

Diffusive feed of reactants and Hopf bifurcations in an oscillatory reaction-diffusion model

B. von Haefen^{a)} and G. G. Izús^{b)}

Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Mar del Plata, Deán Funes 3350, (7600) Mar del Plata, Argentina

(Received 10 June 1998; accepted 14 September 1998)

We study an oscillatory chemical model (the “Brusselator”) with the aim of analyzing the effect of a controlled diffusive feed of reactants in the appearance of chemical oscillations. The reflectivities of the boundary, which adjust the external fluxes, act as control parameters capable to alter the attractive basin of the thermodynamic branch, leading to oscillatory behavior. © 1998 American Institute of Physics. [S0021-9606(98)51247-0]

I. INTRODUCTION

The formation of spatial and temporal structures in extended dissipative systems has become a very active field of research, both from the experimental and from theoretical points of view.^{1–5} The large variety of nonequilibrium systems that one can consider calls for different frameworks in which these phenomena can be analyzed. In particular, the description of dissipative structures in terms of reaction-diffusion (RD) equations has shown to be a very fecund source of tractable models in physics, chemistry, and biology.^{5–7} Typical examples are the conduction of signals by nerve fibers,⁸ laser systems,⁹ the Gunn effect,¹⁰ the ballast resistor,¹¹ and even some genetic and ecological phenomena.^{12,13} The autocatalytic chemical reactions (modeled up by nonlinear RD equations) provide some of the most studied examples.^{14–17} It is well known that chemical systems which are locally in thermodynamic equilibrium, but hold far from chemical equilibrium, can undergo phase transitions toward new stable states which show striking behaviors such as chemical clocks, Turing structures, or even traveling waves. A classical example—and the best known realistic excitable system—is the *Belousov–Zhabotinskii* (BZ) reaction.¹⁸ The overall reaction is the catalytic oxidation of malonic acid in an acidic bromate solution. Limit cycle oscillations are common features of chemically reacting systems like the BZ reaction and glycolysis.^{19–21}

The boundary conditions (BCs) rule over the merging and the stability of nonequilibrium structures in extended dissipative systems. The new generation of unstirred open chemical reactors, based on gel strips, has opened the possibility of controlling the flux of reactants from the boundaries.²² There is already experimental evidence that the BCs play a significant role on the pattern formation: The first unambiguous observation of a genuine Turing structure has been reported in experiments on the chlorite-iodide-malonic acid (CIMA) reaction in an open gel reactor.²³ Moreover, there are reports on the influence of the borders on the selec-

tion and orientation of dissipative structures in RD systems.^{11,24–26}

Of particular interest are the *partially reflecting boundary conditions* (“albedo BCs”), that at the boundary Γ relate the normal derivative of the concentrations with its value:

$$\hat{n}\nabla\rho|_{\Gamma} = -\kappa(\rho - \rho_0)|_{\Gamma}, \quad (1)$$

where $\kappa(>0)$ is the *albedo* parameter, ρ is the concentration of the chemical species, and ρ_0 is some reference concentration of the reservoir that usually lies on the thermodynamic branch. These type of BCs (the most general homogeneous ones) assume that the boundary acts as a partially absorbing or reflecting medium,⁴ which feeds the reaction by diffusion. They have Neumann’s BC (totally reflecting, i.e., $\kappa \rightarrow 0$) and Dirichlet’s BC (totally absorbing of any deviation from ρ_0 , i.e., $\kappa \rightarrow \infty$) as limits. Since these BCs are closely related to diffusion processes, it is our hope that they could be realized in experiments conducted in the new unstirred open reactors (e.g., in a gel ribbon or annulus).²⁷ These BCs have recently been shown to play a relevant role in the appearance and stability (both linear and nonlinear) of stationary patterns in bistable RD systems like the Schlögl model,^{24,25,28–31} the FitzHugh–Nagumo equations,^{32,33} excitable reactions and bimolecular isomerization process.^{34–36}

In recent papers we have been concerned with the role of partially reflecting BCs in pattern selection, and more particularly with the stability properties of the resulting nonequilibrium structures.^{28,30–36} Here we want to analyze for an oscillatory chemical reaction how the controlled fluxes of chemical reagents alter the stability of the homogeneous solution that lies in the thermodynamic branch and produces temporal organization through a Hopf bifurcation. For simplicity, the response of chemical limit cycle oscillations to the diffusive feed in unstirred open reactors will be analyzed for a one-dimensional, two-component RD system.

II. THE BRUSSELATOR

A classical simplified theoretical model used to show cooperative phenomena in chemically reacting systems is a trimolecular reaction model (proposed by Prigogine and Lefever) known as the “*Brusselator*.”^{1,14} It is the simplest

^{a)}Electronic mail: bvhaefte@mdp.edu.ar

^{b)}Corresponding author: electronic mail: izus@mdp.edu.ar

model which exhibits instabilities and transitions to chemical oscillations.¹ The influence of the borders on the selection and orientation of *static* structures in the Brusselator was reported in Refs. 26 and 34.

This chemical reaction takes place in four steps and is held far from equilibrium by allowing the reactions to advance only in one direction. The calculations presented in this paper are carried out for the following dimensionless RD equations for the two species X and Y :

$$\begin{aligned}\frac{\partial X}{\partial t} &= D_1 \nabla_r^2 X + A - (B+1)X + X^2 Y, \\ \frac{\partial Y}{\partial t} &= D_2 \nabla_r^2 Y + BX - X^2 Y,\end{aligned}\quad (2)$$

which model the reaction in an unstirred extended system. D_1 and D_2 are diffusion coefficients, and we assume that A and B (which arise from the kinetics) are in large excess, so that their concentrations are time independent and uniform over the system (pool chemical approximation).²² Although rather unrealistic, this approximation lies at the basis of most theoretical developments for the sake of mathematical tractability. However, experimental setups may fit into this approximation; for example, the well-stirred membrane reactor³⁷ and heterogeneous catalytical reactions over well defined crystalline planes where the feed comes from the gas and induce spatio-temporal symmetry breaking phenomena on the surface.³⁸⁻⁴⁰

Equations (2) have a uniform steady-state solution that lies on the thermodynamic branch:

$$X_0 = A, Y_0 = B/A. \quad (3)$$

Hereafter, we consider the one-dimensional version of Eqs. (2) in the interval $-L \leq z \leq L$ with the following BCs:

$$\begin{aligned}\left. \left(\frac{\partial X}{\partial z} \pm \kappa_X (X - X_0) \right) \right|_{z=\pm L} &= 0, \\ \left. \left(\frac{\partial Y}{\partial z} \pm \kappa_Y (Y - Y_0) \right) \right|_{z=\pm L} &= 0.\end{aligned}\quad (4)$$

Albedo BCs [Eqs. (4)] can be maintained in time by controlling the diffusive flow of X and Y through the boundaries. For these BCs (X_0, Y_0) remain as the homogeneous steady state for $0 \leq \kappa_X \leq \infty$ and $0 \leq \kappa_Y \leq \infty$.

III. STABILITY ANALYSIS OF THE THERMODYNAMIC BRANCH

We wish to investigate the conditions under which the thermodynamic branch becomes unstable and a *nonequilibrium phase transition* occurs to an oscillatory state (temporal organization). B , κ_X , and κ_Y are chosen as control parameters. We look for instabilities in the homogeneous steady-state solution using the linear stability theory. As usual, we propose for X and Y the perturbed forms:

$$\begin{aligned}X(z, t) &= X_0 + \alpha(z, t), \\ Y(z, t) &= Y_0 + \beta(z, t).\end{aligned}\quad (5)$$

This leads to the following linear system for the small space and time-dependent perturbations α and β :

$$\frac{\partial}{\partial t} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{bmatrix} B-1 + D_1 \frac{\partial^2}{\partial z^2} & A^2 \\ -B & -A^2 + D_2 \frac{\partial^2}{\partial z^2} \end{bmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}. \quad (6)$$

By linearity, the BCs to be fulfilled by the perturbations at the boundaries are:

$$\begin{aligned}\frac{\partial \alpha}{\partial z} \Big|_{z=\pm L} &= \mp \kappa_X \alpha \Big|_{z=\pm L}, \\ \frac{\partial \beta}{\partial z} \Big|_{z=\pm L} &= \mp \kappa_Y \beta \Big|_{z=\pm L}.\end{aligned}\quad (7)$$

Equation (6) constitutes a set of linear homogeneous equations of first order in time with constant coefficients. They therefore admit solutions of the form:

$$\begin{pmatrix} \alpha(z, t) \\ \beta(z, t) \end{pmatrix} = \exp(\omega t) \begin{pmatrix} \tilde{\alpha}(z) \\ \tilde{\beta}(z) \end{pmatrix}. \quad (8)$$

As the Laplacian is the only operator acting on space coordinates, we choose its eigenfunctions in order to investigate the stability of the thermodynamic branch:²²

$$\begin{aligned}\frac{d^2}{dz^2} \tilde{\alpha}_n(z) &= -k_n^2 \tilde{\alpha}_n(z), \\ \frac{d^2}{dz^2} \tilde{\beta}_m(z) &= -q_m^2 \tilde{\beta}_m(z),\end{aligned}\quad (9)$$

where n and m are sets of indices labeling the infinite sets of eigenfunctions and the minus signs in front of k_n and q_m accounts that d^2/dz^2 is a dissipative operator having non-positive eigenvalues. The k_n and q_m are functions of L , κ_X , and κ_Y , respectively. The applied BCs originate the following equations for the wave vectors:

$$\begin{aligned}\tan(k_n L) - \frac{\kappa_X}{k_n} &= 0, \text{ for } n=0,2,4, \dots, \\ \cot(k_n L) + \frac{\kappa_X}{k_n} &= 0, \text{ for } n=1,3,5, \dots,\end{aligned}\quad (10)$$

and

$$\begin{aligned}\tan(q_m L) - \frac{\kappa_Y}{q_m} &= 0, \text{ for } m=0,2,4, \dots, \\ \cot(q_m L) + \frac{\kappa_Y}{q_m} &= 0, \text{ for } m=1,3,5, \dots,\end{aligned}\quad (11)$$

respectively. In order to obtain $k_n(\kappa_X)$ and $q_m(\kappa_Y)$ these equations must be solved numerically. By replacing Eqs. (8) and (9) into Eq. (6), we obtain:

$$\begin{bmatrix} c_1^{(n)} & A^2 \\ -B & -c_2^{(m)} \end{bmatrix} \begin{pmatrix} \tilde{\alpha}_n \\ \tilde{\beta}_m \end{pmatrix} = \omega(k_n, q_m) \begin{pmatrix} \tilde{\alpha}_n \\ \tilde{\beta}_m \end{pmatrix}, \quad (12)$$

where

$$\begin{aligned} c_1^{(n)} &= B - 1 - k_n^2 D_1, \\ c_2^{(m)} &= A^2 + q_m^2 D_2. \end{aligned} \quad (13)$$

This system admits nontrivial solutions provided that the following equation is satisfied:

$$\omega^2(k_n, q_m) + (c_2^{(m)} - c_1^{(n)})\omega(k_n, q_m) + A^2 B - c_1^{(n)} c_2^{(m)} = 0. \quad (14)$$

The two solutions of Eq. (14):

$$\omega_{\pm}(k_n, q_m) = \frac{1}{2} [c_1^{(n)} - c_2^{(m)} \pm \sqrt{(c_1^{(n)} + c_2^{(m)})^2 - 4A^2 B}] \quad (15)$$

are physically interesting. Depending on the variables D_1 , D_2 , A , B , κ_X and κ_Y , the frequency can be either real or complex, leading in some particular cases to bifurcations, a frequently observed phenomenon in oscillatory chemical systems out of equilibrium. Hereafter we consider those situations which lead to chemical oscillations (i.e., ω complex).

IV. HOPF BIFURCATION OF THE THERMODYNAMIC BRANCH

The thermodynamic branch is stable if the real part of ω is negative and undergoes a Hopf bifurcation to oscillatory states (limit cycles) when becomes positive.²² $\omega(k_n, q_m)$ will be complex if $c_1^{(n)} c_2^{(m)} - A^2 B < 0$, and the condition that $\omega(k_n, q_m)$ has a positive real part is:

$$B > B_{nm} = A^2 + 1 + k_n^2 D_1 + q_m^2 D_2, \quad (16)$$

where B_{nm} is the boundary (in the space of the parameters) between the regions where the steady state (X_0, Y_0) is stable ($B < B_{nm}$) or unstable ($B > B_{nm}$). It represents a critical surface in the (B, κ_X, κ_Y) -space. Its absolute minimum is $B_{00} = A^2 + 1$, which corresponds to zero-flux BC ($\kappa_X = \kappa_Y = 0$) and represents the onset of oscillatory instability in the spatially uniform Brusselator ($D_1 = D_2 = 0$).

The full symmetric cases: $\kappa_X = \kappa_Y = 0$ (Neumann BC) and $\kappa_X = \kappa_Y = \infty$ (Dirichlet BC) were considered in Refs. 1 and 14. The asymmetric cases, $\kappa_X = \kappa_Y = \kappa$ at the right end and Dirichlet or Neumann BCs at the left end, were considered in Ref. 34.

We consider here the Brusselator subject to nonflux BC and we explore the effect of changing both albedo parameters. In Fig. 1 we show, for the BCs indicated in Eqs. (4), the behavior of $\Delta B_{00} = B_{00}(\kappa_X, \kappa_Y) - B_{00}(0, 0)$ as a function of κ_X and κ_Y . The minimum corresponds to $\kappa_X = \kappa_Y = 0$, indicating which in absence of external fluxes the basin of the thermodynamic branch has its lower extension. The critical value of the control parameter has a monotonous increase with κ_X and κ_Y , and tends asymptotically to its maximum in the nearness of Dirichlet BCs (i.e., $\kappa_X, \kappa_Y \geq 20$).

In the particular case $\kappa_X = 0$, $\kappa_Y = \infty$, the wave vectors satisfy

$$\begin{aligned} k_n &= n\pi/L, \text{ for } n=0, 1, \dots, \\ q_m &= (m+1)\pi/L, \text{ for } m=0, 1, \dots, \end{aligned} \quad (17)$$

and the first bifurcation occurs for $B_{00} = A^2 + 1 + (\pi/L)^2 D_2$. For $\kappa_X = \infty$, $\kappa_Y = 0$, the first bifurcation occurs for $k_0 = \pi/L$, $q_0 = 0$, at $B_{00} = A^2 + 1 + (\pi/L)^2 D_1$.

Figure 2 shows ΔB_{10} as a function of κ_X and κ_Y . The

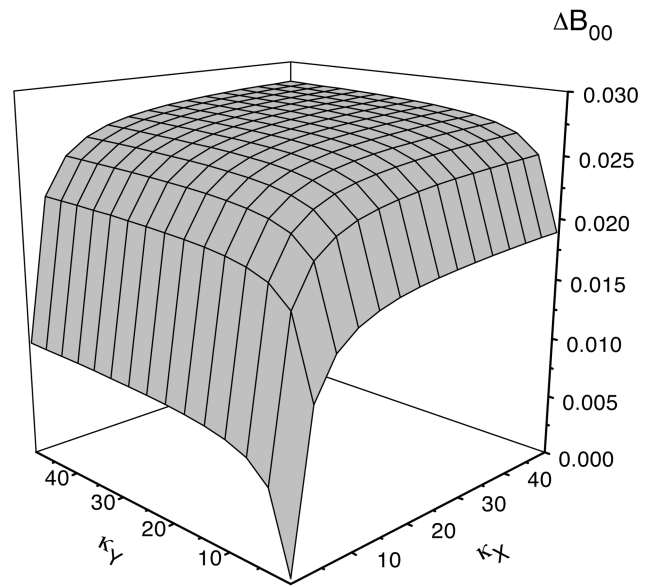


FIG. 1. Plot of ΔB_{00} as a function of κ_X and κ_Y . The surface limits the region where the steady state is stable (below the surface) and unstable (above the surface). The existence of a maximum allowed value of B_{00} can be appreciated for Dirichlet BC. Here $L=1$, $A=0.5$, $D_1=0.008$, and $D_2=0.004$.

behavior is qualitatively similar to the shown in Fig. 1, and the same occurs for the other values of n and m . Therefore, if we increase the albedo parameters κ_X and κ_Y , the critical value of the thermodynamic parameter B increases, and the region where the thermodynamic branch results stable is enhanced. The first (Hopf) bifurcation occurs for $n=m=0$. A similar behavior was obtained for the Brusselator, subject to non-symmetric BCs—but with the same reflectivity for both components—in Ref. 34.

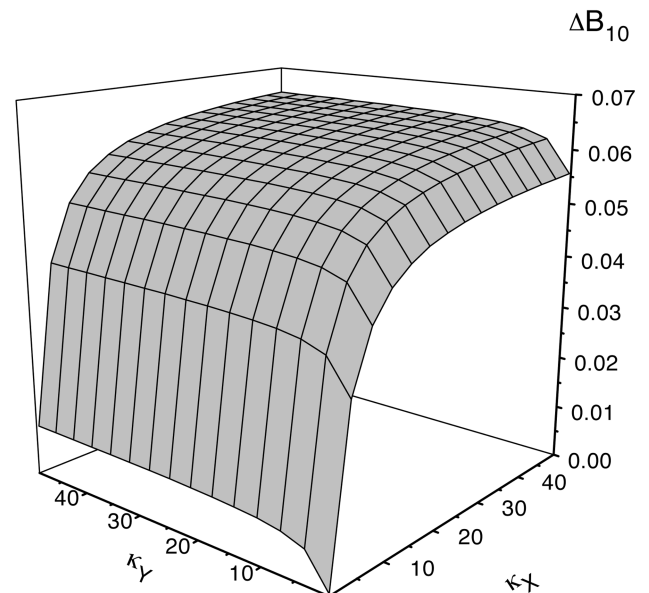


FIG. 2. Plot of ΔB_{10} as a function of κ_X and κ_Y . The values of the parameters are $L=1$, $A=0.5$, $D_1=0.008$, and $D_2=0.004$.

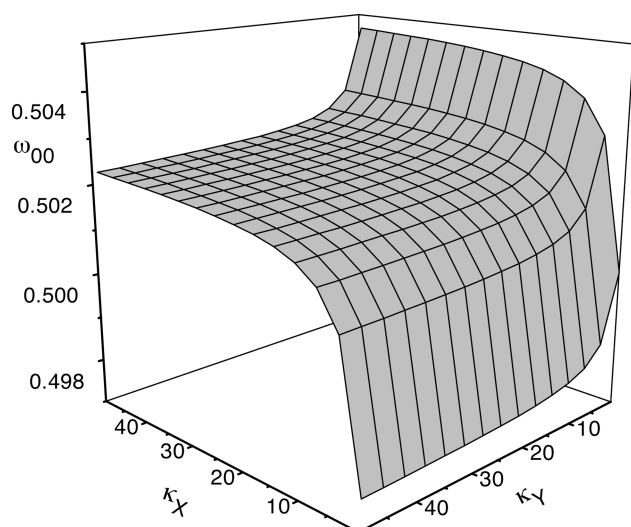


FIG. 3. Plot of the frequency ω_{00} as a function of ω_X and κ_Y . Here $L=1$, $A=0.5$, $D_1=0.008$, and $D_2=0.004$.

The frequency of temporal oscillation for the elementary solutions are $\omega_{nm} = \sqrt{(q_m^2 D_2)^2 + A^2 [(q_m^2 D_2 - k_n^2 D_1) - 1]}$ and can be altered by adjusting the BCs. In Fig. 3 we show ω_{00} as a function of κ_X and κ_Y . The maximum value allowed for that frequency corresponds to $\kappa_X = \infty$ and $\kappa_Y = 0$ ($\omega_{00} \rightarrow \sqrt{-A^2 [(\pi/L)^2 D_1 + 1]}$), and the minimum corresponds to $\kappa_X = 0$ and $\kappa_Y = \infty$ ($\omega_{00} \rightarrow \sqrt{[(\pi/L)^2 D_2]^2 + A^2 [(\pi/L)^2 D_2 - 1]}$). For closed reactors (i.e., Neumann BC) $\omega_{00} = \sqrt{-A^2}$, and for Dirichlet BC ($\kappa_X, \kappa_Y = \infty$), the frequency tends to the asymptotic value $\omega_{00} = \sqrt{[(\pi/L)^2 D_2]^2 + A^2 [(\pi/L)^2 (D_2 - D_1) - 1]}$. Dirichlet BCs can be practically implemented in our system with albedo parameters $\kappa_X, \kappa_Y \geq 20$. That circumstance explains the plateaus in the Figs. 1–3.

V. CONCLUSION

We have studied a prototypical oscillatory reaction-diffusion model (the “Brusselator”) with the aim of identifying the effects of the diffusive feed of reactants on the self-organization processes which occur in autocatalytic chemical reactions, in particular the appearance of temporal patterns. Although the Brusselator does not represent a real chemical reaction, nevertheless it is the best studied and most widely known theoretical model of chemical instability phenomena, and allows a simple numerical treatment of the subject. The BCs considered correspond to adjusting the gradients of the concentrations of the reagents at the boundaries in proportion to the values of the concentrations: the albedo parameters (κ_X, κ_Y) represent these ratio for both reagents.

We have investigated the stability of the thermodynamic branch—in the full space of the reflectivities—for those values of the parameters that allow Hopf bifurcations. The albedo parameters act as control variables capable of enhancing or weakening the self-organization processes without altering the nonlinear dynamics of the system. The basin of the thermodynamic branch in the (B, κ_X, κ_Y) -space—which

is limited by a critical surface—can be altered by adjusting κ_X and κ_Y . Tuning the boundary reflectivities resulted to be a natural way of inducing pattern formation by bifurcation processes.

We have found that the frequency of the chemical oscillations depend on the diffusive regime of the feed, in particular, the frequency of the resulting limit cycle can be adjusted by altering the diffusive fluxes. Only for zero-flux conditions the system is a spatially uniform chemical clock; in other case it is a chemical clock with spatial organization.

We want to remark that albedo BCs have a very important influence on the formation of dissipative structures in RD systems, which has been overlooked recently. Considering the new generation of unstirred open reactors fed by diffusion from the boundaries, the possibility of controlling some aspects of the self-organization processes by adjusting the diffusive feed seems to be feasible. As the dependence of the frequency of the limit cycle oscillations with the reflectivities is essentially determined by the linearized dynamics around the thermodynamic branch and the magnitude of the diffusive feed of reactants, we expect that this phenomenon can be observed in some real extended oscillatory chemical systems. As a first approach, we have restricted our calculations to the Brusselator, but we expect that our results can be qualitatively applied to others chemical oscillators and should open up new experimental possibilities for the study of temporal organization in unstirred nonlinear chemical reactions. The extension of the present analysis to realistic reactions is under way, and will be the subject of forthcoming papers.

ACKNOWLEDGMENTS

The authors thank L. Petcoff for her valuable help with the manuscript. Partial support from CONICET, Argentina, is also acknowledged.

- ¹G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems* (Wiley, New York, 1977).
- ²H. Haken, *Synergetics* (Springer, New York, 1978).
- ³A. S. Mikhailov, *Foundations of Synergetics I* (Springer, New York, 1990).
- ⁴H. S. Wio, *An Introduction to Stochastic Processes and Nonequilibrium Statistical Physics* (World Scientific, Singapore, 1994).
- ⁵M. C. Cross and P. C. Hohenberg, *Rev. Mod. Phys.* **67**, 851 (1993).
- ⁶P. C. Fife, *Mathematical Aspects of Reacting and Diffusing Systems* (Springer, New York, 1979); in *Nonequilibrium Cooperative Phenomena in Physics and Related Fields*, edited by M. G. Velarde (Plenum, New York, 1984).
- ⁷G. Nicolis, T. Erneux, and M. Herschkowitz-Kaufman, in *Advances in Chemical Physics*, Vol. **38**, edited by I. Prigogine and S. Rice (Wiley, New York, 1978).
- ⁸A. Scott, *Neurophysics* (Wiley, New York, 1977).
- ⁹H. Haken, *Z. Phys. B* **21**, 105 (1975).
- ¹⁰B. Knight and G. Peterson, *Phys. Rev.* **155**, 393 (1967).
- ¹¹D. Bedeaux, P. Mazur, and R. A. Pasmantier, *Physica A* **86**, 355 (1977); D. Bedeaux and P. Mazur, *ibid.* **105**, 1 (1981).
- ¹²J. D. Murray, *Mathematical Biology* (Springer, New York, 1985); C. Vidal and A. V. Pecault, *Evolution of Order and Chaos in Physics, Chemistry, and Biology*, Synergetics Series Vol. **17**, edited by H. Haken (Springer, New York, 1982).
- ¹³H. S. Wio *et al.*, in *Instabilities and Nonequilibrium Structures V*, edited by E. Tirapegui and W. Zeller (Kluwer, Dordrecht, 1995); M. Kuperman, B. von Haefen and H. S. Wio, *Bull. Math. Biol.* **58**, 1001 (1996).
- ¹⁴I. Prigogine and R. Lefever, *J. Chem. Phys.* **48**, 1695 (1968).

- ¹⁵F. Schlögl, *Z. Phys.* **253**, 147 (1972); A. Albano *et al.*, *Am. J. Phys.* **52**, 161 (1984).
- ¹⁶R. J. Field and M. Burger, *Oscillations and Traveling Waves in Chemical Systems* (Wiley, New York, 1985).
- ¹⁷Y. Kuramoto, *Chemical Oscillations, Waves and Turbulence* (Springer, New York, 1984).
- ¹⁸B. P. Belousov, in *Collection of Abstracts on Radiation Medicine* (Medzig, Moscow, 1958); A. M. Zhabotinskii, *Biophysics* **9**, 329 (1964).
- ¹⁹A. Goldbeter and G. Nicolis, *Prog. Theor. Biol.* **4**, 65 (1976).
- ²⁰J. Turner, *Lect. Theor. Phys.* **28**, Chap. VI (1974).
- ²¹A. Goldbeter and S. R. Caplan, *Am. Rev. Biophys. Bioeng.* **5**, 449 (1976).
- ²²G. Nicolis, *Introduction to Nonlinear Science* (Cambridge University Press, Cambridge, 1995).
- ²³V. Castets *et al.* *Phys. Rev. Lett.* **64**, 2953 (1990).
- ²⁴C. L. Schat and H. S. Wio, *Physica A* **180**, 295 (1992).
- ²⁵S. Hassan, M. Kuperman, H. Wio, and D. Zanette, *Physica A* **206**, 380 (1994); S. Hassan, D. Zanette and H. Wio, *J. Phys. A* **27**, 5129 (1994).
- ²⁶P. Borckmans, A. De Wit, and G. Dewel, *Physica A* **188**, 137 (1992); A. De Wit, P. Borckmans, and G. Dewel, in *Instabilities and Nonequilibrium Structures IV*, edited by E. Tirapegui and W. Zeller (Kluwer, Dordrecht, 1993).
- ²⁷Z. Noszticzius, W. Horsthemke, W. McCormick, H. Swinney, and W. Tam, *Nature (London)* **329**, 619 (1987); K. Lee, W. McCormick, Q. Ouyang, and H. Swinney, *Science* **261**, 192 (1993).
- ²⁸G. Izús, R. Deza, O. Ramírez, H. Wio, D. Zanette, and C. Borzi, *Phys. Rev. E* **52**, 129 (1995).
- ²⁹D. Zanette, H. Wio, and R. Deza, *Phys. Rev. E* **53**, 353 (1996).
- ³⁰G. Izús, H. Wio, J. Reyes de Rueda, O. Ramírez, and R. Deza, *Int. J. Mod. Phys. B* **10**, 1273 (1996).
- ³¹G. Izús, J. Reyes de Rueda, and C. Borzi, *J. Stat. Phys.* **90**, 103 (1998).
- ³²H. S. Wio, G. G. Izús, J. O. Ramírez, R. R. Deza, and C. Borzi, *J. Phys. A* **26**, 4281 (1993).
- ³³G. Izús, R. Deza, H. Wio, and C. Borzi, *Phys. Rev. E* **55**, 4005 (1997).
- ³⁴G. Izús, O. Ramirez, R. Deza, and H. Wio, *J. Chem. Phys.* **105**, 10424 (1996).
- ³⁵G. Izús, R. Deza, C. Borzi, and H. Wio, *Physica A* **227**, 135 (1997).
- ³⁶B. von Haefen, G. Izús, R. Deza, and C. Borzi, *Phys. Lett. A* **236**, 403 (1997).
- ³⁷R. D. Vigil, Q. Ouyang, and H. Swinney, *Physica A* **188**, 17 (1992).
- ³⁸J. Falta, R. Imbihl, and M. Henzler, *Phys. Rev. Lett.* **64**, 1409 (1990).
- ³⁹S. Jakubith, H. Rothermund, W. Engel, A. von Oertzen, and G. Ertl, *Phys. Rev. Lett.* **65**, 3013 (1990).
- ⁴⁰G. Ertl, *Science* **254**, 1750 (1991).