

Imperfect Bifurcations and Spatial Structures in Dissipative Systems

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One-dimensional reaction-diffusion equations associated with the trimolecular model of Prigogine and Lefever ("Brusselator") are analyzed. A physical description of possibilities of keeping concentrations of initial components constant is discussed. It is shown that the problem considering diffusion of initial components gives rise to an imperfect bifurcation problem. The diffusion equations have been solved numerically by a continuation procedure for the fixed and zero flux boundary conditions. The analysis indicates that the models including diffusion of all reacting components do not admit an occurrence of trivial solutions. These models, as a result, also exclude the possibility of primary bifurcations. The models which consider diffusion of the initial components suppress the number of possible solutions of governing equations. These models may also predict both symmetric and asymmetric states. Apparently this type of models is more suitable for prediction of patterns of spatial organization in growth. Since the number of possible profiles is strongly reduced this principle may lead to a more deterministic way of an evolution process. Symmetric profiles occurring on an isola cannot be reached by an evolution process unless a large perturbation is imposed on the system.

1. Introduction

Over twenty years ago Turing [1] offered a possible explanation how structure may arise in living beings. Turing studied a mathematical model of a growing embryo and suggested that "a system of chemical substances called morphogens, reacting together and diffusing through a tissue is adequate to account for the main phenomena of morphogenesis. Such a system, although it may originally be quite homogeneous, may later develop a pattern of structure due to an instability of homogeneous equilibrium, which is triggered off by random disturbances". The idea of a structure arising as a sequence of instabilities was proposed by the Brussel school of Prigogine who suggested a simplified model, frequently in the literature referred to as the "Brusselator", to illustrate this concept [2]. As a result, the development of the theory of dissipative structures was a rediscovery of the importance of autocatalysis, developed by Lotka [3] seventy years ago for possible explanation of the genesis of spatial forms and structures in living organisms. Prigogine and Nicolis [2] termed the differentiated structures occurring in a reaction-diffusion system "dissipative structures". Evidently, under certain circumstances the usual equilibrium state of a chemical reaction may be unstable with respect to small perturbations and a spatially non-uniform

steady state appears ("symmetry-breaking instability") [4, 5]. Since the classical paper by Prigogine and Nicolis in 1967 [5] a sizeable number of papers on this subject has been published by various authors.

For the "Brusselator" chemical network Herschowitz-Kaufman et al. [6–8] presented a couple of examples of results of numerical solution of the transient reaction-diffusion equation. They have calculated multiple stable solutions for particular values of the governing parameters. A slight change of initial conditions for the relevant parabolic equations very often resulted in widely different steady state profiles. As a result, it was not possible to determine how many solutions exist for given values of the parameters.

Kubicek und Marek in a series of papers [9–12] took advantage of the continuation approach which made it possible to draw a complete bifurcation diagram. They were able to determine all spatial profiles which can exist for given values of the parameters. These authors studied the Brusselator reaction [10], an enzymatic reaction [9] and a reaction describing metabolism of low molecular thiols and proteins [11]. MacPhail et al. [13] studied also the steady state problem for the Brusselator reaction schema, however, they have not been certain how many solutions for a given set of parameters actually exist.

It should be noted however that almost all authors considered the initial components A and B somehow maintained uniformly, so that they can be

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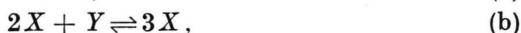
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treated as externally determined parameters. An exception is the paper [8]. Herschkowitz-Kaufman [8] indicated on calculated examples that if diffusion of A is considered the space structures still may exist. Schaeffer and Golubitsky [14] stated that from the point of view of bifurcation analysis further complications in the model would not lead to new behavior.

In this paper we are going to analyze the effect of diffusion of A systematically. A detailed physical discussion of possible maintaining uniform concentration of A and B is presented. The Schaeffer and Golubitsky's theory of an imperfect bifurcation is adopted to analyze qualitatively the Brusselator model. Numerical results are reported both for the constant and zero flux boundary conditions. The calculated results indicate that diffusion of A gives rise to a closed curve (isola). The main result of this study is the fact that the diffusion of A strongly suppresses the number of solutions; for very low values of the diffusion coefficient D_A the isola disappears.

2. Governing Equations

In this paper we consider the one-dimensional reaction-diffusion equations associated to the so called tri-molecular model of Prigogine and Lefever [4], also known as the "Brusselator". The Brusselator corresponds to a single trimolecular scheme:



It is assumed that all forward kinetic constants are set to unity and the inverse reaction rates are neglected. If a bounded one-dimensional medium is assumed, the governing equations describing the reaction and diffusion transport are:

$$\frac{\partial A}{\partial t} = -A + D_A \frac{\partial^2 A}{\partial z^2}, \quad (1)$$

$$\frac{\partial X}{\partial t} = A + X^2 Y - (B + 1)X + D_X \frac{\partial^2 X}{\partial z^2}, \quad (2)$$

$$\frac{\partial Y}{\partial t} = BX - X^2 Y + D_Y \frac{\partial^2 Y}{\partial z^2}, \quad (3)$$

$$\frac{\partial B}{\partial t} = -BX + D_B \frac{\partial^2 B}{\partial z^2}. \quad (4)$$

Two types of boundary conditions for X and Y may be considered:

a) zero flux boundary conditions

$$z = 0, L; t > 0, \partial X / \partial z = \partial Y / \partial z = 0; \quad (5)$$

b) fixed boundary conditions

$$z = 0, L; t > 0, X = X_0 \text{ and } Y = Y_0. \quad (6)$$

For the components A and B only the fixed boundary conditions will be considered here, i.e.:

$$z = 0, L; t > 0, A = A_0 \text{ and } B = B_0. \quad (7)$$

Boundary conditions of the third order will be considered in our next paper [15].

Prigogine et al. [2, 4, 5] and Kubicek and Marek [10] solved the case $D_A \rightarrow \infty$ and $D_B \rightarrow \infty$. For this particular case the concentrations of A and B are constant across the region. Denoting the source terms due to chemical reaction in (2) and (3) as g_1 and g_2 , respectively:

$$g_1 = A + X^2 Y - (B + 1)X, \quad (8a)$$

$$g_2 = BX - X^2 Y, \quad (8b)$$

we may easily show that a trivial solution to the steady state problem (9) and (10)

$$D_X \frac{d^2 X}{dz^2} + g_1 = 0, \quad (9)$$

$$D_Y \frac{d^2 Y}{dz^2} + g_2 = 0, \quad (10)$$

both for boundary conditions (5) and (6) exists:

$$X(z) = X_0; \quad Y(z) = Y_0. \quad (11)$$

This, in chemical kinetics, unexpected result is caused by the fact that the source functions may exhibit zero values, i.e.:

$$g_1 = 0 \quad \text{and} \quad g_2 = 0. \quad (12a, b)$$

A simple calculation yields:

$$X_0 = A_0, \quad Y_0 = B_0/A_0. \quad (13)$$

Uniform solution of (9) and (10) is usually called the basic solution.

Bifurcation of steady state solutions of (9) and (10) can only occur if the linear operator in (9) and (10) is singular. A detailed analysis of this case has been performed by Herschkowitz-Kaufman [8] and by Kubicek and Marek [10].

Now let us try to interpret (9) and (10), i.e. the case of constant values of A and B. Let us suppose that the reaction steps (a)–(d) describe a mechanism of a catalytic reaction of the type gas-solid. Two possible explanations can be suggested:

1) Let us assume that the component A is adsorbed on the catalyst; the reaction rate of the step

(a) can be written

$$r_A = k_1 A / (1 + K_A A). \quad (14)$$

Here k_1 is the rate constant of the surface reaction and K_A is the equilibrium adsorption constant. For the case of a strong adsorption of A , $K_A A \gg 1$, and (14) becomes

$$r_A = k_1 / K_A. \quad (15)$$

In an analogous way we can assume for the step (c)

$$r_B = k_2 B X / (1 + K_B B + K_X X). \quad (16)$$

For a weak adsorption of X , $K_X X \ll 1$ and for a strong adsorption of B , $K_B B \gg 1$. Equation (16) is then approximated by

$$r_B = \left(\frac{k_2}{K_B} \right) X. \quad (17)$$

Here k_2 is the rate constant of the surface reaction and K_B and K_X are the adsorption constants for B and X , respectively. As a result, the term A occurring in (1) must be interpreted as the ratio k_1 / K_A . Similarly the "concentration" B is the value of the ratio k_2 / K_B . Actually, because of the strong adsorption effects the rates of these steps are approximated by a zero order reaction. The same conclusions are true for an interpretation in the language of enzymatic engineering.

2) The second interpretation assumes that our system is imbedded in a system of higher dimension which takes care of an uniform space distribution of concentrations of A and B . This situation is schematically shown for an one-dimensional catalyst in Figure 1. External mass transfer in a turbulent regime may guarantee that the concentrations of A and B are constant along the catalyst. Notice that in this particular case A and B do not diffuse across the boundary (diffusion occurs only in the z direction) but are transported via the external transfer. This interpretation of the "Brusselator" equations can also be used for a two-dimensional body. Failure of this interpretation for a three-dimensional system is obvious. This physical description may also be used for an enzymatic system.

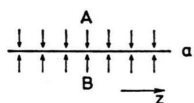


Fig. 1. Schematic picture of the external transport of components A and B to the catalyst surface; a : one-dimensional catalyst.

It should be noted that all reports where the quantitative properties of dissipative structures are studied contain either the assumption that the components are abundant [9–11] or that a rate of certain reaction is constant [9]. An important exception is the paper by Herschkowitz-Kaufman [8].

In our paper we are going to analyze the effect of diffusion of A on the behavior of space structures. Concentration of B is supposed to be kept constant via the external transport (cf. Figure 1). The model under study is thus represented by (1)–(3) subject to boundary conditions (5) and (7) as well as (6) and (7). In this paper only the steady state characteristics of the model will be investigated. For the steady state conditions the governing equations represent a nonlinear boundary value problem. This nonlinear boundary value problem has been approximated by a high order difference scheme and the resulting nonlinear algebraic equations have been solved by the Newton-Raphson method. We feel that for the reaction-diffusion problems this approach works better than the GPM technique used by Kubicek and Marek [9].

3. Imperfect Bifurcations

Bifurcation analysis of the linearized Eqs. (9) and (10) yields results [10] which are schematically drawn in Figure 2. In this figure x is a certain internal state variable (for instance $X'(0)$ for fixed boundary conditions or $X(0)$ for zero flux boundary conditions) and λ is an external variable (here $\lambda \approx L$). Figure 2 represents the familiar pitchfork well known in the theory of buckling [18]. Small perturbations of the pitchfork lead to situations pictured in Fig. 3 [17]. Such problems, which result in bifurcations of the type b illustrated in Fig. 3, are sometimes known as "perfect", a term prevalent in the literature of the theory of elastic stability. If small "imperfections" are added, the problem is usually referred to as an "imperfect". In a number of physical systems, strict bifurcations have not been observed; rather the internal state variable (for instance, amplitude in hydrodynamics [19] or

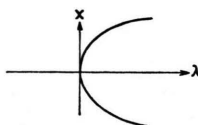


Fig. 2. The bifurcation branches (the pitchfork).

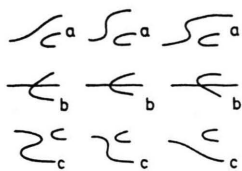


Fig. 3. Classification of perturbations of the pitchfork.

buckling theory [21]) follows a smooth path. For instance, in hydrodynamic observations imperfect bifurcations for the Benard problem may be caused by thermal noise in the plates [20].

In our particular case we replace the parameter A in (9) by the function

$$A(z) = A_0 \frac{\cosh \left[\frac{1}{\sqrt{D_A}} (z - L/2) \right]}{\cosh \left(\frac{L}{2\sqrt{D_A}} \right)}. \quad (18)$$

Since analytical methods based on perturbation analysis [21] and theory for imperfect bifurcations via singularity theory [18] may give rise only to the qualitative results we have performed in this work a complete study.

4. Solution for the Fixed and Zero Flux Boundary Conditions

Numerical computations were performed for the parameters which were used both by Herschkowitz-Kaufman [8] and by Kubicek et al. [10]: $A=2$, $B=4.6$, $D_X=1.6 \cdot 10^{-3}$, $D_Y=8 \cdot 10^{-3}$.

Numerical calculations for this type of problem are much more difficult than those for the problem considered by Kubicek et al. [10]. In the latter case we can analytically calculate the values of the bifurcation lengths, start the calculation in the vicinity and by a continuation strategy calculate the particular dependences. For the problem given by (1)–(4) a trivial solution does not exist. The trivial solution can be used as a first guess for concentration profiles at very low values of the space coordinate z . The calculated solution, which is close to the trivial one, may be easily calculated by a continuation procedure.

Numerical experiments indicated that the imperfect bifurcation caused by diffusion of the component A may result in the creation of a closed curve. It is not easy to find these curves since we have in fact no simple guiding principle to locate them.

One possibility is, of course, to continue in the value of the parameter D_A , starting at very high values of D_A . For these values the results by Herschkowitz-Kaufman [8] and Kubicek [10] can be used as a first approximation.

a) Fixed Boundary Conditions

The dependence $Y'(0)$ and $X'(0)$ as a function of L is drawn by a solid line in Fig. 4 ($D_A=0.1$). The results calculated by Kubicek et al. [10] for the case $D_A \rightarrow \infty$ are drawn here by a dashed line.

We can notice that the branch of symmetric solutions closely follows the dependences calculated by Kubicek [10]. The branch of solutions arising through primary bifurcation from the trivial solution, curve A, decomposes because of the imperfect

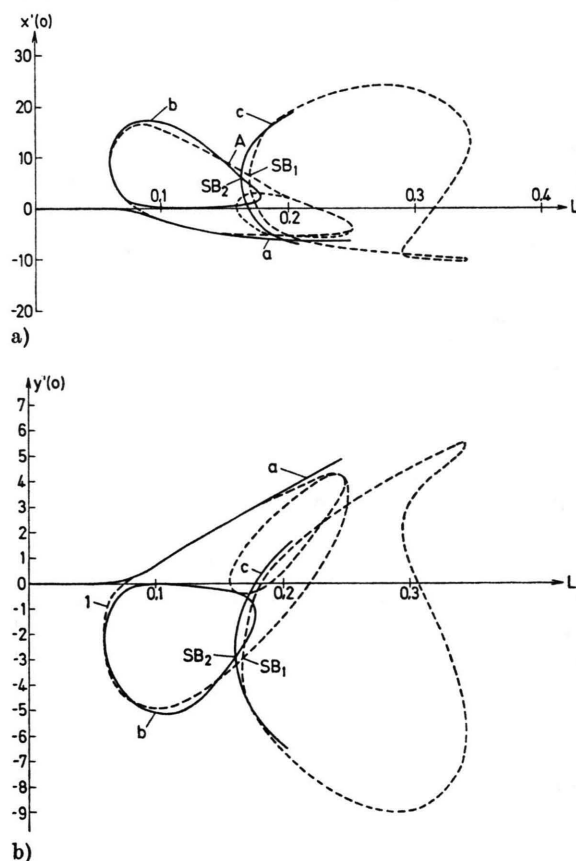


Fig. 4. Dependences $X'(0)$ and $Y'(0)$ on the characteristic dimension of the system L . Fixed boundary conditions (full line): a) branch of symmetric solutions, b) isola, c) branch of asymmetric solutions, SB_1 , SB_2 points of secondary bifurcation. — The results calculated by Kubicek et al. [10] are drawn by a dashed line.

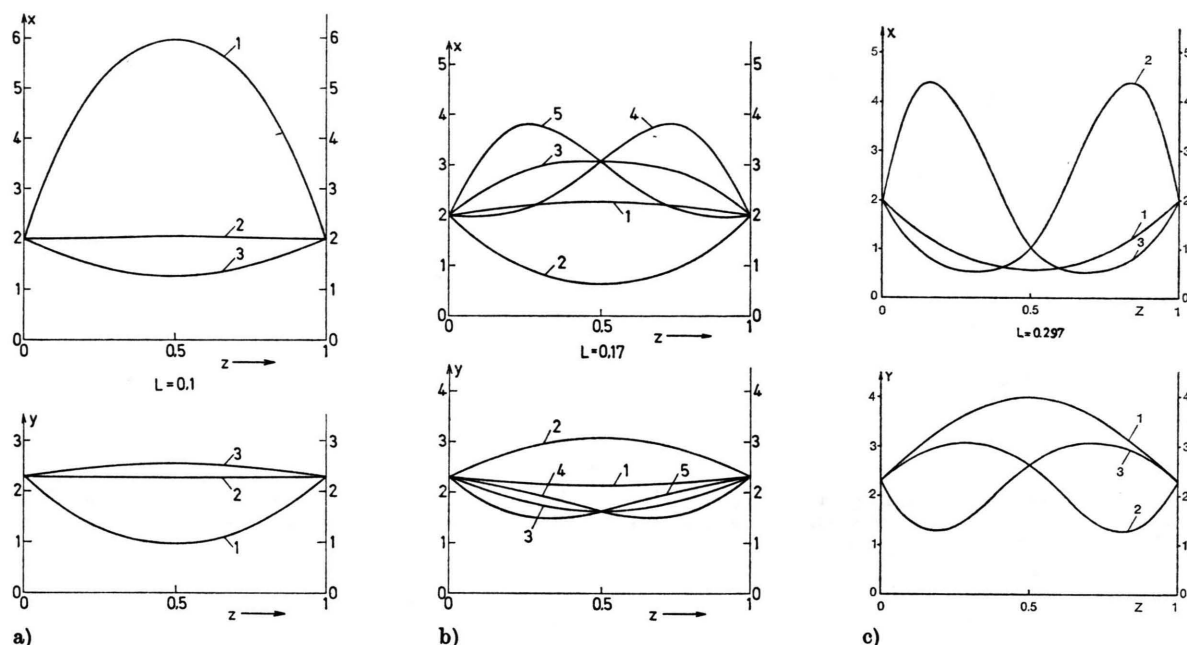


Fig. 5. Spatial profiles X and Y for fixed boundary conditions. a) $L=0.1$. b) $L=0.17$. c) $L=0.297$.

bifurcation into two separated branches of symmetric solutions, namely branch a and closed branch (isola) b. A branch of asymmetric solutions, curve c, results through a secondary bifurcation from the isola, cf. point SB_2 in Fig. 4. As a result, the more realistic model which considers also diffusion of the component A does not suppress the existence of asymmetric solutions. This fact is in agreement with the observation of Herschkowitz-Kaufman [8]. The concentration profiles calculated for different values of L are drawn in Figure 5.

The effect of the magnitude of the diffusion coefficient D_A on the behavior of the system is

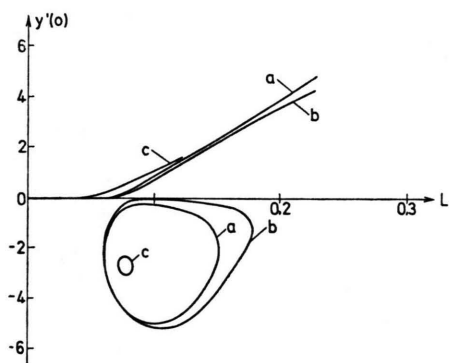


Fig. 6. The effect of the magnitude of D_A on the behavior of the system. — a) $D_A=0.02$, b) $D_A=0.1$, c) $D_A=0.0007$.

drawn in Figure 6. This figure reveals that for low values of D_A the dimension of the isola decreases; for approximately $D_A=7 \cdot 10^{-4}$ the isola disappears. Since the asymmetric solutions appear through secondary bifurcation from the isola it is obvious that a high diffusion resistance for A suppress the occurrence of asymmetric solutions.

We have performed calculations for $D_A=10$; in the vicinity of the points 1 and 2 the numerical algorithm did not work properly, since the classical Brusselator model is only weakly perturbed and the Jacobian matrix is almost singular.

b) Zero Flux Boundary Conditions

The dependence $Y(0)$ and $X(0)$ as a function of L is drawn by a solid line in Fig. 7 ($D_A=0.02$). The results calculated by Kubicek et al. [10] for the case $D_A \rightarrow \infty$ are drawn here by a dashed line. Figure 7 reveals that for the case of finite values of D_A isolated branches of solutions may exist.

The asymmetric solutions appear again via the secondary bifurcation from the symmetric isolated solutions (cf. points SB_1 , SB_2). The space profiles for different values of L are drawn in Figure 8. We may note that for a certain value of L (cf. the situation for $L=0.2$) three symmetric and two asymmetric profiles may exist.

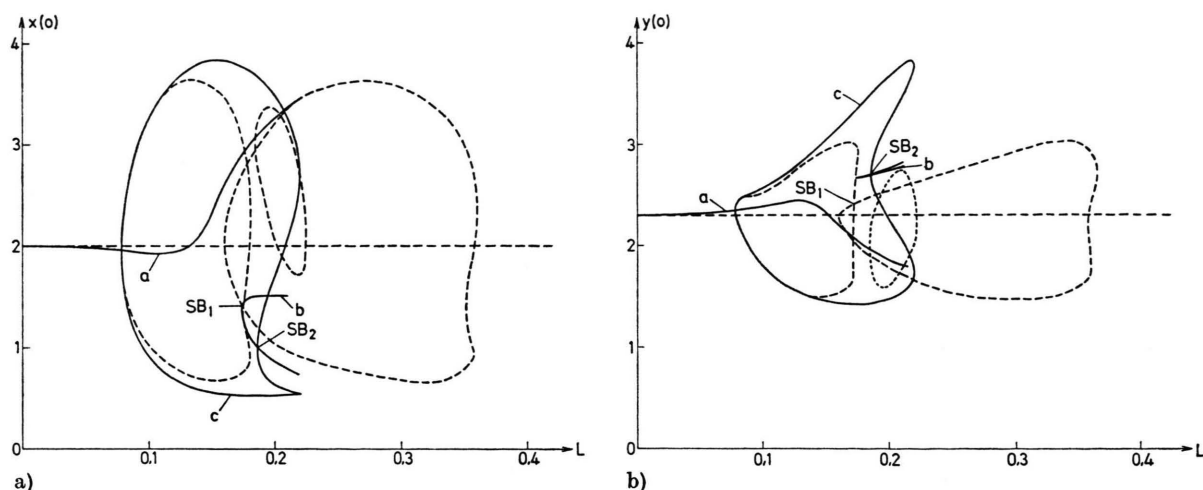


Fig. 7. Dependences $X(0)$ and $Y(0)$ on the characteristic dimension of the system L . — Zero flux boundary conditions (full line). a) branch of symmetric solutions, b) isola, c) branch of asymmetric solutions. The results calculated by Kubicek et al. [10] are drawn by a dashed line.

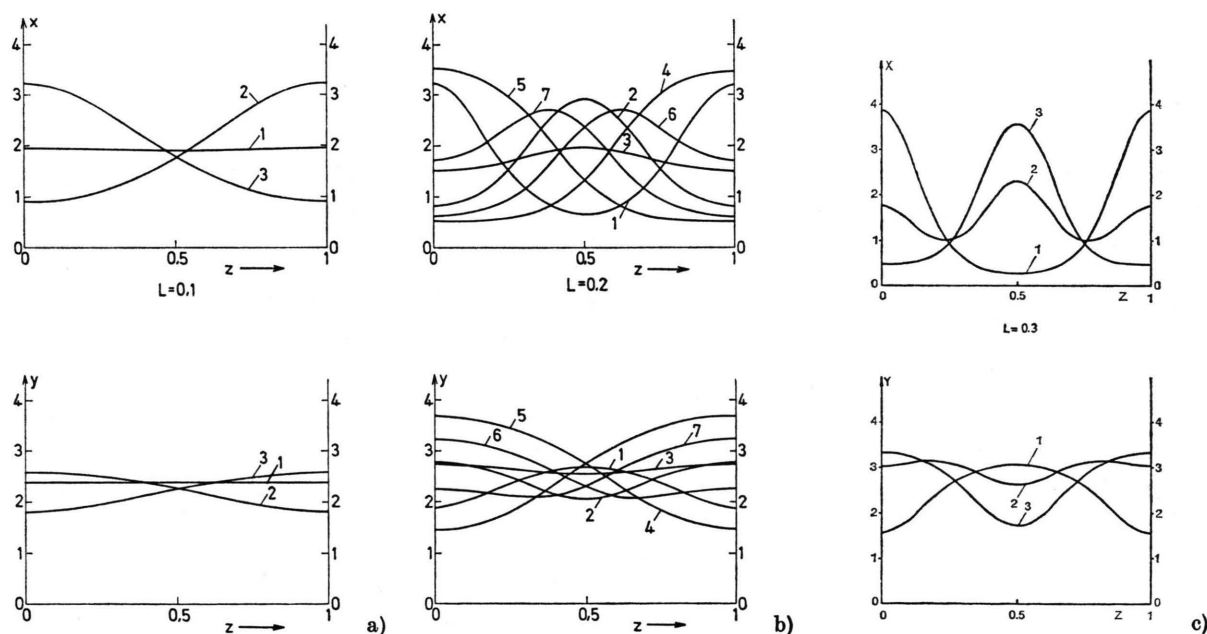


Fig. 8. Spatial profiles X and Y for zero flux boundary conditions. a) $L=0.1$, b) $L=0.2$, c) $L=0.3$.

5. Conclusion and Discussion

As shown in the preceding sections models including diffusion of all reaction components do not admit an occurrence of a trivial branch (i.e. existence of an initially homogeneous system). These models, as a result, also exclude the possibility of primary bifurcations. In recent papers Kubicek et al. [10, 11] calculated the bifurcation diagrams for four cases: i) simple trimolecular scheme (Brusselator), ii) model describing metabolism of low

molecular thiols and proteins, iii) simple enzymatic reaction [9], iv) activator-inhibitor model [22]. In the majority of cases described by Kubicek and associates the calculated bifurcation diagrams exhibited a rather bizarre shape. Generally, for these models the number of possible (stable) solutions is very high. Roughly speaking, the higher is the value of the space coordinate, the more strange behavior may be expected. These models are capable of predicting asymmetric space profiles, however

certain of them may lead to a spectrum of possible patterns of spatial concentration profiles in growth.

The models which consider diffusion of the initial components suppress the number of possible solutions of the governing equations. Evidently, for large values of the space coordinate L , the concentration of the component A decreases to low values and thus the possibility of a rich spectrum of solutions is restricted. Apparently, this conclusion is generally valid.

The modified models may also predict both symmetric and asymmetric states. We have proved the possibility of existence of both states for a modified Brusselator model. Apparently this type of models is more suitable for prediction of patterns of spatial organisation in growth. Using this type of models the system follows the branch of symmetric solutions as long as this branch is stable. After losing stability a jump to another symmetric or asymmetric branch occurs. Since the number of possible profiles is strongly reduced we feel that this principle may lead to a more deterministic way of an evolution process. We can also note that the symmetric profiles occurring on the isola cannot be reached by an evolution process unless a large perturbation is imposed on the system.

There is a number of models developed for chemically reacting systems where an inhomogeneous constant term is considered. To mention only a few, let us present enzymatic problems [9], [22] (constant reaction rate of a certain reaction or constant production rate of a certain component) and chain branching in the theory of branching reactions [25]. In the latter case the constant term represents an "inflow" to the system [26]. Since this term may give rise to a number of strange phenomena, a careful analysis of its physical meaning should be performed.

This paper is the first communication in the literature on a systematic analysis of dissipative structures in chemically reacting systems where also the diffusion of the inlet component(s) is considered. We cannot guarantee that we have found all solutions of the equations, however, a procedure for a systematic evaluation of all steady state profiles is in progress [23].

In a next paper we are going to present the results for the boundary conditions of the third kind, evaluate the effect of the component B , calculate the bifurcation diagram also for higher values of the space coordinate L and analyze the stability of the calculated steady states [15].

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