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ANALYSIS OF CRITICAL PHENOMENA IN A DYNAMIC SYSTEM UNDER THE INFLUENCE OF RANDOM PERTURBATIONS

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Abstract. The paper is devoted to the study of stochastic models of an electrochemical reaction with a perturbation described by a generalized white-noise random process. Noise-induced transitions are analyzed, the influence of external perturbations on limit cycles is examined, and the sensitivity of the cycle to noise was found. The dependence of the threshold value of the noise intensity on the control parameter of the system is established. The critical value of the noise intensity at which small-amplitude oscillations turn into mixed-type oscillations is obtained. The critical value of noise corresponding to the transition from canard trajectories to relaxation oscillations in the model is found. It is shown that an increase in the intensity of random perturbations can lead to significant changes of oscillation modes of the model up to their destruction.

***Keywords and phrases*:** random perturbation, white noise, stochastic sensitivity, critical phenomenon, canard trajectory, differential equation, stochastic equation.

***AMS Subject Classification*:** 35Q92, 35R60

1. Introduction. Analysis of changes in the behavior of dynamic systems under the influence of random perturbations is of great interest to researchers in various fields of natural science. Stochastic models are used for studying various physical, chemical, and biological processes that are characterized by the presence of random deviations (errors, noise, instability of factors influencing the process). Stochastic fluctuations often cause unexpected results in the operation of electronic generators and lasers, lead to a change in the dynamic modes of functioning of the chemical and biological system.

As a rule, unstable operation of any industrial unit is accompanied by some losses. In some cases, the unstable behavior of an electrochemical reactor leads to its shutdown or reduction in productivity, product defects, or various accidents. Therefore, the search for stability conditions is an important part of the complex problem concerning the reliability and efficiency of technological processes.

Even small random perturbations can lead to qualitative changes in the nonlinear dynamics of the system. The situation can become unstable not only due to incorrect actions, but also due to small changes of some parameters. In chemical systems, the role of such random perturbations can be played by various impurities, thermal fluctuations, and many other external factors.

In this paper, we study the effect of noise (see [5, 13]) on the critical mode of the dynamic model of the Koper–Sluyters electrochemical reaction (see [6]) in electrochemical reactors. Electrochemical reactors are used for the electrochemical conversion of various liquids (milk, vegetable and mineral oils, solutions of carbohydrates, ammonia, alcohols, organic and inorganic fertilizers, and many others).

2. Deterministic model. Consider a model of an electrochemical reaction of the Koper–Sluyters type (see [14]) without random fluctuations. In the dimensionless form, the dynamic model of an

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electrochemical reaction is the following system of differential equations:

$$\frac{du}{dt} = -k_a e^{\gamma\theta/2} u(1-\theta) + k_d e^{-\gamma\theta/2}\theta + 1 - u = f(u,\theta), \quad (1)$$

$$\beta\frac{d\theta}{dt} = k_a e^{\gamma\theta/2} u(1-\theta) - k_d e^{-\gamma\theta/2}\theta - k_e e^{\alpha_0\zeta E}\theta = g(u,\theta), \quad (2)$$

where u is the dimensionless surface concentration of the electrolyte X and β is the dimensionless volume concentration of X. The dimensionless variable θ is the amount of the substance X adsorbed on the electrode surface, E is the electrode potential, β is the adsorbate coverage coefficient, α_0 is the symmetry coefficient for the electron transfer, k_a, k_d, and k_e are the rates of adsorption, desorption, and electron transfer, respectively. The parameter γ is called the interaction parameter; positive (negative) values of γ correspond to the attractive (repulsive) adsorption interaction. The dimensionless current density is $J = k_e e^{\alpha_0\zeta E}\theta$, where $\zeta = F/(RT)$, R is the universal gas constant, F is the Faraday constant and T is the temperature.

Since the parameter β is small, the system (1)–(2) is a singularly perturbed system.

In [8–11], a detailed analysis of the deterministic model was performed by methods of the theory of singular perturbations and numerical methods. It was shown that the critical modes is modeled by a duck trajectory; this mode separates two main types of reaction modes: stable cycles and relaxation oscillations (see [12, 15–18]).

3. Critical mode in the model. It was shown in [8] that there are several locations for a singular point of the system. In the first case, singular point is located on the stable part of the zero approximation of the slow invariant manifold (see [20]); the type of the singular point is a stable ficus. In the second case, the singular point lies in the unstable part of the zero approximation of the slow invariant manifold. If it is removed from the breakdown points at a considerable distance, then relaxation oscillations are observed in the system.

With further minor changes in the control parameter (the values of all other parameters are fixed), the singular point moves to the unstable part of the zero approximation of the slow invariant manifold but remains in a small neighborhood (of order $O(\beta)$ as $\beta \to 0$) of the breakdown point. The singular point becomes an unstable focus, and a closed trajectory is separated from it; the amplitude of this closed trajectory grows proportionally to the square root of the increment of the control parameter, i.e., the Andronov–Hopf bifurcation appears. The Andronov–Hopf bifurcation establishes a connection between the loss of stability of equilibrium positions and the occurrence of periodic solutions in the system. In experiments where values of the parameter are close to the bifurcation value, the periodic solution appeared differs little from the stationary solution since its amplitude is very small and can be lost in the experimental noise. However, when the parameter reaches the "duck" value, the situation changes dramatically: a small change in the parameter leads to the so-called *duck explosion*, when the amplitude of concentration fluctuations almost instantly takes sufficiently large values. This means that the "duck" value of the parameter should be considered as the boundary of the safe flow of the process (see [12, 15–18]).

The duck trajectory and the value of the control parameter k_e^* can be represented in the form of an asymptotic decomposition in powers of a small parameter β (see [19]):

$$u = \Phi(\theta,\beta) = u_0(\theta) + \beta u_1(\theta) + \beta^2 u_2(\theta) + \ldots, \quad (3)$$

$$k_e^* = \chi(\beta) = \chi_0 + \beta\chi_1 + \beta^2\chi_2 + \ldots. \quad (4)$$

To find an asymptotic representation of the duck trajectory, we substitute Eqs. (3) and (4) into the invariance equation

$$\frac{du}{d\theta} g(u,\theta) = \beta f(u,\theta)$$

obtained from the system (1)–(2). After the substitution we obtain

$$u_0(\theta) = \frac{k_d e^{-\gamma\theta/2} + \chi_0 e^{\alpha_0 \zeta E}}{k_a e^{\gamma\theta/2}(1-\theta)}\theta, \tag{5}$$

$$u_1(\theta) = \frac{-k_a u_0(\theta)(1-\theta)e^{\gamma\theta/2} + k_d e^{-\gamma\theta/2}\theta + 1 - u_0(\theta) + \chi_1 e^{\alpha_0\zeta E}\theta u_0'(\theta)}{k_a e^{\gamma\theta/2} u_0'(\theta)}, \tag{6}$$

$$\chi_0 = \frac{k_a(1-\bar\theta)e^{\gamma\bar\theta/2} - k_d e^{-\gamma\bar\theta/2}\bar\theta}{(k_a(1-\bar\theta)e^{\gamma\bar\theta/2} - 1)e^{\alpha_0\zeta E}\bar\theta}, \tag{7}$$

$$\chi_1 = -\frac{k_a u_1(\bar\theta)(1-\bar\theta)e^{\gamma\bar\theta/2} + u_1(\bar\theta) + k_a u_1(\bar\theta)u_1'(\bar\theta)(1-\bar\theta)e^{\gamma\bar\theta/2}}{e^{\alpha_0\zeta E}\bar\theta u_1'(\bar\theta)}, \tag{8}$$

where $\theta = \bar\theta$ is the value at the breakdown point. Equations (5)–(8) determine the first approximation for the duck trajectory passing through the breakdown point $(u(\bar\theta), \bar\theta)$ of the system (1)–(2).

During the study, we encountered the problem of the influence of external noises on the critical mode of the model. Since this mode is modeled by a duck trajectory, it is necessary to study how its shape, size, and the possibility of existence change under the influence of external perturbations (see [7, 13]).

4. Stochastic model. Let us modify the model considered in the previous section from the point of view of the influence of medium fluctuations on the chemical reaction. Since these fluctuations are random, their inclusion in the modification proposed leads to the fact that the new model will be considered stochastic. Naturally, such a perturbation must be introduced as an additive term to the stationary process. Assume that the system is also affected by a white noise of low intensity:

$$\frac{du}{dt} = -k_a e^{\gamma\theta/2}u(1-\theta) + k_d e^{-\gamma\theta/2}\theta + 1 - u + \epsilon\xi_1 = f(u,\theta), \tag{9}$$

$$\beta\frac{d\theta}{dt} = k_a e^{\gamma\theta/2}u(1-\theta) - k_d e^{-\gamma\theta/2}\theta - k_e e^{\alpha_0\zeta E}\theta + \epsilon\xi_2 = g(u,\theta). \tag{10}$$

The scalar random process $\xi(t,\omega)$, $t \in T = [0,\infty]$, is a stationary white noise; its spectral density $\epsilon \in [0,1]$ (called the intensity of the white noise) is constant.

The study of the influence of external noises on the behavior of the system was performed with the following values of the parameters proposed in [6]: $\epsilon = 0.2$, $\gamma = 8.99$, $k_a = 10$, $k_d = 100$, $k_e = 0.85, \alpha_0 = 0.5$, $\zeta = 38.7$, $E = 0.207$ (unless other values are indicated in captions).

We start the study with an analysis of the stochastic sensitivity of the equilibrium depending on the control parameter k_e.

5. Theoretical noise sensitivity. For noise sensitivity analysis of a stochastic equilibrium of the dynamic system, the method of stochastic sensitivity functions was used in [3, 4]. It is based on the calculation of the stochastic sensitivity matrix W, which is a positive definite matrix characterizing the spread of random trajectories of system around the equilibrium position. The eigenvalues of the matrix W are theoretical characteristics of the noise sensitivity.

The matrix W is the solution of the matrix equation

$$FW + WF^T + S = 0, \tag{11}$$

where

$$F = \begin{pmatrix} \dfrac{\partial f}{\partial u} & \dfrac{\partial f}{\partial \theta} \\ \dfrac{\partial g}{\partial u} & \dfrac{\partial g}{\partial \theta} \end{pmatrix}_{(\bar u,\bar\theta)}, \quad S = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad W = \begin{pmatrix} w_{11} & w_{12} \\ w_{12} & w_{22} \end{pmatrix}. \tag{12}$$

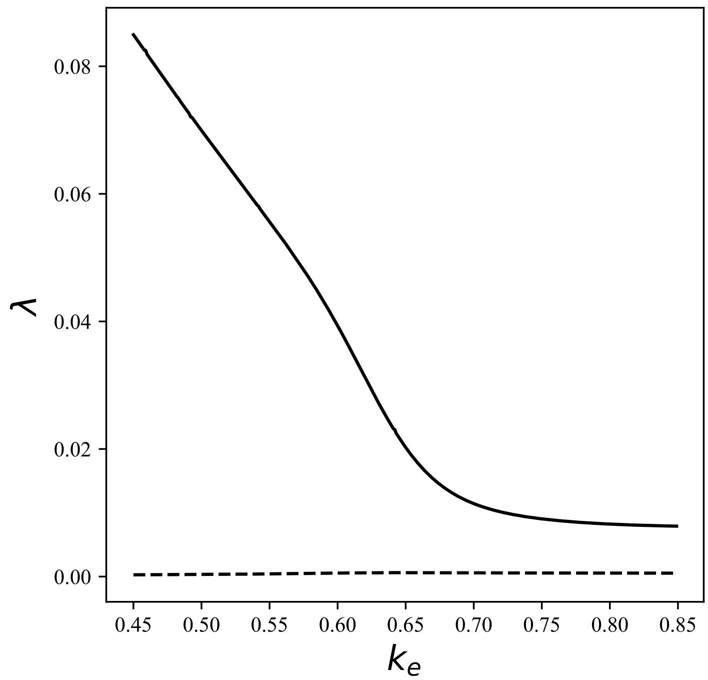

Fig. 1. Theoretical noise sensitivity

The elements of the matrix W can be found from (11):

$$w_{11} = \frac{-1 - 2f_\theta w_{12}}{2f_u}, \quad w_{22} = \frac{-1 - 2g_u w_{12}}{2g_\theta}, \quad w_{12} = \frac{f_u f_\theta + g_u g_\theta}{2(f_\theta^2 g_\theta + g_\theta^2 f_u - f_u f_\theta g_u - f_u g_u g_\theta)};$$

its eigenvalues are

$$\lambda_{1,2} = \frac{1}{2}\left(w_{11} + w_{22} \pm \sqrt{(w_{11} + w_{12})^2 - 4(w_{11}w_{22} - w_{12}^2)}\right). \tag{13}$$

where

$$f_u = \frac{\partial f}{\partial u}(\bar{u}, \bar{\theta}), \quad f_\theta = \frac{\partial f}{\partial \theta}(\bar{u}, \bar{\theta}), \quad g_u = \frac{\partial g}{\partial u}(\bar{u}, \bar{\theta}), \quad g_\theta = \frac{\partial g}{\partial \theta}(\bar{u}, \bar{\theta}).$$

Results obtaining by the theoretical method are presented in Fig. 1.

Note that one of the eigenvalues (13) is very small (see Fig. 1, dashed line); thus, the stochastic sensitivity is defined by the largest eigenvalues. The graph shows that the stochastic equilibrium becomes more sensitive to noise as the control parameter k_e increases.

6. Noise-induced transitions. In the stochastic model, under the influence of noise, qualitative changes are possible: if of the noise intensity ϵ_{cr} reaches a certain critical value, a transition occurs from one deterministic attractor (rest point) to another (limit cycle). Such qualitative changes in the system are called noise-induced transitions. Consider the change in the stochastic phase portrait depending on the noise intensity.

At low noise, random states always lie in a neighborhood of the equilibrium. As the noise intensity grows, rare transitions through the unstable cycle to the limit cycle and vice versa appear, i.e., mixed-type oscillations are observed (see Fig. 2). However, if the bifurcation parameter increases and approximates the zone where the rest point loses its stability, the amplitude of oscillations becomes large (see Fig. 3). As the noise intensity increases further, transitions become more frequent.

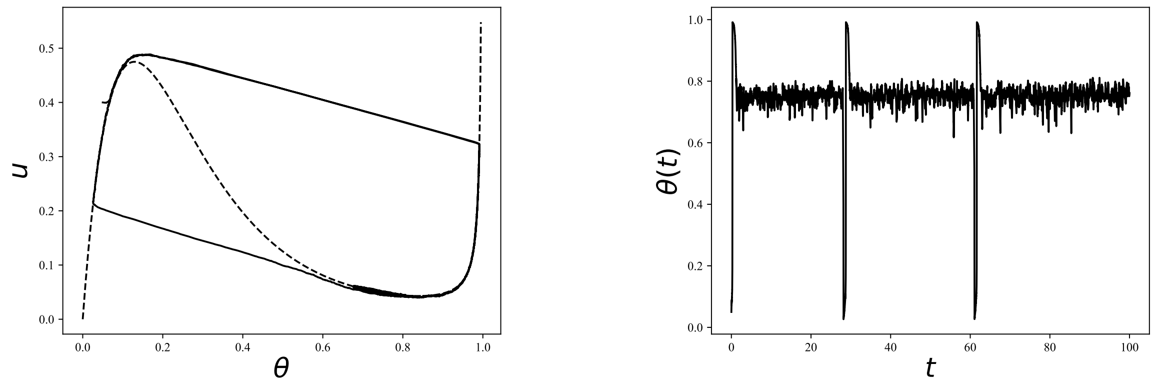

Fig. 2. Noise-induced transition for $k_e = 0.85$ and $\epsilon = 0.0098$

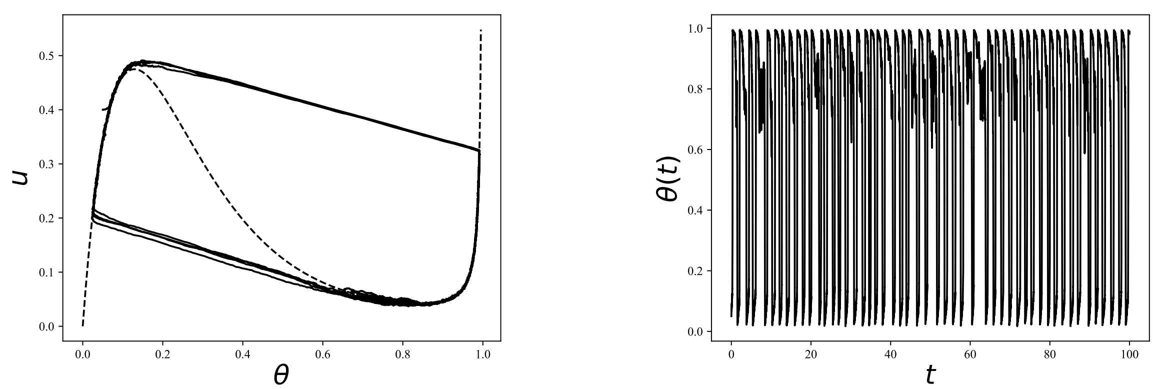

Fig. 3. Noise-induced transition for $k_e = 0.85$ and $\epsilon = 0.02$

Thus, applying the techniques of stochastic sensitivity functions, we can predict the value of the noise intensity ϵ_{cr} corresponding to the appearance of transitions. For example, for the control parameter $k_e = 0.85$, at which noise-induced transitions were demonstrated, the critical value of the noise intensity is approximately equal to $\epsilon_{cr} \approx 0.009495$.

Having searched for the critical values of the noise intensity for the values of the parameter k_e from the stable zone, we obtained the dependence of ϵ_{cr} on the control parameter. Figure 4 shows that as the value of the bifurcation parameter increases, the value of the noise intensity, at which transitions between attractors appear, decreases.

7. Study of stochastic cycles. We are interested in the stochastic dynamics of the system considered in the zone of critical cycles. Under the action of random perturbations, trajectories leave the deterministic cycle and form a certain bundle around it, called a stochastic cycle. Figure (5) shows stochastic cycles for the fixed noise intensity $\epsilon = 0.00225$ and three values of the parameter k_e, namely, $k_e = 0.92$, $k_e = 0.92053$, and $k_e = 0.93$. Note that the spread of random trajectories changes significantly along the cycle. To an even greater extent, this spread depends on the parameter k_e.

A convenient quantitative characterization of the spread of random trajectories around a deterministic cycle at low noise is the stochastic sensitivity function (see [1–3]).

If the intensity of noise in the system increases, in addition to quantitative changes, new effects can occur.

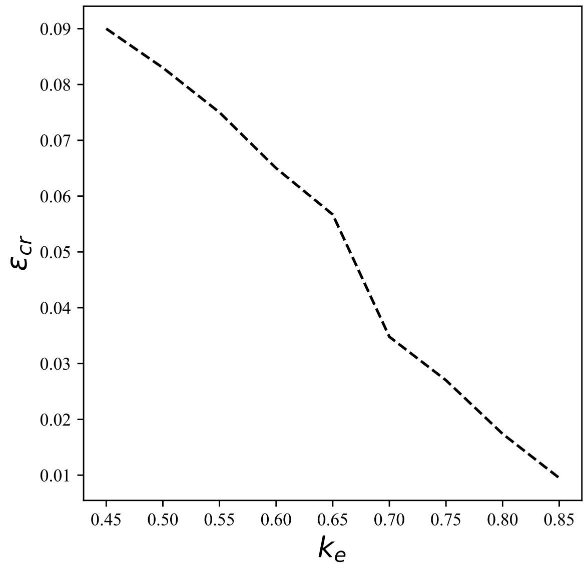

Fig. 4. Dependence of the critical noise value on the control parameter k_e

Now we study in more detail the distribution of trajectories of the stochastically perturbed critical cycle for $k_e = 0.92053$ for various values of the noise intensity ϵ. The corresponding graphs are presented in Fig. (6).

Note that the distribution of random trajectories changes as the noise intensity increases, namely, the spread of trajectories expands and the range of amplitudes of stochastic oscillations grows. At $\epsilon = 10^{-5}$, two concentration zones appear in the bundle of random trajectories. Thus, a qualitative change in the phase portrait of the stochastic system—a stochastic bifurcation—is observed. The bifurcation point lies between $\epsilon = 10^{-8}$ and $\epsilon = 10^{-5}$.

The changes in the dynamics of the stochastic system can be illustrated by time series. In Fig. (7), the graphs of the coordinate $\theta(t)$ are presented.

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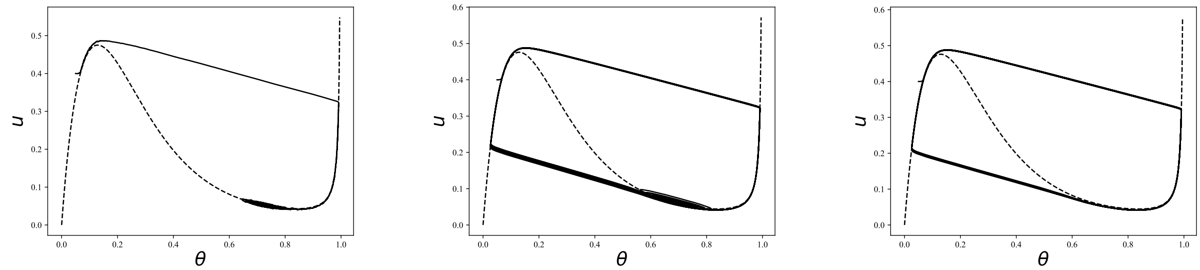
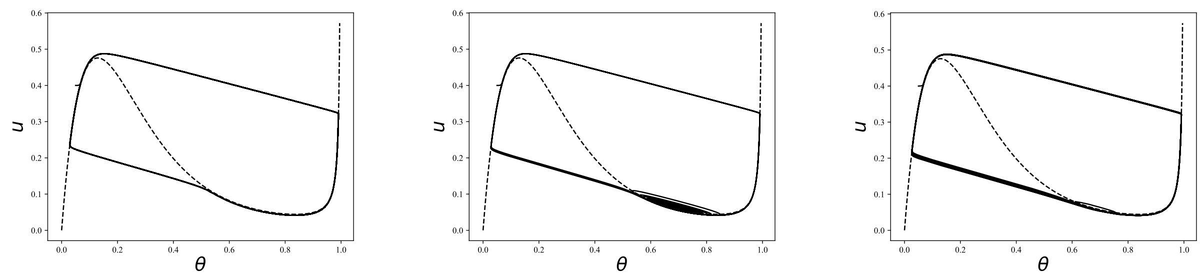
REFERENCES

1. I. A. Bashkirtseva, "Stochastic sensitivity analysis: theory and numerical algorithms," *IOP Conf. Ser. Mater. Sci. Eng.*, **192**, 012024 (2017).
2. I. A. Bashkirtceva and T. V. Perevalova, "Analysis of stochastic attractors at bifurcation rest point-cycle," *Avtomat. Telemekh.*, No. 10, 53-69 (2007).
3. I. A. Bashkirtseva and L. B. Ryashko, "Sensitivity analysis of the stochastically and periodically forced brusselator," *Phys. A.*, **278**, 126–139 (2000).
4. I. A. Bashkirtseva and L. B. Ryashko, "Stochastic sensitivity analysis of noise-induced excitement in a preypredator plankton system," *Front. Life Sci.*, **5**, 141-148 (2011).
5. N. Berglund, B. Gentz, and C. Kuehn, "Hunting french ducks in a noisy environment," *J. Differ. Equations.*, **252 (9)**, 4786–4841 (2012).



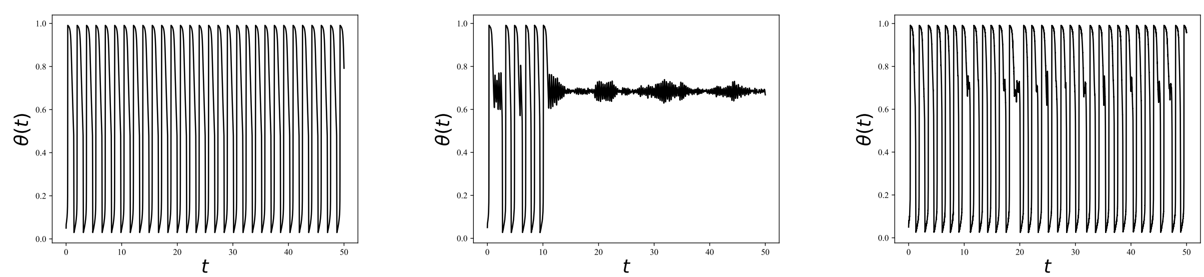
(a) (b) (c)

Fig. 5. Stochastic cycles for the noise intensity $\epsilon = 0.00225$



(a) (b) (c)

Fig. 6. Splitting of the stochastic cycle for $k_e = 0.92053$



(a) (b) (c)

Fig. 7. Graphs of $\theta(t)$ for $k_e = 0.92053$

6. F. Berthier, J. P. Diard, and S. Nugues, “On the nature of the spontaneous oscillations observed for the Koper–Sluyters electrocatalitic reaction,” *J. Electroanal. Chem.*, **436 (1)**, 35–42 (1997).
7. H. E. De Swart, and J. Grasman, “Effect of stochastic perturbations on a low-order spectral model of the atmospheric circulation,” *Tellus.*, **39A**, 10–24 (1987).
8. N. M. Firstova, “Study of critical phenomena in a model of an electrochemical reactor,” *Vestn. Samar. Univ. Estestvennonauch. Ser.*, **110**, No. 9/2, 221–226 (2013).
9. N. Firstova and E. Shchepakina, “Conditions for the critical phenomena in a dynamic model of an electrocatalytic reaction,” *J. Phys. Conf. Ser.*, **811**, 012002 (2017).
10. N. Firstova and E. Shchepakina, “Modelling of critical conditions for an electrochemical reactor model,” *Proc. Eng.*, **201**, 495–502 (2017).
11. N. Firstova and E. Shchepakina, “Study of oscillatory processes in the one model of electrochemical reactor,” *CEUR Workshop Proc.*, **1638**, 731–741 (2016).

12. E. S. Golodova and E. A. Shchepakina, "Simulation of safe combustion processes with maximal temperature," *Mat. Model.*, **20**, No. 5, 55–68 (2008).
13. J. Grasman, "Asymptotic analysis of nonlinear systems with small stochastic perturbations," *Math. Comput. Sim.*, **31**, 41–54 (1989).
14. M. T. M. Koper and J. H. Sluyters, "Instabilities and oscillations in simple models of electrocatalytic surface reactions," *J. Electroanal. Chem.*, **371 (1)**, 149 (1994).
15. E. A. Shchepakina, "Safety conditions for the ignition of a flammable liquid in a porous insulating material," *Sib. Zh. Industr. Mat.*, **5**, No. 3 (11), 162-169 (2002).
16. E. A. Shchepakina, "Singular perturbations in modeling of safe combustion processes," *Mat. Model.*, **15**, No. 8, 113–117 (2003).
17. E. A. Shchepakina, "Singularly perturbed models of combustion processes in in multiphase media," *Sib. Zh. Industr. Mat.*, **6**, No. 4 (16), 142–157 (2003).
18. E. Shchepakina, "Black swans and canards in self-ignition problem," *Nonlinear Anal. Real World Appl.*, **4**, 45–50 (2003).
19. E. Shchepakina, "Critical phenomena in a model of fuel's heating in a porous medium," *CEUR Workshop Proc.*, **1490**, 179-189 (2015).
20. V. A. Sobolev and E. A. Shchepakina, *Model Reduction and Critical Phenomena in Macrokinetics* [in Russian], Fizmatlit, M. (2010).

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