Weakly Stable Dynamics in a Three-Dimensional Kinetic Model of Catalytic Hydrogen Oxidation

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Abstract

Some new results concerning complex dynamics in a kinetic model of heterogeneous hydrogen oxidation over metallic catalysts are presented. Relaxation oscillations with a high sensitive dependence on the initial conditions arise in the three-variable system with fast, intermediate and slow variables due to existence of the canard cycles that occur in the one-parameter family of two-variable subsystems. A key feature of the weakly stable dynamics appearance will be successive period doubling bifurcations in which the system behavior becomes progressively more complex until the attractor appears.

INTRODUCTION

A detailed study of a mathematical model of a heterogeneous catalytic system in the form of three-variable nonlinear ordinary differential equations is presented with special attention to weakly stable dynamics, a type of complex irregular behavior frequently encountered in oscillating chemical reactions. One of the most important properties of the weakly stable dynamics is "a sensitive dependence on the initial conditions" [1–4].

In the model considered we find numerically periodic orbits of rather complex structure. Bifurcation theory and precise numerical analysis of the global error in long-term numerical integration show that a high sensitive dependence on the initial conditions and weakly stable dynamics appear in the three-variable systems with fast, intermediate and slow variables due to existence of the canard cycles which occur close to the Hopf bifurcation in the one-parameter family of two-variable subsystems [5].

In this paper we study another way to weakly stable dynamics and show the role of successive period doubling bifurcations in the creation of weakly stable dynamics.

MATHEMATICAL MODEL

In this paper we present some new results concerning complex dynamics in a three-dimensional kinetic model of heterogeneous hydrogen oxidation on metallic catalysts [11]:

$$\dot{x} = k_1(1 - x - y)^2 - k_{-1}x^2 - 2k_3(y) \cdot x^2 y$$
$$\dot{y} = k_2(1 - x - y)^2 - k_{-2}y^2 - k_4(y,z) \cdot y$$
$$\quad - k^3(y) \cdot x^2 y \qquad (1)$$
$$\dot{z} = \varepsilon[y(1 - z) - az(1 - x - y)]$$

where x and y are the catalyst surface coverages by hydrogen and oxygen adsorbed, respectively, so that $x \geq 0$, $y \geq 0$ and $x + y \leq 1$; z is the concentration of oxygen dissolved into the subsurface layer, $0 \leq z \leq 1$; $k_{\pm 1}$, $k_{\pm 2}$, k_3, k_4, and $k_{\pm 5}$ are the rate constants of the reaction mechanism steps, $\alpha = k_{-5}/k_5$, $\varepsilon = k_5$ and

$$k_3(y) = k_{30} \exp(-\mu_3 y),$$
$$k_4(y,z) = k_{40} \exp(-\mu_4 y - \mu_5 z)$$

due to the assumption that the activation energies of the reaction rates depend upon the oxygen concentrations y and z. Note that ε is a small parameter because the dissolution into the subsurface layer is a relatively slow process as compared to the chemical reaction or adsorption onto the catalyst surface.

An original iterative method for solving periodical boundary-value problem for autonomous ordinary differential equations is applied to calculations of periodic orbits and their stability in the three-dimensional kinetic model of catalytic hydrogen oxidation [6−8]. This method develops the concept of the well known multishooting method [4, 14, 15].

The model (1) has served as an important motivation for the simplest possible geometrical interpretation of weakly stable dynamics in nonlinear heterogeneous catalytic reactions [9−13, 5, 8].

PERIODIC ORBITS

We let parameters k_1 and k_{40} vary while fix the other parameters $k_{-1} = 0.008$, $k_2 = 20$, $k_{-2} = 0$, $k_{30} = 100$, $\mu_3 = 30$, $\mu_4 = 12$, $\mu_5 = -10$, $\alpha = 7.88$, and $\varepsilon = 0.0024$. Physically it means that the hydrogen partial pressure in the gas mixture over the catalyst surface is varied. Note that k_1 and k_{40} depend linearly upon it.

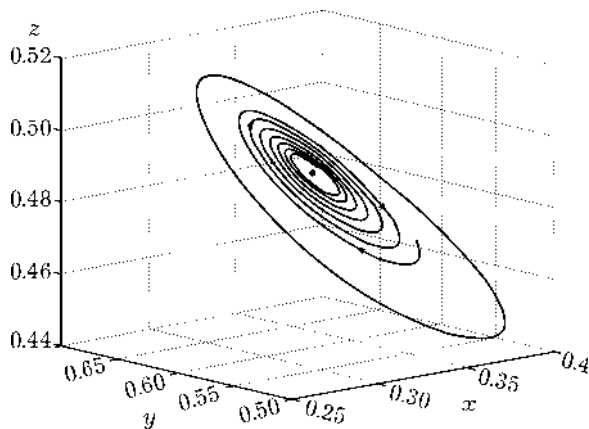Now we give an example to illustrate that an unstable limit cycle exists (Fig. 1). Using the

Fig. 1. Unstable limit cycle of the system (1) with a trajectory inside it for $k_1 = 0.135824260$ and $k_{40} = 2$. The stable steady state is (0.3252466, 0.5958083, 0.4892114) with the eigenvalues -1.9004268 and $-1.9769 \cdot 10^{-4} \pm i \cdot 5.05856 \cdot 10^{-3}$.
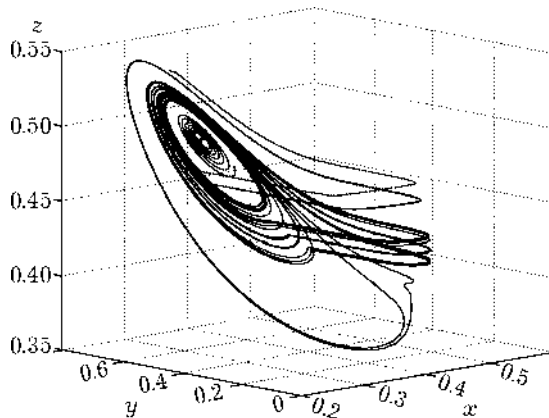

Fig. 2. Unstable limit cycle of the system (1) with two trajectories around it. Parameters are the same as in Fig. 1.

computational technique developed in [6−8], we take three local cross-sections π_1, π_2 and π_3 of the trajectories (1) passing through the points $a_1 = (0.28899502, 0.64086281, 0.51238075)$, $a_2 = (0.33714826, 0.57187779, 0.49312216)$ and $a_3 = (0.38548260, 0.52092294, 0.44677296)$. It allows us to find the periodic orbit decomposed into three pieces with intervals of integration T_i from π_i to π_{i+1} where $T_1 = 395.66180572$, $T_2 = 283.61493869$ and $T_3 = 598.30280382$. Thus, the period equals 1277.57954823. We remark that in this example the multipliers of the unstable closed orbit are (1.8133, 0, 1) and hence a two-dimensional stable invariant manifold exists. The local dynamical behavior "transverse" to this manifold is relatively simple, since it is controlled by the exponentially contracting flow in the local stable manifold (Fig. 2). Trajectories in the stable manifold are expanding.

WEAKLY STABLE DYNAMICS

Numerical integration of the system (1) appears to yield trajectories that are not asymptotically periodic. In fact, in some cases we observe weakly stable dynamics followed by asymptotically periodic motions (Fig. 3). Following [1, 2] we refer to the local expansion and consequent "independent" behavior of orbits starting arbitrary close together as sensitive dependence on the initial conditions or weakly stable dynamics. Since such "simple" differential equations of dimension three play an important role in the kinetic modeling of hete-
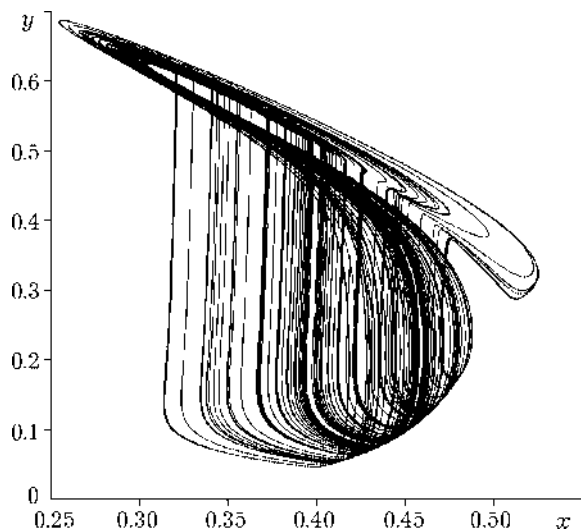
Fig. 3. Weakly stable dynamics: (x, y)-projection of the numerical solution of the system (1) for $k_1 = 0.144$ and $k_{40} = 1.92$ with the initial conditions chosen arbitrary close to the attractor.

rogeneous catalytic reactions [13] and can posses solutions of stunning complexity, an understanding of typical structures of their solutions is essential.

PERIOD DOUBLING SEQUENCE

We consider the role of successive period doubling bifurcations in the creation of weakly stable dynamics in Fig. 3. Following [3], we make first one remark about relationship of the Poincare return map with eigenvalue -1 at a fixed point, to the continuous flow around the corresponding periodic orbit. The trajectories of the Poincare map alternate from one side of the fixed point to the other along the direction of the eigenvector to -1. It means that the two-dimensional center manifold for the periodic orbit of the three-variable system is twisted around the periodic orbit like a Mobius band around its center line.

We have found numerically a sequence of flip bifurcations in the system (1). In Fig. 4−6 we show periodic orbits for several values of k_1 and k_{40}. Using the techniques of previous paragraphs we show that for a value k_1' where $0.146 < k_1' < 0.147045$ the periodic orbit of period T has bifurcated to an orbit of period $2T$ and then for k_1'' where $0.145 < k_1'' < 0,146$ the periodic orbit of period $2T$ has bifurcated to
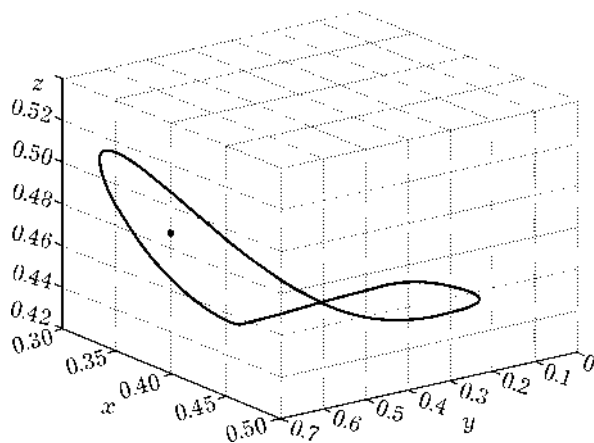

Fig. 4. T-periodic solution of the system (1) for $k_1 = 0.147045$ and $k_{40} = 1.9606$. The unstable steady state is (0.3487194, 0.5699204, 0.4706045) with the eigenvalues -1.931873 and $7.17146 \cdot 10^{-4} \pm i \cdot 5.14812 \cdot 10^{-3}$. Period equals 970.4344.
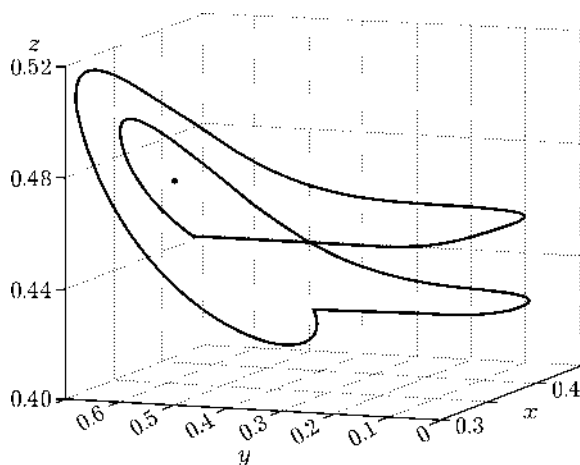

Fig. 5. $2T$-periodic solution of the system (1) for $k_1 = 0.1460$ and $k_{40} = 1.94666$. Period equals 1931.1277.
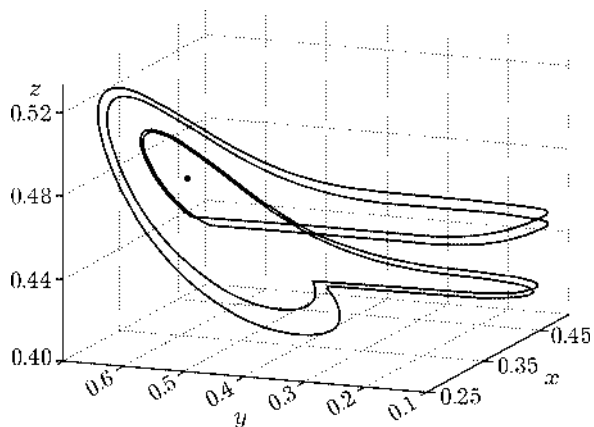

Fig. 6. $4T$-periodic solution of the system (1) for $k_1 = 0.1450$ and $k_{40} = 1.9334$. Period equals 3949.9572.

an orbit of period $4T$. In such a way, an infinite number of families of periodic orbits can be created in flip bifurcations as k_1 decrease. Note, that k_{40} should very simultaneously with the changes of k_1. Thus, a stable orbit with period longer then any pre-assigned period can be found if we let k_1 vary in the interval $0.144 < k_1 < 0.145$. Such orbits are indistinguishable in the numerical integration from bounded non-periodic motions.

We suggest that for $k_1 = 0.144$ such orbits may constitute the attractor observed in a long-term numerical integration (see Fig. 3).

CONCLUSION

In the paper an original iterative algorithm proved to be efficient and accurate for long-term calculations of rather complex periodic orbits and their stability in a three-dimensional kinetic model of catalytic hydrogen oxidation.

Our analysis of this model demonstrates that for some parameters there exists an attractor with the region of high sensitive dependence on initial conditions. To get a clearer idea of the structure of the attracting set we find successive period doubling bifurcations in which the flow becomes progressively more complex until the attractor appears.

We believe that the results obtained are of importance for understanding the reasons of weakly stable dynamics in different heterogeneous catalytic systems.

Acknowledgements

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