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Explosion of limit cycles and chaotic waves in a simple nonlinear chemical system

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We consider a simple model of an autocatalytic chemical reaction where a limit cycle rapidly increases to infinite period and amplitude, and disappears under variation of a parameter. We show that this bifurcation can be understood from seeing the system as a singular perturbation problem, and we find the bifurcation point by an asymptotic analysis. Scaling laws for period and amplitude are derived. The unphysical bifurcation to infinity disappears under generic modifications of the model, and for a simple example we show is replaced by a canard explosion, that is, a narrow parameter interval with an explosive growth of the amplitude. The bifurcation to infinity introduces a strong sensitivity that may result in chaotic dynamics if diffusion is added. We show that this behavior persists even if the kinetics is modified to preclude the bifurcation to infinity.

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I. INTRODUCTION

Reaction schemes based on the cubic autocatalator as defined in Eq. (1) below have been widely used as prototypes for investigations into nonlinear dynamics of chemical reactions. The central part of the scheme is a cubic autocatalytic step and a first-order decay of the catalyst,

\[ A + 2B \rightarrow 3B \quad \text{(with rate } k_1 a b^2), \quad B \rightarrow C \quad \text{(with rate } k_2 b), \]

where \( a, b \) are the concentrations of the reactants \( A, B \) and \( k_1, k_2 \) are the rate constants. Here we are interested in studying reactions in closed systems where the reactant \( A \) is produced by a slow first-order decay of a precursor \( P \),

\[ P \rightarrow A \quad \text{(rate } k_0 p). \]

Clearly, the reaction based on the schemes (1) and (2) will eventually stop as \( P \) is consumed. However, if the reactant \( P \) is initially present in a large amount, it is customary to invoke the \textit{pooled chemical approximation} and assume that \( P \) retains its initial concentration \( p_0 \) throughout the reaction. Introducing dimensionless variables, the differential equations for the reaction scheme assuming the reactor is well stirred become

\[ \frac{du}{dt} = \mu - u v^2, \quad \frac{dv}{dt} = u v^2 - v, \]

where \( u = \sqrt{k_1/k_2} a, \quad v = \sqrt{k_1/k_2} b, \quad t \) is the dimensionless time scaled from physical time by \( k_1 \) and \( \mu = \sqrt{k_1/k_2 p_0/k_2}. \) This system allows limit cycles, corresponding to an oscillating reaction, for certain values of \( \mu. \) The oscillations are, of course, artefacts from the pooled approximation, but even if the slow consumption of \( P \) is included in a model the transient behavior will for a long time resemble the dynamics of the system (3) closely.

The system (3) has been studied in detail by Merkin, Needham, and Scott [1]. It was shown that the limit cycles rapidly increase to infinite amplitude and period as \( \mu \) approaches a critical value \( \mu_c \) from above. Clearly, this unphysical bifurcation to infinity limits the applicability of the model (3), and it becomes interesting to establish whether the reaction scheme can be modified to avoid this bifurcation while still retaining the simplicity of the pooled approximation. To this end, Merkin, Needham, and Scott [2] added the uncatalyzed reaction

\[ A \rightarrow B \quad \text{(rate } k_3 a) \]

yielding the differential equations

\[ \frac{du}{dt} = \mu - u v^2 - ru, \quad \frac{dv}{dt} = u v^2 - v + ru, \]

with \( r = k_3/k_4). \) It was shown that, as long as \( r \neq 0, \) an interval close to \( \mu_c \) with rapid growth of amplitude and period persisted. However, the bifurcation to infinity did not occur as the amplitude of the limit cycles remains bounded. Gray, Roberts, and Merkin [3] further added a quadratic autocatalytic reaction,

\[ A + B \rightarrow 2B \quad \text{(rate } k_4 a b) \]

resulting in

\[ \frac{du}{dt} = \mu - u v^2 - ru - s u v, \quad \frac{dv}{dt} = u v^2 - v + ru + s u v, \]

with \( s = k_4/\sqrt{k_1 k_2} \) and again obtained bounded trajectories only.

The rapid but bounded growth of limit cycles over a short parameter interval as it occurs in the systems (5) and (7) is
known as a canard explosion. This is mathematically well understood in singular perturbation systems of the form

\[
\frac{du}{dt} = f(u, v, \mu, \epsilon), \quad \frac{dv}{dt} = \epsilon g(u, v, \mu, \epsilon),
\]

in the limit \( \epsilon \to 0 \) [4]. Canard explosions in chemical systems have been identified in the Oregonator [5] and the Edblom-Orbán-Epstein (EOE) reaction [6].

In the present paper we show that it is possible to rewrite the system (3) as a singular perturbation system. This point of view gives rise to a simple geometric interpretation of the bifurcation to infinity and allows an asymptotic determination of \( \mu' \). We also obtain scaling laws for amplitude and period of the limit cycle as the bifurcation to infinity is approached that deviate from the results in [1], and we confirm our results by numerical computations. The singular perturbation analysis is basically the same as is applied in the analysis of the canard explosion. We also analyze the modified system (5) and give a simple geometric explanation why modifications of the original system (3), such as Eqs. (5) and (7), behave as they do.

We have previously [7,8] analyzed bifurcations to infinity in models from mathematical economics and biochemistry. In those studies we have, as in [1], introduced critical points at infinity and seen the bifurcation as being associated with heteroclinic connections of the separatrices of these critical points. The present analysis is simpler in that it only involves objects in the Euclidean plane.

If the reactor is not well mixed, diffusion must be taken in account. If the reactor is spatially one dimensional the pooled kinetics of Eq. (3) leads to the reaction-diffusion system

\[
\frac{\partial u}{\partial t} = \lambda_u \frac{\partial^2 u}{\partial x^2} + \mu - u v^2, \quad \frac{\partial v}{\partial t} = \lambda_v \frac{\partial^2 v}{\partial x^2} + u v^2 - v, \tag{9}
\]

where \( \lambda_u, \lambda_v \) are diffusion coefficients. The basic pattern formation from local bifurcations subject to the no-flux boundary conditions

FIG. 1. Explosion and disappearance of the limit cycle of Eq. (3) for decreasing values of \( \mu \). (a) \( \mu = 0.92 \). (b) \( \mu = 0.9005 \). (c) \( \mu = 0.9 \). Top row: Trajectories in the \((u, v)\) phase plane. Middle row: Time trace of \( u \). Bottom row: Trajectories in the \((p, q)\) phase plane, defined by the coordinate transformation (16). Also shown is the slow manifold \( S_2 \) from (18).

FIG. 2. Sketches of the \( p \) and \( q \) phase plane. (a) For the system (3), the branches \( S_1 \) and \( S_2 \) of the slow manifold with stable manifold \( M_S \) and the unstable manifold \( M_U \), both in the boundary layer of \( S_2 \). The configuration shown with \( M_S \) above \( M_U \) allows a limit cycle. (b) The slow manifold for the system (5) with turning point \( T \) where the branches \( S_1 \) and \( S_2 \) meet.
TABLE I. Results of the asymptotic calculation of $\mu_\infty$ for $\epsilon = 1$.

| Order $k$ | Contribution $\mu_k$ | Approximation $\mu_\infty^{(k)} = \sum_{k=0}^{\infty} \mu_k$ | Relative error $|\frac{\mu_\infty^{(k)} - \mu_\infty}{\mu_\infty}|$ |
|-----------|----------------------|-----------------------------------------------|-----------------------------------------------|
| 0         | 1.00000000           | 1.00000000                                   | 0.11072139                                    |
| 1         | -0.12500000          | 0.87500000                                   | 0.02811877                                    |
| 2         | 0.03125000           | 0.90625000                                   | 0.00659126                                    |
| 3         | -0.00488281          | 0.90136718                                   | 0.00116781                                    |
| 4         | -0.00449970          | 0.89666748                                   | 0.00054224                                    |
| 5         | 0.07579800           | 0.90424728                                   | 0.0036680                                     |
| 6         | -0.00622034          | 0.89802694                                   | 0.00254226                                    |
| 7         | 0.00072032           | 0.89874726                                   | 0.00174218                                    |
| 8         | 0.00958743           | 0.90334771                                   | 0.00890678                                    |
| 9         | -0.02425103          | 0.88403836                                   | 0.01802935                                    |
| 10        | 0.03671743           | 0.92080109                                   | 0.02275347                                    |

\[ \frac{\partial u}{\partial x} = \frac{\partial v}{\partial x} = 0 \text{ for } x = 0, 1, \] (10)

has been studied in some detail \[9,10\]. In [11] it was noted that

the amplitude of limit cycles born in a Hopf bifurcation may obtain large amplitudes as $\mu$ is decreased. We analyze this behavior for a case where both the diffusion constants are small and show that the bifurcation to infinity introduces a sensitivity that may result in chaotic dynamics. Finally, we show that this behavior is basically linked to the singular perturbation nature of the problem, as it persists even if the kinetics is modified to the form (5).

II. DYNAMICS OF THE WELL-STIRRED REACTOR

A. Singular perturbation of the pooled model

The system (3) has a critical point $(u, v) = (1/\mu, \mu)$ which is stable for $\mu > 1$ and loses stability in a Hopf bifurcation at $\mu = 1$. By standard procedures [1] one finds the bifurcation to be supercritical, so stable limit cycles exist for $\mu < 1$. As $\mu$ is decreased the amplitude and period grows rapidly, and when $\mu$ is decreased beyond the numerically obtained value

\[ \mu_\infty = 0.900 \, 315 \, 780 \, 772 \, 2; \] (11)

the limit cycle disappears and only unbounded trajectories remain. See Fig. 1.

The limit cycles display the characteristics of relaxation oscillations: a slow phase is followed by fast, almost linear motion. A formulation as a singular perturbations problem can be achieved by following the analysis of [6] for the EOE reaction. The key is the fact that the right hand sides of the differential equations are almost identical, except for a sign. Indeed, the system can be written in the form

\[ \frac{du}{dt} = f(u, v) + g(u, v, \mu), \quad \frac{dv}{dt} = -f(u, v), \] (12)

with

\[ f(u, v) = v - uv^2, \quad g(u, v, \mu) = \mu - v. \] (13)

If $g$ is replaced by 0 in Eq. (12) the isolated critical point is replaced by two curves of critical points,

\[ v = 0 \text{ and } 1 - uv = 0. \] (14)

Hence, if we modify (12) to include an auxiliary parameter $\epsilon$ as

\[ \frac{du}{dt} = f(u, v) + \epsilon g(u, v, \mu), \quad \frac{dv}{dt} = -f(u, v), \] (15)

we obtain a singular perturbation problem in the limit $\epsilon = 0$, and we recover the original problem when $\epsilon = 1$. With the change of variables

\[ p = \frac{u - v}{2}, \quad q = \frac{u + v}{2}, \] (16)

we obtain the system in the standard singular perturbation form,

\[ \frac{dp}{dt} = f(q + p, q - p), \quad \frac{dq}{dt} = \epsilon \frac{g(q + p, q - p, \mu)}{2}. \] (17)

The curves of equilibria (14) become

\[ S_1 : p = q, \quad S_2 : q = \sqrt{p^2 + 1}, \] (18)

and are denoted by slow manifolds. In the limit $\epsilon = 0$ it is not difficult to see that the critical points on $S_1$ are stable and the critical points on $S_2$ are stable when $p < 0$ and unstable when $p > 0$. When $\epsilon$ is sufficiently small and nonzero, there are boundary layers close to the slow manifolds with slow dynamics. Close to a stable part there is an attracting trajectory and close to an unstable part there is a repelling trajectory. This is the content of Tikhonov’s theorem (see, e.g., [4] or

FIG. 3. Scaling of amplitude $A$ and period $T$

Close to the bifurcation to infinity. The markers show numerical simulations. The lines show least-squares fit from the data with $\ln(\mu - \mu_\infty) \approx -5$ yielding $A = -0.9189 \ln(\mu - \mu_\infty) - 0.0506$, $T = -1.120 \ln(\mu - \mu_\infty) + 5.547$. 

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at the end of the unstable boundary layer below trajectories coming from the stable boundary layer enters the can exist. This is shown in where unbounded motion occurs. In this case no limit cycles are collected. To order expansions of the trajectory and hence makes the trajectory well defined for all

\[ q(p) = q_0(p) + \epsilon q_1(p) + \epsilon^2 q_2(p) + \cdots, \]

and the bifurcation point

\[ \mu_c = \mu_0 + \epsilon \mu_1 + \epsilon^2 \mu_2 + \cdots, \]

are inserted in the Eqs. (17), and terms of the same order in \( \epsilon \) are collected. To order \( \epsilon^k \), this gives rise to an algebraic equation for \( q_k(p) \). In general, this has a singularity at \( p = 0 \), but \( \mu_{k-1} \) can be chosen in a unique way to remove the singularity and hence makes the trajectory well defined for all \( p \).

Implementing this procedure in a computer algebra program yields the results in Table I, where the expansion of the parameter is shown for \( \epsilon = 1 \). The asymptotic nature of the series is apparent, as the agreement with the numerical result becomes poor if too many terms in the series are included. If the series for \( \mu \) is truncated when the absolute value of the contribution is minimal at order 4, the error is only about 0.4%.

### Table II. Asymptotic calculation of \( \mu_c \) for Eq. (5) for \( r = 0.005 \).

<table>
<thead>
<tr>
<th>Order</th>
<th>Basic term ( \mu_k^{(0)} )</th>
<th>Correction term ( \mu_k^{(1)} )</th>
<th>( \mu_c ) for ( r = 0.005 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00000000</td>
<td>-1.50000000</td>
<td>0.99250000</td>
</tr>
<tr>
<td>1</td>
<td>-0.12500000</td>
<td>1.81250000</td>
<td>0.85843750</td>
</tr>
<tr>
<td>2</td>
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<td>-1.23437500</td>
<td>0.88351563</td>
</tr>
<tr>
<td>3</td>
<td>-0.00488281</td>
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<td>0.87804443</td>
</tr>
<tr>
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<td>0.25778198</td>
<td>0.87463364</td>
</tr>
<tr>
<td>5</td>
<td>0.00757980</td>
<td>-0.12490487</td>
<td>0.88158874</td>
</tr>
<tr>
<td>6</td>
<td>-0.00622034</td>
<td>-0.04510999</td>
<td>0.87512824</td>
</tr>
<tr>
<td>7</td>
<td>0.00072032</td>
<td>0.17333773</td>
<td>0.87672986</td>
</tr>
<tr>
<td>8</td>
<td>0.00958744</td>
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<td>0.88525366</td>
</tr>
<tr>
<td>9</td>
<td>-0.02425103</td>
<td>0.11999141</td>
<td>0.86160259</td>
</tr>
<tr>
<td>10</td>
<td>0.03671743</td>
<td>-2.310.22742</td>
<td>-0.10.6528170</td>
</tr>
</tbody>
</table>

![Figure 4](image-url)  
**FIG. 4.** Bifurcation diagram of Eq. (5) for \( r = 0.005 \). The light line is the steady state (full line stable, dashed line unstable.) The heavy line is the limit cycle. The vertical line is the asymptotic canard point from Table II, \( \mu_c \approx 0.875 \).

### B. Scaling

From the geometric analysis it is also possible to understand the scaling close to the bifurcation. As the bifurcation is approached, the limit cycle spends more and more time in the unstable boundary layer of \( S_2 \). Returning to the original \( (u,v) \) variables, we have here that \( v \approx 1/\mu \), and from the first equation of Eq. (3) we get \( u(t) \approx K + \mu t \) for some constant \( K \). Let \( \eta = v - 1/\mu \) denote the deviation of the trajectory from the slow manifold. We get

![Figure 5](image-url)  
**FIG. 5.** Solutions of Eq. (9) showing \([u(x = 0.5, t), v(x = 0.5, t)]\). (a) \( \mu = 0.904 \), simple limit cycle. (b) \( \mu = 0.9001 \), period-2 limit cycle. (c) \( \mu = 0.90007 \), period-4 limit cycle. (d) \( \mu = 0.900 055 \), chaos.
Then a trajectory leaves the boundary layer when $h \sim D$. Let the thickness of the boundary layer be denoted by $D$ where $t \sim S$. Hence, if $M_S$ is below $M_U$ limit cycles of large but finite amplitude will occur. If $M_S$ is above $M_U$ there are smaller limit cycles that never reach $S$, and the boundary between these two kinds of limit cycles occur again exactly when $M_S = M_U$. The parameter value where this occurs has previously been denoted the canard point $\mu_c$ [6]. This may be determined asymptotically with the method we used before, since the procedure depends only on the system in a neighborhood of $p = 0$. By this we have computed the canard point for small values of $r$ by further expanding each term of Eq. (20) in $r$ as $\mu_k = \mu_k(0) + \mu_k(1) r + \cdots$. The results of the computations are shown in Table II. Again the series is clearly asymptotic, and breaking at $k = 4$ where the contribution $\mu_k$ is minimal we obtain $\mu_C \approx 0.875$. The numerically obtained bifurcation diagram in Fig. 4 confirms the interpretation of $\mu_c$.

III. THE REACTION-DIFFUSION SYSTEM

The homogeneous branch of steady solutions $[u(x,t),v(x,t)] = (1/\mu, \mu)$ for the reaction-diffusion system (9) and (10) can loose stability in both pitchfork and Hopf bifurcations. Further, the bifurcating steady branches have secondary bifurcations, and a very rich set of possible structures exists, as described in [9,10]. Here we consider the complex dynamics associated with the bifurcation to infinity in a case with small diffusion coefficients.
We have performed simulations with the program reaction diffusion system solver [13], which employs a Crank-Nicholson scheme with a Runge-Kutta method for the time integrations. We have used 50 spatial grid points and verified the computations by making sample runs with 100 points that yielded almost identical results. The Galerkin method used in [11] turned out to give incorrect results for positive concentrations for the present choice of diffusion coefficients.

Results from the simulations are shown in Fig. 5. For a high value of \( m \) a simple limit cycle exists, but as \( m \) is decreased, period doubling bifurcations leading to chaos occur. Further decreasing \( m \) yield chaotic transients, with a long time behavior as in Fig. 5(d), but with solutions eventually having \( u \rightarrow \infty, v \rightarrow 0 \).

The spatial structure of the solutions in the chaotic regime can be seen from Fig. 6, where a few oscillations are shown. Most of the time the concentrations are almost homogeneous, and the system essentially behaves as if no diffusion was present with slow changes of concentrations. However, as \( u \) becomes sufficiently large and \( v \) becomes sufficiently small a fast wave moves across the domain, \( u \) becomes small and \( v \) becomes large, and an almost homogeneous state is reestablished. This is repeated in an irregular pattern, and the slow/fast behavior again confirms the singular perturbation nature of the system.

The unbounded solutions allowed by the reaction-diffusion system will again disappear if the reaction scheme is modified. However, the chaotic dynamics may persist, as it stems from the sensitivity of the system to the relative positions of \( M_S \) and \( M_U \). To demonstrate that we have performed simulations with the reaction-diffusion system where the kinetics is given by Eq. (5). Results are shown in Fig. 7, where essentially the same behavior as without the modification is found. Hence, the chaotic dynamics is not related to the bifurcation to infinity itself, but is rather associated with the sensitivity of trajectories in a parameter region where a stable and an unstable boundary layer are close and interact strongly, and may as well occur in a system that exhibits a canard explosion.

\[
\lambda_u = \frac{0.009}{\pi^2} = 0.0091189065, \quad \lambda_v = \frac{9}{10} \lambda_u = 0.0082070159. \tag{26}
\]

References