ∇^2 for the Laplacian in the scaled spatial variable $\boldsymbol{\rho}$.

For the case of autonomous phenomena, l in the above development corresponds to the characteristic length of the concentration profile.

2. Multiple Time Scales

The scaled formulation (4.13) is convenient for introducing a multiple time theory. One time (on the order of the cycle period) is τ , which we denote as τ_0 . A slower time τ_1 is associated with the dimensionless time νt which is related to τ via $\tau_1 = \varepsilon \tau$. Further, we note that even for the simple case of homogeneous evolution ($\nabla^2 C = 0$) with G independent of $\boldsymbol{\rho}$ we must be able to account for the shift of frequency $\omega_c \rightarrow \omega(\varepsilon)$ that we expect in general will occur. To include this possibility we must, furthermore, introduce an infinite sequence of time scales such that

$$\tau_n = \varepsilon^n \tau. \tag{4.15}$$

This will allow for the recovery of the renormalized frequency $\omega(\varepsilon)$ in an expansion of the form

$$\omega = \sum_{n=0}^{\infty} \omega_n \varepsilon^n \tag{4.16}$$

where $\omega_0 = \omega_c$, as we shall see later in our development.

With this we write C in the form

$$C = C(\boldsymbol{\rho}, \tau_0, \tau_1, \tau_2, \dots)$$

and seek an expansion in the form

$$C = \sum_{n=0}^{\infty} C_n \varepsilon^n \quad (4.17)$$

where $C_n = C_n(\mathbf{p}, \tau_0, \tau_1, \dots)$. In terms of the times τ_n , (4.13) becomes

$$\sum_{n=0}^{\infty} \varepsilon^n \frac{\partial C}{\partial \tau_n} = \varepsilon D \nabla^2 C + R[C] + \varepsilon G[\mathbf{p}, C]. \quad (4.18)$$

3. Derivation of an Augmented Phase Diffusion Equation

To order $\varepsilon^0 = 1$ we obtain

$$\partial C_0 / \partial \tau_0 = R[C_0]. \quad (4.19)$$

Since we seek solutions that locally lie close to the limit cycle at all points, we have

$$C_0 = \psi_c(\tau_0 + \alpha) \quad (4.20)$$

where the local phase α depends on \mathbf{p} and the slow times

$$\alpha = \alpha(\mathbf{p}, \tau_1, \tau_2, \dots). \quad (4.21)$$

To order ε we have [with $\Omega = (\partial R / \partial \psi)_{\psi = \psi_c}$]

$$\begin{aligned} \left(\frac{\partial}{\partial \tau_0} - \Omega \right) C_1 = & - \left(\frac{\partial C_0}{\partial \tau_0} \right) \frac{\partial \alpha}{\partial \tau_1} \\ & + D \left\{ \frac{\partial C_0}{\partial \tau_0} \nabla^2 \alpha + \frac{\partial^2 C_0}{\partial \tau_0^2} |\nabla \alpha|^2 \right\} + G[\mathbf{p}, C_0]. \end{aligned} \quad (4.22)$$

Equation (4.22) is a differential equation for C_1 with respect to τ_0 parametrized by \mathbf{p} and the slow times. Noting that the quantity $(\partial C_0 / \partial \tau_0)$ satisfies the homogeneous equation

$$(\partial / \partial \tau_0 - \Omega)(\partial C_0 / \partial \tau_0) = 0, \quad (4.23)$$

we see that we cannot solve for C_1 unless the right-hand side of (4.22) is orthogonal to the solution of the adjoint equation corresponding to $(\partial C_0 / \partial \tau_0)$

$$(\partial / \partial \tau_0 - \Omega^T) f = 0. \quad (4.24)$$

The calculations are similar to those given earlier (Ortoleva and Ross, 1973; 1974; Ortoleva, 1976), and the solubility condition for (4.22) in light of the null space of $(\partial / \partial \tau_0 - \Omega)$ as seen in (4.23) leads to

$$\partial \alpha / \partial \tau_1 = D_p \nabla^2 \alpha + \Delta |\nabla \alpha|^2 + g(\mathbf{p}) \quad (4.25)$$

where

$$\begin{pmatrix} D_p \\ \Delta \\ g(\rho) \end{pmatrix} = \frac{1}{2\pi} \int_0^{2\pi} d\tau_0 f \begin{pmatrix} D(\partial\psi_0/\partial\tau_0) \\ D\Omega(\partial C_0/\partial\tau_0) \\ G[\rho, C_0] \end{pmatrix}. \tag{4.26}$$

The notation fA for any vector A implies a summation over indices where f is given by (4.24). Equation (4.25) is a diffusionlike equation for the phase α with nonlinear transport term $\Delta|\nabla\alpha|^2$ and source term $g(\rho)$ due to the perturbation \mathcal{G} . This ‘‘augmented phase diffusion’’ equation is a generalization of a linear theory that did not include the nonlinear transport term (Ortoleva and Ross, 1973a; Ortoleva, 1976). In another treatment the equivalent to (4.25) for the special case of temporarily periodic solutions was obtained (Ortoleva and Ross, 1974). Finally we note that the result (4.25) similar to that obtained by Kuramoto and Yamada (1976) for the case of no inhomogeneity, $\mathcal{G} = 0$, and two chemical species. The treatment of the latter authors was not a consistent theory in that, for example, it neglected corrections in C of order ϵ and higher.

4. Special Cases of the Augmented Phase Diffusion Equation

Let us now consider some simple cases in order to clarify the meaning of the various terms.

a. Homogeneous Renormalization. Suppose we uniformly raise the temperature of a homogeneous oscillation. Thus G would be independent of space. Then what is the effect of the perturbation on the homogeneous evolution? For this simple case (4.25) becomes

$$\partial\alpha/\partial\tau_1 = g \tag{4.27}$$

and hence

$$\alpha = g\tau_1 + \alpha_1(\tau_2, \tau_3, \dots). \tag{4.28}$$

Neglecting the phase shift α_1 (which is a constant to order ϵ), we obtain in lowest order

$$C \underset{\epsilon \rightarrow 0}{\rightsquigarrow} \psi_c((1 + \epsilon g)\omega_c t) \tag{4.29}$$

and we see that the system oscillates with the renormalized frequency $\omega(\epsilon)$ such that

$$\omega \underset{\epsilon \rightarrow 0}{\rightsquigarrow} \omega_c(1 + g\epsilon). \tag{4.30}$$

b. Periodic Autonomous Phenomena. Since gradients of frequency eventually lead to infinite gradients, the most general periodic solution to the reaction diffusion equation (4.7) takes the form

$$C = \chi[\rho, \tau + p(\rho)] \tag{4.31}$$

where χ is periodic in $\tau + p(\boldsymbol{\rho})$ with a constant frequency ω . The spatially dependent distribution of phase of oscillation is denoted $p(\boldsymbol{\rho})$. To lowest order $\chi \sim \psi_c(\tau_0 + \alpha)$ and hence for periodic solutions we must have

$$\alpha = \sum_{n=1}^{\infty} \beta_n \tau_n + p. \quad (4.32)$$

From (4.25) we obtain

$$\beta_1 = D_p \nabla^2 p + \Delta |\nabla p|^2. \quad (4.33)$$

This is the equation derived earlier by directly seeking periodic solutions (Ortoleva and Ross, 1974). For plane waves of wavelength l we have $p = \mathbf{n} \cdot \boldsymbol{\rho}$ where \mathbf{n} is a unit vector along the direction of propagation. Hence

$$\beta_1 = \Delta, \text{ plane waves.} \quad (4.34)$$

Similarly, for one- or two-dimensional centers or spiral waves with essentially planar form far from the core we see that $\beta_1 = \Delta$ also.

5. Reduction of the Phase Equation to Linear Form

Interestingly enough we can transform the nonlinear phase equation into a linear equation. Letting

$$\begin{aligned} \alpha &= (D_p/\Delta) \ln A, \\ \boldsymbol{\rho} &= (D_p/\Delta)\mathbf{y}, \quad \alpha(\mathbf{y}) = (\Delta/D_p)g[(D_p/\Delta)\mathbf{y}], \end{aligned} \quad (4.35)$$

we find

$$\partial A/\partial \tau_1 = [\nabla_y^2 + \alpha(\mathbf{y})]A. \quad (4.36)$$

This equation warrants further investigation and applications. It is rather surprising that the nonlinear equation (4.25) can so generally be transformed to linear form.

6. Breakdown of the Theory

This theory breaks down under situations where new length scales enter the problem and shock structures develop. An example arises in applying the theory to find periodic centers. The theory yields divergent phase at the core of a circular wave for some systems and always does so for spiral waves (Ortoleva and Ross, 1974). The theory is believed to be valid far from the core of these phenomena, however.

A second source of breakdown is the presence of shorter time scales in the chemical kinetics or diffusion coefficients. For example, in the case of relaxation oscillations one has a periodic sequence of very short time scale changes separating regions of smooth variation on the time scale of the period of the cycle. Such problems have been treated using matched asymptotic

techniques and catastrophe theory [see Hanusse *et al.* (1978) and Feinn and Ortoleva (1977) for a review and references].

7. Application of the Theory

The augmented phase diffusion theory may be used to study the transient evolution toward periodic states. It thus may be applied to the study of the stability of chemical waves (Ortoleva, 1976). A variety of other applications suggest themselves, including the ability of a limit-cycle system to preserve phase coherence over long distances in the presence of random fluctuations [Ortoleva, 1972 (unpublished)][†] and the response of a limit-cycle system in the presence of gradients in conditions such as temperature or catalyst concentrations. Note that the phase diffusion coefficient D_p is not necessarily positive. Thus for the case $D_p < 0$ inhomogeneities in the phase will be amplified, leaving these systems inherently unstable to pattern formation. This is an alternate explanation of the tendency in the melonic acid wave medium for homogeneous oscillation to become unstable to pattern formation.

V. Membrane and Surface Localized Structures

Interfaces between a bulk phase and a membrane, dust particle, and catalytic particles or wires provide special localized sites of reaction. It appears that all the phenomena that occur in bulk media may also occur in association with these localized sites. For example, it is found in Liesegang experiments with chromate ions imposed on a silver nitrate gel solution that the bands of precipitate may be localized to the walls of the tube and not in the gel itself. In fact, the pattern may take the form of a corkscrew curling down the tube. Clearly, under situations where this may occur, the conditions at the glass-gel interface provide a favorable localized site for nucleation of precipitate particles. In this section we discuss some theoretical results that have been obtained on pattern formation, propagating waves, and other nonequilibrium phenomena that occur in association with the interaction of localized sites and bulk media.

A. BULK AND SURFACE KINETICS

We consider an isothermal medium at rest, the "bulk," in contact with an object (such as a wall, membrane or wire) through an interface defined by

[†] Using a Langevin approach one may calculate the phase correlation function. The random source term is identified with G in (4.7). In the limit when the noise is small in mean square amplitude one obtains simple, physically transparent results. It is an instructive exercise and may be of interest in certain applications such as chemical and ecological oscillatory systems.

the surface S . In the bulk we have the continuity equation for the chemical concentrations which we assume to be described by Fick diffusion (with constant diffusion coefficient matrix D) according to

$$\partial C/\partial t = D\nabla^2 C + \mathcal{R} \quad (5.1)$$

where \mathcal{R} is the rate of bulk phase reaction.

We distinguish two processes that can occur at the surface. If σ_i is the surface area density (moles/area) of species i that is immobilized to the surface, then we have (neglecting surface diffusion for simplicity)

$$\partial\sigma/\partial t = g(\sigma, C) \quad (5.2)$$

where g is the rate of incorporation of material into the surface (moles/area-time) and depends on the bulk concentrations at S and on σ (and for electrochemical systems on the voltage difference between the surface and the bulk across the interface). A second kind of surface reaction does not lead to incorporation in the surface and has a rate denoted by $h(\sigma, C)$ (in moles consumed per unit time per unit area). For example, g may represent the rate of surface precipitation in the Liesegang problem mentioned above and h may represent the rate of surface catalyzed reaction. Finally, g may have two distinct types of contributions— g_1 representing reactions among interfacially bound species that do not consume bulk phase molecules and g_2 that do consume the latter. Let the total rate of loss of bulk phase species per unit area be denoted G ; we have

$$G = g_2 + h. \quad (5.3)$$

Since the amount of bulk material consumed must be just balanced by the flux $\mathbf{n} \cdot D\nabla C$ from the bulk (\mathbf{n} is the unit normal to S at the point in question directed into the bulk), we obtain at a point \mathbf{r} on S

$$\mathbf{n} \cdot D\nabla C = G(\sigma, C), \quad \mathbf{r} \in S. \quad (5.4)$$

With this the local site problem consists of solving the continuity equation (5.1) in the bulk consistent with the boundary condition (5.4) and the surface kinetics (5.2). It is clear that the three sources of nonlinearity (\mathcal{R} , g , and G) yield the possibility for a richness of phenomena in this system.

It is convenient to incorporate the boundary condition (5.4) directly into the continuity equation (Ortoleva and Ross, 1972; Ortoleva, 1976). The method involves replacing (5.4) by the boundary condition $\mathbf{n} \cdot D\nabla C = 0$ for an impenetrable wall and adding a delta function localized source term to the continuity equation (5.1). Let S^+ be a surface parallel to S a distance 0^+ in the bulk and let $\delta^+(\mathbf{r})$ be the one-dimensional delta function localized to S^+ so that for any path integral $\int A(\mathbf{r})\delta^+(\mathbf{r}) ds$ passing through S^+ at \mathbf{r}^+

we obtain the value $A(\mathbf{r}^+)$. Then, if we replace (5.1) by

$$\partial C/\partial t = D\nabla^2 C + \mathcal{R} + G\delta^+(\mathbf{r}), \quad (5.5)$$

it is easy to show that (5.4) is satisfied by integrating (5.5) along a small path in the direction \mathbf{n} passing through S^+ .

B. LINEAR BULK KINETICS

We now show that under certain circumstances the present problem reduces to the solution of integral equations involving only σ and the surface values of the bulk concentrations. We assume that the absence of surface localized processes, $G = 0$, there is a steady state $C_b(\mathbf{r})$,

$$D\nabla^2 C_b + \mathcal{R} = 0. \quad (5.6)$$

Furthermore, if we introduce the relative concentration $C - C_b$, which we denote C for convenience, we have, neglecting nonlinearities in the bulk,

$$\partial C/\partial t = LC + G\delta^+(\mathbf{r}) \quad (5.7)$$

$$L(\mathbf{r}) = D\nabla^2 + \Omega(\mathbf{r}) \quad (5.8)$$

$$\Omega = (\partial\mathcal{R}/\partial C)_{C=C_b(\mathbf{r})} \quad (5.9)$$

where Ω is the matrix of the linearized bulk kinetics.

We introduce a bulk propagator $\Xi(\mathbf{r}, \mathbf{r}'; t)$ such that

$$\partial\Xi/\partial t = L(\mathbf{r})\Xi \quad (5.10)$$

$$\Xi(\mathbf{r}, \mathbf{r}'; 0) = I\delta(\mathbf{r} - \mathbf{r}') \quad (5.11a)$$

$$\mathbf{n} \cdot D\nabla\Xi = 0, \quad \mathbf{r} \in S, \mathbf{r}' \in V \quad (5.11b)$$

where $\delta(\mathbf{r} - \mathbf{r}')$ is the three-dimensional Dirac delta function, I is the identity matrix, and V is the volume of the bulk. With this, the solution to (5.7) may be written

$$C(\mathbf{r}, t) = \int d^3r' \Xi(\mathbf{r}, \mathbf{r}'; t)C(\mathbf{r}', 0) + \int_0^t dt' \int_S d^2r' \Xi(\mathbf{r}, \mathbf{r}'; t - t')G[\sigma(\mathbf{r}', t'), C(\mathbf{r}', t')]. \quad (5.12)$$

The first term in (5.12) is the initial value contribution, whereas the second term is the accumulated effect of the surface reaction propagated into the system volume V from S . This is a great simplification of the problem since if we locate \mathbf{r} on the surface, then (5.12) represents a closed equation for the bulk concentrations at the surface coupled to σ . A complete solution for the system is obtained by simultaneously solving (5.12) for the bulk concentra-

tions at the surface consistent with (5.2), the latter of which may be converted into an integral equation by integration with respect to t . This reduces the problem to the solution of coupled nonlinear integral equations for surface quantities only.

1. Steady States

A reduction of (5.12) comes about for steady states. Let $\sigma^*(\mathbf{r})$, $C^*(\mathbf{r})$ be a steady-state solution of (5.12). Let P be the projection operator (in the N -dimensional concentration space) onto the subspace of species that have no bulk reaction [or, more generally, onto the null space of L , which for simplicity we assume to correspond to homogeneous (\mathbf{r} independent) eigenfunctions]. Then $\Xi \rightarrow V^{-1}P$ as $t \rightarrow \infty$.

For simplicity we consider the case where such species are not present. Then since $\Xi \rightarrow 0$ as $t \rightarrow \infty$ for a stable bulk, we have by evaluating (5.12) in the limit as $t \rightarrow \infty$

$$C^*(\mathbf{r}) = \int_S d^2r' Z(\mathbf{r}, \mathbf{r}') G[\sigma^*(\mathbf{r}'), C^*(\mathbf{r}')] \quad (5.13)$$

where

$$Z(\mathbf{r}, \mathbf{r}') \equiv \int_0^\infty dt \Xi(\mathbf{r}, \mathbf{r}'; t). \quad (5.14)$$

To solve (5.13) we need a second equation for σ^* . This comes straightforwardly from (5.2) and reads

$$g(\sigma^*, C^*) = 0. \quad (5.15)$$

The solution of (5.15) allows elimination of σ^* in favor of C^* to derive a closed equation for C^* from (5.13). Since (5.13) and (5.15) are nonlinear, it is clear that the system can have multiple solutions in certain cases (Shymko and Glass, 1974; Bimpong-Bota *et al.*, 1974; Bimpong-Bota *et al.*, 1977).

2. Stability of the Steady States

The stability of the steady states to infinitesimal perturbations may be studied by linearizing (5.12) about the steady-state solution

$$\begin{aligned} C &= C^* + \delta C \\ \sigma &= \sigma^* + \delta \sigma. \end{aligned} \quad (5.16)$$

Introducing the rectangular stability matrices as follows,

$$\begin{aligned} M &= (\partial G / \partial C)^* \\ N &= (\partial G / \partial \sigma)^* \\ \mu &= (\partial g / \partial C)^* \\ \nu &= (\partial g / \partial \sigma)^*, \end{aligned} \quad (5.17)$$

we have

$$\delta C(\mathbf{r}, t) = \int d^3r' \Xi(\mathbf{r}, \mathbf{r}', t) \delta C(\mathbf{r}', 0) + \int_0^t dt' \int_S d^2r' \Xi(\mathbf{r}, \mathbf{r}'; t - t') \{M\delta C(\mathbf{r}', t') + N\delta\sigma(\mathbf{r}', t')\} \quad (5.18)$$

$$\partial\delta\sigma/\partial t = \mu\delta C + \nu\delta\sigma. \quad (5.19)$$

It is easy to see that $\delta\sigma(\mathbf{r}, t) = e^{\nu t}\delta\sigma(\mathbf{r}, 0) + \int_0^t dt' e^{\nu(t-t')}\mu\delta C(\mathbf{r}, t')$ and we obtain a closed equation for δC from (5.18) by eliminating $\delta\sigma$. For general surface geometry the problem is rather formidable. The theory can be carried out in great detail for regular arrays of local sites (Bimpong-Bota *et al.*, 1977) and for the planar case which we now consider.

C. PLANAR SURFACES

We now consider the simple case of a planar interface. Let the system be bounded by a plane at $x = 0$ with a bulk in $x > 0$. For the case of a homogeneous bulk steady state $C_b(\mathbf{r}) = C_b$ the propagator Ξ takes the form

$$\Xi(\mathbf{r}, \mathbf{r}'; t) = \Xi_0(\mathbf{r} - \mathbf{r}', t) + \Xi_0(\mathbf{r} - \bar{\mathbf{r}}', t) \quad (5.20)$$

where Ξ_0 is the propagator for an infinite medium and $\bar{\mathbf{r}}'$ is the image point to \mathbf{r}' , i.e., if $\mathbf{r}' = (x', y', z')$, then $\bar{\mathbf{r}}' = (-x', y', z')$. Since at the surface $x' = 0$, $\bar{\mathbf{r}}' = \mathbf{r}'$ and for points $(0, y, z)$ (5.20) simplifies as follows. Introducing a two-dimensional vector $\mathbf{r}_S = (0, y, z)$, we obtain

$$C(\mathbf{r}_S, t) = \int_0^\infty dx' \int d^2r'_S [\Xi_0(\mathbf{r}_S - \mathbf{r}', t) + \Xi_0(\mathbf{r}_S - \bar{\mathbf{r}}', t)] C(\mathbf{r}', 0) + 2 \int_0^t dt' \int d^2r'_S \Xi_0(\mathbf{r}_S - \mathbf{r}'_S, t - t') G[\sigma(\mathbf{r}'_S, t'), C(\mathbf{r}'_S, t')]. \quad (5.21)$$

This equation provides a convenient framework for studying questions of stability in the planar surface problem by linearizing this equation around a given reference state. Instability may arise due either to perturbations uniform along the wall or to those corresponding to spatial patterning, either static or propagating, parallel to the wall (Bimpong-Bota *et al.*, 1974). These disturbances decay as one goes away from the surface.

1. Spatio-temporally Periodic Patterns

To illustrate the application of the nonlinear methods developed for pure bulk phase systems we consider the phenomena of surface localized periodic patterns. For the case of waves or patterns periodic in the y direction and constant in the z direction we seek solutions

$$C = \chi(\phi, x) \quad (5.22)$$

$$\phi = ky - \omega t \quad (5.23)$$

where χ is 2π periodic in ϕ and where k and ω are the wave vector and frequency, respectively. Assuming the bulk kinetics in the absence of local reactions yields a homogeneous state, the stability matrix Ω is independent of \mathbf{r} and χ obeys the equation

$$D\{(\partial^2/\partial x^2) + k^2(\partial^2/\partial \phi^2)\}\chi + [\Omega + \omega(\partial/\partial \phi)]\chi = -2G[\chi]\delta(x) \quad -\infty < x < \infty \quad (5.24)$$

where for simplicity we have neglected the dependence of G on σ . We have used the convenient device of extending the domain of the system into the unphysical region $x < 0$ with the proviso that we must seek solutions symmetric in x . (Integrating this equation over a small interval about $x = 0$ shows that the boundary condition $D\partial\chi/\partial x = G$ is satisfied, provided χ is symmetric in x .) Taking Fourier series transforms with respect to ϕ and Fourier integral transforms with respect to x , we may show that for the surface value of the pattern $\chi(\phi) \equiv \chi(\phi, 0)$ we have, including the factor of 2 in G for convenience,

$$\chi(\phi) = \int_{-\pi}^{\pi} d\phi' S_{k^2, \omega}(\phi - \phi') G[\chi(\phi')] \quad (5.25)$$

$$S_{k^2, \omega}(\phi) = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} dq \sum_{n=-\infty}^{\infty} e^{in\phi} [(nk)^2 + q^2] D - in\omega - \Omega)^{-1}. \quad (5.26)$$

It is useful to write (5.25) as an operator equation

$$\chi = \mathcal{S}_{k^2, \omega} G[\chi] \quad (5.27)$$

with the ϕ convolution being accounted for in the operator $\mathcal{S}_{k^2, \omega}$. Equation (5.27) presents itself as a convenient starting point for the study of surface waves and static patterns ($\omega = 0$).

a. Bifurcation Analysis of Surface Structures. Consider a bifurcation analysis of the onset of patterning as a small deviation of the concentrations from a static state uniform along the surface. In analogy to the bulk formalism (Kopell and Howard, 1973; Ortoleva and Ross, 1974; Achmuty and Nicolis, 1975; Keener, 1976) (see also Appendix A) we consider a family of solutions that arise in the vicinity of a wave vector k_0 with corresponding frequency ω_0 and expand all quantities in terms of an amplitude parameter A [Ortoleva (1974, unpublished)],

$$\begin{pmatrix} \chi \\ \omega \\ k^2 \end{pmatrix} = \sum_{n=0}^{\infty} \begin{pmatrix} \chi_n \\ \omega_n \\ k_n^2 \end{pmatrix} A^n. \quad (5.28)$$

In carrying out the expansion care must be taken not to neglect the dependence of $S_{k^2, \omega}$ on A via k^2 and ω . With this procedure it may be shown that there exists a complex conjugate pair of eigenvalues (of the stability prob-

lem) with imaginary part $\pm i\omega_0$ at k_0 and with real part passing through the origin linearly with $k^2 - k_0^2$ at k_0^2 , then a family of wave solutions typically bifurcates at k_0^2 with an amplitude proportional to $|k^2 - k_0^2|^{1/2}$. The bifurcation may occur for $k^2 \geq k_0^2$, depending on the particular system (i.e., Ω , D , and G). The result is very similar to the results of the Hopf bifurcation theorem [see Hopf (1942), Stakgold (1971), Sattinger (1973), and Appendix A] as applied to chemical waves in a bulk medium [see Hanusse *et al.* (1978) for a review].

b. Limit-Cycle Perturbation Scheme. It has been shown that there can exist uniform oscillations along a wall (Bimpong-Bota *et al.*, 1974). Using techniques closely related to those in Section IV,C, Kopell and Howard (1973), and Ortoleva and Ross (1974), one may show [Ortoleva (1974, unpublished)] that there must be a family of long wavelength extensions of this solution for $k^2 > 0$ at least for k^2 near the origin. In deriving this result one must account for the dispersion (i.e., k^2 dependence of ω). The theory proceeds by expanding $S_{k^2, \omega}$, ω , and χ in powers of k^2 and putting the result in (5.27). The coefficients of ω are fixed by the condition of solubility of the theory to various orders. The only kinetic assumption is that the uniform oscillation be a limit-cycle stable modulo a uniform shift of phase.

c. Soluble Models. Using local kinetics as in Section II,B for the variables X and Y and letting X and Y decompose and diffuse with the same rate in the bulk one may construct model systems with periodic wave train solutions (Bimpong-Bota *et al.*, 1974) which verify the bifurcation and limit-cycle calculations outlined in the two preceding paragraphs. One may also construct models like those in Section II,A to find multiple steady state and other features of bifurcation-diagrams discussed in Section II,A (Bimpong-Bota *et al.*, 1974).

d. Multiple-Site Systems. When there are multiple localized sites of reaction a variety of interesting phenomena can occur (Bimpong-Bota *et al.*, 1977). Oscillations and multiple steady states may exist due to the interaction of two or more sites that cannot occur for one site (Shymko and Glass, 1974). For infinite arrays of sites the transition to new far from equilibrium states as a function of density of sites has the features of cooperative and critical behavior (Bimpong-Bota *et al.*, 1977). For the case of a dispersion of catalyst particles, the system may be described in terms of effective or renormalized transport and reaction in a coarse grained description (Ortoleva, 1978b).

e. Future Developments. Interesting problems to be solved in this area by applying or extending the results cited here include phenomena at electrode surfaces, periodic precipitation on surfaces, BZZ or other chemical waves on surfaces due to localized ferroin or other reagents on a surface, and mem-

brane waves associated with a membrane containing an enzyme and placed in a bath of reactants. Systems with localized kinetics are of great importance in biological and chemical engineering systems.

VI. The Morphological Stability of Growing Bodies

Crystal growth under conditions far from equilibrium leads to stellar, dendritic, hollow, or feathery crystals. In contrast to this, near-equilibrium growth yields solid prismatic crystals. Tumor or colony growth (such as in corals) seem to be closely related to this type of phenomena in that the colony often grows in a dendritic or undulated pattern rather than with a smoother surface. We now discuss these types of situations in terms of the morphological stability of a growing body.

For growing bodies there are two opposing tendencies regarding the stability of simple geometries to the outcropping of dendritic protrusions. The gradient of growth material away from the object makes it advantageous for the growth of a protrusion relative to growth at a larger radius of curvature. Furthermore, in systems with a high heat of fusion a protrusion can eliminate heat more rapidly than a flatter surface. However surface tension tends to maximize the radius of curvature, hence opposing the tendency towards outcropping. Morphological instability in physico-chemical systems comes about when the balance between these two tendencies is turned in favor of outcropping. An analogous tendency towards outcropping to take advantage of nutrient gradients occurs in biological systems. The analog to surface tension is less straightforward and involves factors such as sharing of metabolites to advantage and the resistance to loss of essential chemical species or external attack when the surface area is minimized.

A. KINEMATICS OF GROWING BODIES

We consider first the growth of a pure amorphous solid from a solution of concentration $C(\mathbf{r}, t)$ (Mullins and Sakerka, 1967; Langer and Turski, 1976; Langer, 1976; Chadam *et al.*, 1978). Consider a body defined by a surface S with unit normal $\mathbf{n}(\mathbf{r})$ at points \mathbf{r} on S directed out of the body. Because of the incorporation of material from the environment, a surface area element δA moves a distance $v\delta t$ in the direction \mathbf{n} where v is the local velocity of advancement of the surface. Associated with this advance, $\rho_s v\delta A\delta t$ moles of material are incorporated where ρ_s is the density of the growing body material. The material that was incorporated came from both diffusion to the surface, $-\mathbf{n} \cdot \mathbf{J}\delta A\delta t$ (where \mathbf{J} is the flux of material), plus the material already present in the swept out volume $v\delta t\delta AC$ (where C is the concentration of the material in the bulk near the surface). Equating these to the quantity

of moles incorporated we obtain

$$\rho_s v = Cv - \mathbf{n} \cdot \mathbf{J}. \quad (6.1)$$

This kinematic relation between the advancement velocity v and the flux of material from the solution can be further developed into a boundary condition for the reaction transport equations in the bulk. Let G be the rate of incorporation of material (moles per unit area per unit time). Because of surface tension effects, G can depend on the radius of curvature as well as the solution concentration at the surface. Since $G\delta A\delta t$ is the amount of moles incorporated in time δt on an area δA and since this is also given by $\rho_s v\delta A\delta t$, we see that

$$v = G/\rho_s \quad (6.2)$$

and hence we obtain the boundary condition

$$(1 - C/\rho_s)G = -\mathbf{n} \cdot \mathbf{J}. \quad (6.3)$$

This boundary condition differs from that found in the previous section for fixed boundaries. The new term is due to the fact that the motion of the surface sweeps out material in addition to that which comes to the surface by the flux \mathbf{J} . The term C/ρ_s can be ignored without much loss of accuracy for growth from a vapor or from a dilute solution, but cannot be ignored for growth from a concentrated solution or from a pure melt of the growth material.

Next we must introduce an equation for the surface defining the growing body. A surface can always be written as the set of points \mathbf{r} such that

$$S(\mathbf{r}, t) = 0. \quad (6.4)$$

By convention we take S to be ≥ 0 outside/inside the growing body. In a time δt a point \mathbf{r} on S moves to a point $\mathbf{r} + v\mathbf{n}\delta t$. Since at time $t + \delta t$ S also satisfies (6.4) we have, after expanding in δt and setting the coefficient of δt to zero since this must hold for arbitrary but small δt ,

$$\partial S/\partial t + v\mathbf{n} \cdot \nabla S = 0. \quad (6.5)$$

Noting that $\mathbf{n} = \nabla S/|\nabla S|$ and using (6.2), we obtain

$$\partial S/\partial t + G|\nabla S| = 0. \quad (6.6)$$

Since G depends on radius of curvature, it is a functional of S and hence (6.6) is a nonlinear equation in S (from the $|\nabla S|$ term as well as from G).

B. DIFFUSION LIMITED GROWTH THEORY

In many cases of far from equilibrium growth the incorporation rate G is much more rapid than the rate of transport of material to the surface of the

growing body. Since this case has been the most widely studied (Mullins and Sekerka, 1967; Langer and Turski, 1976; and Langer, 1976), it is derived here as a special case of the more general theory presented above (Chadam *et al.*, 1978).

Since there is a time scale in G that is fast relative to the other processes in the system, we introduce a smallness parameter ε to emphasize this fact:

$$G = \varepsilon^{-1} \bar{G}. \quad (6.7)$$

The parameter ε represents the ratio of time scale associated with the attainment of equilibrium near the surface to that of crystal growth. For example, if $G = q(C - C^{eq})$, where C^{eq} is the (radius of curvature dependent) equilibrium concentration, then ε^{-1} is τq and $\bar{G} = \tau^{-1}(C - C^{eq})$ where τ is a typical time scale on which the object grows. Using (6.7), the boundary condition becomes

$$-\varepsilon \mathbf{n} \cdot \mathbf{J} = (1 - C/\rho_s) \bar{G}. \quad (6.8)$$

If we expand C and S in ε ,

$$\begin{aligned} C &= \sum_{m=0}^{\infty} C_{(m)} \varepsilon^m \\ S &= \sum_{m=0}^{\infty} S_{(m)} \varepsilon^m \end{aligned} \quad (6.9)$$

and similarly for \mathbf{J} and \bar{G} we obtain to lowest order

$$\bar{G}_{(0)} = \bar{G}(C_{(0)}, S_{(0)}) = 0 \quad (6.10)$$

which states that at each point \mathbf{r} on the solid surface C is at equilibrium with the solid at the local radius of curvature,

$$C_{(0)} = C^{eq}(S_{(0)}). \quad (6.11)$$

To the next order we obtain

$$-\mathbf{n} \cdot \mathbf{J}_{(0)} = (1 - C_{(0)}/\rho_s) G_{(1)} \quad (6.12)$$

and to lowest order from the surface equation we have, using (6.10),

$$\rho_s (\partial S_{(0)}/\partial t) = |\nabla S_{(0)}| \mathbf{n} \cdot \mathbf{J}_{(0)} / (1 - C_{(0)}/\rho). \quad (6.13)$$

Finally, recalling that $\mathbf{n} = \nabla S / |\nabla S|$, we obtain

$$\frac{\partial S_{(0)}}{\partial t} = \frac{\nabla S_{(0)} \cdot \mathbf{J}_{(0)}}{(\rho_s - C_{(0)})}. \quad (6.14)$$

This equation coupled with the continuity equation

$$\partial C_{(0)}/\partial t = -\nabla \cdot \mathbf{J}_{(0)} \quad (6.15)$$

and the boundary condition (4.11) provides a complete theory for the study of morphological stability for the case of transport limited growth. Thus we have arrived at the starting point for the classical morphological stability theory of Mullins and Sykerka (1967).

C. DISCUSSION

Morphological stability is an interesting free boundary problem, the latter term referring to the fact that the determination of the location of the boundary is part of the problem to be determined. It seems of great importance in its biological applications. This problem has been considered in materials science where important problems including the shape of precipitate particles and the roughness of the surface of solid deposited from vapors and melts have been studied (Mullins and Sekerka, 1967; Langer and Turski, 1976; Langer, 1976).

It is important to note that crystal anisotropy often plays a very dominant role in the determination of shape and that this effect is not covered by the simple theory presented here. Furthermore, special sites of rapid growth such as skew dislocations may lead to the growth of whiskerlike projections out of an otherwise smooth surface (Ruth and Hirth, 1964). It is possible that the growth rate G can be made anisotropic and heterogeneous accounting for special localized sites, but this will not be developed here. Finally, the theory presented here does not account for the growth of solid mixtures. This can be handled in a manner similar to that presented above, although the results are not presented here for brevity and can be found in Walkind and Segal (1970) and Hasse *et al.* (1978).

It is clear that this area presents a wealth of possibilities for interesting and important nonequilibrium structures in physico-chemical and biological systems.

VII. Mechano-Chemical Phenomena

There are several phenomena involving center of mass motion of the system that is sustained because of the far from equilibrium conditions of the chemical reactions. When chemical reactions are taking place that involve heats of reactions or changes in numbers of moles, it was shown that acoustic modes in gases could become unstable and that such a system would spontaneously emit sound or amplify it as an acoustic pulse passed through such a reacting medium (Toong, 1972; Gilbert *et al.*, 1973). Another type of mechano-chemical coupling apparently occurs in peristaltic motion. Here slow waves of contraction sweep along various organs like the stomach and the large intestine. These motions are believed to be autonomous and

not directly coordinated by the central nervous system. Clearly if a composition wave passes through the tissue comprising such an organ and if the associated concentration changes affect the contractile mechanism, one could readily see how such a peristaltic motion could take place.

A. DESTABILIZATION OF A DAMPED OSCILLATOR BY A CHEMICAL REACTION: MODEL OF INSECT FLIGHT

For the purpose of illustration we consider a simple model of a mechanochemical instability that may, in fact, be of interest in understanding the mechanism of flight of certain insects (Pringle, 1968; Wigglesworth, 1972). It is known that the wing beat rate of some insects is much greater than the maximum rate at which individual nerve signals can be transmitted. For these insects the wing thorax system acts like an oscillator (often a nonlinear click oscillator) with frequency typically close to that of the wing beat frequency of flight. However the question arises as to how can the energy losses due to internal friction and losses to the demands of flight be overcome? In what follows we consider a simple model of a mechanical oscillator that is coupled to a contractile system in such a way that just enough energy is added in each cycle to overcome energy losses. In this model the neural impulses would, for example, serve to change the resonance frequency through the tension of the indirect flight muscles and nonequilibrium conditions, but not trigger individual wing beats.

Consider a harmonic oscillator characterized by a coordinate X with linear damping coefficient γ , frequency ω , and rest position $\bar{X}(Y)$ that depends on the composition of a chemical species Y (specifying the state of the contractile fibrils in the muscle):

$$(d^2X/dt^2) + \gamma(dX/dt) + \omega^2(X - \bar{X}(Y)) = 0. \quad (7.1)$$

The chemical species Y (located within the spring) undergoes a reaction whose rate depends on the extension of the spring and hence on X ,

$$dY/dt = F(X, Y). \quad (7.2)$$

At rest (steady state) the configuration is X^* , Y^* where

$$X^* = \bar{X}(Y^*) \quad (7.3)$$

$$F(\bar{X}(Y^*), Y^*) = 0. \quad (7.4)$$

The question arises under what conditions, if any, will the system spontaneously lapse into auto-oscillation?

Carrying out ordinary linear stability analysis, we can find the stability eigenvalues that answer the above question. The answer is particularly simple in the case where ω is large relative to all the other inverse times in

the system—i.e., γ and those in F . First we expand the stability eigenvalues z in powers of ω^{-1} ,

$$z = \omega\zeta_{-1} + \zeta_0 + \omega^{-1}\zeta_1 + \dots$$

with coefficients ζ_m . Keeping the first two terms in the oscillatory roots z_{\pm} , we have

$$z_{\pm} \approx \pm i\omega + \frac{1}{2}[(\partial F/\partial X)^*(\partial \bar{X}/\partial Y)^* - \gamma].$$

For instability, $\text{Re } z_{\pm} > 0$, we must have

$$(\partial F/\partial X)^*(\partial \bar{X}/\partial Y)^* > \gamma,$$

i.e., the product of the change in rate of reaction with distension times the change in the rest position with the active species concentration (Y) must exceed the damping factor γ . Thus with each cycle the distension changes the concentration of Y which in turn shifts the rest position just enough to give the oscillator a kick to overcome damping.

This simple result is analogous to the results found for the coupling of reaction to acoustic modes (Toong, 1972; Gilbert *et al.*, 1973). There X is replaced by pressure or density and γ by viscosity. The quantity $\partial \bar{X}/\partial \bar{Y}$ is analogous to the heat or volume change of reaction.

The connection of the present model to the problem of insect flight obviously requires a more detailed and realistic analysis of the biological system. However the experiments on flight muscle clearly point out this tendency toward auto-oscillation (Pringle, 1968; Wigglesworth, 1972). Finally, mechano-chemical instabilities appear to play an important role in fibril auto-oscillation in sperm and other systems (Brakaw and Benedict, 1968).

B. REMARKS

It appears that the variety of nonlinear methods have not been applied to problems in mechano-chemical instabilities. Furthermore, biological mechano-chemical (i.e., peristaltic) waves present themselves as interesting and important problems for future research in applied nonlinear analysis.

VIII. Concluding Remarks

The spate of activity over the past decade in the field of physico-chemical instabilities has served to greatly increase our understanding of these phenomena. Perhaps one of the greatest recent contributions has been to put a variety of engineering, biological, geological, and other widely varying problems within a unified framework.

It is important to note that the developments within the macroscopic or phenomenological theory has been paralleled by advances in the fundamental studies in nonequilibrium statistical mechanics of instabilities. Preliminary results along these lines have demonstrated the close analogy of nonequilibrium transitions to various types of equilibrium phase changes (McQuarrie, 1967; Nitzan *et al.*, 1974; Nitzan, Ortoleva, and Ross, 1974b; Keizer, 1975; Malek-Mansour and Nicolis, 1975; Gardiner *et al.*, 1976; Ortoleva and Yip, 1976; Van Kampen, 1976; Oppenheim *et al.*, 1977).

The great wealth of phenomena in chemically reacting systems can be traced for the most part to the almost limitless nonlinear analytical forms that chemical reaction rates may take on and still be consistent with basic physical principles of conservation and symmetry. Thus it should not be a surprise if in the next decade many examples of oscillatory, propagating, and other media are discovered. In fact, the surprise would be if this were not the case.

In light of this I believe that theory in this field will play a very important role in terms of its ability to predict new phenomena and to classify the multiplicity of possibilities according to rather general properties of the phenomenological relations for reaction and transport. An attempt along these lines has been done for chemical waves using catastrophe theory (Feinn and Ortoleva, 1977).

An area of great importance is the application of the theory and concepts of the study of nonlinear physico-chemical phenomena to explain processes in biological, geological, ecological, and other systems. In order to make useful contributions along this line, close collaboration between experimental and theoretical efforts must be made. Not only should the experimental data guide the theorist, but theoretical results should be used as a guide in the design of experiments so that central conceptual points may be resolved. In surveying possible areas of application and from work in progress in our and in other's laboratories, I believe that major advances along these lines are forthcoming in the next few years. And furthermore, there is much more room for other efforts along these lines.

In conclusion, it is a reasonable approximation of reality to assert that "Oh, nonlinear partial differential equations—anything can happen" and I would furthermore add that it is beautiful that it indeed does.

Appendix

A. BIFURCATION ANALYSIS

To introduce the ideas of bifurcation theory we consider a most simple example, that of homogeneous steady-state systems. Let λ be a homogeneous constraint. We wish to study the bifurcation behavior of the steady-

state solutions of the equation

$$dC/dt = \mathcal{R}(C, \lambda) \tag{A.1}$$

as a function of λ . We assume there is a known branch of solutions $C^*(\lambda)$ and rewrite the equation in terms of the deviation from this state. Letting

$$C = C^* + c,$$

we obtain for the steady-state value of c

$$L(\lambda)c + \mathcal{N}(c, \lambda) = 0 \tag{A.2}$$

where

$$L(\lambda) \equiv (\partial \mathcal{R} / \partial C)_{C^*(\lambda)} \tag{A.3}$$

$$\mathcal{N} \equiv \mathcal{R} - Lc. \tag{A.4}$$

Note that \mathcal{N} is of order c^2 or higher and that for the present case of a single variable that if $L(\lambda)$ passes through zero at a critical value λ_c , then the state C^* is marginally stable there. We assume that C^* becomes unstable beyond λ_c and let

$$z' \equiv (dL/d\lambda)_{\lambda_c} > 0. \tag{A.5}$$

We expect that in the vicinity of λ_c we might have the onset of a new branch of steady states. This is indeed the case under the assumptions given thus far. We introduce a parameter A measuring the amplitude of the new bifurcating branch and expand c and λ in A :

$$c = \sum_{n=1}^{\infty} c_n A^n \tag{A.6}$$

$$\lambda = \lambda_c + \sum_{n=1}^{\infty} \lambda_n A^n. \tag{A.7}$$

Substitution into (A.2) yields to lowest order

$$L(\lambda_c)c_1 = 0 \tag{A.8}$$

which is automatically satisfied since $L(\lambda_c) = 0$ when the steady state C^* is marginally stable at λ_c . To second order we have

$$\lambda_1 z' c_1 + bc_1^2 = 0, \quad b \equiv \frac{1}{2}(\partial^2 \mathcal{N} / \partial c^2)_{c=0, \lambda=\lambda_c}. \tag{A.9}$$

If $b \neq 0$, we have a new branch of states (i.e., $c_1 \neq 0$)

$$c_1 = -\lambda_1 z' / b \tag{A.10}$$

since $z' \neq 0$ by assumption. Thus the onset of a new branch (solution) requires both a loss of stability of one branch and a condition on the nonlin-

earity ($b \neq 0$) in the vicinity of the marginal stability point. To complete the theory we must make a more specific assumption about the relation between λ and A . A convenient choice is to let $\lambda_n = 1$ for the first value of n for which λ_n may be chosen to be nonzero. Since this is the case for λ_1 , we put $\lambda_1 = 1$ and obtain

$$c \underset{\lambda \rightarrow \lambda_c}{\sim} -(z'/b)(\lambda - \lambda_c). \quad (\text{A.11})$$

The new branch of steady states bifurcates with a critical index of one in this case since c is linear in $(\lambda - \lambda_c)$. The new branch $C^* + c$ transverses the reference branch C^* at λ_c . Furthermore, by performing linear stability analysis from the new state as calculated from (A.11), one may easily show that the small deviations δc from the new state obey

$$d\delta c/dt = -z'(\lambda - \lambda_c)\delta c \quad (\text{A.12})$$

and hence while the reference branch C^* is stable for $\lambda < \lambda_c$, the new branch is stable for $\lambda > \lambda_c$. Thus the two branches exchange stability.

Consider the simple example for which $\mathcal{R} = \lambda C - C^2$. The system has a steady state at $C^* = 0$. Here $L = \lambda$ and $\mathcal{N} = -C^2$. Thus $z' = 1$, $b = -1$, and the above theory predicts a new branch will bifurcate at $\lambda_c = 0$ in the form $c = \lambda$ which is obviously correct for this simple case.

The simple theory presented here for illustrative purposes may be extended to multicomponent systems and to spatio-temporally varying behavior and may be applied to the theory of homogeneous chemical oscillations [see Hopf (1942) and the Appendix of DelleDonne and Ortoleva (1977)], chemical waves (Kopell and Howard, 1973; Ortoleva and Ross, 1974; Hanusse *et al.*, 1978) and static structures in bounded (Achmuty and Nicolis, 1975; Keener, 1976) and unbounded media and for surface localized phenomena [see Ortoleva (1974, unpublished) and Section V,C,1].

B. LIMIT-CYCLE PERTURBATION THEORY

We now discuss a perturbation theory for systems with a homogeneous limit-cycle oscillation. Let the equation

$$d\chi_c/dt = \mathcal{R}[\chi_c] \quad (\text{B.1})$$

have a stable limit-cycle solution χ_c with frequency ω_c . Then what is the effect of adding a correction term γG to the equation? Thus we seek C as a solution to

$$dC/dt = \mathcal{R}[C] + \gamma G[C] \quad (\text{B.2})$$

and in particular seek periodic solutions in the limit as $\gamma \rightarrow 0$. First it is convenient to work with 2π -periodic functions. We let

$$\tau \equiv \omega(\gamma)t \quad (\text{B.3})$$

where $\omega(\gamma)$ is the γ -dependent frequency. This γ dependence of ω is important since the coefficients of the series development of the 2π -periodic solutions $\psi(\tau)$ to (B.2),

$$\psi = \chi_c(\tau) + \sum_{n=1}^{\infty} \psi_n \gamma^n, \tag{B.4}$$

may be determined only if a solubility condition involving the expansion coefficients ω_n ,

$$\omega = \omega_c + \sum_{n=1}^{\infty} \omega_n \gamma^n, \tag{B.5}$$

is satisfied. To lowest order in γ we obtain

$$\omega_c(d\psi_0/d\tau) = \mathcal{R}[\psi_0] \tag{B.6}$$

which is known to have a limit-cycle solution χ_c .

In next order we find

$$[\omega_c(d/d\tau) - \Omega(\tau)]\psi_1 = -\omega_1(d\psi_0/d\tau) \tag{B.7}$$

$$\Omega(\tau) \equiv (\partial\mathcal{R}/\partial C)_{C=\chi_c(\tau)}. \tag{B.8}$$

However we note that $[\omega_c(d/d\tau) - \Omega]d\psi_0/d\tau = 0$ and hence ψ_1 can only be determined as a 2π -periodic function if the right-hand side of (B.7) is appropriately orthogonal to $(d\chi_c/d\tau)$. Hence $\omega_1 = 0$ and thus the frequency shift due to $|\gamma| > 0$ occurs in order γ^2 . The coefficient ω_2 is then determined in the next order by assuming that the right-hand side of

$$[\omega_c(d/d\tau) - \Omega]\psi_2 = -\omega_2(d\psi_0/d\tau) + (\partial^2\mathcal{R}/\partial C^2)_{C=\chi_c(\tau)}\psi_1\psi_1 \tag{B.9}$$

is orthogonal to the adjoint eigenvector f corresponding to $d\chi_0/d\tau$ (see below). We obtain

$$\omega_2 = \frac{1}{2\pi} \int_{-\pi}^{\pi} [f(\tau), (\partial^2\mathcal{R}/\partial C^2)_{C=\chi_c(\tau)}\chi_1(\tau)\chi_2(\tau)] d\tau \tag{B.10}$$

where (A, B) implies a sum over components and f is the solution of

$$\omega_c(df/d\tau) = \Omega^T(\tau)f(\tau) \tag{B.11}$$

where Ω^T is the transpose of Ω . The function f is 2π periodic and is normalized such that

$$\frac{1}{2\pi} \int_{-\pi}^{\pi} (f, d\chi_c/d\tau) d\tau = 1. \tag{B.12}$$

This type of expansion has been applied to develop spatio-temporal solutions to reaction diffusion equations with limit-cycle kinetics. With it both

planar and more complex geometric chemical waves have been studied as long wavelength extensions of the limit-cycle solution [see (Kopell and Howard, 1973; Ortoleva and Ross, 1974; Hanusse *et al.*, 1978), and Section IV.C].

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