Investigation of the Internal Hierarchy of Chemical Kinetics Mechanisms

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Abstract—**In this work we present a framework for global model reduction based on the Singular Perturbed Vector Fields (SPVF) method developed by the authors. This method aims at a global transformation of the system to new coordinates, which are suitable to perform further reduction and mechanism simplification. Furthermore two well established methods of chemical kinetics mechanisms reduction - PEA and QSSA methods are analyzed in the context of SPVF. The method is verified by the analysis of the methane/air and n-heptane/air combustion systems. The results show that considerable dimension reduction is possible without any significant damage to the overall mechanism performance.**

I. Introduction

The interest in numerical simulations of reacting flows has grown considerably in the last years. Numerical experiments are considered a powerful tool and take a leading role in science, engineering and industry. The underlying models get more and more detailed and in the case of chemical kinetics for combustion systems the dimension of the considered system of governing equations increases tremendously [1,2]. The understanding and interpretation of results of simulations of such detailed systems becomes problematic.

In many cases, however, one does not need such a complicated description of the phenomenon under consideration. Most likely the detailed model has been developed to cover and to 'fit' all possible ranges of observations and experimental data. In particular simulations, however, one would typically need a certain 'sub-model' that can be used efficiently to reach a required accuracy and level of prediction. On one hand, one has a detailed system reflecting the current situation of the detailed model/mechanism development for the whole range of observations. On the other hand, in particular numerical simulations only a 'small part' of this model is actually involved and important, while the rest is not relevant and even redundant. In order to formalize this observation and develop a tool of automatic model reduction a coordinate free singular perturbation approach has been developed [3].

The basic idea behind the approach is the decomposition of motions and the identification of low dimensional invariant (integral) manifolds embedded into the detailed system phase space. In other words, the phase space of the detailed system is assumed to be split asymptotically into families of fast/slow invariant manifolds representing relatively slow and fast system motions.
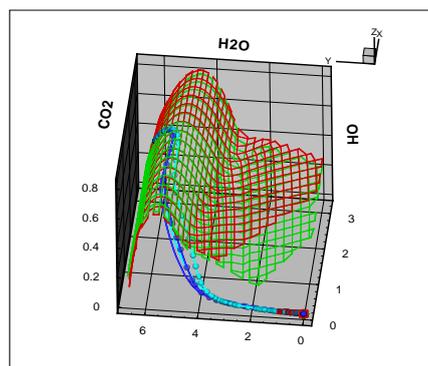

Fig. 1. 2D ILDM (red) and 2D GQL (green) manifolds with system (fast/slow) trajectories in projection to species specific mole numbers.

This decomposition of motions is the main assumption of various model reduction approaches (see e.g. [4,5,6]). Based on this assumption one concludes that if there is a simplified (in terms of dimension) or reduced model describing the detailed one with reasonable accuracy, it should correspond to the invariant manifold of low dimension and the overall system dynamics can be restricted to this manifold (see Fig. 1). The problem of model reduction, in this context, reduces to the identification of such manifolds in the system's phase space and the analysis of their properties. One would be interested in an approach which for a given detailed model (system of governing equations, range of initial, boundary and system parameters are supposed to be known) allows to perform a global decomposition of motions in an explicit form. The global and constant transformation to the standard form of singularly perturbed systems (SPS) by using singularly perturbed vector fields approach is suggested as a main theoretical framework.

It should be clearly stated that the main aim of the study is not in improving existing tools of model reduction (e.g. of QSSA, PEA etc.) or of local analysis (see e.g. CSP, ILDM etc.). But the aim is to develop a global constant decomposition approach.

II. System decomposition

A. Global Quasi-Linearisation (GQL)

The main result of the SPVF method [3] is a transformation defined by invariant subspaces $\tilde{Z}_f$, $\tilde{Z}_s$ of the GQL approximation of the chemical source term [7]

$$\frac{d\psi}{dt} = F(\psi), \;\; F(\psi) = S \cdot R(\psi) \qquad (1)$$

here $\psi = ([c_1],...,[c_{n_s}])$ is the state vector and $S = (\gamma_{j,i})_{j=1,..n_s,\, i=1,...,n_r}$ is the matrix of stoichiometric coefficients, and R is the vector of reaction rates.

For a given function $F(\psi)$ one performs a linearization (called GQL): $T \cdot \psi \approx F(\psi)$ (see [7] for more detail). The invariant subspaces relevant to two groups of eigenvalues, sorted according to their order of magnitude, define corresponding transformation matrices $\widetilde{Z}_f, \widetilde{Z}_s$:

$$T = \left(Z_s \; Z_f\right)\begin{pmatrix}\Lambda_s & 0 \\ 0 & \Lambda_f\end{pmatrix}\begin{pmatrix}\widetilde{Z}_s \\ \widetilde{Z}_f\end{pmatrix}, \;\; \varepsilon = \frac{\max(|\lambda(\Lambda_s)|)}{\min(|\lambda(\Lambda_f)|)},$$

here Λ_f, Λ_s are $m_f \times m_f, m_s \times m_s$ block matrices relevant to eigenspaces and ε measures the difference in time scales.

If a gap condition is satisfied $\varepsilon << 1$, then the invariant subspaces allows us to represent explicitly both fast and slow manifolds

$$\begin{aligned} M_{GQL}^0 &= \left\{\widetilde{Z}_f \cdot F(\psi) = 0\right\} \\ M_{GQL}^{0,fast} &= \left\{\widetilde{Z}_s \cdot \psi = \widetilde{Z}_s \cdot \psi_0\right\} \end{aligned} \qquad (2)$$

The knowledge of the explicit global decomposition can not only be used to determine the fast and slow manifolds as in (2), but it can be used to improve the approximation of the slow manifold. For instance, the approximation of first order (with respect to the defined system small parameter [7]) is given by the system Jacobian in the form

$$M_{GQL}^1 = \left\{\widetilde{Z}_f \cdot F_\psi(\psi) \cdot F(\psi) = 0\right\}. \qquad (3)$$

Additionally, the stability of the slow manifold can be studied in a straightforward way [7]. In the following, two methods are reviewed based on the suggested point of view.

B. QSSA in the conext of GQL

The QSSA assumes that some species $\left[c_{j_1}\right],...,\left[c_{j_{m_f}}\right]$ of chemical systems (1) are in quasi-steady states. It allows an approximation of both the fast system motions and the slow manifold:

$$\begin{aligned} M_{QSSA}^0 &= \left\{F_{j_1}(\psi) = 0,..., F_{j_{m_f}}(\psi) = 0\right\} \\ M_{QSSA}^{0,fast} &= \left\{[c_{j_1}] = const,...,[c_{j_{m_f}}] = const\right\} \end{aligned} \qquad (4)$$

Thus, an empirically defined dimension of the reduced model is $m_s = n_s - m_f$, i.e. the number of independent variables minus the number of constraints. The question whether one obtains a good approximation of the manifold in this way can be investigated by post-processing step comparing the performance of the detailed (1) and reduced (4) systems. It is obvious, however, that the problem of choice of steady states is not trivial. However, there are efficient tools to identify species in steady state

like Computer Singular Perturbation (CSP) technique [4] and Level of Importance Index (LOI) method [8].

Now, if one assumes that the QSSA method based on the right decomposition, then it can be easily verified by

$$\widetilde{Z}_f \cdot S \approx (\gamma_{j,i})_{j=\{j_1,...,j_{m_f}\}, \, i=1,...,n_r}. \qquad (5)$$

C. PEA in the context of GQL

The standard PEA method approximates the manifold of (1) by assuming that some ($m_f < n_s$) elementary reactions of (1) are in partial equilibrium

$$M_{PEA}^0 = \left\{R_{i_1}(\psi) = 0, ..., R_{i_{m_f}}(\psi) = 0\right\}. \qquad (6)$$

This defines an ($m_s = n_s - m_f$) dimensional manifold of slow motions, while the fast motions are those bringing the elementary reactions $R = (R_1,...,R_{n_r})^T$ in partial equilibrium, assuming other elementary reactions are dormant. In the implementation, however, it is suggested to use not the elementary rates directly as defined in (6), but their differentiations along the flow (1)

$$M_{PEA}^1 = \left\{\frac{dR_{i_1}(\psi)}{dt} = 0, ..., \frac{dR_{i_{m_f}}(\psi)}{dt} = 0\right\}, \qquad (7)$$

i.e. reactions might go in two directions very fast to be neglected, but they stay at partial equilibrium Similar as for the QSSA above, by assuming that the PEA method describes satisfactory the slow manifold as well as fast motions, one obtains an equation equivalent to (3)

$$\widetilde{Z}_f \cdot S = (a_{i,j})_{m_f \times n_r}, a_{i,j} = \begin{cases} 0, i = k, j \neq i_k \\ 1, i = k, j = i_k \end{cases}. \qquad (8)$$

Hence, whenever $\widetilde{Z}_f$ satisfies (8) the GQL and PEA slow/fast manifold equations coincide, i.e. $M_{GQL}^0 = M_{PAE}^0$, moreover, (7) corresponds directly to the GQL of the first order approach (3)

$$\begin{aligned} \frac{dR_{i_j}(\psi)}{dt} &= \frac{dR_{i_j}(\psi)}{d\psi} \cdot \frac{d\psi}{dt} = \frac{dR_{i_j}(\psi)}{d\psi} \cdot F(\psi) \Leftrightarrow \\ &\Leftrightarrow \widetilde{Z}_f \cdot \frac{dF(\psi)}{d\psi} \cdot F(\psi)\Big|_{i,j} = 0 \end{aligned} \qquad (9)$$

This explains the use of the derivatives of the elementary reactions in (7): According to the SPVF (3), equation (7) defines a higher order approximation of the slow manifold with respect to a fixed decomposition; this is why (7) is typically used.

III. APPLICATIONS

The method of the GQL analysis has been implemented in the ILDM code [4]. In order to verify the method and investigate its applicability limits it has been applied to the methane and n-heptane auto-ignition problem. In the tested mechanisms three calculations have been made for different initial temperatures and pressures: first the detailed system (1) has been integrated and the delay time was determined based on the OH radicals. In order to

obtain an appropriate approximation of the RHS of (1) the GQL analysis has been implemented yielding fast and slow subsystems given by (2) (see [7] for detail); finally, both fast and slow subsystems have been integrated, the delay times have been determined and the results were compared.
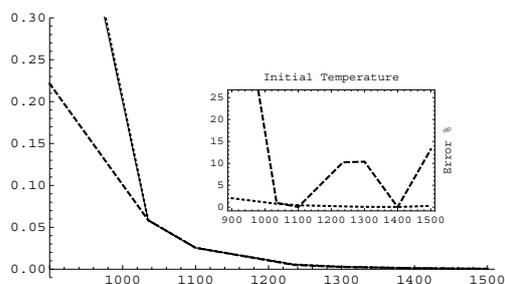

Fig. 2. Delay times versus initial temperature and relative errors, the detailed model – black line, slow subsystem delay times – dotted line, fast subsystem delay times – dashed line.

A. Warnatz's C₁-C₂ Methane/Air mechanism

Warnatz's C_1-C_2 mechanism comprises $n_s = 34$ species and $n_r = 302$ reactions [1]. For the auto-ignition problem at an initial temperature of 1034 K (and pressure 3.12 bar) it has been found that the mechanism has a fast subsystem of co-dimension of 6, i.e. $m^1_f = 28$, $m^1_s = 6$, while the slow subsystem yields $m^1_f = 15, m^1_s = 19$ with relative gaps (estimation of the system small parameter) $\varepsilon^1 = 0.021$ and $\varepsilon^2 = 0.038$ correspondingly. This allows to conclude that an efficient global system dimension is about $n - m^1_s - m^2_f$, 34-6-15, i.e. 13. Fig. 2 shows the performance of relevant fast and slow subsystems in terms of the delay times. It is important to note that the decomposition used for fast and slow subsystem was the same as for the reference case (1034 K, 3.12 bar). Note, however, that mixtures were stoichiometric for all cases.

B. Peters's n-heptane/Air mechanism

The n-heptane combustion system [9,10] of $n_s = 35$ has been already investigated in previous work (see e.g. [11]), but only with respect to the slow subsystem integration yielding a 14-dimensional slow manifold, which is found to perform accurately enough (relative error was about 10%). This model represents a tough test case because of the negative temperature dependence of the ignition delay time (see Fig. 3 and [10]). However, the current analysis (for stoichiometric mixtures with an initial temperature of 833 K and a pressure of 13.5 bar) reveals 6 quasi-conserved quantities as in the previous case $m^1_f = 29, m^1_s = 6$. The invariant subspace analysis of the GQL approximation of the system ($\varepsilon^1 = 0.036$ and $\varepsilon^2 = 0.083$) yields $m^2_f = 19, m^2_s = 16$. It provides us with a better estimate of the reduced system dimension, which equals now to $35 - 6 - 19 = 10$, because $n - m^1_s - m^2_f$ fast modes are considered to relax while "quasi-conserved" quantities do not change.
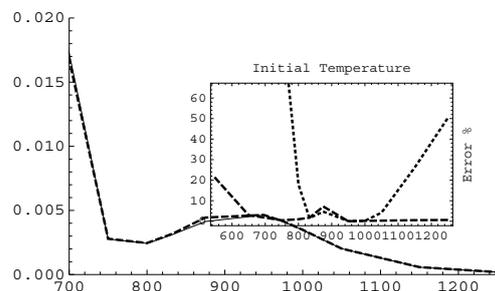

Fig. 3. Delay times versus initial temperature and relative errors, the detailed model – black line, slow subsystem delay times – dotted line, fast subsystem delay times – dashed line.

IV. Conclusion

The problem of model reduction is treated in a general framework. Multi-scale phenomena and the decomposition of motions allow the decoupling of the fast motions and reduce the system's dimension and stiffness making it treatable numerically. A global framework for model reduction has been discussed and used to investigate the conventional tools of QSSA and PEA. Numerical examples show the potential of the framework for developing of schemes of globally reduced kinetic mechanisms.

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