

Decomposition of chemical kinetics models in the auto-ignition problem

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Introduction

Mathematical modeling of complex reacting systems of combustion processes has gained importance in the recent years due to the requirements of economical use of available energy resources and reducing the overall pollution impact caused by combustion processes. The most complicated part of the modeling is obviously the chemical kinetic model. In order to improve agreement of simulated and experimental results one inevitably has to increase the complexity and the dimension of the mathematical model. In this way, reaction mechanisms reach in some cases more than thousand chemical species, which participate in several thousands of elementary reactions (see e.g. [1]). This leads to very large dimensions of the partial differential equation system. As a result typical mathematical models of reacting flows with detailed mechanisms cannot be treated analytically and even the numerical treatment is limited to academic problems. Accordingly, the need for reduction methods providing with reduced models, which are simple (low dimensional, less complex etc.), but nevertheless, describe quantitatively the underlying combustion process, has been constantly increased.

At present there are a lot of realizations of model reduction that use existence of multiple time scales, which is an important feature of chemical kinetic mechanisms. Although this complicates a lot the numerical treatment of the reacting flow system due to the stiffness of the resulting mathematical model, it allows also to construct low-dimensional approximations of the detailed model describing the so-called long-term and rate limiting dynamics accurately. Most precise methods, however, have local character and are based on an analysis of eigenspaces of the Jacobi matrix of the chemical source term (see below). In fact, local information about the decomposition makes such methods quite accurate in the description of the slow system dynamics, but for fast motions, which become very important in the context of ignition/extinction problems, there are up to now no reliable methods. The current work is devoted to applying such a method [2], which can be efficiently used for global analysis of the reaction mechanisms with subsequent formulation of explicit reduced models for unsteady combustion regimes like ignition processes.

Problem statement and suggested solution

A typical mathematical model of a reacting system under consideration (pure homogeneous system of the auto-ignition problem) is presented by a system of ordinary differential equations that describes the chemical system evolution based on the mass action law

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

These equations describe the evolution in linear vector space $\psi = (\psi_1, \dots, \psi_n)$, 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. Positive invariance of the domain Ω (composed by vectors with nonnegative components) to ensure a dissipative nature of the reaction mechanism is additionally assumed.

Theoretically, a final purpose of model reduction is a reformulation of the system (1) 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 (1) will be accurately described by the following reduced model

$$\frac{d\theta}{dt} = \tilde{F}(\theta), \quad \theta \in \mathbb{R}^m. \quad (2)$$

The main question then arises: how the systems (1) and (2) relate to each other, namely, what is the relation between detailed $\psi = (\psi_1, \dots, \psi_n)$ and reduced spaces $\theta = (\theta_1, \dots, \theta_m)$ and how they can be compared. In the case the reduced space can be represented by a low-dimensional manifold in the detailed linear vector space and given in explicit form $M = \{\psi = \psi(\theta)\}$ the system (1) can be projected to the manifold M yielding

$$\frac{d\theta}{dt} = \psi_\theta^+(\theta) F(\psi(\theta)) \equiv \tilde{F}(\theta), \quad \theta \in \mathbb{R}^m. \quad (3)$$

The Moore-Penrose pseudo-inverse $\psi_\theta^+(\theta)$ has been used in (3), which is a well defined function unless the tangent space TM specified by $\psi_\theta(\theta)$ degenerates. Obviously, the reduction of an arbitrary system with prescribed dimension and accuracy is almost always impossible in principle, fortunately, states of systems governed by chemical reactions access not the entire possible range of the thermo-chemical state space, but only a part of it. This part usually has a low-dimensional structure or can be efficiently approximated by low-dimensional manifolds. Therefore, low-dimensional manifolds with certain properties (invariance, attractiveness, stability, slowness etc.) are very important for model reduction. Although the existing methods can be used to obtain a low-dimensional approximation of the accessed space by the system (1), they can not be used to investigate these properties. The QSSA method (Quasi Steady State Assumption), for instance, assumes that some of the species are already in steady state, while the PEA (Partial Equilibrium Assumption) defines the reduced dynamics by considering some elementary reactions in partial equilibrium, meaning that the rates of forward and reverse reactions are equal etc. In our approach, however, a simple mathematical model for the decomposition of motions leads to a very special system representation of the system (1) as a Singular Perturbed System (SPS) with the system small parameter $0 < \varepsilon \ll 1$ controlling the difference in time scales:

$$\begin{cases} \frac{dU}{dt} = F_s(U, V) \\ \varepsilon \frac{dV}{dt} = F_f(U, V) \end{cases}. \quad (4)$$

Thus, in order to investigate the system (1) we apply a global (in Ω) and automatic method [2, 3] to find a transformation of the system to the most suitable for the analysis form (4) and then use powerful theory of singular perturbations to access the reduced space and study the properties of the chemical kinetic model.

Results and conclusions

As an example for the application of the method we have chosen auto ignition process in heptane/air mixture. For the analysis, the $n_r = 56$ step skeletal mechanism with $n_s = 35$ species of n-heptane/air system [4] has been used. The global analysis yields the reduced model dimension as $m = 20 - n_c = 14$, where $n_c = 6$ is a number of the conserved quantities. The system small parameter for the described dimension decomposition is estimated as $\varepsilon = 3.42 \times 10^{-2}$. In order to compare the detailed and reduced models the system has been integrated on the approximation $F_r(U, V) = 0$ of the m -dimensional slow manifold. Figure compares two delay times for initial relatively low temperatures ranging from 800 K to 1300 K. It shows relative errors of the reduced model by comparison of delay times. One sees the accuracy is about a few percent, while typically for conventional methods they can vary within several orders of magnitude. Thus, the simulations of the ignition times are in very good agreement with those obtained with the detailed mechanism.

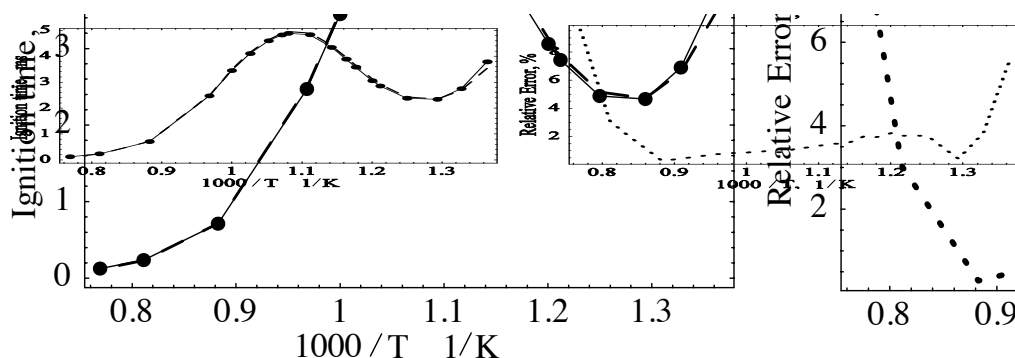


Fig. Initial gas temperature dependence of the ignition delay time and the relative error. Black lines with filled circles are the reduced model delay time prediction; dashed lines are the detailed model results and the relative error.

The suggested method [2] allows more than two times reduction of the skeletal mechanism for relatively low initial temperatures. It provides an explicit form of the decomposition of motions and, therefore, it can be and has been used for the detailed analysis of the system internal hierarchy. Furthermore, the problems of the implementation of the global analysis and finding an optimal transformation as well as the definition of the positively invariant domain to automatically identify the important range of the physical system's parameters for the auto-ignition phenomenon have been overcome successfully.

References

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