Non-hyperbolic Singularities in Fast-Slow Chemical Oscillators

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Summary. In this contribution we shall outline recent results on two chemical oscillation models: the autocatalytic model and the Olsen model. For the autocatalator, we extend the local theory of singularities in fast-slow polynomial vector fields to classes of unbounded manifolds which lose normal hyperbolicity due to an alignment of the tangent and normal bundles. A projective transformation is used to localize the unbounded problem. Then the blow-up method is employed to characterize the loss of normal hyperbolicity for the transformed slow manifolds. Our analysis yields a rigorous scaling law for all unbounded manifolds which exhibit a power-law decay for the alignment with a fast subsystem domain. Furthermore, the proof establishes a practical growth bound for the oscillations in autocatalytic reactions. For the Olsen model, we are just going to state the main results in the presentation. The Olsen model is four-dimensional, not in a standard form required by geometric singular perturbation theory and contains multiple small parameters. These three obstacles are the main challenges we resolve by our analysis. Scaling and the blow-up method are used to identify several subsystems. The results presented here provide a rigorous analysis for two oscillatory modes. In particular, we establish the existence of non-classical relaxation oscillations in two cases.

Introduction

Dynamics with separated time scales is ubiquitous in applications. One area, where several time scales naturally appear in the modelling process are chemical reactions. It often occurs, and is quite reasonable also from an abstract point of view, to encounter different chemical reactions occurring at widely separated reaction rates. After using mass-action kinetics to derive ordinary differential equations (ODEs) from the abstract reactions and by using a suitable non-dimensionalization, one frequently obtains systems with multiple time scales. The basic case in this context are fast-slow systems with two time scales. The general form can be written as:

$$\begin{array}{rcccl} \varepsilon\frac{\mathrm{d}x}{\mathrm{d}\tau} & = & \varepsilon\dot{x} & = & f(x,y;\varepsilon), \\ \frac{\mathrm{d}y}{\mathrm{d}\tau} & = & \dot{y} & = & g(x,y;\varepsilon), \end{array} \tag{1}$$

where f, g are smooth maps, $\varepsilon > 0$ is a small parameter indicating the time scale separation between the fast variables $x \in \mathbb{R}^m$ and the slow variables $y \in \mathbb{R}^n$. In the singular limit $\varepsilon \to 0$, one obtains from (1) a differential-algebraic equation constrained to the critical set

$$C_0 := \{(x,y) \in \mathbb{R}^{m+n} : f(x,y;0) = 0\}. \tag{2}$$

As long as the set C_0 is a sufficiently smooth manifold and if it satisfies the normal hyperbolicity condition that the matrix $\mathrm{D}_x f(x,y;0) \in \mathbb{R}^{m\times m}$ has no eigenvalues with zero real part for $(x,y) \in C_0$, Fenichel's Theorem converts (1) into a regular perturbation problem near C_0. However, if normal hyperbolicity is lost, then one requires specialized analysis. Essentially, this loss of normal hyperbolicity is directly connected to bifurcations/singularities of the fast subsystem, which can be obtained from (1) by changing the time scale to $t := \tau/\varepsilon$ and then taking the singular limit $\varepsilon \to 0$

$$\begin{array}{rcl} \frac{\mathrm{d}x}{\mathrm{d}t} & = & f(x,y;0), \\ \frac{\mathrm{d}y}{\mathrm{d}t} & = & 0. \end{array} \tag{3}$$

In this contribution, we shall focus on the analysis of several different situations, where normal hyperbolicity is lost. In both chemical systems we study, the understanding of the associated singular parts of the critical manifold is crucial to describe the formation of oscillatory patterns, which are much more complicated than classical relaxation oscillations.

The Autocatalator

A prototypical case of an autocatalytic system is given by four reactions

$$P \to Y, \quad Y \to X, \quad Y + 2X \to 3X, \quad X \to Z \tag{4}$$

where X, Y are the two main reactants, P is a constant 'pool'-chemical and Z is the product. Then it can be shown, using standard mass-action kinetics and non-dimensionalization, that (4) leads to a two-dimensional system of ODEs

$$\begin{array}{rcl} \varepsilon\dot{x} & = & yx^2 + y - x, \\ \dot{y} & = & \xi - yx^2 - y, \end{array} \tag{5}$$

where the phase space variables x, y are dimensionless concentrations associated to X, Y respectively and ξ is a parameter. It is natural to assume that the concentrations are non-negative $x, y \in \mathbb{R}_0^+$. Furthermore, note that the nonlinear term arises due to the autocatalytic reaction part $Y + 2X \to 3X$. It is well-known that the 2D-autocatalator (5) can exhibit an attracting periodic orbit for certain ranges of the parameters. The critical manifold is given by

$$C_0 = \{yx^2 + y - x = 0\} = \left\{ y = \frac{x}{1+x^2} \right\}. \tag{6}$$

Observe that C_0 is an unbounded smooth manifold. The angle between the tangent spaces T_pC_0 and the hyperplanes $\{p \in C_0 : y = \text{const.}\}$ decays to zero as $x \to +\infty$. This alignment, which is expected to imply a loss of normal hyperbolicity in the system at infinity, already causes substantial difficulties in the rigorous analysis of the dynamics of the 2D autocatalator model. Given these examples, it is desirable to build a general theory of fast-slow systems with unbounded critical manifolds. The main contributions summarized in this work, stated here in a non-technical form, are: (a) we study a general class of critical manifolds, which may have an arbitrary power-law decay $y \sim 1/x^s$ (as $x \to \infty$) for the alignment with a fast subsystem domain. This includes the autocatalytic critical manifolds as special cases and answers open questions arising from various numerical studies; (b) using the blow-up method we give a rigorous proof when normal hyperbolicity for a perturbation of the critical manifold fails i.e. which is the largest region up to which a slow manifold, obtained as a perturbation of the critical manifold, is normally hyperbolic. The relevant scaling law turns out to be given by

$$(x, y) \asymp \left(\mathcal{O}(\varepsilon^{-1/(s+1)}), \mathcal{O}(\varepsilon^{s/(s+1)})\right), \qquad \text{as } \varepsilon \to 0, \tag{7}$$

where $-s$ is the power law exponent for the asymptotic decay of the critical manifold; (c) on a technical level we contribute to a further development of the blow-up method by augmenting it with an 'optimality-criterion' of blow-up coefficients which have to be chosen in the analysis; (d) the scaling (7) also has immediate consequences for the asymptotics of oscillatory patterns.

The Olsen Model

Experimental observation of oscillatory dynamics in the peroxidase-oxidase (PO) reaction

$$2\ \mathrm{NADH} + 2\ \mathrm{H^+} + \mathrm{O_2} \to 2\ \mathrm{NAD^+} + 2\ \mathrm{H_2O} \tag{8}$$

led to further interest in the dynamical mechanisms. Various models have been proposed to capture the dynamics of (8). We are going to present results for a model of the PO reaction initially proposed by Degn, Olsen and Perram. The four ODEs are

$$\begin{array}{rcl} \frac{\mathrm{d}A}{\mathrm{d}T} &=& -k_3ABY + k_7 - k_{-7}A, \\ \frac{\mathrm{d}B}{\mathrm{d}T} &=& -k_3ABY - k_1BX + k_8, \\ \frac{\mathrm{d}X}{\mathrm{d}T} &=& k_1BX - 2k_2X^2 + 3k_3ABY - k_4X + k_6, \\ \frac{\mathrm{d}Y}{\mathrm{d}T} &=& -k_3ABY + 2k_2X^2 - k_5Y, \end{array} \tag{9}$$

where $(A, B, X, Y) \in (\mathbb{R}^4)^+_0$ are chemical concentrations and $k_i > 0$ are parameters. A and B denote concentrations of the substrates $NADH$ and O_2 while X and Y are concentrations for two free radicals. Olsen used k_1 as a bifurcation parameter and found three main distinct regimes consisting of mixed-mode oscillations (MMOs), chaos and relaxation-type periodic oscillations. From the numerical results, it was conjectured that multiple time scales are crucial for the the understanding of the oscillations. However, the Olsen model had resisted rigorous mathematical analysis for over thirty years, despite it being a key motivating example to study multiple time scale dynamics in general and for the development of the blow-up method in particular. The main obstacle for the analysis of the Olsen model is that many problems occur simultaneously. It is four-dimensional, in nonstandard form, contains several non-folded degenerate singularities, has three natural small parameters and a return mechanism without an S-shaped manifold. It even has multiple regimes of different geometric multiple time scale decompositions due to the relative asymptotic limits of the small parameters. In this contribution, we survey recent results providing a first detailed multiscale analysis of the Olsen model. We establish existence results for several special types of periodic solutions.

Literature Summary

The contribution is a summary of results obtained recently in several works. Here we provide a very brief overview of this body of work to which the author has contributed. The literature also contains some pointers to background results and related extensions:

- General background on fast-slow systems [Kue15].
- Main results on the autocatalator [Kue14].
- Main results on the Olsen model [KS15].
- An introduction to the blow-up method and a calculation for hyperbolic spaces [Kue16].

References

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