

Global analysis of chemical kinetic mechanisms

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1 Introduction

Mathematical modeling and numerical simulation of combustible reacting systems has become very important due to the requirement of economical use of available natural energy resources and the task of reducing the overall pollution impact caused by combustion processes. In order to improve the technology, more detailed and reliable modeling of the combustion phenomena is needed that agrees better with experimental data. One of the most complicated parts of such models is obviously the chemical kinetic model [1]. Accordingly, very complex and detailed mathematical models of chemical kinetics mechanisms are available. There are a lot of methods and almost automatic procedures to devise detailed mechanisms, however, in this way such reaction mechanisms comprise in some cases more than thousand chemical species, which participate in several thousands of elementary reactions [2]. Such mechanisms cannot be longer treated analytically and even the numerical treatment is limited to academic problems.

Consequently, the need for methods of mechanism analysis with intention to use the results of the analysis for detailed mechanism improvement and also model reduction has been constantly increasing. For instance, sensitivity analysis [3, 4], Computational Singular Perturbation (CSP) [5] and Intrinsic Low-Dimensional Manifolds (ILDM) methods [6, 7] are some of the methods that appear during last decades in order to analyze the dynamics of reaction mechanisms. The first method permits to study the influence of the system parameters and the initial conditions onto the system behavior. The second properly answers the question of which species and reactions are most important over the evolution of the system, while the third describes low dimensional manifold in the state space as approximations of the detailed model describing the so-called long-term and rate limiting dynamics accurately. It is interesting to note that in spite of the fact the methods above (as well as many others) have different orientation and realization/implementation strategies, but, nevertheless, a basic tool of the system analysis still the same its linearization, i.e. the system's Jacobian matrix. This local character in our opinion considerably diminishes the value of the analysis, especially with respect to the reduction context.

In the current study we present and investigate a complimentary tool to the methods above that has a global character and, therefore, is appropriate for the analysis of the system hierarchy, which is needed for the decomposition of the system and its dimension reduction. The presented method, which we call Global Quasi-Linearization (GQL) [8], decomposes the system dynamics, serves as a relatively simple tool of definition of the low-dimensional manifold of the reduced dynamics and what is more important it allows to explore the properties of such low-dimensional manifolds like attractiveness, stability, invariance etc. Hence, the GQL method illustrated in this work is a powerful

tool for the comprehensive global analysis of the detailed kinetic mechanisms that can be used efficiently in model the reduction context as well as in the comparative analysis and improvement of the detailed mechanisms and study their properties.

2 Problem statement, importance of the system analysis

A typical mathematical model describing the evolution of the thermo-chemical state vector in linear vector space $\psi = (\psi_1, \dots, \psi_n)$ in time, where ψ_j represents such quantities as the pressure of the mixture, the enthalpy, the mass fraction/mole concentration of chemical species or their specific mole numbers reads

$$\frac{d\psi}{dt} = F(\psi), \quad \psi \in \Omega \subset R^n$$

Here F stands for the chemical source term. First of all, let us outline the meaning of the system/model reduction from a mathematical point of view, such that the relation of the global analysis to the model reduction becomes clear.

In general a final aim of model reduction is a reformulation of the original system in an appropriate reduced form by introducing the reduced space $\theta = (\theta_1, \dots, \theta_m)$ $m \ll n$ such that the solution of the system will be accurately described by the following reduced model

$$\frac{d\theta}{dt} = \tilde{F}(\theta), \quad \theta \in R^m$$

The main question then arises: how these systems relate to each other, namely, what is the relation between the detailed $\psi = (\psi_1, \dots, \psi_n)$ and reduced spaces $\theta = (\theta_1, \dots, \theta_m)$, i.e. one needs to describe a relation between these spaces in order to reduce the system. If the reduced space can be represented by a low-dimensional manifold in the detailed linear vector space, which is given in explicit form $M = \{\psi = \psi(\theta)\}$, then the original system is restricted/projected to the manifold M yielding

$$\frac{d\theta}{dt} = \psi_\theta^+(\theta) F(\psi(\theta)) \equiv \tilde{F}(\theta), \quad \theta \in R^m$$

The Moore-Penrose pseudo inverse $\psi_\theta^+(\theta)$ [9] has been used here, which is a well defined function unless the tangent space TM given by $\psi_\theta(\theta)$ degenerates. The reduction of a given arbitrary system with prescribed dimension and accuracy is a very complicated task, but the existence of various time scales, which is a typical feature of chemically reacting flows, restricts the thermo-chemical state space to the system states that has a low-dimensional structure or can be efficiently approximated by low-dimensional manifolds. This important feature of reaction mechanisms and the existence of low-dimensional manifolds make the model reduction task realistic.

Therefore, the information about the decomposition and identification of this variety of time scales leads directly to the model reduction as a model reformulation on the manifolds defined through the decomposition, i.e. manifold can be defined as a set of states where fast processes have already relaxed which is called as a slow manifold (see, for instance, ILDM manifolds definition [7]). The set of the systems states where the slow processes are frozen defines the so-called fast motions or a manifold of fast motions of the system. In this respect, low-dimensional manifolds with certain properties (invariant, attractive, stable, slow, fast etc.) are extremely important for model reduction. Moreover, an efficient method of model analysis should not only provide with approximation of the manifold potentially useful for model reduction, but it also should supply us with the tool for its analysis with respect to the key properties listed above.

In the following, the method of global analysis of kinetic mechanisms and low-dimensional manifolds useful for model reduction will be presented, applied to a number of combustible systems (H_2/H_2+CO and CH_4/Air) and compared to the ILDM approach.

3 Global linear approximation instead of local Jacobian

The central idea of the GQL is the identification of fast manifolds or subspaces in the linear vector space of the original system that represents mathematical model of the kinetic mechanism. In order to find such fast subspaces, or in the other words fast processes splitting it, a set of n points from the accessed by the system states domain of the state space is used $\{\psi^1, \dots, \psi^n\} \in \Omega$ together with their images under the vector field $\{F(\psi^1), \dots, F(\psi^n)\}$ (see e.g. [8] for more detail). Then properties of linear transformation which maps the n points into their images $T: \psi^i \rightarrow F(\psi^i)$, $i=1, \dots, n$ are investigated instead of the Jacobian matrix. This linear transformation is based on the states (points) uniformly distributed in the accessed domain and, therefore, defines the global properties of the system. The matrix form of the transformation T is given in the original coordinate system by

$$T = [F(\psi^1), \dots, F(\psi^n)] [\psi^1, \dots, \psi^n]^{-1},$$

where first matrix in the product represents the matrix whose columns are the vector field (RHS of the original system) calculated at different states and the second $[..]^{-1}$ denotes inverse of the matrix, which comprises the states themselves. The specific problem of the choice of n points for appropriate definition of the transformation has been investigated in [10] and is not discussed in the present study. However, it must be admitted that this is a crucial issue of the method and therefore in a few sentences we address the role of this choice. There are several criteria for this choice that have to be satisfied by the choice.

- Uniformity; it is guaranteed by quasi-uniform distribution.
- Separation from the possible slow manifold; only points having RHS values above an average values are considered.
- Degeneration; the second matrix in the definition comprises vectors that spans the simplex of the volume which is compared to the volume of the accesses domain Ω .
- Optimality; a sequence of transformations T is generated and then the best of the sequence is chosen.

After the transformation T has been found the rest follows the ILDM method [7]. Eigenvalue analyses of the transformation T answer the question about the system hierarchy, the decomposition and dimensions of the reduced model are defined on the basis of the so-called gap condition between the eigenvalues. Invariant slow (related to the group of relatively small eigenvalues) and fast (related to the group of large eigenvalues) subspaces of the transformation matrix can be used efficiently to define the fast subspaces and slow manifolds correspondingly (see e.g. [7] for slow manifold definition). Moreover, as it was shown in [10] the constant fast subspace can be efficiently used for stability and attractiveness analysis of the slow manifold.

4 Implementation and comparison

In order to illustrate the method described above three typical combustion kinetics mechanisms have been tested, namely, the H₂/air, H₂+CO/air and CH₄/air systems. The results of the GQL analysis and ILDM method are summarized in figure 1, where the typical result for the slow manifold and fast motions are shown in projection to some species specific mole numbers.

As a main outcome of the implementation, it has been found that decompositions for the chosen mechanisms exist. Moreover, the constant approximation can be efficiently used in order to describe both slow and fast manifolds of the system (compare GQL manifold, ILDM slow manifolds and fast motions with the detailed system solution in Fig. 1). Additionally, the domain of the GQL slow manifold existence typically is large compare to the ILDM. Right near the boundary of the existence, where manifolds start deviate one from the other, both loose their stability properties and become unstable that means the states reach the so-called turning manifold.

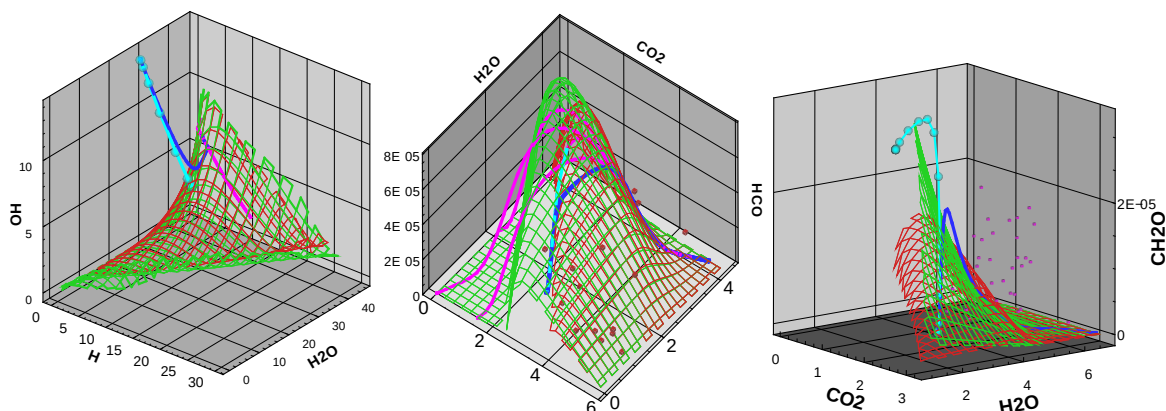


Figure 1. State space projection onto some species specific mole numbers. Red mesh is the 2D ILDM manifold, green mesh shows 2D GQL manifold, blue solid line represent the detailed system solution, light blue line shows the fast subsystem solution defined on the basis of the GQL analysis. Colored small cubes indicate the states used for the GQL transformation. Left: hydrogen, middle: syngas and right: methane/air systems are illustrated.

This indicates the need to increase the dimension of the slow manifold and requires a more careful study of the dynamical properties of the slow manifold in this part of the domain. Another interesting observation concerns the syngas/air system. For this system the results for laminar free flames are shown as magenta lines. Thus, one can see that even for non-homogeneous case the results of the pure homogeneous system analysis produces reliable manifold for an open system.

To summarize, an efficient algorithm of the global analysis of the chemical kinetic mechanisms has been presented and applied to real combustion kinetic mechanisms. It allows investigation the system hierarchy and answers the question whether the assumption about the decomposition of motions is valid. If the answer is positive, then it decouples the fast motions/processes and as a result reduces the system's dimension and stiffness of such models making them treatable numerically for complex reacting flow problems. The comparison of the projections of the state space is in good agreement with those obtained with the standard ILDM method as well as with the detailed system simulation.

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