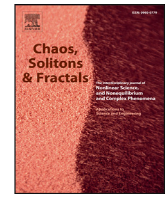
Chaos, Solitons and Fractals 87 (2016) 84–91

Contents lists available at ScienceDirect

Chaos, Solitons and Fractals

Nonlinear Science, and Nonequilibrium and Complex Phenomena

journal homepage: www.elsevier.com/locate/chaos



Complex bifurcations in the oscillatory reaction model

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ARTICLE INFO

Article history:
Received 18 November 2015
Revised 29 February 2016
Accepted 9 March 2016
Available online 24 March 2016

***Keywords*:**
Oscillatory reaction
Bifurcations
Non-linear dynamics
Law of mass conservation

ABSTRACT

The mixing of different types of bifurcations, i.e. supercritical Andronov–Hopf (SAH), double loop (DL) and saddle-loop (SL) bifurcations in the vicinity of their total annihilation, is examined on the highly nonlinear six-variable model for the Bray–Liebhafsky (BL) oscillatory reaction under continuously well-stirred tank reactor (CSTR) conditions. For this kind of the reaction system where the law of mass conservation is additional constraint that must be satisfied and where because of that, some simple bifurcations cannot be formed independently to the others, the considered transformations of the bifurcations are particularly important. That is why as the control parameters for bifurcation analysis, the specific flow rate (j_0), as well as the inflow hydrogen peroxide concentration ($h = [H_2O_2]_{in}$), were used. The complex bifurcations obtained from numerical simulations are compared with some experimental results. It was shown that these complex bifurcations cannot be easily recognized in experimental investigations without knowing their evolution.

1. Introduction

In almost all complex nonlinear reaction systems with feedback, when they are far from thermodynamic equilibrium, numerous dynamic states can be found [1–10]. Despite the corresponding state space such systems should be mostly in stable steady states, there are lots of them (particularly in biological and social sciences, including population phenomena) which are always in various periodic and aperiodic oscillatory dynamic states. Such are the double oscillatory evolution of endocrine hormones at humans with different periods on the ultradian and circadian levels [11–14], neural spiking and bursting [15], oscillations of glycolytic intermediates [16], heart beating, fluctuations in the density of population of *Paramecium aurelia* and *Saccharomyca exiguous* [17], etc. In these systems the transition from one to the other dynamic states can be of vital importance for their existence [11–15]. Therefore, we need to examine qualitative changes in the dynamics (*bifurcations*) and the parameter values at which they occur (*bifurcation points*). As already mentioned, dynamical systems are very complex; some simpler systems such as oscillatory chemical reactions are more appropriate models for the analysis of bifurcations.

In general, bifurcations are important phenomena that provide scenario of transitions between dynamic states and emerging of instabilities as some *control parameter* (the specific flow rate, the inflow concentration of the feed substances, temperature, etc.) is varied. The most examined and most frequently encountered are bifurcations that appear when the stable steady state becomes unstable and *vice versa*. The most common representatives of such transitions are the *supercritical* and *subcritical Andronov–Hopf, saddle-loop* (SL)[1], *saddle-node infinite period* (SNIPER)[2] and *double loop* (DL)[3] bifurcations [1–10,14,15,18–53]. Their determinations in the reaction systems are based on the examinations of Maselko and other authors [24–39,50] founded on the Poincaré–Andronov–Hopf theoretical investigations of two-variable systems [18–20]. They explained how the mentioned bifurcations can be identified experimentally by means of the amplitudes (A) and the oscillatory period (τ) of the periodic orbits, emerging in the bifurcation point, together with the presence/absence of hysteresis in region of bifurcation. For this purpose, they also analyzed both, the limit values of A and τ in the bifurcation point, as well as scaling laws near the bifurcation point governing their values as the function of the distance from bifurcation point. Position of the dynamical system is given by

[1] also known as *infinite period bifurcation* [52], *homoclinic* [36,53], *or saddle-homoclinic bifurcation*.

[2] also known as saddle-node on the invariant circle (SNIC) and as saddle-node central homoclinic bifurcation [53].

[3] also known as *loop-loop, jug handle* or *stable-unstable limit cycle bifurcation* [35].

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http://dx.doi.org/10.1016/j.chaos.2016.03.013
0960-0779/

Table 1
Characteristics of different types of bifurcations (supercritical Andronov–Hopf, SAH, saddle-loop, SL and saddle-node infinite period, SNIPER bifurcation) [4,9,24,35–37,39]

Type of bifurcation	Characteristics of A[a] and τ[b] in the bifurcation point	Dependence of A and τ on $\Delta\mu$[c] or δ[d] near the bifurcation point	Existence of hysteresis
Supercritical Andronov–Hopf (SAH) [4,9,24,35,37,39]	$A \to 0$ $\tau \to$ finite value	$A \propto \Delta\mu^{1/2}$ $\tau \propto \Delta\mu$	No
Saddle-loop (SL) [9,35–37,39]	$A \to$ finite value $\tau \to \infty$	$\tau \propto \ln \delta$	Yes
Saddle-node infinite period (SNIPER) [37,39]	$A \to$ finite value $\tau \to \infty$	$\tau = \delta^{-1/2}$	No

[a] Amplitude of oscillations.
[b] Period of oscillations.
[c] Bifurcation parameter displacement $\Delta\mu = |\mu - \mu_c|$, i.e. absolute value of the control parameter μ distance from its value in bifurcation point μ_c.
[d] Dimensionless value of the bifurcation parameter displacement $\delta = |\mu - \mu_c|/\mu_c$.

the control parameter μ having the value μ_c in bifurcation point. The distance of the dynamical system from bifurcation point is given by the bifurcation parameter displacement, $\Delta\mu = |\mu - \mu_c|$ or its dimensionless value $\delta = |\mu - \mu_c|/\mu_c$. The behaviour of the nonlinear reaction system in the vicinity of bifurcation point for *supercritical Andronov–Hopf* (SAH), *SL* and SNIPER types of bifurcations is presented in Table 1. Thus, the SAH bifurcation can be recognized when in the vicinity of the bifurcation point, the amplitude of oscillations (A) is linearly proportional to the square root of the control parameter value (μ). By extrapolation of this interdependence on zero amplitude, the exact value of the control parameter at the bifurcation point (μ_c) can be determined. There, the oscillation period (τ) has finite value, whereas there is linear dependence between τ and control parameter in vicinity of bifurcation point. Besides, no hysteresis is observed [4,9,35,39]. The *saddle-node infinite period* (SNIPER) as well as SL bifurcation are both characterized by abrupt vanishing of large-amplitude oscillations in the vicinity of the bifurcation point as the control parameter is being varied [9,27,35–37,39]. These bifurcations differ from each other by different relationships between period of oscillations and bifurcation parameter displacement in the vicinity of the bifurcation point (Table 1). Besides, the presence of hysteresis in SL bifurcation distinguishes SL from the SNIPER bifurcation, where hysteresis is not found. In reaction systems, the subcritical Andronov–Hopf (sAH) and the DL bifurcations are in combination with each other due to the mass conservation. Although, their mathematical definitions are clear for each separately [50], they will be discussed in the following together (see Section 4).

Moreover, bifurcations can be examined as a function of two or more control parameters. The bifurcation, well defined as a function of the first selected parameter, can be essentially transformed or even destroyed under influence of the other parameter(s). Consequently, the related bifurcation point can be only slightly shifted, but can also disappear under influence of other control parameter(s).

Besides, in chemical, physico-chemical and biochemical reaction systems, where the concentrations of independent intermediate species play the role of variables, their number is mostly larger than two. Moreover, in these nonlinear reaction systems, the combinations of simple bifurcations are required by the law of mass conservation. Therefore, in such systems the identification of bifurcations types is not as simple as in prototype mathematical models, and their interesting merging as well as transitions between them must be carefully analyzed. We intend to show that beside the methods proposed by Maselko and other authors, the process of formation of complex bifurcations with respect to at least two control parameters (historical development) is also necessary. Thus, by analyzing well-known bifurcations that appear in the model of the Bray–Liebhafsky (BL) oscillatory reaction, we have unexpectedly found very interesting transformations of SAH bifurcation into some complex bifurcation consisted of one SAH and two double-loop (DL) ones, as well as one kind of their annihilation in combination with other complex bifurcation emerging by mixing the other SAH and the SL one.

2. The model of the Bray–Liebhafsky oscillatory reaction

The BL oscillatory reaction [54,55], that is, the hydrogen peroxide decomposition in the presence of both, iodate and hydrogen ions:

$$2H_2O_2 \xrightarrow{IO_3^-,\, H^+} 2H_2O + O_2$$

is complex nonlinear process in which the numerous intermediate species, such as I_2, I^-, HIO, HIO_2 and I_2O, take place. If this reaction is performed in the open reactor, more precisely in the continuously well-stirred tank reactor (CSTR), where the inflow of basic constituents (here hydrogen peroxide) and outflow of all species is present, the time evolution of their concentrations can be described by the following set of differential equations based on the earlier proposed model [56] (Appendix 1) and mass-action kinetics [57,58]:

$$\frac{dx_1}{dt} = -k_5x_1x_4 - k_6x_1x_6 - k_7x_1x_5 - k_8x_1 + j_0h - j_0x_1 \tag{1a}$$

$$\frac{dx_2}{dt} = k_4x_3x_4 - k_{11}x_2 - j_0x_2 \tag{1b}$$

$$\frac{dx_3}{dt} = -k_1x_3 - k_2x_3x_5 - k_4x_3x_4 + k_5x_1x_4 + k_9x_4x_5 + k_{11}x_2 - j_0x_3 \tag{1c}$$

$$\frac{dx_4}{dt} = k_1x_3 + 2k_3x_6 - k_4x_3x_4 - k_5x_1x_4 + k_6x_1x_6 - k_9x_4x_5 - 2k_{10}x_4^2 + k_{11}x_2 - j_0x_4 \tag{1d}$$

$$\frac{dx_5}{dt} = k_1x_3 - k_2x_3x_5 + k_6x_1x_6 - k_7x_1x_5 + k_8x_1 - k_9x_4x_5 - j_0x_5 \tag{1e}$$

$$\frac{dx_6}{dt} = k_2x_3x_5 - k_3x_6 - k_6x_1x_6 + k_{10}x_4^2 - j_0x_6 \tag{1f}$$

Here x_i ($i = 1-6$) denotes the concentration of species X_i, that is H_2O_2, I_2, I^-, HIO, HIO_2 and I_2O, respectively; h, k_m ($m = 1$–11) and j_0 denotes the inflow hydrogen peroxide concentration, the rate constants and a specific flow rate, respectively. The concentrations x_i ($i = 1-6$) and h are given in mol $\times$ dm^{-3} i.e. M, whereas the rate constants k_m ($m = 1$–11), as well as j_0, have dimensions which provide that each term in Eq. (1) has dimensions of reaction rates, that is, concentration $\times$ time^{-1}, here given in: M $\times$ min^{-1} (see Appendix 1). In these equations k_m, j_0 and h are parameters, whereas x_i is variable. Thus, we are dealing with the six-dimensional system where under defined conditions all six variables can be in the oscillatory dynamic states [56,59–61].