Invariant characteristics of self-organization modes in Belousov reaction modeling

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Abstract. We consider the problem of mathematical modeling of oxidation-reduction oscillatory chemical reactions based on the mechanism of Belousov reaction. The process of the main components interaction in such reaction can be interpreted by a phenomenologically similar to it "predator-prey" model. Thereby, we consider a parabolic boundary value problem consisting of three Volterra-type equations, which is a mathematical model of this reaction. We carry out a local study of the neighborhood of the system's non-trivial equilibrium state and construct the normal form of the considering system. Finally, we do a numerical analysis of the coexisting chaotic oscillatory modes of the boundary value problem in a flat area, which have different nature and occur as the diffusion coefficient decreases.

1. Introduction

The reaction we are interested in was discovered by B.P. Belousov in 1951, but gained a wide popularity much later — a detailed article on this topic was published only 30 years later (see [1]). An experimental analysis of this reaction was done in the works of A.M. Zhabotinsky (see [2]).

We study a fairly simplified mathematical model in terms of the reaction components composition. The relations between the considering substances that enter into Belousov reaction (namely: bromo acid $HBrO_2$, cerium Ce^{4+}, and bromide Br^- [2]) can be clearly described by the following scheme (see Fig. 1), where the sign "+" means that the presence of one substance contributes to the emergence of another, and the sign "−" indicates the oppression of one substance by another. A system of differential equations was proposed in [3] to describe this reaction on the assumption of phenomenological proximity of the substances interaction resulting scheme to the "predator-prey" problem. Later the system was modified in [4] for more accurately modeling of the ongoing chemical processes.

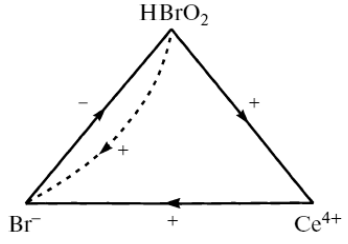


Figure 1. The nominal scheme of substances interaction in the modeling reaction.

2. Problem statement

We consider a boundary value problem of the form:

$$\begin{aligned} \dot{x} &= D_1\Delta x + r_1(1 + a(1 - z) - x)x, & \left.\frac{\partial x}{\partial \nu}\right|_{\partial\Omega} &= 0, \\ \dot{y} &= D_2\Delta y + r_2(x - y)y, & \left.\frac{\partial y}{\partial \nu}\right|_{\partial\Omega} &= 0, \\ \dot{z} &= D_3\Delta z + r_3(\alpha x + (1 - \alpha)y - z)z, & \left.\frac{\partial z}{\partial \nu}\right|_{\partial\Omega} &= 0, \end{aligned} \tag{1}$$

where $x(t, s)$, $y(t, s)$, and $z(t, s)$ stand for the concentration density of $HBrO_2$, Ce^{4+}, and Br^- respectively, $s \in \Omega \subset \mathbb{R}^2$, $t > 0$; parameters r_1, r_2, r_3, a, D_1, D_2, D_3 are positive; $\alpha \in (0, 1)$; $(D_1, D_2, D_3) = d(D_1^0, D_2^0, D_3^0)$, $d > 0$; Δ is a Laplace operator; and ν is a direction of the outer normal to the border $\partial\Omega$ of bounded flat area Ω with measure equals to 1.

Our goal is to carry out the local study of limit cycle genesis in the neighborhood of the nontrivial equilibrium state of the system (1) at value of parameter a close to the critical a_{cr}. In [4] for case of $a \gg a_{cr}$ the corresponding cycle was studied using the large parameter method. Moreover, it is required to consider the typical chaotic oscillatory modes with different structures at small diffusion value in a flat area using numerical analysis.

We introduce auxiliary notations: $p = r_1r_2r_3$, $q = r_1r_2 + r_1r_3 + r_2r_3$, $r = r_1 + r_2 + r_3$. A local analysis of the problem (1) will be performed near the equilibrium state $(1, 1, 1)$, since at

$$a > a_{cr} = (qr - p)/(p(1 - \alpha) - \alpha r_1r_3(r_1 + r_3)) \tag{2}$$

the system without diffusion terms loses stability in an oscillatory manner.

The main result of numerical analysis is as follows: the boundary value problem (1) has coexisting chaotic oscillations that retain the dynamic characteristics of spatially homogeneous cycle of the system, and self-organization type modes that are, in some way, more effective: the minima of the average value by area Ω increase and the maximum burst values decrease.

3. A local analysis of neighborhood of equilibrium state $(1, 1, 1)$ at a close to critical

We clarify the problem statement in this case. We consider the problem for the spatially homogeneous solution of the system (1), in which we assume $a = a_{cr} + \varepsilon$, where ε is a positive small parameter, a_{cr} is determined by the formula (2), and the stability is getting lost in an oscillatory manner in the neighborhood of the equilibrium state $(1, 1, 1)$ at this value of a. To do this, we make replacements: $x = u + 1$, $y = v + 1$, $z = w + 1$. The resulting system has the form:

$$\begin{aligned} \dot{u} &= r_1(u + 1)(-u - (a_{cr} + \varepsilon)w), \\ \dot{v} &= r_2(v + 1)(u - v), \\ \dot{w} &= r_3(w + 1)(\alpha u + (1 - \alpha)v - w). \end{aligned} \tag{3}$$

In (3) we use the standard replacement of the normal forms method, and we search the solution in the form

$$(u, v, w)^T = \sqrt{\varepsilon}(he^{i\omega t}\xi(\tau) + \text{c.c.}) + \varepsilon U_1(t, \tau) + \varepsilon^{3/2}U_2(t, \tau) + \dots, \tag{4}$$

where c.c. is a complex conjugate to the expression in the same bracket, $\tau = \varepsilon t$ is a slow time, $U_j(t, \tau)$ $(j \geq 1)$ are the trigonometric polynomials by t, $h = (h_1, h_2, h_3)^T$ is the eigenvector of matrix of the linearized system (3) corresponding to eigenvalue $i\omega$, and $\omega = \sqrt{q + r_1r_3a\alpha}$.

After equalization of the coefficients by same powers of $\sqrt{\varepsilon}$, on the third step (at $\varepsilon^{3/2}$) we obtain the problem for U_2, from the solvability condition of which in the class of trigonometric polynomials we get the equation for complex amplitude:

$$\xi' = (\varphi_0 + i\psi_0)\xi + (d_0 + ic_0)|\xi|^2\xi,$$

which has a self-similar solution of the form $\xi = \rho e^{i\varphi}$, where $\rho(\tau)$ and $\varphi(\tau)$ satisfy the following equations: $\rho' = \varphi_0\rho + d_0\rho^3$, $\varphi' = \psi_0 + c_0\rho^2$. Here ρ determines the amplitude, and φ determines the correction to the oscillation frequency. Parameters φ_0 and d_0 have the form:

$$\varphi_0 = \frac{r_1 r_3 (r_2 - \alpha r)^2}{2(r_2(r^2+q) - \alpha(r^3+p))},$$

$$d_0 = \frac{(1-\alpha)^2 r_2^3 (r_1+r_2)^4 (r_1+r_3)^2 (r_2+r_3)^3 r((1+\alpha)r_1 + (\alpha-3)r_2 + (3\alpha-1)r_3)(q - r_1 r_3 \alpha)^2}{2r_3^2(r_2-\alpha r)^3(r_2(r^2+q) - \alpha(r^3+p))(r_2(r^2+4q) - \alpha(r^3+4p))}.$$

Hereinafter, we will only be interested in the amplitude of the oscillatory mode, therefore we do not give the form of ψ_0 and c_0 due to its cumbersomeness.

For the case $r_1 = 1$, $r_2 = 2$, $r_3 = 3$ the dependence of φ_0 and d_0 on the parameter α is represented on Fig. 2 and Fig. 3. Here, the solid line indicates a zone of positive values, and dotted line indicates a zone of negative values.

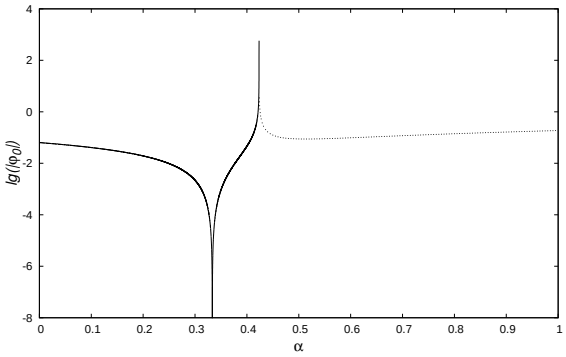


Figure 2. Dependence of φ_0 on α at $r_1 = 1$, $r_2 = 2$, $r_3 = 3$.

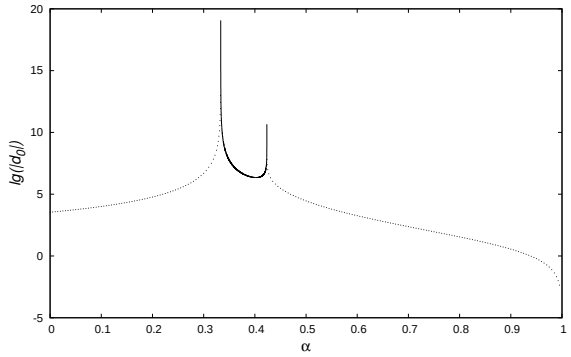


Figure 3. Dependence of d_0 on α at $r_1 = 1$, $r_2 = 2$, $r_3 = 3$.

Thereby, the following statement is proved.

Theorem 1. *Let these inequalities are satisfied:* $r_1, r_2, r_3 > 0$, $(r_2(r^2+q) - \alpha(r^3+p)) > 0$, $((\alpha+1)r_1 + (\alpha-3)r_2 + (3\alpha-1)r_3)(r_2(r^2+4q) - \alpha(r^3+4p)) < 0$, $r_2 \neq \alpha r$, *and* $a = a_{cr} + \varepsilon$, *where* a_{cr} *is defined by the formula* (2). *Then there exists* $\varepsilon_0 > 0$ *such that for all* $\varepsilon \in (0, \varepsilon_0]$ *within some sufficiently small neighborhood of zero there exists an orbitally asymptotically stable limit cycle of the system* (3) *bifurcating from it with asymptotics* (4).

Note that a value of the oscillation amplitude of the system's limit cycle is determined by $\sqrt{-\varepsilon\varphi_0/d_0}$. To illustrate Theorem 1, we calculated the analytical and numerical values of the oscillation amplitude for a fixed set of parameters in order to determine the limits of applicability of this theorem. Based on Table 1, it is not difficult to see that the asymptotic formulas are satisfied within rather wide limits.

Suppose that $D_1 = \varepsilon d D_1^0$, $D_2 = \varepsilon d D_2^0$, $D_3 = \varepsilon d D_3^0$. After that, using the methods of asymptotic analysis we can find the value d, at which the constructed by us spatially homogeneous cycle with the asymptotics (4) loses stability. By analogy with the assumptions of the article [5], we can find such a critical value d and the asymptotics of a spatially

Table 1. Values of the cycle oscillation amplitudes at $r_1 = 1$, $r_2 = 2$, $r_3 = 3$.

α	ε	analytical result	numerical result
0.1	10^{-2}	0.22090794	0.22116161
0.1	10^{-1}	0.69869911	0.69937442
0.3	10^{-2}	0.08908736	0.08855718
0.3	10^{-1}	0.28086436	0.28004238

inhomogeneous cycle bifurcating from a homogeneous one. Unfortunately, asymptotic methods do not allow us to study the problem by further decreasing the parameter d and increasing the parameter a. Thereby, we have to apply numerical methods. It should also be noted that asymptotic formulas for spatially homogeneous and spatially inhomogeneous cycles were obtained in [4] assuming that r is a large parameter.

Spatially inhomogeneous modes bifurcating from the homogeneous cycle of the system (3) usually inherit the properties of a spatially homogeneous cycle relatively to the average value, minima and maxima of the oscillatory modes. In a numerical experiment, it is interesting to find spatially inhomogeneous modes of another structure, which we conventionally call self-organization modes. The next section is devoted to a numerical analysis of the boundary value problem (1) and to finding such modes.

4. Numerical analysis of the boundary value problem (1)

We study the boundary value problem (1) using numerical methods in the square area Ω ($\Omega = \{(x_1, x_2) \mid 0 \le x_1 \le 1,\ 0 \le x_2 \le 1\}$). For the numerical analysis of the boundary value problem (1) we replace Laplace operator with its difference analogue. Suppose the number of partition points m gets such greater, than the diffusion coefficient gets smaller. Also we assume that the values in the appropriate rectangles of the region Ω are the same. Such approach allows us to apply the methods of parallel calculations.

Numerical analysis showed that the cycle constructed by us with the increasing of parameter a becomes relaxational and turns into the modes described in [4]. Therefore, we further consider the case of finite r_1, r_2, r_3 and a relatively large a. Based on this, we set in (1)

$$d = 0.002,\ D_1^0 = 0.01,\ D_2^0 = 0.08,\ D_3^0 = 0.01,\ r_1 = 1,\ r_2 = 2,\ r_3 = 3,\ \alpha = 0.2,\ a = 100.$$

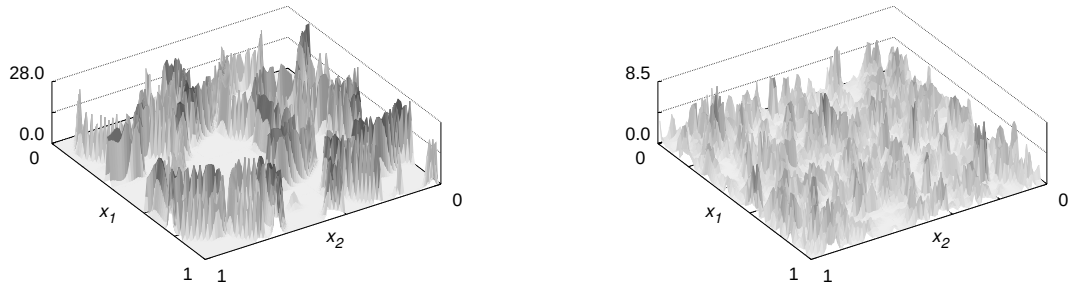
As the diffusion coefficient d decreases, the oscillating modes of distributed model become more complicated. Coexisting chaotic modes of different nature arise including chaotic oscillations with relaxation properties and self-organization modes.

- The solutions of the first type are similar in their properties to the homogeneous stable relaxation cycle of the system (deep minima and high δ-like bursts of the average by space value $x(t, s)$) (see Fig. 4 a), Fig. 5 a), and Fig. 6 a)).
- In self-organization modes the minima of the average by space value $x(t, s)$ are separated from zero, and the bursts are not so large by amplitude as in other solutions (see Fig. 4 b), Fig. 5 b), and Fig. 6 b)).

A comparison of their dynamic characteristics is given in Table 2. Here $\widehat{x}(t)$ is the average by space defined by the formula $\widehat{x}(t) = 1/(\text{mes}\ \Omega) \int\limits_\Omega x(t, s)ds$ and $M(\widehat{x}(t))$ is the average by time. The largest Lyapunov exponents (see [6, 7, 8, 9]) of these modes are calculated for various number of partition points (see Fig. 7). These graphs clearly show the difference in the chaotic structure of considered modes.

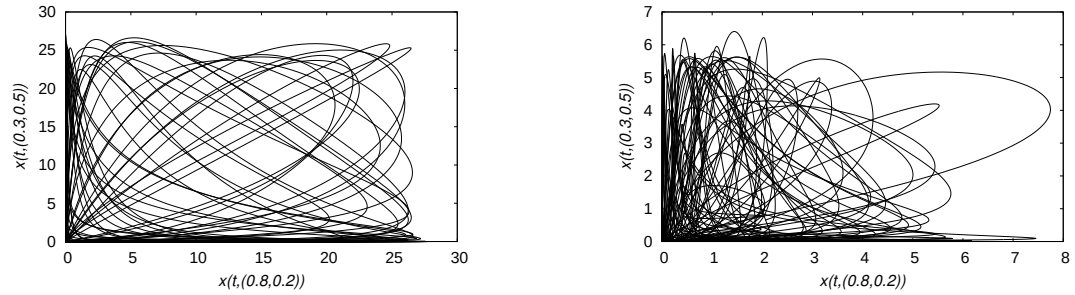
Table 2. Comparison of modes dynamic characteristics.

Mode type	$M(\widehat{x}(t))$	$\min \widehat{x}(t)$	$\max \widehat{x}(t)$	$\min x(t,s)$	$\max x(t,s)$
Relaxation mode	0.9540	10^{-11}	3.44373	10^{-12}	29.81307
Self-organization mode	0.9722	0.79906	1.15436	10^{-12}	18.03019



a) b)

Figure 4. Distribution of $x(t,s)$ by area Ω at $t = T_*$ in case of mode with a) relaxation properties; b) self-organization.

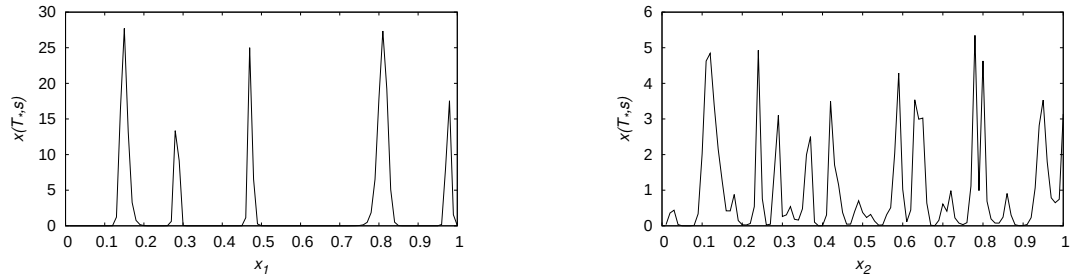


a) b)

Figure 5. Phase portrait of $x(t,s)$ (built on $x(t,(0.8,0.2))$ and $x(t,(0.3,0.5))$) in case of mode with a) relaxation properties ($0 \le t \le 200$); b) self-organization ($0 \le t \le 50$).

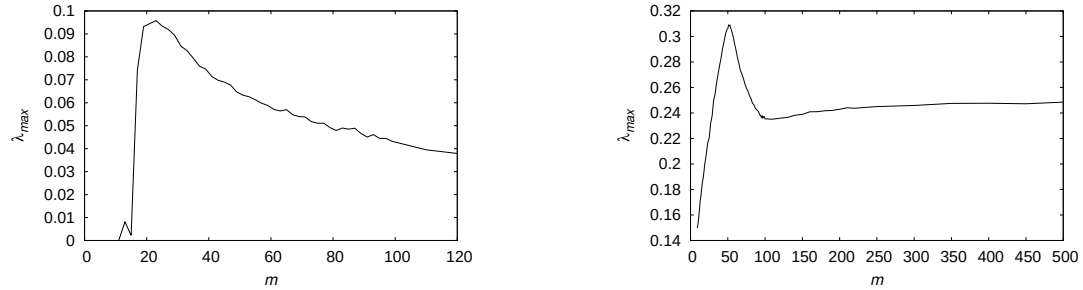
5. Conclusion

We summarize obtained results. First of all, we note the found for a point model asymptotic formulas for a stable periodic solution. For this solution, which is a spatially homogeneous cycle of a model system, we determine the conditions on which a spatially inhomogeneous cycle bifurcates from it. These asymptotics are used as a starting point for a numerical experiment. The main result of numerical modeling of the boundary value problem is as follows: it has more complex oscillatory modes (self-organization modes) along with spatially inhomogeneous modes bifurcating from spatially homogeneous ones. These modes are unordered both by time and space. The largest Lyapunov exponent, calculated for them, turned out to be positive, and that just represents its disorder. At the same time, these solutions have a more explicit biophysical meaning. This allows us to consider the offered approach for oscillatory chemical reactions modeling as fairly adequate.



a) b)

Figure 6. Cross-section of $x(t, s)$ along one of area Ω axes at $t = T_*$ in case of mode with a) relaxation properties; b) self-organization.



a) b)

Figure 7. Dependence of largest Lyapunov exponent on the number of partition points in case of mode with a) relaxation properties; b) self-organization.

Acknowledgments

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