Cusp-Shaped Return Maps with Period Adding in a Model of a Chemical System

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Abstract. Period adding with the coexistence of successive attracting periodic orbits is observed in the model of a chemical system when the bifurcation parameter is changed. This phenomenon is characterized by a family of one-dimensional return maps having a cusp shape with positive Schwarzian derivative that exhibits a saddle-node bifurcation.

1. Introduction

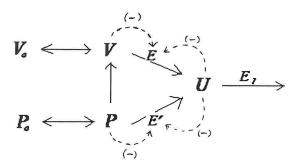
Period adding has been observed in chemical systems [1, 2] and in an electrochemical system [3–5]. Period adding means the following phenomenon: a limit cycle, or an asymptotically periodic behavior, is composed of an oscillation of large amplitude followed by a number of small amplitude oscillations; this number increases by one or by a fixed quantity as an appropriate bifurcation parameter is changed. The observed period-adding oscillations of concentrations of intermediate species or electrical currents were stable in some windows of the parameter. These windows were separated by ranges of the parameter in which oscillations were chaotic.

We have found a similar period-adding phenomenon in a model of a chemical system [6]. Windows with successive attracting periodic orbits were separated by intervals of the bifurcation parameter in which orbits were chaotic. In some windows the period-doubling cascade appeared; moreover, the dynamical behavior of the system was characterized by a family of one-dimensional return maps having a cusp shape.

In the present paper we show new results concerning the same model [6]: we find that the period adding also appears at different ranges of the bifurcation parameter. In contrast to the previous case [6], successive windows of attracting periodic orbits are not separated by chaotic trajectories, but overlap so the coexistence of an n-periodic orbit with an (n+1)-periodic orbit is observed in some intervals of the bifurcation parameter.

2. Model and results

The model describes an open chemical system with coupled enzymatic reactions whose full scheme is given elsewhere [6, 7]. The block scheme is the following:



Substrates V and P are transformed by enzymatic reactions to the same product U. Each of these reactions is inhibited by an excess of its substrate and common product. Moreover, P is transformed into V by a monomolecular reaction. The system is open due to inflows of V and P and the simple enzymatic reaction that transforms P into some inert product. Such a scheme can be useful in the modeling of time evolution of metabolytes that are produced in two or more metabolic pathways.

It is assumed that total concentrations of all enzymes are much lower than concentrations of substrates and product. With this assumption the concentrations of all enzymes and all their complexes with substrates and product become fast variables. In a slow time scale (appropriate for the description of changes of substrates and product) they take their quasi-stationary values and can be eliminated from kinetic equations using the Tikhonov theorem [8]. The dynamical behavior of the system is then described by three kinetic equations. In dimensionless form they are given by

$$\frac{dv}{dt} = A_1 - A_2 v - \frac{v}{(1+v+A_3 v^2)(1+u)},$$

$$\frac{du}{dt} = \epsilon_2 \left(\frac{v}{(1+v+A_3 v^2)(1+u)} + B \left(\frac{p}{(1+p+B_3 p^2)(1+Ku)} \right) + Dp - \frac{Cu}{L+u} \right),$$

$$\frac{dp}{dt} = \epsilon_3 \left(B_1 - B_2 p - B \left(\frac{p}{(1+p+B_3 p^2)(1+Ku)} \right) \right),$$

where v, p, and u are dimensionless concentrations of V, P, and U, respectively. The parameters are defined elsewhere [6, 7].

The same values of the parameters as in the previous works [6, 7] have been assumed:

$$A_1 = 0.08928606601$$
, $A_2 = 0.01486767767$, $A_3 = 4$, $B = 0.04$, $B_1 = 0.000701754$, $B_2 = 0.000140351$, $B_3 = 4$, $C = 0.122$, $D = 0.001$, $K = 10$, $L = 0.74$, and $\epsilon_2 = 0.2$.

 ϵ_3 plays the role of the bifurcation parameter. We change ϵ_3 within the interval [2.7, 2.85].

Orbits obtained by numerical integrations can be roughly characterized by sequences of small (S) and large (L) loops or short and long ones, respectively. Looking at the coordinate u(t) along the orbit, one can see that it has local maxima at approximately the same level (1.45 to 1.5) and local minima at two different levels (the first at about 1.1 to 1.4 and the second at about 0.7 to 0.8). Small (short) loops correspond to maximum—upper minimum—maximum, whereas large (long) loops correspond to maximum—lower minimum—maximum.

At $\epsilon_3 = 2.7$ the system approaches the periodic trajectory with the sequences SL for all initial conditions, whereas at $\epsilon_3 = 2.85$ the periodic trajectory with the sequences LSL is the sole attractor. The examples of attracting periodic orbits are shown in figure 1.

To characterize the behavior of the system we made the Poincaré section at the plane u=1.4343, looking only at those cases in which trajectories cross this plane with u(t) decreasing. Examples are shown in figure 2.

The apparent line shape of the Poincaré sections is caused by the very strong contraction of trajectories in one direction. In the Poincaré section we distinguish three disjoint sets of points (see figure 2). Counting these sets from left to right we call them I_1 , I_2 , and I_3 . The sets I_1 and I_3 consist of intersections of large loops, whereas the set I_2 consists of intersections of small ones.

The first return diffeomorphism F_{ϵ_3} gives the following picture. For all ϵ_3 only the sequences $L(SL)_n$ are seen and

$$F(I_1) \subset I_2, \ F(I_2) \subset I_3, \ F(I_3) \subset I_1 \cup I_2.$$

For most values of ϵ_3 the set I_1 consists of one point. Then the point of set I_3 furthest to the right is transformed to the set I_1 , whereas all remaining points are transformed to I_2 . There are, however, subintervals of ϵ_3 in which two successive attracting periodic trajectories coexist. In this case the Poincaré section contains two points in the set I_1 and 2n+1 points in each of the sets I_2 and I_3 . The two far right points of I_3 are transformed to I_1 . An example of the coexistence of attracting periodic trajectories is shown in figure 1.

Note that at a given ϵ_3 the trajectory intersects the plane u=1.4343 at different values of coordinate p. So the changes in this coordinate (at the Poincaré section) with ϵ_3 can be used to characterize the appearing bifurcations. In order to avoid transient behavior some initial intersections are omitted. The results of the numerical calculations are shown in figure 3.

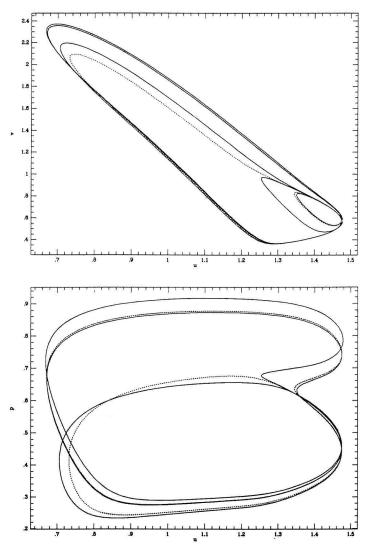


Figure 1: Projections of attracting periodic trajectories on the planes (u,v) and (u,p) for $\epsilon_3=2.765$. The coexistence of the periodic LSL-orbit (dotted line) and the $L(SL)_2$ -periodic orbit is seen. Both orbits are attracting, and the system evolves toward one of them depending on initial conditions.

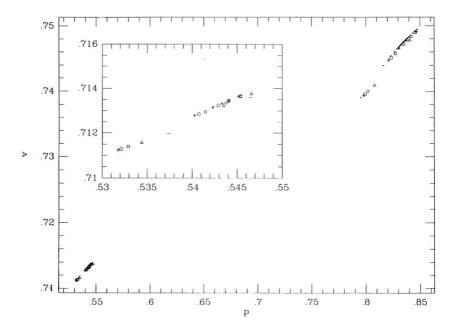


Figure 2: The Poincaré sections at the plane u=1.4343 for given values of ϵ_3 : $\epsilon_3=2.737$ (black points), $\epsilon_3=2.753$ (stars), $\epsilon_3=2.76$ (pentagons), $\epsilon_3=2.77$ (squares), $\epsilon_3=2.8$ (triangles), and $\epsilon_3=2.84$ (dashes). The three sets of points I_1 , I_2 , and I_3 are circled. In the inset are shown the enlargement of I_1 and I_2 .

The values of p at the intersections are grouped into three bunches corresponding to sets I_1 , I_2 , and I_3 . If we decrease ϵ_3 we see that one additional intersection appears in each of the two bunches of p values corresponding to sets I_2 and I_3 . This corresponds to the appearance of the new subsequence SL, which is added to the previous sequence $L(SL)_n$. If we change ϵ_3 in the opposite direction the hysteresis is seen. In some subintervals of ϵ_3 the n-periodic orbit coexists with (n+1)-periodic orbit.

We can parameterize a bunch I_2 by coordinate p and induce a onedimensional return map on this bunch. In this way a map of the interval of p into itself is constructed. Figure 4 shows examples of maps for different ϵ_3 . Each map is of the cusp shape type; they appear continuous, but the derivative at the maximum changes discontinuously from very large positive to very large negative (probably infinite). With ϵ_3 decreasing, the left branch of the maps of the family changes its position and tends toward tangency with the diagonal. This change of ϵ_3 is accompanied by the period adding. A new attracting orbit appears with one more fixed point for appropriate iteration of the map when we go from one window to the next. The changes of the

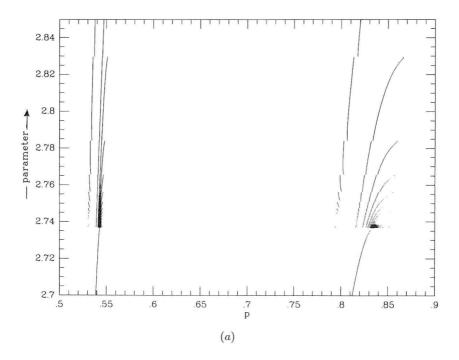


Figure 3: (a) The changes in "asymptotic" values of p at the Poincaré section for ϵ_3 belonging to [2.7, 2.85]. The initial 150 loops were omitted. Three bunches of p values corresponding to the three sets I_i are seen.

shape of a map with ϵ_3 can be described by the following formula:

$$f(x) = d - a \left(\frac{k - x}{k}\right)^{0.335} \quad \text{if } x \le k$$

$$f(x) = d - \left(\frac{x - k}{d - k}\right)^{0.335} \quad \text{if } x > k,$$

where k is the abscissa of the maximum.

The coexistence of two attracting periodic orbits in some intervals of ϵ_3 can be explained by the fact that the Schwarzian derivative of the family of one-dimensional return maps is positive.

With decreasing ϵ_3 in the interval [2.7, 2.85], the sequence SL appears more and more frequently. At the tangency of the left branch with the diagonal ($\epsilon_{3,t} = 2.7366...$) the loop L disappears; only the sequence SL remains, which composes the attracting periodic trajectory.

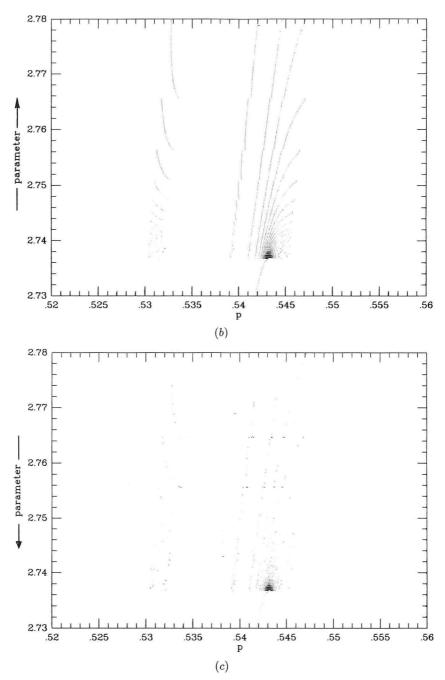


Figure 3: (Continued.) (b) The enlargement of the I_1 and I_2 sets when ϵ_3 is increasing. (c) The enlargement of the I_1 and I_2 sets when ϵ_3 is decreasing. The hysteresis and the coexistence of successive orbits

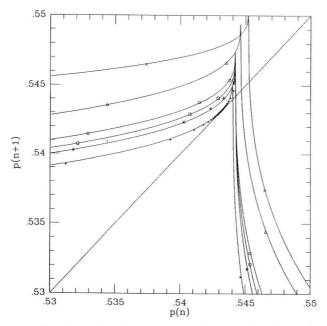


Figure 4: One-dimensional return maps of the p values along the set I_2 : $\epsilon_3 = 2.737$ (black points), $\epsilon_3 = 2.753$ (stars), $\epsilon_3 = 2.76$ (pentagons), $\epsilon_3 = 2.77$ (squares), $\epsilon_3 = 2.84$ (x).

3. Discussion

The family F_{ϵ_3} is hard to analyze in a quantitative way. However, the complex behavior of our model can be described by a family of one-dimensional return maps that exhibit a saddle-node bifurcation. Sufficiently close to the tangency of the branch of the map with the diagonal, the appearance of an $L(SL)_n$ -periodic attracting orbit can be scaled according to the scaling law [9, 10]

$$\epsilon_{3,n+1} - \epsilon_{3,n} = \text{constant} (n^{-2} - (n+1)^{-2})$$

where $\epsilon_{3,n+1}$ and $\epsilon_{3,n}$ denote values of ϵ_3 at which $L(SL)_{n+1}$ - and $L(SL)_n$ -periodic orbits appear.

The adding subsequence in the interval investigated here is different from that found for ϵ_3 belonging to the interval [1.28, 1.36] in the same model [6]. Instead of the sequence SSLSL [6], now the sequence SL is added. The more important difference is that the windows of successive attracting periodic orbits are now no longer separated by chaotic orbits, but overlap. This is the consequence of the fact that the one-dimensional return maps probably have infinite derivatives at the critical point. In fact, this condition implies positive Schwarzian derivative [10]: the positive Schwarzian derivative is necessary to have different attracting orbits [11].

Since the one-dimensional return maps in both intervals of ϵ_3 have a cusp-shape form, we observe the period adding that is a typical phenomenon for this type of map [12, 13].

Our model is an example of a continuous system in which various periodadding phenomena are found. As one-dimensional return maps with a cusp shape have been found in such different systems as the Lorenz model [14] and experimental chemical system [15], and the period adding has also been found in experiments [1–5], it seems that many dynamical systems can be characterized by maps with a shape of this kind.

Acknowledgments

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References

- H. L. Swinney, "Observation of Order and Chaos in Nonlinear Systems," *Physica*, 17D (1986) 3–15.
- [2] I. R. Epstein, "Oscillations and Chaos in Chemical Systems," Physica, 17D (1986) 47–56.
- [3] F. N. Albahadily and M. Schell, "An Experimental Investigation of Periodic and Chaotic Electrochemical Oscillations in the Anodic Dissolution of Copper in Phosphoric Acid," *Journal of Chemical Physics*, 88 (1988) 4312–4319.
- [4] F. N. Albahadily, J. Ringland, and M. Schell, "Mixed-Mode Oscillations in an Electrochemical System. I. A Farey Sequence Which Does Not Occur on a Torus," *Journal of Chemical Physics*, 90 (1989) 813–821.
- [5] M. Schell and F. N. Albahadily, "Mixed-Mode Oscillations in an Electrochemical System. II. A Periodic-Chaotic Sequence," *Journal of Chemical Physics*, 90 (1989) 822–828.
- [6] F. Aicardi and A. L. Kawczynski, "Period-Adding Phenomenon in a Model of Chemical System," Complex Systems, 4 (1990) 1–10.
- [7] A. K. Kawczynski, M. Misiurewicz, and K. Leszcynski, "Periodic and Strange Attractors in a Model of Chemical System," *Polish Journal of Chemistry*, 63 (1989) 239–247.
- [8] A. N. Tikhonov, Mathematics of the USSR Sbornik, 31 (1952) 575-594 (in Russian).
- [9] H. G. Schuster, Deterministic Chaos: An Introduction (Weinheim, 1984).

- [10] M. Misiurewicz and A. L. Kawczynski, "Periodic Orbits for Interval Maps with Sharp Cusps," Physica, 52D (1991) 191–203.
- [11] P. Collet and J. P. Eckmann, Iterated Maps on the Interval as Dynamical Systems (Basel, 1980).
- [12] M. Misurewicz and A. L. Kawczynski, "At the Other Side of a Saddle-Node," Communications in Mathematical Physics, 131 (1990) 605–617.
- [13] A. L. Kawczynski and M. Misiurewicz, "Period-Adding Phenomenon in 1D Return Maps," Zeitschrift fur Physikalische Chemie (Leipzig), 271 (1990) 1037–1046.
- [14] E. N. Lorenz, "Deterministic Nonperiodic Flow," Journal of Atmospheric Sciences, 20 (1963) 130–141.
- [15] J. Maselko, M. Alamgir, and J. R. Epstein, "Bifurcation Analysis of a System of Coupled Chemical Oscillators: Bromate-Clorite-Iodide," *Physica*, 19D (1986) 153–161.