Two-dimensional model of a reaction-diffusion system as a typewriter

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Pattern formation is a common phenomenon, which appears in biological systems, especially in cell differentiation processes. The proper level for understanding the creation of patterns seems to be a physicochemical description. The most fundamental models should be based on systems, in which only chemical reactions and diffusion transport occur (reaction-diffusion systems). In order to present a richness of patterns, we show here the asymptotic patterns in the form of capital letters obtained in two-dimensional reaction-diffusion systems with zero-flux boundary conditions. All capital letters are obtained in the same model, but initial conditions and sizes of the systems are different for each letter. The chemical model consists of elementary reactions and is realistic. It can be realized experimentally in continuous-flow unstirred reactor with an enzymatic reaction allosterically inhibited by an excess of its reactant and product.
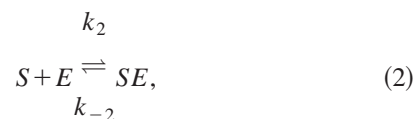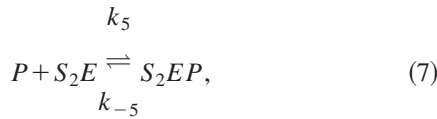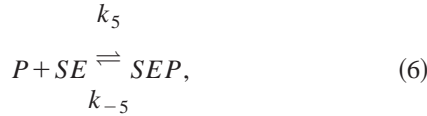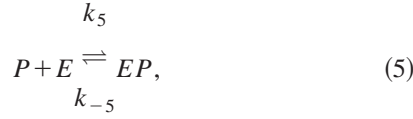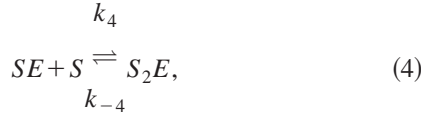
In 1952 Alan Turing pointed out that reaction-diffusion systems might be treated as minimal models of the pattern formation in biological systems [1]. He showed that stationary periodical distributions of variables (reactant concentrations) appeared as asymptotic solutions to nonlinear partial differential equations of the parabolic type (reaction-diffusion systems). Almost forty years later the Turing patterns have been found in open, continuous-flow, unstirred reactors (CFUR), in which the chloride–iodide–malonic acid reaction (CIMA) occurred [2,3]. Meantime target patterns (traveling concentric rings) [4] and spiral waves [5] have been observed in the Belousov-Zhabotinsky (BZ) reaction in closed systems. Now, various patterns, such as oscillating waves [6], lamellar structures [7], self-replicating spots [8], and others [9] are know to appear in chemical systems. Almost all these patterns have been found by chance. The main reason is that the theory of the reaction-diffusion systems is still far from complete. Small amplitude patterns can be described by the linear perturbation analysis of the systems close to bifurcations of homogeneous stationary states [10]. However, large amplitude patterns, which appear in excitable, bistable, or oscillatory systems, have been obtained mainly in numerical simulations of corresponding reaction-diffusion equations. There are well-known theorems by Fisher [11], Kolmogorov, Petrovsky, and Piskunov [12], and Kanel [13], but they describe traveling fronts in one-variable systems only. The theorem by Kanel was helpful in the construction of large amplitude stationary periodical structures in at least three-variable reaction-diffusion systems provided there was the possibility to separate time scales for each variable [14,15]. The other approach of construction of stationary structures in one-dimensional (1D) and 2D two-variable (activator-inhibitor) systems in an excitable regime with one stationary state has also been considered [16–19].

Large amplitude stationary periodical structures have been found numerically in 1D and 2D two-variable reaction-diffusion models in the excitable regime with three stationary states for periodic boundary conditions, provided that there is a sufficiently large difference in diffusion coeffi-

cients [20,21]. They appear due to division and stopping of a traveling impulse. These results are very important, because every pattern observed in a n-variable reaction-diffusion system can always be found in a $(n+1)$-variable reaction-diffusion system, but not *vice versa*. Recently, we have explained in a qualitative way, reasons of the division and the stopping of a traveling impulse and found large amplitude stationary periodical structures in a two-variable, one-dimensional model for zero-flux boundary conditions [22]. Moreover, we have found that for various initial conditions different patterns may coexist in the same system. Each pattern exists in a limited interval in space. There are subintervals on which subsequent patterns coexist. The number of the coexisting structures strongly increases with a size of the system. The coexistence of the large amplitude stationary periodical structures in 1D systems is the crucial property, which allows us to construct two-dimensional patterns with desired forms. In order to illustrate possibilities of the creation of various patterns in 2D systems we show in the present paper the large amplitude stationary patterns in the form of all capital letters. It is noteworthy, that the all capital letters have been created in the same reaction-diffusion model. Each letter has been obtained in a system with appropriate sizes as the result of local excitations of a homogeneous stationary state, which is stable to small perturbations. Some letters have been obtained by local excitations separated in time.

Our model consists of the following elementary, monomolecular and bimolecular reactions (excluding autocatalysis) [22]:

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

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

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

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

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

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

$$P + S_2E \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} S_2EP, \tag{7}$$

$$P + E' \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} E'P, \tag{8}$$

$$E'P \xrightarrow{k_7} E' + R, \tag{9}$$

$$P \xrightarrow{k_8} Q. \tag{10}$$
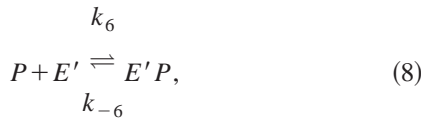
In step (1) S_0 is treated as the reservoir variable, whose concentration is maintained constant. The steps (2)–(7) describe a catalytic (enzymatic) reaction with the inhibition by an excess of the reactant S and the product P. For simplicity we assume that the rate constants in steps (5)–(7) are the same, which is a reasonable assumption for allosteric inhibition by the product. The product P is consumed by another enzymatic reaction with the enzyme E' producing inreactive product R [steps (8) and (9)]. It is assumed that these reactions occur in its saturation regime. Moreover, P is transformed directly to some product Q in the step (10). This second enzymatic reaction allows the simplification of formulas for a nullcline for the product. Due to steps (1) and (8)–(10), the scheme describes an open chemical system.

According to the mass action law, the behavior of the system is described by ten kinetic equations for S, P, E, SE, EP, S_2E, SEP, S_2EP, E', and SE'. It is easy to see that $E(t) + SE(t) + EP(t) + S_2E(t) + S_2EP = E_0$ and $E'(t) + E'P(t) = E_0'(t)$ are two first integrals, so the dynamics of the system is described by eight kinetic equations. Usually, total concentrations of the enzymes (catalysts) E_0 as well as E_0' are much smaller than the concentrations of the reactant S and the product P. In this case one can separate scales of time, in which the concentrations of the reagents change. The variables E, SE, EP, S_2E, SEP, S_2EP, and E' become fast

variables, whereas S and P are the slow ones. According to the Tikhonov theorem [23], the fast variables in a slow time scale are equal to their quasistationary values and in this scale the dynamics can be described by a reduced system of slow variables.

Assuming that diffusion coefficients for catalysts (enzymes) and all their complexes with the reactant and the product are negligible, the dynamics of inhomogeneous 2D system is described by the following reaction-diffusion equations:

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

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

where s and p are dimensionless concentrations of the reactant S and the product P, respectively, t, x, and y are dimensionless time and space coordinates, D_s and D_p are dimensionless diffusion coefficients, and A_1, A_2, A_3, B, B_1, and B_2 are the parameters. In all calculations described in the present paper we assume the following values for the parameters $A_1 = 0.01$, $A_2 = 10^{-4}$, $A_3 = 0.505$, $B = 0.625$, $B_1 = 7.99 \times 10^{-3}$, and $B_2 = 4.65 \times 10^{-5}$ and the diffusion coefficients $D_s = 10^{-5}$ and $D_p = 5 \times 10^{-5}$. For the given values of the parameters the homogeneous system is in an excitable regime with three stationary states. One of them is a stable node and the other ones are a saddle point and an unstable focus [22]. In the sequel we consider the initial-boundary value (Fourier) problem with zero-flux (Neumann) boundary conditions. In all calculations the same values of the parameters have been used, but we have changed the sizes of the system and positions of local excitations of the homogeneous stable stationary state. We assume that in all regions, which are initially excited $s(0,x,y) = 20$ and $p(0,x,y) = 35$. Outside of excited regions the homogeneous stationary values of both variables have been assumed as initial conditions. The letters shown in Fig. 1 have been generated for the data presented in the Table I. L_x and L_y denote the sizes of the rectangles in x and y directions; "No." numbers rectangular regions excited initially (without star) or with a time delay (with star); x_l and y_l denote position of the lower left apex of excited regions; and l_x and l_y denote the sizes of excited rectangles in x and y directions, respectively. The letters "A" and "F" have been constructed in two steps. Initially the system was excited in the given region and after some time (T) the next excitation was introduced with $s(T,x,y) = 40$ and $p(T,x,y) = 35$. The patterns obtained in the calculations have been a little deformed (squeezed or/and elongated in one or two dimensions) in order to get letters with proper height and width. It is easy to check that our equations are symmetrical with respect to translations and reflections in x and y. If

FIG. 1. The set of asymptotic patterns generated in twenty-six 2D systems. The patterns have been obtained in the systems with different sizes and different initial conditions (see Table I). The patterns are a little deformed to give the letters with close height and width. All letters are formed from the patterns by separations of asymptotic values of $s(t,x,y)$ into two regions with values of s higher or lower than 2. One of these two regions is marked in black.

$s(t,x,y)$ is a solution in a given system, then its mirror reflection is also the solution. Owing to the zero-flux boundary conditions, a given solution together with its mirror reflection is also the solution on the enlarged region. This property allows us to not only save computer time, but also to compose some letters from parts by mirror reflections along one or both space directions. It is evident that an initial, local excitation positioned symmetrically in a 2D system evolves according to the initial symmetry and asymptotically gives a symmetrical pattern. An unsymmetrical initial disturbance with small asymmetry evolves asymptotically to a symmetric pattern, whereas that with strong asymmetry sometimes gives unsymmetrical asymptotic patterns. We have assumed that a given pattern has an asymptotic form if the maximal local changes in $s(t,x,y)$ and $p(t,x,y)$ appear at the 8th digit at most and continue decreasing in time. It is noteworthy that some letters may be generated in a few ways which means with different sizes of the system and local excitations positioned in various places. Small changes in the size of the system as well as in places of initial excitations usually give small differences in calculated values of $s(t,x,y)$ and do not change the ''geometry'' of the pattern. However, if one size of the system is close to the interval on which the 1D pattern becomes unstable, then in this case small changes of the sizes may give completely different asymptotic patterns. Our model is structurally stable, which means that there are sufficiently small changes of the right hand sides of the equations as well as the diffusion coefficients, which do not cause qualitative differences in asymptotic patterns. The asymptotic values of $s(t,x,y)$ and $p(t,x,y)$ change in the ranges (0.1–40) and (8–30), respectively. All letters are formed from the asymptotic patterns by separation of asymptotic values of $s(t,x,y)$ into two regions. The regions in the (x,y) plane in which $s(t,x,y)$ is higher or lower than 2 are marked in black. Not all of our letters have elegant forms. Some of them are similar to scribble, but they are readable, especially when used in sets meaning words. Our model should be treated as an example of an inhomogeneous distributed chemical system in which various patterns may appear. In real systems inhomogeneities may appear due to internal, local fluctuations. Such fluctuations can induce the spontaneous formation of large amplitude patterns. The patterns in the form of all capital letters may appear in various dynamical systems, provided that the necessary conditions are fulfilled. The properties of the translation and reflection symmetries are satisfied in all nonlinear parabolic type par-

TABLE I. Sizes of the system, number of excited regions, their positions, and sizes.

	L_x	L_y	No.	x_l	y_l	l_x	l_y
A	4.00	4.00	1	1.76	1.76	0.48	0.48
			2*	1.60	0.00	0.88	0.80
B	2.80	4.28	1	1.28	0.00	0.24	0.60
			2	1.28	3.64	0.24	0.60
C	1.52	3.04	1	1.40	1.28	0.24	0.48
D	3.44	3.04	1	1.48	1.44	0.48	0.48
E	4.24	1.60	1	1.56	0.00	0.32	0.48
			2	2.56	0.00	0.32	0.48
F	2.00	4.00	1	1.76	1.76	0.24	0.24
			2*	1.56	0.00	0.44	0.24
G	2.00	4.00	1	0.00	0.00	0.48	0.48
			2	1.52	1.76	0.48	0.48
H	2.80	4.00	1	1.28	1.40	0.24	1.20
I	4.00	2.00	1	1.52	1.76	0.48	0.48
			2	0.00	1.76	4.00	0.24
J	3.20	1.00	1	0.00	0.00	1.20	0.76
			2	0.00	0.76	3.20	0.24
K	4.00	4.00	1	1.76	0.00	0.48	0.48
			2	3.52	1.52	0.48	0.96
			3	1.76	3.52	0.48	0.48
L	3.20	1.00	1	0.00	0.00	3.20	0.24
			2	0.00	0.24	1.20	0.76
M	5.60	2.00	1	1.18	1.40	0.24	0.60
			2	4.08	1.40	0.24	0.60
N	5.92	2.48	1	1.36	0.00	0.24	0.60
			2	4.32	1.88	0.24	0.60
O	4.00	4.00	1	1.76	1.76	0.48	0.48
P	4.00	4.00	1	0.00	0.00	0.48	0.48
			2	1.52	1.76	0.96	0.48
			3	3.52	0.00	0.48	0.48
Q	4.00	4.00	1	1.76	1.52	0.48	0.96
			2	3.52	0.00	0.48	0.48
			3	3.32	3.52	0.48	0.48
R	4.65	3.04	1	1.36	1.36	0.32	0.32
			2	4.36	1.36	0.16	0.32
S	2.48	5.92	1	0.00	1.36	0.60	0.24
			2	1.88	4.32	0.60	0.24
T	3.20	2.00	1	0.00	0.00	3.20	0.24
			2	0.00	0.24	1.20	1.52
			3	0.00	1.76	3.20	0.24
U	2.80	2.00	1	1.28	0.00	0.24	0.60
V	5.00	5.00	1	0.00	0.00	0.24	0.24
W	5.60	2.00	1	1.18	0.00	0.24	0.60
			2	4.08	0.00	0.24	0.60
X	3.44	3.44	1	1.60	1.60	0.24	0.24
Y	3.44	1.72	1	1.60	0.00	0.24	0.12
Z	2.48	5.92	1	0.00	4.32	0.60	0.24
			2	1.88	1.36	0.60	0.24

tial differential equations (reaction-diffusion systems) for the Neumann boundary conditions. The particular property, namely, the coexistence of stationary patterns, that is the dependence of asymptotic solutions on initial conditions is

the crucial point. In the case of a two-variable system the generation of the large amplitude patterns and, as a consequence, their coexistence is achieved due to a sufficiently large difference in the diffusion coefficients. For equal or very close diffusion coefficients an initial local excitation always evolves to the traveling impulse, that is, to the pulse of excitation running through the system with constant velocity. Of course, not only patterns in the form of the letters are possible in our model. These patterns should be considered only as examples of the variety of asymptotic structures possible in chemical systems. They are constructed in order to convince the reader that rather simple, but nonlinear chemical systems are sufficiently rich to produce the desired patterns. Of course, much more important is a modeling of patterns observed in biological systems, especially in cell differentiation processes, which seems to be governed by the positional information [24]. On the other hand, it does not escape our notice that the possibility to create patterns in the form of the letters open new prospects for encoding information in chemical systems.

The model can be accomplished experimentally by two coupled enzymatic reactions proceeding in a 2D CFUR. One of them should be a enzymatic (catalytic) reaction of Michaelis-Menten type (Langmuir-Hinshelwood) with the inhibition by an excess of its reactant and product, whereas the other one can be a simple enzymatic (catalytic) reaction. Moreover, the values of the diffusion coefficients are reasonable for the diffusion transport of compounds in liquid or gel systems used in typical CFURs. The feed of a CFUR can be assured by step (1), which describes the influx of the reactant S from reservoirs through the x,y planes. Step (10) describes the outflow of the product P to the reservoirs, in which its concentration can be neglected. These assumptions are reasonable approximations, if the size of the CFUR in the direction perpendicular to the x,y plane is so small that the concentration gradients in this direction caused by the diffusion flows from the reservoirs can be neglected. It is noteworthy that our model is realistic in the sense that all its basic assumptions can be accomplished in real CFURs. Therefore, we hope that our results will be a stimulus for experimentalists to look for the patterns discussed in the present paper in real systems.

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