

Global and comparative analysis of chemical kinetics models in the self-ignition problem

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Abstract

In the present work a novel method of a global analysis of detailed and skeletal chemical kinetics mechanisms is discussed. The method is applied to the analysis and reduction of detailed model of the self ignition phenomena. It is well known, that most methods (sensitivity analysis, CSP, ILDM etc.) of the chemical kinetic model analysis although they are widely used and produce quite good results have a local character, i.e. most of the existing methods are based on the analysis of the system Jacobian. Therefore, they are limited in the applications and interpretation of results to a neighbourhood of a particular system state. Questions of how the system dynamics can be decomposed and what is a global hierarchy of the system are still open. In the current work, the gap between a local and global analysis is narrowed by considering the so-called global linearization procedure that allows describing explicitly the decomposition into fast and slow motions that present in the combustion system. The introduced method addresses issues of global analysis and is implemented within a code for the standard ILDMs method. In order to verify the method it has been applied to a simple, but meaningful n-heptane/air self ignition problem.

1. Introduction

Detailed chemical kinetic models of complex combustion phenomena have become a powerful tool for the simulation and of reacting flows [1]. However, there are many factors which complicate considerably the use of detailed chemical kinetics. For instance, the large number of species and reactions, i.e. the system dimension, increases the computational cost and typically prohibits the use of very detail chemistry in engineering applications with complicated geometries. Furthermore, the mathematical model of the conservation laws of reacting flows with very detailed chemical models is highly nonlinear which results in time scales differing by many orders of magnitude. These drastic differences in time-scales and nonlinearities course stiffness and difficulties in the numerical solution [2].

Accordingly, as an ultimate purpose of a chemical kinetic model analysis, simpler overall chemical kinetic models, which reduce stiffness and the system dimension, are required. The need of mechanism analysis and reduction methodologies has grown, and a range of methods has been developed in the last several decades to obtain simplified models of chemical kinetic (see e.g. [3] for more references and reviews). Evident progress in theoretical [4, 5] as well as in practical and numerical aspects (see e.g. [6]) has been made recently. As a main achievement of these studies is an observation that the thermo-chemical state of the reacting system in the full state space accesses ONLY a small part of the state space during the combustion process. This is because of and the wide range of differing in orders time scales such that in a typical combustion system the system's states form a low-dimensional manifold in the detailed state space. These

manifolds often possess very important properties like invariance and exponentially attractiveness for the system trajectory flow. Usually, following the evolution of the fast transient period, the system is governed by the slow reactions along the so-called slow manifold of considerably low dimension. By using such manifolds the state space can be described by means of a smaller number of system parameters and the reduced system of differential equations is required to describe merely the behaviour of those parameters. The other species concentrations or the whole state space can be recast from values of these parameters by using functional relations defining the manifold and, therefore, do not require the solution of expensive differential equation system of higher dimension.

This picture illustrates that the long term or rate limiting dynamics of the chemical kinetics can be reduced / confined efficiently onto these slow manifolds by using the local analysis defining the slow manifold structure [6], but how the transient period can be handled is an open question and it requires more sophisticated tools. Thus, a suitable combination of a local and global analysis is needed for an accurate reduced model formulation. In this respect, the fast motions/manifolds are very important and merely are in the focus of the current study.

Additionally, although the knowledge about the fast motions (defining fast manifolds) can be used for reduction purposes themselves, the most important feature of fast manifolds is that they allow exploring the asymptotical properties of the slow manifolds with respect to stability and attractiveness. Without this knowledge the properties of the slow manifolds can not be properly studied, which can increase the probability of a wrong use of the slow manifolds. Hence fast manifolds are powerful tool of the detailed model

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analysis and methods that allow their approximation are very important.

2. Preliminary remarks

It is important in many engineering applications to construct a tool which allows a comparative analysis of the detailed mechanisms using the manifold calculation (of slow and fast motions respectively) in very fast and robust way. In order to formulate such a method and construct a suitable procedure to decompose the system, the basics of the model reduction by the decomposition of motion have to be understood and studied properly. In particular, the following questions are very important

- Which properties of the original system characterize the fast and slow motions of the system?
- Which mathematical models can be used to model these specific properties of the chemical kinetics models and efficiently catch the fast/slow decomposition?
- Is there a suitable theoretical concept that can help to delineate a typical hierarchical structure with its subsequent use for model reduction?
- How can the theory be implemented in the most appropriate and efficient way?

These and other questions were extensively studied in previous works on the so-called Singular Perturbed Vector Fields [7-9]. This framework answers the most theoretical questions above. In particular, decomposition means that we are looking for new coordinates representing the original system in a special form of a Singular Perturbed System (SPS) [10, 11]. In a number of works [7-9], the theory of SPS [12, 13] has been reviewed, extended and applied with special emphasis on a coordinate free approach. The key idea of the approach is an evaluation of such change of the system coordinates that provides with a necessary decomposition. After this coordinate change has been found all the machinery of powerful methods of SPS can be applied to analysis, formulation of the reduction procedure and evaluation of the reduced system dynamics.

3. Implementation of the Singularly Perturbed Vector Field approach in conventional coordinate form

3.1 Mathematical model

Let us consider a general form of the system of governing equations in vector notation

$$\frac{d\psi}{dt} = F(\psi), \quad \psi \in \Omega \subset R^n. \quad (1)$$

Here the state vector ψ is the n-dimensional vector of natural system variables having obvious physical meaning $\psi = \left(h, p, \frac{w_1}{M_1}, \dots, \frac{w_{n_s}}{M_{n_s}} \right)$, where h denotes the enthalpy, p the pressure, w_1, \dots, w_{n_s} are the species mass fractions and M_1, \dots, M_{n_s} the molar masses ($n = n_s + 2$). $F(\psi)$ is the n-dimensional vector of the thermo-chemical source term and t denotes the time.

As it follows from the general framework [9], the suggested approach is based on two main assumptions, first of all on the assumption that there exist a decomposition because of the different time scales present in the system (1) and, secondly, we suppose that it is valid (within a certain accuracy) everywhere inside an a priori fixed domain Ω accessed by the system states.

3.2 Global linearization

The main tool of the analysis, namely, a linear approximation to the vector field given by the RHS of (1) (so called Global Quasi-Linearization) is presented in this subsection. A variation of the GQL procedure [9] is discussed here. This has been motivated by numerical simulations, because in many practical situations the system has a dimensional form and, therefore, cannot be used for a global multi-scale analysis without a proper non-dimensionalization procedure. In this case the system hierarchy might be perturbed by naturally different scales of the system variables or parameters. This problem is easily overcome by suggesting a proper normalization procedure for a linearization matrix of the system given in dimensional form.

Accordingly, suppose the $F(\psi)$ is a vector field, which satisfies our assumptions about a "hidden" small parameter of the system, which determines the main disparity of time scales. The main steps of the analysis are the following.

- First, we select n linearly independent points (vectors) $\psi_1, \dots, \psi_n \in \Omega$ in such a way that the set of vectors defined by the vector field $F(\psi_1), \dots, F(\psi_n)$ is also linearly independent, which is possible because we assume additionally that all linear integrals which define the conserved subspace of the system have been removed prior to its final form (1).
- These vectors form the columns partitioning of

the matrices

$$\bar{F} = [F(\psi_1), \dots, F(\psi_n)], \bar{\Psi} = [\psi_1, \dots, \psi_n].$$

(iii) The matrix $T = \bar{F} \left(\bar{\Psi} \right)^{-1}$ is the GQL of the

system (1). It has a simple geometrical interpretation. It is the matrix for the linear mapping that transforms the set of vectors ψ_1, \dots, ψ_n into the set of results under the RHS of the system (1) $F(\psi_1), \dots, F(\psi_n)$;

(iv) As a final point, we study the invariant eigenspaces of the matrix T and exploit the decomposition in terms of the vectors which span eigenspaces, i.e. if the matrix T is decomposed into invariant subspaces

$$T = \begin{pmatrix} Z_s & Z_f \end{pmatrix} \begin{pmatrix} N_s & \\ & N_f \end{pmatrix} \begin{pmatrix} \tilde{Z}_s \\ \tilde{Z}_f \end{pmatrix}. \quad (2)$$

Then, similar to the assumption of the ILDMs method (see e.g. [14 - 16] for more details), the fast relaxed processes define an approximation of the low dimensional manifold within the state space as

$$\tilde{Z}_f F(\psi) = 0, \quad (3)$$

This defines the manifold in the state space where the reaction rates in direction of the fast processes vanish defines an approximation to the slow manifold. The invariant eigenspaces define a reduced system dimension since Z_s and \tilde{Z}_s are the right and left invariant subspaces belonging to the m_s eigenvalues having the smallest real parts (N_s) and Z_f and \tilde{Z}_f are the right and left invariant subspace, correspondingly, related to the fast relaxing processes with m_f eigenvalues (N_f) having the largest negative real parts respectively ($m_s + m_f = n$). The equation (3) is then defined globally in Ω , it implicitly represents an m_s -dimensional slow manifold in the state space.

Furthermore, the fast invariant subspace (defined by Z_f and \tilde{Z}_f) can be used for the analysis of any approximation of the slow manifold for the system (1) as it is shown below. Suppose one has the slow manifold approximation in an implicit form:

$$M = \{\psi \in \Omega : \Phi(\psi) = 0\}, \quad (4)$$

Then, asymptotical properties of any low dimensional manifold (stability, attractiveness etc.) under consideration are completely described by the eigenvalue analysis of the following matrix:

$$\tilde{Z}_f F_\psi(\psi) Z_f \Big|_{\Phi(\psi)=0}, \quad (5)$$

Therefore the proposed method is not only an efficient tool for the slow manifold approximation, but in addition it provides important asymptotical properties of low dimensional manifolds. Furthermore, it has to be mentioned that because the present algorithm is similar to the ILDMs concept with only difference of using GQL matrix - T instead of the system Jacobian. Therefore, all previous developments of the ILDM can be applied to implement the method with only minor changes in the numerical code structure.

3.3 Accessed domain and the reference set definition

It is clear that the efficiency and the accuracy of this procedure depends essentially on choice of ψ_1, \dots, ψ_n . Roughly speaking, practical recommendations for the choice are following: $F(\psi_1), \dots, F(\psi_n)$ should not be too close because it can result in degeneration of the matrix $\bar{\Psi}$. Additionally, the values of vector field $F(\psi_i)$ should represent "different" behavior for different $i = 1, \dots, n$. This choice is a crucial point of the algorithm and must be adapted to every particular model. At present, the following algorithm for choice of reference set of points/vectors has been suggested. Note that other possibilities of the choice of reference points can exist, but theoretically, their results differ only in higher orders of approximations with respect the system small parameter (see e.g. [9] for details and the definition).

First, by performing a quasi-stochastic uniform distribution, an "initial set" $S_N = \{\psi_1, \dots, \psi_N\}$ consisting of points ($N \gg n$) uniformly distributed in the domain Ω is formed. Then we calculate mean value of the vector field over the sequence S_N as $\bar{F} = \frac{1}{N} \sum_{i=1}^N F(\psi_i)$, and take a subset of S_N as following

$$S_K = \{\psi_i \in S_N : \|F(\psi_i)\| > \|\bar{F}\|\} \quad (6)$$

where $i = 1, \dots, K$, $K = k \cdot n$, $k \gg 1$. The set S_K is called the "control set". It consists of the points, which are sufficiently far away from the slow manifold and, therefore, can be safely used to estimate the fast subspace (see e.g. [7, 9] for more details). Any subset of

length of n of the control set S_K can be used as the reference set to obtain T , but there is also a degeneration problem of the chosen subset of the control set if some of points/vectors are close to or some points are still close to the slow manifold. This can lead

to a degeneration of the matrix $\bar{\Psi}$ and, consequently, to a wrong decomposition. Accordingly, not every subset of S_K of length of n can be used as the reference one. In order to solve this problem a subset of vectors is needed such that it spans the simplex of volume that can be compared to the volume of the domain Ω . To resolve this problem we suggest exploiting the assumed decomposition further. For that reason, arbitrarily sequences of length n from the control set are created and the best one is chosen by the best decomposition (small parameter) condition. Namely, the sequence of GQL approximations $T_i, i=1, \dots, k$ are defined by subsets of the control set

$$\{\psi_{(i-1)n+1}, \dots, \psi_{in}\}, i=1, \dots, k;$$

The final reference sequence $\{\psi_{(i^*-1)n+1}, \dots, \psi_{i^*n}\}$ and the final GQL approximation are found simultaneously as $T=T_{i^*}$ by a maximal gap for given dimension of the reduced model m_s :

$$i^* : \max_i \left(\frac{|\lambda_{m_s+1}(T_i)|}{|\lambda_{m_s}(T_i)|} \right), \quad (7)$$

where $\lambda_j(T_i), j=1, \dots, n$ are eigenvalues of T_i ordered in increasing order by absolute values. Finally,

the reciprocal value $\varepsilon = \left(\frac{|\lambda_{m_s+1}(T_{i^*})|}{|\lambda_{m_s}(T_{i^*})|} \right)^{-1}$ defines a

small system parameter.

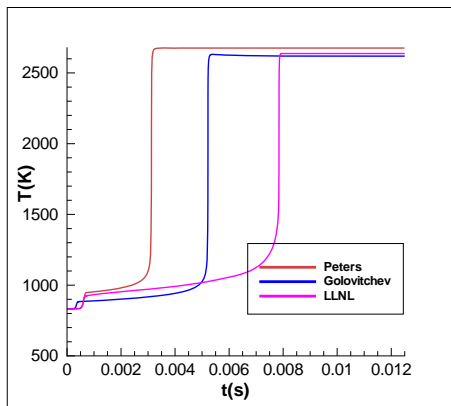


Fig. 1. Temperature time histories of different detailed mechanisms of n-heptane self ignition at initial temperature of $T_0 = 833 K$ and constant pressure $13.5 \times 10^5 Pa$.

4. Self ignition problem

In this section the method of global analysis outlined in the previous sections is applied to the auto-ignition of the n-heptane/air homogenous system. The elementary kinetic mechanism of this system is relatively well studied (see e.g. [17 – 20] for more references), the complex two stage ignition of a stoichiometric mixture represents a quite interesting and challenging task for any reduction procedure (see Fig. 1).

This type of two stage auto-ignition occurs in the so-called Negative Temperature Coefficient (NTC) regime due to the fact that the oxidation process slows down while the temperature slightly increases (see Fig. 1, 2 for profiles and comparisons). In the second stage, the formation of H_2O_2 becomes more important, which then slowly dissociates to OH radicals [17] leading to the second and final stage of thermal runaway. For current analysis the $n_r = 56$ step skeletal mechanism with $n_s = 35$ species of [18] has been used. It is comparatively small but, nevertheless, until the second stage of the ignition it describes the kinetics qualitatively and quantitatively reasonably well (see e.g. [18] for detail and Fig. 1 for illustration).

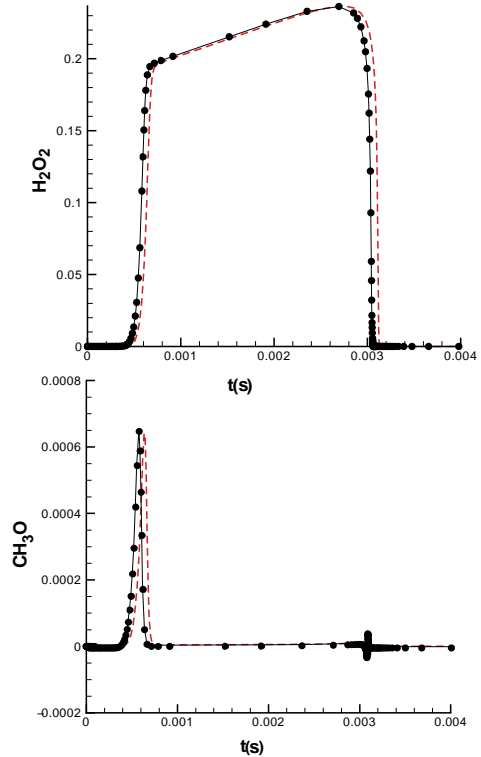


Fig. 2. Profiles of some species of n-heptane self ignition at initial temperature of $T_0 = 833 K$ and pressure $13.5 \times 10^5 Pa$. Red dashed line represents the detailed system profile, while the black line with filled circles shows the GQL reduced model solution.

Figure 1 shows comparisons of the chosen kinetic mechanism with the others given by LLNL [19] and

Golovichev [20] of $n_s = 159$ and $n_s = 57$ species correspondingly. It is interesting to note that although all these mechanisms are well accepted they predict ignition delay times varying by a factor of 3.

5. Results and Discussion

A detailed system solution and the manifold mesh are generated by using the HOMREA code [21 - 23]. The program was originally developed to simulate homogeneous reactors, later it was extended to tackle the ILDM table generation and then used for the IC engine cycle simulation.

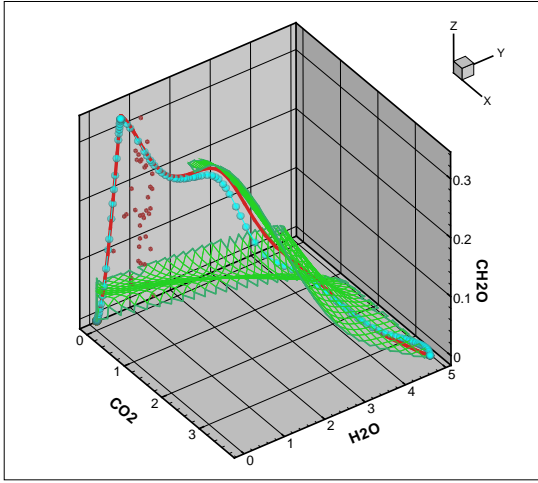


Fig. 3. State space projection onto 3D space with detailed system solution trajectory shown by the red line, 2D GQL slow manifold is the green mesh, red cubes are the reference set of the GQL analysis, cyan line with spheres is the reduced model solution trajectory.

The Global Quasi Linearization (GQL) procedure has been applied in order to set up a decomposed system for the auto-ignition problem. The domain of interest has been defined by a system trajectory yielding the maximum values for the species molar numbers over this trajectory for all species. The detailed system solution is analyzed until the middle stage of the second induction time (see Fig. 1 and 2) $t = t^* = 2ms$ in order to insure that the domain of interest will cover the essential part of the ignition and will not include the slow processes close to the equilibrium point. In this respect the domain definition problem becomes a crucial point because the information on the vector field near the equilibrium, where the major products have been already build up, is not important for the ignition stage, therefore the random points are selected from the domain (8) of the state space close to the trajectory during the ignition phase (see Fig. 3 for illustration).

$$\psi_i^{\max} = \max_{0 \leq t \leq t^*}(\psi_i(t)),$$

$$\Omega = \left\{ \psi : 0 \leq \psi_i \leq \psi_i^{\max}, i = 1, \dots, n_s \right\} \quad (8)$$

In order to predict accurately the delay time one needs to keep the overall dimension of the reduced model relatively high in comparison, for instance, to a flame propagation problem. This is because the stationary flame propagation is mainly controlled by a few rate limiting slow reactions, which are described reasonably well by relatively low dimensional slow manifolds [22].

At the same time to describe the ignition process important fast modes have to be included in the reduced model as well. This feature is shown in the Fig. 3, where the 2D GQL approximation of the slow system manifold is presented together with the detailed and the reduced model solutions trajectories as well as with the reference set used for the GQL analysis. One can see that during the first ignition and the transient second delay period where H_2O_2 and CH_2O are being formed (Fig. 2 and 3), the system solution deviates significantly from the 2D slow manifold. However, close to equilibrium the 2D manifold represents the system quite well.

In the following ignition delay times of the original and reduced models will be compared in order to verify the model reduction strategy. An accurate choice of the reference set (see Fig. 3) has been performed as defined in (8) yielding the reduced model dimension as $m_s = 20 - n_c = 14$, where $n_c = 6$ is the number of the conserved quantities, which corresponds to an $m_f = 17$ dimensional fast manifold structure ($n = m_s + m_f + n_c = 37$).

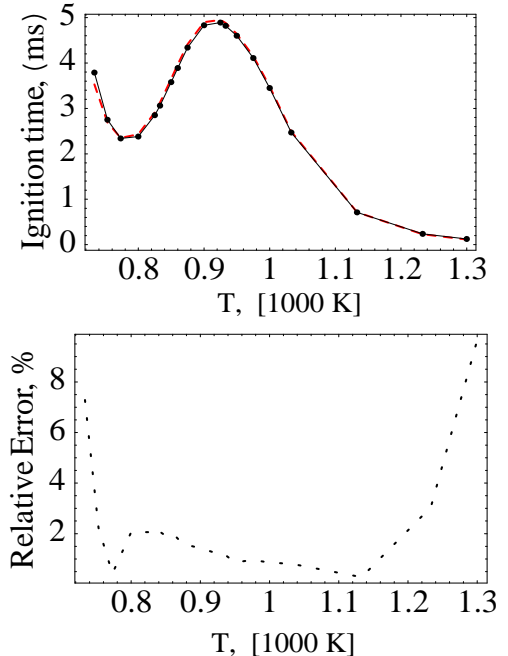


Fig. 4. Temperature dependence of the ignition delay time and the relative error. Black lines with filled circles are the reduced model delay time prediction; red dashed lines are the detailed model results.

The gap between the eigenvalues of the GQL based on the reference set defines the system small parameter

equals to $\varepsilon = 3.42 \times 10^{-2}$. The invariant subspaces of the GQL define the decomposition (2) and have been used to compare the detailed and reduced solutions, namely, the system has been integrated on the GQL approximation $\tilde{Z}_f F(\psi) = 0$ of the m_s -dimensional slow manifold (see Fig. 2 for comparison of typical profiles of the detailed and the reduced models).

The results of the solution of two systems (1) and the GQL reduced model based on (3) are compared, the second of the reduced model corresponds to the integration of the system on the 14-dimensional slow manifold (excluding the conserved quantities i.e. it is considered in the reacting space only) which defines a 14-dimensional reduced model for the ignition process. Figure 5 compares the ignition delay times for relatively low temperatures ranging from 800 K to 1300 K. It shows the relative errors of the reduced model as well. One sees that there are some deviations for high temperatures because the delay time becomes very small and a relative error is plotted, but they are still within an acceptable level of accuracy. It is interesting that the relative error in most of the range is less than a few percent and significantly smaller than the differences in the results obtained from different mechanisms shown in Fig. 1

6. Conclusions

An efficient algorithm of the global analysis of the chemical kinetic mechanisms has been presented and applied to the problem of self ignition. It is based on the natural assumption of the decomposition of motions. It can efficiently be used to decouple fast motions/processes and as a result to reduce the system's dimension and stiffness of such models making them treatable numerically even for complex reacting flow problems. The main feature of the novel approach compared to other approaches is its global character and the capability of approximating not only the slow system manifolds (used to reduce the system), but the explicit decomposition and the fast manifolds as well, which are extremely important for the analysis of asymptotical properties of the decomposition and system hierarchy.

The skeletal chemical reaction mechanism (35 species, 56 reactions) for n-heptane/air auto-ignition problem is considered for verification. The reduced model is formulated and studied on a basis of special system representation as a standard SPS system. The global analysis yields a 14-dimensional reduced model. The results show that the proposed method is an effective and promising tool for mechanisms analysis and model reduction.

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