MOLECULAR MOVEMENTS
AND CHEMICAL REACTIVITY
AS CONDITIONED BY MEMBRANES
ENZYMES AND OTHER MACROMOLECULES

XVIth SOLVAY CONFERENCE ON CHEMISTRY
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VOLUME XXXIX
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XVIth SOLVAY CONFERENCE ON CHEMISTRY

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VOLUME XXXIX
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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more, and be broadly educated with respect to a large domain of science, has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, thus the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, which field we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest, and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

ILYA PRIGOGINE

STUART A. RICE
PREFACE

The papers and discussions in this volume were presented at the XVIth Solvay Conference on Chemistry held at the Free University of Brussels from November 22 to November 26, 1976.

The main objective of the Scientific Committee was to stress in this meeting the structure-environment relationships that condition the chemical reactivity in molecular and supramolecular assemblies such as polymers, enzymes, and membranes. Remarkable achievements have been made over the last few years. They demonstrate the subtleties of the molecular events that take place in such systems and account for highly specific and coordinated processes of catalysis, transport, and recognition. In usual chemical systems, reactivity and reaction rate are simple functions of the molecular species involved and of their relative abundance. In processes involving macromolecules or supramolecular organizations the dynamic behavior is controlled by a much more complex interplay of short and long range interactions, be it at the intramolecular or supramolecular level. Furthermore, these interactions are at the heart of the fascinating feedback mechanisms by which it becomes possible, under nonequilibrium conditions, for some chemical systems to come to "life," that is, to self-organize and adapt their functional, spatial, and temporal order to their environment.

To explore these mechanisms is of fundamental importance and interest. This field is at present giving rise to great expectations also from the technological point of view. A better understanding of the problems involved is indeed needed for the successful realization of many progresses envisioned in medical and industrial research.

These problems therefore are great challenges to physicists, chemists, and biologists. We hope that this volume will help in finding the road to their solution.

Great thanks are due to Professors A. R. Ubbelohde, S. Claesson, and V. Prelog for their decisive role in the organization and running of the conference.

Brussels, Belgium
April 1978

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MOLECULAR MOVEMENTS AND CHEMICAL REACTIVITY AS CONDITIONED BY MEMBRANES, ENZYMES AND OTHER MACROMOLECULES

ADVANCES IN CHEMICAL PHYSICS
VOLUME XXXIX
COUPLING BETWEEN DIFFUSION AND CHEMICAL REACTIONS

I. PRIGOINE and R. LEFEVER

Service de Chimie-Physique II Brussels, Belgium

I. INTRODUCTION

One of the main themes of this volume is the influence of the environment on chemical reactivity. Such a question is of special interest for chemical systems in far from equilibrium conditions. It is today well known that, far from equilibrium, chemical systems involving catalytic mechanisms may lead to dissipative structures.\textsuperscript{1,2} It has also been shown—and this is one of the main themes of this discussion—that dissipative structures are very sensitive to global features characterizing the environment of chemical systems, such as their size and form, the boundary conditions imposed on their surface, and so on. All these features influence in a decisive way the type of instabilities, called bifurcations, that lead to dissipative structures.

Far from equilibrium, there appears an unexpected relation between chemical kinetics and the space-time structure of reacting systems. It is true that the interactions that determine the values of the relevant kinetic constants and transport coefficients result from short-range interactions (valency forces, hydrogen bounds, Van der Waals forces). However, the solutions of the kinetic equations depend in addition on global characteristics. This dependence, which near equilibrium on the thermodynamic branch is trivial, becomes decisive in chemical systems working under far from equilibrium conditions. For example, the occurrence of dissipative structures generally requires that the system’s size exceed some critical value, the latter being a complex function of the parameters describing the reaction-diffusion processes. Therefore chemical bifurcations imply long-range order involving the system as a whole.

We review in Section II the basic results of nonequilibrium thermodynamic stability theory and recall the thermodynamic and kinetic conditions necessary to the occurrence of cooperative coherent behaviors in chemical systems. We briefly indicate some known experimental systems that meet these requirements and in which dissipative structures
may be observed. Throughout these notes we focus on qualitative rather than quantitative aspects and draw our conclusions from the study of idealized models involving a minimal number of ingredients. The prototype of these models is the so-called Brusselator. It corresponds to a reaction chain involving two chemical intermediates and a trimolecular step. This is the simplest stoichiometric reaction (in two variables systems) having an instability of the thermodynamic branch. The Brusselator reads

\begin{align}
A & \rightarrow X \\
2X + Y & \rightarrow 3X \\
B + X & \rightarrow Y + D \\
X & \rightarrow E
\end{align}

where \(X\) and \(Y\) are the intermediate composition variables and \(A, B, D, E\) the initial and final products whose concentration remains constant in time. Many remarkable properties of this model are shared qualitatively by numerous experimental (both biological and nonbiological) systems in which dissipative structures have been described.

In Sections III to V we analyze the properties of dissipative structures in one-dimension reaction mediums. As shown originally by Auchmuty and Nicolis, Herschkowitz-Kaufman, Keener, and Mahar and Matkowsky, the methods of bifurcation theory permit us to evaluate the new regimes that bifurcate from a homogeneous equilibrium type of steady state as well as regimes that branch off an already organized state and correspond to secondary bifurcations. We see that a great variety of solutions may be observed by slight modifications in boundary conditions or size parameters. Furthermore, as is also shown in Section V, this multiplicity increases and qualitatively new behaviors appear when chemical and diffusion processes take place in two dimensions.

Bifurcation theory can only provide information on the solutions that appear in the neighborhood of a point of bifurcation and whose amplitude goes to zero at that point. Other approximate analytical methods, like singular perturbation theory, have permitted the calculation of solutions of large amplitude, but for conditions that postulate large differences in the values of the diffusion coefficients of the reacting species. Only under special conditions can one go beyond the limitations of such descriptions and find an exact solution to the steady-state problem in general. These conditions are often met in one-variable systems. Examples of both first- and second-order phase transitions in such systems have been discussed by Schlögl. In Section VI we

* More recently a remarkably simple experimental example of spatial order in a one-variable system that presents an electrothermal instability has been analyzed by Bedaux et al.
Consider a simplified version of the Brusselator, which belongs to a class of systems described by equations of the form:

\[ \frac{dx}{dt} = f(x, y) + D_1 \frac{\partial^2 x}{\partial r^2} \quad (2a) \]

\[ \frac{dy}{dt} = cf(x, y) + D_2 \frac{\partial^2 y}{\partial r^2} \quad (2b) \]

Although these systems involve two variables, their steady-state solutions can be calculated in general and a more complete mathematical analysis of dissipative structures is possible. From a practical point of view it is interesting to note that systems obeying equations of the form (2) may be found in artificial membrane reactors. Examples are presented by D. Thomas in this volume.

II. THERMODYNAMIC AND KINETIC ASPECTS OF SELF-ORGANIZATION

In open systems the total entropy variation

\[ dS = d_\text{S} + d_\text{s} \quad (3) \]

decomposes into an entropy flow \( d_\text{S} \) exchanged with the environment and an entropy production \( d_\text{s} \) due to the irreversible processes. The explicit evaluation of (3) yields the balance equation

\[ \frac{d_\text{s}}{dt} = \int \sum J_\rho X_\rho \, dV = \frac{\partial S}{\partial t} + \phi[S] \geq 0 \quad (4) \]

where the sign of \( \frac{d_\text{s}}{dt} \) is imposed by the second law of thermodynamics. The \( J_\rho \)'s and \( X_\rho \)'s are the conjugate thermodynamic fluxes and forces of the irreversible processes. The flow term \( \phi[S] \) corresponds to the entropy flux across the boundaries. Equation (4) has two immediate consequences:

1. Any decrease of the entropy in the system \( \left[ (\partial S/\partial t) < 0 \right] \) requires a negative entropy flux with the environment i.e., the system has to be open and \( d_\text{s}/dt = -\phi[S] < 0 \).
2. Once a state of low entropy has been achieved it can only be sustained in an open system, the condition \( \partial S/\partial t = 0 \) requiring necessarily

\[ \int \sum J_\rho X_\rho \, dV = \phi[S] > 0 \quad (5) \]

We thus see that nonequilibrium may be a source of order. Two kinds of situations and two kinds of order must then be distinguished. In the first place, we have situations that correspond to slight deviations from an equilibrium state between the system and its environment. In that case
the thermodynamic forces $X_\rho$ and fluxes $J_\rho$ obey linear relations

$$J_\rho = \sum_\alpha L_{\alpha \rho} X_\alpha$$

(6)

in which the phenomenological coefficients $L_{\alpha \rho}$ are constants satisfying Onsager's reciprocity relations $L_{\alpha \rho} = L_{\rho \alpha}$. This guarantees the existence of a state function, the entropy production, that has the properties of a potential. Accordingly,

$$\frac{\partial X_i}{\partial t} = -\frac{\delta P(X_i)}{\delta X_i} ; \quad P = \frac{dS}{dt}$$

(7)

and

$$\frac{\partial P}{\partial t} = \sum_i \frac{\delta P}{\delta X_i} \frac{\partial X_i}{\partial t} = -\sum_i \left( \frac{\delta P}{\delta X_i} \right)^2 \leq 0$$

(8)

Under those conditions $P$ behaves as a Lagrangian in mechanics. Furthermore, as $P$ is a nonnegative function for any positive value of the concentrations $\{X_i\}$, by a theorem due to Lyapounov, the asymptotic stability of nonequilibrium steady states is ensured (theorem of minimum entropy production). These steady states are thus characterized by a minimum level of the dissipation; in the linear domain of nonequilibrium thermodynamics the systems tend to states approaching equilibrium as much as their constraints permit. Although entropy may be lower than at equilibrium, the equilibrium type of order still prevails. The steady states belong to what has been called the thermodynamic branch, as it contains the equilibrium state as a particular case.

Beyond the domain of validity of the minimum entropy production theorem (i.e., far from equilibrium), a new type of order may arise. The stability of the thermodynamic branch is no longer automatically ensured by the relations (8). Nevertheless it can be shown that even then, with fixed boundary conditions, nonequilibrium systems always obey to the inequality

$$\frac{d_P}{dt} = \int \sum_\rho J_\rho \frac{dX_\rho}{dt} \leq 0$$

(9)

![Fig. 1. Entropy production as a function of some concentration $X_i$ (in the linear range). Here $P_0$ and $X_s$ are the steady-state values of $P$ and $X_i$.](image-url)
This is the so-called *evolution criterion*. The equality sign applies only to steady states. Two cases may then arise:

1. Here \( d_xP/dt = d\phi/dt \leq 0 \) is reducible to the total differential of some scalar potential \( \phi \) (kinetic potential). We have a generalization of the behavior found near equilibrium with the important difference that the steady-state solutions are no longer necessarily unique for a set of values of the constraints.

2. In this case \( d_xP/dt \) cannot be reduced to an exact differential and the criterion simply expresses that in the course of time the variation of the thermodynamic forces tends to diminish the entropy production.

A stability criterion for nonequilibrium steady states can readily be deduced from (9). Suppose that for all small departures from the steady state considered we have

\[
\delta x P \geq 0 \quad \text{or} \quad \int \left[ \sum_p \delta I_p \delta X_p \right] dV \geq 0
\]  

where the \( \delta I_p, \delta X_p \) are excess quantities evaluated around the reference steady state. Then, as a consequence of inequality (9), asymptotic stability with respect to small deviations is ensured. Far from equilibrium, however, negative terms in the sum (10) may become dominant and, as represented in Fig. 2, an instability of the thermodynamic branch may appear. As a result, beyond some threshold value of the deviation from equilibrium, there may be a spontaneous evolution toward a new state of organization with properties completely different from those of the thermodynamic branch. This opens a new field, nonequilibrium physical chemistry. These transitions to a new type of dynamic structure are very similar to the usual equilibrium transitions. However, let us stress again that these new types or organization of matter, called dissipative structures, can persist only if the coupling with the outside world through flows of matter and energy is sufficiently strong.

Let us mention a few relevant examples:

One of the best understood kinds of chemical instability that leads to

![Fig. 2. Stability of the thermodynamic branch as a function of some parameter \( \lambda \) that measures the chemical system's distance from equilibrium. In the linear range (i.e., for \( 0 \leq \lambda \leq \lambda^* \)) the steady states belong to the thermodynamic branch (a) and are stable. Beyond this domain there may exist a threshold point \( \lambda_c \) at which a new stable nonequilibrium branch of solutions (b) appears while the thermodynamic branch becomes unstable.](image-url)
temporal order involves allosteric enzymes regulated by a positive feedback of the reaction product.\textsuperscript{24} The enzyme phosphofructokinase is a representative system of this type and its catalytic properties can be summarized in Fig. 3.\textsuperscript{26} The enzyme is part of the glycolytic chain; $\sigma_1$ and $k_5$ stand, respectively, for the rate of supply of ATP and the rate of product decay (assumed to take place through a monomolecular consumption step). The product ADP binds preferentially to the active form of the enzyme; as a result, its accumulation displaces the conformational equilibrium in favor of the active form and promotes a positive feedback effect. When some conditions on the kinetic constants are satisfied, this feedback can appropriately be described by a trimolecular step.\textsuperscript{11,26} A vast class of instabilities in enzymatic systems arises from the pH dependence of enzymatic activity. In general, protein molecules contain a number of ionizing groups, such as (\text{--COOH}), which can be ionized to give the negatively charged (\text{--COO}\textsuperscript{-}) ion, and (\text{--NH}_2), which can add on a proton to give (\text{--NH}_3\textsuperscript{+}). The active enzyme may be represented as in Fig. 4; then addition of acid or base to the active enzyme may be depicted as in Fig. 5, or schematically

$$EH_2 \xrightarrow{OH^-} EH \xrightarrow{H^+} E$$  \hspace{1cm} (11)

The enzymatic activity versus pH is thus generally a bell-shaped curve as in Fig. 6. An autocatalytic effect may appear when the reaction products have an acid-base effect (often the case). A simple example is the glucose oxidase reaction, shown in Fig. 7. Notably, the rate versus product (H\textsuperscript{+}) curve indicates an autocatalytic effect on the alkaline branch, that is, for $pH > pH_0$ (see Fig. 6). Systems presenting analogous properties have been studied by R. Caplan et al.\textsuperscript{27} and we also learn more about them from D. Thomas in this volume.

Fig. 4. Enzyme in active form.

Fig. 5. Schematic representation of the acid-base equilibrium of enzymes.
COUPLING BETWEEN DIFFUSION AND CHEMICAL REACTIONS

III. GENERAL FORMULATION

The systems considered here are isothermal and at mechanical equilibrium but open to exchanges of matter. Hydrodynamic motion such as convection are not considered. Inside the volume $V$ of Fig. 8, $N$ chemical species may react and diffuse. The exchanges of matter with the environment are controlled through the boundary conditions maintained on the surface $S$. It should be emphasized that the consideration of a bounded medium is essential. In an unbounded medium, chemical reactions and diffusion are not coupled in the same way and the convergence in time toward a well-defined and asymptotic state is generally not ensured. Conversely, some regimes that exist in an unbounded medium can only be transient in bounded systems. We approximate diffusion by Fick’s law, although this simplification is not essential. As a result, the concentration of chemicals $X_i$ ($i = 1, 2, \ldots, r$ with $r \leq N$) will obey equations of the form

$$\frac{\partial X_i}{\partial t} = \sum_p v_{pl}v_p(\{X_j\}) + D_i \frac{\partial^2 X_i}{\partial z^2} \quad (i = 1, \ldots, r; \quad j = 1, \ldots, N) \quad (12)$$
where $v_p$ is the rate of the $p$th chemical reaction and $v_{pi}$ is the corresponding stoichiometric coefficient of $X_i$. Two types of boundary conditions are considered on the surface $S$: Dirichlet conditions
\begin{equation}
\{X_1, \ldots, X_r\} = \{\text{const}\}_s
\end{equation}
or Neumann boundary conditions
\begin{equation}
\{n \cdot \nabla X_1, \ldots, n \cdot \nabla X_r\} = \{\text{const}\}_s
\end{equation}
These conditions together with those concentrations $X_i$ ($i = N - r, \ldots, N$) whose value is maintained constant inside $V$ constitute the constraints applied to the system by the environment. Only for some particular set of values of these constraints is an equilibrium state realized between $V$ and its external world. Although we refer here only to chemical systems, the class of phenomena obeying parabolic differential equations of the form (12) is much broader. A discussion of or references to self-organization phenomena in other fields (e.g., ecology, laser theory, or neuronal networks) can be found in Ref. 2.

In fact, the variety of phenomena that may be described by this sort of reaction diffusion equation is properly amazing. Some order can be brought into the results by considering as the "basic solution" the one corresponding to the thermodynamic branch. Other solutions may then be obtained as successive bifurcations from this basic one, or as higher-order bifurcations from a nonthermodynamic branch, taking place when the distance from equilibrium is increased. Investigations along such lines of thought have been made by Ortoleva and Ross and inside our group. On the other hand, the relation between chemical instabilities and the nature of the catalytic properties appearing in the reaction scheme has been investigated by Tyson.

As we have mentioned, in the last two years much work has been done on the reaction scheme (1) from the point of view of the mathematical study of bifurcations and numerical computations. For this reason we start with a review of these results.

**IV. DISSIPATIVE STRUCTURES IN A SIMPLE MODEL SYSTEM**

Let us go back to the Brusselator (1). In a one-dimensional medium of unit length the reaction-diffusion equations (12) become
\begin{equation}
\begin{aligned}
\frac{\partial X}{\partial t} &= A + X^2 Y - (B + 1)X + D_1 \frac{\partial^2 X}{\partial z^2} \\
\frac{\partial Y}{\partial t} &= BX - X^2 Y + D_2 \frac{\partial^2 Y}{\partial z^2}
\end{aligned}
\end{equation}
We take the boundary conditions

\[ X(0, t) = X(1, t) = A; \quad Y(0, t) = Y(1, t) = \frac{B}{A} \]  

(15)

These values correspond to the homogeneous steady-state solution of (14), which belongs to the thermodynamic branch. We first determine the conditions under which this solution becomes unstable and subsequently the properties of the new regimes that branch off at the point of instability.

A. Linear Stability Analysis

Setting

\[
\begin{pmatrix}
X \\
Y
\end{pmatrix}
= \begin{pmatrix}
A \\
B \\
A
\end{pmatrix} + \begin{pmatrix}
x(z, t) \\
y(z, t)
\end{pmatrix}
\]

(16)

with

\[
\begin{array}{c}
\frac{x}{A}, \quad \frac{y}{B} \ll 1 \\
\frac{x}{A}
\end{array}
\]

and \( x(0) = x(1) = y(0) = y(1) = 0 \)

the linearization of (14) yields

\[
\begin{pmatrix}
\frac{\partial x}{\partial t} \\
\frac{\partial y}{\partial t}
\end{pmatrix}
= L \begin{pmatrix}
x \\
y
\end{pmatrix}
\]

(17)

where \( L \) is the differential matrix operator

\[
L = \begin{pmatrix}
D_1 \frac{d^2}{dz^2} + B - 1 & A^2 \\
-B & D_2 \frac{d^2}{dz^2} - A^2
\end{pmatrix}
\]

(18)

The solutions of (17) satisfying the boundary conditions are of the form

\[
\begin{pmatrix}
x(z, t) \\
y(z, t)
\end{pmatrix}
= \begin{pmatrix}
x_0 \\
y_0
\end{pmatrix} e^{\omega_n t} \sin n\pi z
\]

(19)

where \( \omega_n \) is the eigenvalue of (18) corresponding to the wave number \( n \). In order for the homogeneous steady-state solution to be unstable it is sufficient that the real part of some particular \( \omega_n \) be positive. The critical point at which the exchange of stability takes place is thus determined.
from the condition

\[
\text{Re} \, \omega_n = 0 \tag{20}
\]

This exchange of stability may correspond to the branching of a time periodic solution when

\[
A^2 + 1 + (n\pi)^2(D_1 + D_2) < B < A^2 + 1 - (n\pi)^2(D_2 - D_1) + 2A[1 - (n\pi)^2(D_2 - D_1)]^{1/2} \tag{21}
\]

or of a new steady-state solution when

\[
B > B(n) = \left[1 + \frac{D_1}{D_2} A^2 + \frac{A^2}{D_2(n\pi)^2} + D_1(n\pi)^2 \right] \tag{22}
\]

These conditions have been plotted in Figs. 9 and 10 for two values of the

Fig. 9. Linear stability diagram illustrating (21). The bifurcation parameter $B$ is plotted against the wave number $n$. (a) and (b) are regions of complex eigenvalues $\omega_n$; (b) shows region corresponding to an unstable focus; (c) region corresponding to a saddle point. The vertical lines indicate the allowed discrete values of $n$. $A = 2$, $D_1 = 8 \cdot 10^{-3}$, $D_2 = 1.6 \cdot 10^{-3}$. 
COUPLING BETWEEN DIFFUSION AND CHEMICAL REACTIONS

Fig. 10. Linear stability diagram illustrating the branching of a new inhomogeneous steady-state solution. The regions (a), (b), (c) are defined as in Fig. 9. \( A = 2; \, D_1 = 1.6 \cdot 10^{-3}, \, D_2 = 8 \cdot 10^{-3} \). The critical mode \( \mu \) is the integer that gives to \( B(n) \) its minimal value \( B_c \).

ratio of diffusion coefficients \( D_2/D_1 \). It is seen that when this ratio increases (Fig. 10), we first encounter (for increasing values of \( B \)) the critical point (22) suggesting the appearance of an inhomogeneous pattern of concentration. This situation as well as the one corresponding to Fig. 9 has been studied analytically by the methods of bifurcation theory.\textsuperscript{13,14} We shall limit our analysis here to the branching of steady-state solutions and report in the next section some interesting numerical results on time periodic solutions in a one- and two-dimensional reacting medium.

The surprising result we would like to emphasize here is that quite different properties arise depending solely on the symmetry characteristics of the critical mode \( n \). It is clear from Fig. 10 that there exists a critical mode \( \mu \) for which \( B(n) \) assumes its minimal value \( B_c(n) \). We shall proceed to evaluate the steady-state solutions branching off near this critical point. Inserting the decomposition (16) into the rate equations and keeping the nonlinear contributions in \( x \) and \( y \), we obtain

\[
L_c \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -h(x, y) \\ h(x, y) \end{pmatrix}
\]

(23)
where $L_c$ is the operator (18) evaluated for the critical mode $\mu$ and

$$h(x, y) = (B - B_c)x + 2Ax y + \frac{B}{A} x^2 + x^2 y$$  \hfill (24)

The vector $\begin{pmatrix} x \\ y \end{pmatrix}$ is a solution of (23), provided $L_c$ satisfies the solubility condition

$$\left( x^+, y^+ \right) \begin{pmatrix} h \\ -h \end{pmatrix} = \int_0^1 dz (y^+ - x^+) h(x, y) = 0$$  \hfill (25)

where $(x^+, y^+)$ is the eigenfunction corresponding to a null eigenvalue of the adjoint of $L_c$. Both $L_c$ and its adjoint have the same critical wave number $\mu$ whereas the amplitudes $(x_0^+, y_0^+)$ and $(x_0, y_0)$ are in general different. In order to calculate the solutions explicitly we introduce the expansions

$$\begin{pmatrix} x \\ y \end{pmatrix} = \epsilon \begin{pmatrix} x_0 \\ y_0 \end{pmatrix} + \epsilon^2 \begin{pmatrix} x_1 \\ y_1 \end{pmatrix} + \cdots$$  \hfill (26)

$$B - B_c = \gamma = \epsilon \gamma_1 + \epsilon^2 \gamma_2 + \cdots$$  \hfill (27)

into (23) and on identifying terms with equal powers of $\epsilon$, we obtain the system of equations

$$L_c \begin{pmatrix} x_k \\ y_k \end{pmatrix} = \begin{pmatrix} -a_k \\ a_k \end{pmatrix}, \quad 0 \leq k \leq \infty$$  \hfill (28)

The validity of the solubility condition (25) to each order [i.e., for each $a_k(z)$] leads to the determination of the coefficients $\gamma_i$ and permits us to express $\epsilon$ in terms of $B - B_c$ from (27). The explicit form of the bifurcating solution is then obtained by substituting $\epsilon$ as well as $\begin{pmatrix} x_i \\ y_i \end{pmatrix}$ of the successive approximations of (23) into (26). The results can then be summarized as follows.

If the critical wave number $\mu$ is even, one finds

$$x(z) = \pm \left( \frac{B - B_c}{\phi} \right)^{1/2} \sin \mu \pi r - \frac{B - B_c}{\phi} \frac{8(\mu \pi)^2}{\pi^2 D_1 A} \times \left[ 2[D_1(\mu \pi)^2 + 1] - B_c \right] \sum_{n, odd} \frac{n}{(n^2 - \mu^2)^2} \frac{1}{n^2 - 4\mu^2} \sin n \pi z$$  \hfill (29)

and a similar expression for $y(z)$. The function $\phi$ involves $A$, $D_1$, $B_c$, and $\mu$. Depending on its sign, two types of bifurcation diagram are obtained.

When $\phi > 0$ the amplitude of the new solution grows in the supercritical region $B > B_c$ as $(B - B_c)^{1/2}$. Furthermore, these solutions possess the