

G-Scheme-based Analysis of Hydrocarbon Ignition

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Abstract—Using the G-Scheme, we have developed a specific procedure to generate simplified mechanisms for chemical kinetics processes, to analyze them in order to understand the role of the most important reactions, and to identify the most important reactions paths of the processes. The procedure is based on participation indices specifically created for a G-Scheme generated database. The effectiveness of the procedure is demonstrated by applying it to auto-ignition problems for homogeneous hydrocarbon/air mixtures.

I. INTRODUCTION

Detailed chemical reactions mechanisms involve a large number of species and reactions. The use of a simplified kinetic model is a common simplification in reactive flow computations, although it may introduce significant errors in subsequent simulations. As an example, phenomenological models such as one- and two-step reactions are not able to capture all relevant dynamics inherent in the full mechanism, so that the simulations are only qualitatively representative of the physical phenomena. However, inclusion of even moderately complex detailed chemistry in the numerical simulation of reactive flows makes the computational cost extremely difficult to afford. Currently there are several methods employed to reduce the CPU time and the memory overhead required to solve reactive flows with detailed kinetics. This is achieved by reducing the number of species and reactions in the detailed mechanism and at the same time decreasing the stiffness of the system.

II. G-SCHEME-BASED ANALYSIS METHODOLOGY

The *G-Scheme* [1] is a time accurate computational tool that exploits, adaptively, opportunities for reduction from the presence of fast/active and slow/active spectral gaps. The characterization of the local structure (of the tangent space) of the subspaces associated with the slow, active, and fast scales can be of great significance in the analysis of the dynamics with the aim of obtaining a low-dimensional description. The specific features of the *G-Scheme* provide a time-scale-aware sensitivity analysis of the problem, which might be used to simplify/reduce/understand the problem at hand.

The *G-Scheme* decomposes the space in 4 subspaces according to the time scale of each mode: the active subspace \mathbb{A} contains all the active scales, the subspaces \mathbb{H} contains all scales slower than the active ones, while faster scales are in the subspace \mathbb{T} , and lastly, the invariant subspace \mathbb{E} containing the invariant modes. The active and the slow/fast modes are projected on the invariant subspace. Subsequently, only the active subspace is numerically integrated using as time step

of the order of the time scale of the fastest mode in this subspace. The contributions of the slow and fast subspaces are evaluated using asymptotic corrections. The time evolution of the species provides the data base used for the analysis and simplification procedure.

In the *G-Scheme* we modify the CSP Participation Index [2] to define the G-Scheme Participation Index (GPI) [3] of the k -th reaction relative to the dynamics of subspace s :¹

$$\widehat{\mathcal{P}}_k^s(\mathbf{x}) = \frac{\sum_{i=N_{s,b}}^{N_{s,e}} C_k^i(\mathbf{x}) r^k(\mathbf{x})}{\sum_{i=N_{s,b}}^{N_{s,e}} \sum_{k'=1}^{\mathbb{R}} |C_{k'}^i(\mathbf{x}) r^{k'}(\mathbf{x})|} \quad (1)$$

with

$$C_k^i = \mathbf{b}^i(\mathbf{x}) \cdot \mathbf{S}_k, \quad (2)$$

where $\mathbb{R} = 2N_r$, N_r being the number of reversible reactions, \mathbf{b}^i the contravariant basis vector, \mathbf{S}_k the stoichiometric vector, and r^k the rate associated with the k -th reaction. Note that $0 < P_k^i(\mathbf{x}) < 1$. Equation (1) provides a measure of the contribution of the k -th reaction to the subspace s normalized by the contribution of all reactions in the same subspace. In other words, the GPI provides a criterion to identify if the k -th reaction is *active*, *slow*, *fast*, or as *negligible* if it doesn't have a relevant value in any of the subspaces. The concept of an *important reaction* is not an inherent property of the reaction but a function of the local state.

We can rank the reactions according to the maximum value of $\widehat{\mathcal{P}}_k^s$ in a time interval considered as follows:

$$\overline{\mathcal{P}}_k^s = \max_{t_b < t < t_e} \left(|\widehat{\mathcal{P}}_k^s(\mathbf{x})| \right). \quad (3)$$

This choice is more conservative than the time-weighted averages of the index along the trajectory. Equation (3) provides a value that summarizes all the information given by (1). By identifying the maximum value of the participation index calculated for any reaction along the process, we obtain an objective measure of the importance of the reaction for the analyzed problem.

Based on (3), we can create a very simple iterative procedure to obtain a simplified mechanism that satisfies objective criteria defined by the analyst.

¹The index $s = h/a/t$ identifies one of the three subspaces as follows: h for \mathbb{H} , a for \mathbb{A} , and t for \mathbb{T} .

In this study we choose the error in the equilibrium temperature and ignition time as criteria, defined as:

$$err_T = \frac{T_{f,s} - T_{f,c}}{T_{f,c}} \quad \text{and} \quad err_t = \frac{t_{e,s} - t_{e,c}}{t_{e,c}}, \quad (4)$$

where $T_{f,s}$ and $T_{f,c}$ are the equilibrium temperatures for the simplified and complete mechanisms respectively, while $t_{e,s}$ and $t_{e,c}$ are the ignition times for the simplified and complete mechanisms respectively.

III. HYDROCARBON IGNITION

In a homogeneous chain-branched explosion, it is possible to identify a short period, the *explosive* stage, in which most of the chemical heat is released. Before this occurs, two other stages are noted: in the first, the *initiation* stage, the change of state is very slow, while in the second, the *chain-branching* stage, there is a rapid increase in the chain-carrier species concentration. The explosive stage itself is followed by the *termination* stage, where stable species are ultimately produced.

The explosive stage is characterized by a very short time scale, with the dynamics controlled by a pair of real distinct positive eigenvalues. During this period these two eigenvalues, of decreasing magnitude, are responsible for the increase in the chain-carrier species (and a decrease of the associated time scales) until they merge to form a pair of complex conjugate eigenvalues with positive, and still decreasing, real parts. Eventually, their real parts become negative and the imaginary parts reduce to zero and thus, subsequently, become a pair of real distinct negative eigenvalues.

In this work, we analyze and construct simplified mechanisms on the basis of the information extracted from the numerical solution of the ignition process by using the *G-Scheme* solver. Applying the *G-Scheme* analysis to the four stages allows us to identify a simplified mechanism that reproduces the complete combustion process.

Simplified mechanisms for hydrogen, methane, propane, and n-heptane is obtained by taking the union of all the reactions that have a value of the GPI above a selected threshold in at least one *G-Scheme* subspace. The accuracy of the reduced mechanism depends on the selected GPI threshold: increasing the threshold decreases the number of reactions in the skeletal mechanism and also decreases the accuracy of the results. However, above a certain threshold the skeletal mechanism is not able to reproduce the explosion. Therefore, we will look for the threshold value corresponding to the smallest skeletal set of reactions able to reproduce the explosion stage within the given error tolerance. These simplified mechanisms are shown to be robust with respect to different initial conditions.

By applying the same analysis focused at the *explosion stage* only, it is possible to identify the species and reactions that play crucial roles in the explosion process. Such analysis allows us to obtain a much smaller skeletal kinetics mechanism that reproduces the explosion process, which is a subset of the respective global simplified mechanism, formed

by reactions that play the most important role in the burning of the mixture.

We emphasize the fact that in all cases studied we have found two eigenvalues with positive real parts that are key to the evolution described above. The modes associated with these eigenvalues are the *explosive* modes, they drive the evolution of the species and they provide the time scale of the process. We evaluate the GPI only for the modes associated with the positive eigenvalues to determine a subset of reactions that form the skeletal mechanism of the explosion stage. This set of reactions is contained in the skeletal mechanism for the *explosive* stage and are the reactions that drive the ignition process.

Lastly, we note that for n-heptane, in the case of a low initial temperature, two explosions occur. In this case we are able to identify a skeletal mechanism for each explosion stage.

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