# Stationary Periodical Structure Emitting an Infinite Number of Traveling Impulses in a Model of a One-Dimensional Infinite Excitable Reaction−Diffusion System

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A two-variable model of a one-dimensional infinite excitable reaction−diffusion system describing an expanding stationary periodical structure emitting traveling impulses is presented. The model is based on two coupled catalytic (enzymatic) reactions. The chemical scheme consists of mono- and bimolecular reactions.

## Introduction

The Turing bifurcation is the best known scenario leading to the formation of small amplitude stationary periodical structures in reaction−diffusion systems.[1] In this bifurcation, a homogeneous stationary state corresponding to a stable focus, being stable with respect to perturbations of the reactant concentration over time, loses its stability due to infinitesimal spatial perturbations. One should distinguish, however, between small and large amplitude stationary periodical structures. Whereas small amplitude stationary periodical structures emerge due to infinitesimal perturbations and "wind" around the stable focus, large amplitude structures appear far from the Turing bifurcation in excitable or bistable reaction−diffusion systems perturbed by excitations larger than some threshold value. Large amplitude stationary periodical structures have been observed experimentally in three different chemical systems: the chlorite−iodide−malonic acid reactions (CIMA),[2] the ferrocyanide−iodate−sulfite reaction,[3,4] and in the Belousov−Zhabotinsky reaction dispersed in a water-in-oil reverse microemulsion. [5]

There are three known scenarios in which large amplitude stationary periodical structures appear in excitable systems. A stationary periodical structure may be built by the creation of the next subsequent pulse ahead of previously created pulses forming part of the structure. This scenario has been realized in excitable[19] as well as homogeneously oscillating models[20] and may be called forward firing. In the second scenario stationary periodical structures are created by a traveling impulse which splits periodically, leaving behind subsequent stationary pulses.[2−20,23] The term "backfiring" has been coined for this scenario. The Ising−Bloch bifurcation of a stationary front into two counterpropagating fronts may generate a stationary periodical structure in the third scenario.

It is noteworthy that chemical models of stationary periodical structures consist of many variables.

The creation of a complex pattern is shown in the present paper. An expanding stationary periodical structure emits an infinite number of traveling impulses in an infinite system. A similar effect has been observed in the $Ru(bpy)_3^{2+}$-catalyzed BZ-AOT finite system.[22] The stationary periodical structure generates single phase waves behind which new fragments of the stationary periodical structure appear. The difference between the phenomenon observed in the $Ru(bpy)_3^{2+}$-catalyzed BZ-AOT system and the effect described in the present paper is that in the first case a single phase wave is generated, whereas in the latter case an infinite number of traveling impulses appear. Moreover, the model of the $Ru(bpy)_3^{2+}$-catalyzed BZ-AOT finite system consists of four variables and is much more difficult to analyze than the two-variable model presented below. The model considered here describes an excitable system and has three stationary states (a stable node, a saddle point, and an unstable focus).

In the next chapter we describe the model of a 1D infinite system. The results are presented in the next chapter. The last chapter presents the conclusions.

## Model

The model describes an open, infinite chemical system in which two catalytic (enzymatic) reactions occur.

$$S_0 \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} S \tag{1}$$

$$S + E \underset{k_{-2}}{\overset{k_2}{\Leftrightarrow}} SE \tag{2}$$

$$SE \xrightarrow{k_3} P + E \tag{3}$$

$$S + SE \underset{k_{-4}}{\overset{k_4}{\Leftrightarrow}} S_2E \tag{4}$$

$$P + E \underset{k_{-5}}{\overset{k_5}{\Leftrightarrow}} EP \tag{5}$$

$$P + SE \underset{k_{-5}}{\overset{k_5}{\Leftrightarrow}} SEP \tag{6}$$

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$$P + S_2E \underset{k_{-5}}{\overset{k_5}{\Leftrightarrow}} S_2EP \quad (7)$$

$$P + E' \underset{k_{-6}}{\overset{k_6}{\Leftrightarrow}} PE' \quad (8)$$

$$PE' \xrightarrow{k_7} R + E' \quad (9)$$

$$P \xrightarrow{k_8} Q \quad (10)$$

An excess of the reactant S (activator) and the product P (inhibitor) inhibits the transformation of S to P (eqs 2−7). For simplicity we assume that the other catalytic (enzymatic) reaction (8 and 9) occurs in its saturation regime. The system is open due to reaction 1, in which $S_0$ plays the role of the reservoir variable for the reactant S, and reaction 10, in which the product P is irreversibly transformed into inactive reagent Q. Note that the chemical scheme consists of elementary reactions, which are monomolecular and bimolecular reactions without autocatalytic steps.

We assume that the total concentrations of catalysts (enzymes) E and E′ are much smaller than the concentrations of the reactant S and the product P. On the basis of the Tikhonov theorem[23] the concentrations of both catalysts (enzymes) and their complexes may be eliminated as fast variables, and the dynamics of the system in the slow time scale may be described by the two kinetic equations for the reactant S and the product P only.

The time−space behavior of the system for dimensionless concentrations of the reactant $s$ and the product $p$ is described by the following equations

$$\frac{\partial s}{\partial t} - D_s\frac{\partial^2 s}{\partial x^2} = A_1 - A_2 s - \frac{s}{(1 + s + A_3 s^2)(1 + p)} \quad (11)$$

$$\frac{\partial p}{\partial t} - D_p\frac{\partial^2 p}{\partial x^2} = B\left(-B_1 - B_2 p + \frac{s}{(1 + s + A_3 s^2)(1 + p)}\right) \quad (12)$$

where $s = S/K_m$ and $p = K_5P$ are dimensionless concentrations of the reactant S and the product P, respectively, $D = D_p/D_s$ is the ratio of the diffusion coefficients for the product $D_p$ and the reactant $D_s$, $x = (k_3E_0/D_sK_m)^{1/2}$ is the space coordinate, $t = k_3E_0/K_mt'$ is dimensionless time, $K_5 = k_5/k_{-5}$, and $K_m = (k_{-2} + k_3)/k_2$, $K_m' = (k_{-6} + k_7)/k_6$ are the Michaelis constants. $A_1 = k_1S_0/(k_3E_0)$. $A_2 = k_{-1}K_m/(k_3E_0)$, $A_3 = k_4/k_{-4}K_m$, $B = K_mK_5$, $B_1 = k_7E_0'/(k_3E_0)$ and $B_2 = k_8/(k_3E_0K_5)$ are dimensionless parameters. The assumption that reactions 8 and 9 occur in its saturation regime means that $K_m'$ is much smaller than $p$. Therefore, the rate of this reaction is constant and equal to $-B_1$.

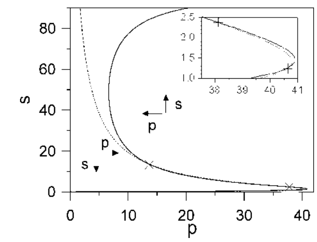


**Figure 1.** The nullclines for $s$ (continuous line) and $p$ (dotted line) on the phase plane $(p,s)$ for eqs 11 and 12 with neglected diffusion terms. The unstable focus (UF) positioned at (13.36431468, 13.88559325) is visible. The inset shows that the nullclines have two additional intersection points: the stable node (SN) with coordinates (40.5859278, 1.22754247) and the saddle point (SP) at (38.144272305, 2.362912366).

Note that parameters $B$ and $D$ do not have any influence on the stationary states or on the nullclines of the system (11 and 12). Therefore, $B$ and $D$ can be treated as bifurcation parameters. For the remaining parameters the following values are assumed

$$A_1 = 10^{-2},\ A_2 = 10^{-4},\ A_3 = 0.505,\quad B_1 = 7.99 \times 10^{-3},\ B_2 = 4.65 \times 10^{-5}$$

At these values of the parameters the system (11 and 12) has three stationary states: a stable node ($p_{sn}$ = 40.5859278, $s_{sn}$ = 1.22754247), a saddle point at ($p_{sp}$= 38.144272305, $s_{sp}$= 2.362912366), and a third stationary state ($p_{ss}$= 13.36431468, $s_{ss}$= 13.88559325) whose stability depends on $B$. For $B <$ 0.66935961 the third stationary state is the unstable focus and the stable node is the sole attractor. At $B$ = 0.66935961 the unstable focus becomes stable but an unstable limit cycle appears whose radius grows from 0 for larger $B$. The nullclines for the activator $s$ and the inhibitor $p$ for the above values of the parameters are shown in Figure 1. Only a small part of the upper attracting branch of the nullcline for $s$ is shown. The arrows on the plane $(p,s)$ show the vector direction fields for $s$ (up or down) and $p$ (left or right). The unstable focus is visible in Figure 1. The inset in Figure 1 shows the positions of the stable node and the saddle point.

The initial value (Cauchy's) problem for the system (11 and 12) in $x \in (0,\infty)$ is considered. Of course, no numerical approach can be used for an infinite system. However, it is possible to characterize asymptotic solutions for an infinite system by solutions to a sufficiently large finite system with zero-flux boundary conditions. The considered finite system should be of a size guaranteeing that its solutions are sufficiently close to the asymptotic solutions considered in the initial value problem. In numerical calculations the following initial-boundary value problem is solved numerically

$$s(0, x) = 20.0;\ p(0, x) = 35.0 \text{ for } x \in [0, 0.5] \quad (13)$$

$$s(0, x) = 1.22754;\ p(0, x) = 40.5859 \text{ for } x \in [0.5, L] \quad (14)$$

$$\left.\frac{\partial s}{\partial x}\right|_0 = \left.\frac{\partial s}{\partial x}\right|_L = \left.\frac{\partial p}{\partial x}\right|_0 = \left.\frac{\partial p}{\partial x}\right|_L = 0 \quad (15)$$

The initial values of $s$ and $p$ in the unexcited interval $x \in [0.5, L]$ are approximately equal to their values at the stable node. The numerical calculations are performed for increasing sizes of the system $L$. The numerical solutions are realized for

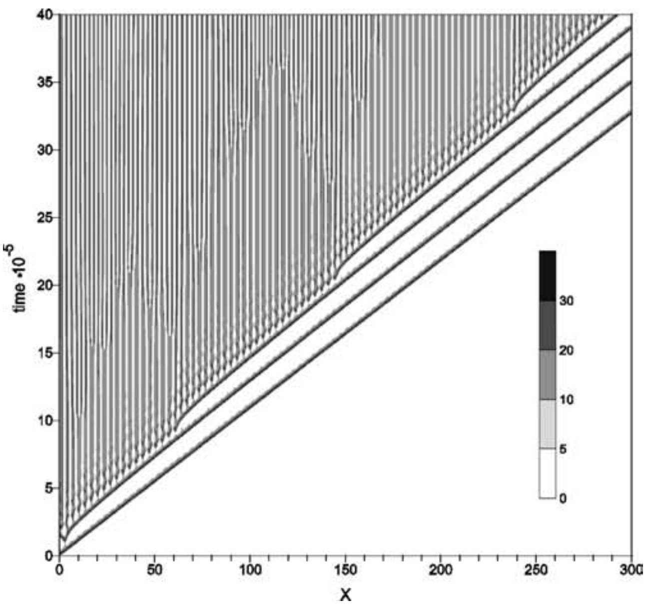


**Figure 2.** Time−space evolution of *s*(*t*,*x*) in the system for $B = 0.65$ and $D = 1.876$. Four subsequent traveling impulses are seen which leave behind an expanding stationary periodical structure. In an infinite system an infinite number of traveling impulses will be generated by the expanding stationary periodical structure.

*L* at which the properties of a given asymptotic solution are clearly visible.

Equations 11 and 12 are solved using the Cranck−Nicholson scheme for the diffusion terms and the fourth-order Runge−Kutta algorithm for the kinetic terms. In order to avoid numerical artifacts we have changed (decreasing and increasing) the spatial step in the range from 0.0025 to 0.01 and the time step in the range from 0.5 to 2. The results of the numerical calculations presented below do not depend on the used spatial and time steps in the ranges given above.

## Results

An example of space−time evolutions of the initial excitation given by (13) and (14) of eqs 11 and 12 with $B = 0.65$ and $D = 1.876$ is shown in Figure 2 for $L = 300.0$. The initially formed impulse leaves behind it a single surviving pulse from which a new impulse is created. This new impulse divides periodically, leaving behind several surviving pulses from which a stationary periodical structure is formed asymptotically. The periodical division of the new impulse occurs several times. However, some successive pulses do not survive and the new impulse continues its spreading and leaves behind decaying pulses. The last surviving pulse forms the next new impulse, which again leaves behind surviving pulses. And again some successive pulse decays but the new impulse spreads, leaving behind decaying pulses. The last surviving pulse formed before the creation of the decaying pulse generates the next new impulse. The above scenario of the creation of surviving pulses followed by the generation of decaying pulses repeats infinitely. An infinite number of traveling impulses is generated asymptotically, behind which a stationary periodical structure forms. The stationary periodical structure occupies an increasing area. The interval in space occupied by the stationary periodical structures grows with velocity equal to the velocity of the first traveling impulse. One may treat the asymptotic pattern as a source of traveling impulses generated by the expanding stationary periodical structure. The generation of only the first four traveling impulses is shown in Figure 2, but the stationary periodical structure will spread to infinity and an infinite number of traveling impulses will be emitted in infinite systems. Patterns of the type shown in Figure 2 appear in a very narrow range of *B* and *D* inside the tetragon limited by ($B_a = 0.627$, $D_a = 2.01$), ($B_b = 0.66935961$, $D_b = 1.73$), ($B_c = 0.66935961$, $D_c = 1.74$), ($B_d = 0.63$, $D_d = 2.03$). With increasing *D* the traveling impulses are more and more rarely generated in space and their number grows more and more slowly in time. If *B* crosses the upper side of the tetragon, the stationary periodical structure is built up just behind the first traveling impulse. Below the lower side of the tetragon the traveling impulse leaves decaying pulses behind.

## Discussion

The existence of an expanding stationary periodical structure emitting traveling impulses follows from the theorem about the dependence of asymptotic solutions on parameters, which for the infinite system considered above may be formulated as follows. If a traveling impulse which periodically leaves behind it exclusively decaying pulses exists for some range of the diffusion coefficient, and a traveling impulse which periodically leaves behind it exclusively surviving pulses (forming an expanding stationary periodical structure) exists for another range of the diffusion coefficient, then for the diffusion coefficient range between these two ranges the survival of the pulses may be interrupted by the decaying of the pulses, and patterns of the type shown in Figure 2 may appear. The transition from one range of the diffusion coefficient to the other is very sharp, and it is difficult to decide if the number of surviving pulses grows by 1 or by some number greater than 1.

The model described in the present paper can be treated as an example of an excitable dynamical system. Due to the presence of saddle point, perturbations of the system above the separatrix going to the saddle point cause the trajectory of the system to evolve around the unstable focus before returning to the stable node. This property of the model causes the traveling impulses generated in it to display features which are not found in excitable systems with one stable stationary state. The model (11 and 12) has been used previously for the generation of large amplitude stationary periodical structures created by subsequent divisions of the traveling impulse.[14] Moreover, two-dimensional (2D) stationary patterns mimicking all capital Latin[24] as well as Old Hebrew[25] letters have been generated in the same model. We have also shown that the absolutely stable traveling impulse in a 1D system becomes unstable in a 2D system provided that the size of the system perpendicular to the impulse propagation is sufficiently large.[26]

It is worth noting that our model is also realistic and could be realized in experiments in a 1D CFUR with two enzymatic reactions. One of them should be inhibited by its reactant and product. There are many enzymes which are inhibited by an excess of their reactants and products. Examples include invertase inhibited by sucrose (reactant) and by fructose and glucose (products), xantine oxidase inhibited by xantine (reactant) and ureate (product), acetylcholinesterase inhibited by acetylcholine and choline, and many others.[27,28]

The list of possible asymptotic behaviors in nonlinear reaction−diffusion systems is far from complete. The effect described above supplements the list by adding to it a previously unknown asymptotic solution. We hope that our result will be helpful in searches for the described phenomenon in experiments.

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## References and Notes

(1) Turing, A. M. *Philos. Trans. R. Soc. London, Ser. B* **1952**, *237*, 37.
(2) Winfree, A. T. *The geometry of biological time*; Springer: New York, 1980.
(3) Murray, J. D. *Mathematical biology*; Springer: Berlin, 1993.
(4) Field, R. J.; Burger, M. *Oscillations and traveling waves in chemical systems*; Wiley: New York, 1985.
(5) Kapral, R.; Showalter, K. *Chemical waves and patterns*; Kluwer: Dordrecht, 1995.
(6) Keener, B. S.; Osipov,W. W. *Autosolitons*; Kluwer: Dordrecht, 1994.
(7) Petrov, V.; Scott, S. K.; Showalter, K. *Philos. Trans. R. Soc. London, Ser. A* **1994**, *347*, 631.
(8) Górski, J.; Kawczyński, A. L. *Pol. J. Chem.* **1985**, *59*, 61.
(9) Bär, M.; Hildebrant, M.; Eiswirt, M.; Falcke, M.; Engel, H.; Neufeld, M. *Chaos* **1994**, *4*, 499.
(10) Reynolds, W. N.; Pearson, J. E.; Ponce-Dawson, S. *Phys. Rev. Lett.* **1994**, *72*, 2797.
(11) Doelman, A.; Kaper, T. J.; Zegeling, P. A. *Nonlinearity* **1997**, *10*, 523.
(12) Reynolds, W. N.; Ponce-Dawson, S.; Pearson, J. P. *Phys. Rev. E* **1997**, *56*, 185.
(13) Nishiura, Y.; Ueyama, D. *Physica D* **1999**, *130*, 73.
(14) Kawczyński, A. L.; Legawiec, B. *Phys. Rev. E* **2001**, *63*, 021405.
(15) Ei, S. I.; Mimura, M.; Nagayama, M. *Physica D* **2002**, *165*, 176.
(16) Nishiura, Y.; Teramoto, T.; Ueda, K. *Chaos* **2003**, *13*, 137.
(17) Nishiura, Y.; Teramoto, T.; Ueda, K. *Phys. Rev. E* **2003**, *67*, 056210.
(18) Teramoto, T.; Ueda, K.; Nashiura, Y. *Phys. Rev. E* **2004**, *69*, 056224.
(19) Kawczyński, A. L.; Gŏrski, J. *Pol. J. Chem.* **1983**, *57*, 523.
(20) Kawczyński, A. L.; Comstock, W. S.; Field, R. J. *Physica D* **1992**, *54*, 220.
(21) Manz, N.; Steinbock, O. *Chaos* **2006**, *16*, 037112.
(22) Vanag, V. K.; Epstein, I. R. *Phys. Rev. Lett.* **2004**, *92*, 128301.
(23) Tikhonov, A. N. *Math. Sbor.* **1952**, *31*, 573.
(24) Kawczyński, A. L.; Legawiec, B. *Phys. Rev. E* **2001**, *64*, 056202.
(25) Kawczyński, A. L.; Legawiec, B. *Pol. J. Chem.* **2004**, *78*, 733.
(26) Kawczyński, A. L.; Leda, M.; Legawiec, B. *Phys. Rev. E* **2006**, *73*, 046128.
(27) Selkov, E. E. *Oscillatory Processes in Biological and Chemical Systems*; Science Publishers: Moscow, 1967.
(28) Golbeter, A. *Biochemical Oscillations and Cellular Rhythms*; Cambridge: University Press: Cambridge, 1996.

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