Chemical kinetics mechanism simplification via CSP

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Abstract

An algorithm was developed to generate simplified (skeletal) mechanisms, from a given detailed one, able to replicate the dynamics of a user-specified set of species (chosen from the original set) to within a user-specified error tolerance when a finite set of sampling points, U, in the chemistry configuration space is given. The simplification procedure involves discarding elementary reactions and species that are deemed unimportant in the set U. The criteria used in deciding which elementary reactions or species to discard are based on the Computational Singular Perturbation (CSP) method. The procedure involves applying the CSP analysis to each point in U and an algorithm to assemble the simplified mechanism that is valid for all the points in U and is optimized for the set of scalars specified. This algorithm provides a convenient way to construct comprehensive simplified mechanisms, applicable over a wide range of parameters and combustion processes. The effectiveness of this new algorithm is demonstrated by constructing simplified mechanisms that are optimized for two reactive flow systems – namely a perfectly stirred reactor and a premixed flame of methane and air.

Keywords: Chemical kinetics reduction; Auto-ignition; Laminar flames; Numerical methods

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1. Introduction

Detailed chemical kinetic mechanisms for hydrocarbon oxidation can be composed of hundreds of species and thousands of elementary reactions. This and the extremely wide time scale spectrum, leading to stiff governing equations, lead to severe limitations in the applicability of detailed kinetics in numerical simulations of even simple combustion phenomena.

Several reduction techniques have been developed over the years aimed at reducing the dimensionality and stiffness of the equations to ease the task of numerical integration. A typical approach is the QSSA, which replaces the original mechanism involving N species with a far smaller set of global reaction steps, not involving steady state species. Still, the latter are required to determine the rates of the global steps. The evaluation of these species, through a system of complex algebraic relations, decreases the computational time savings through reduction from a theoretical $\mathcal{O}(1 - N_{QSSA}^2/N^2)$ to an effective $\mathcal{O}(1 - N_{QSSA}/N)$, where N_{QSSA} is the number of species retained in the global steps [1,2,3].

An alternative route to kinetics simplification is the construction of skeletal mechanisms (also required as a preliminary step before QSSA reduction) obtained by discarding all ‘unimportant’ species and elementary reactions from the detailed mechanism. The degree of reduction is not as high as in the QSSA, since typically $N_{sk} > N_{QSSA}$, where N_{sk} is the number of species in the skeletal mechanism, but no complex rate computations are necessary, so that the computational time saving is indeed $\mathcal{O}(1 - N_{sk}^2/N^2)$.

The present study introduces a skeletal reduction algorithm, which utilizes a criterion to select the elementary reactions important to the dynamics of a prescribed subset of species of interest which explicitly takes into account the CSP splitting between fast and slow components of the kinetic system.

2. Theoretical background

A thorough description of the CSP method may be found in [4,5,6,7]. In its classical formulation, CSP is

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especially devoted to the analysis of spatially homogeneous finite dimensional systems (e.g. perfectly stirred reactors) governed by a set of stiff ODEs for which an invariant slow manifold exists leading to a fixed equilibrium within the composition space. The asymptotic behavior of the system is represented by a non-stiff, slowly evolving manifold-constrained system. Extension to more complex PDE-governed systems which involve convective-diffusive transport was discussed in [6,8,9,10].

CSP introduces an ordered set of time-dependent basis vectors $\{\boldsymbol{a}_i\}_{i=1}^{N}$ (and their duals $\{\boldsymbol{b}^i\}_{i=1}^{N}$) found by a refinement procedure described in [11,12,13], which, to leading order accuracy, are equivalent to the time-dependent eigenvectors of the Jacobian matrix of the chemical source term. The basis vectors induce a decomposition of the N-dimensional phase space into an M and an $(N - M)$-dimensional subspace, spanned by the first M and the remaining $(N - M)$ basis vectors and associated with the M fastest and $N - M$ slowest time scales, respectively. The ensuing $(N - M)$-dimensional slow subspace, approximating the invariant slow manifold, is identified as the phase space locus where the chemical source term has no projection onto the fast subspace and where the trajectory is forced to lie under the action of the fast scales.

Such a decomposition prompts the introduction of a 'slow' importance index $(I_k^i)_{slow}$ assessing the relative influence of the slow component of a given reaction k to the production/depletion of a given species i. In addition, it prompts the introduction of a 'fast' importance index $(I_k^i)_{fast}$ assessing the relative influence of the fast component of the k-th reaction to the M species affected the most by these time scales (CSP radicals [10]). The indices are defined as:

$$(I_k^i)_{slow} = \sum_{s=M+1}^{N} a_s^i(\boldsymbol{b}^s \cdot \boldsymbol{S}_k)R^k \Big/ \sum_{j=1}^{N_r} \left| \sum_{s=M+1}^{N} a_s^i(\boldsymbol{b}^s \cdot \boldsymbol{S}_j)R^j \right| \tag{1}$$

$$(I_k^i)_{fast} = \sum_{r=1}^{M} a_r^i(\boldsymbol{b}^r \cdot \boldsymbol{S}_k)R^k \Big/ \sum_{j=1}^{N_r} \left| \sum_{r=1}^{N} a_r^i(\boldsymbol{b}^r \cdot \boldsymbol{S}_j)R^j \right| \tag{2}$$

where N_r is the total number of reactions, counting the forward and reverse reactions separately, $\boldsymbol{S}_k$ the N-dimensional stoichiometric vector of the k-th reaction, and R^k is the rate of the k-th reaction.

For a given species, 'the elementary reactions with the largest $(I_k^i)_{slow}$ are the rate controlling reactions for that species' [14]. On the other hand, elementary reactions with the largest $(I_k^i)_{fast}$ will quickly damp any perturbation of the system state off the manifold, mainly through adjustment of the CSP radical species.

Using these indices, skeletal mechanisms can be constructed by retaining the most important kinetic components to both the slow and fast dynamics of the problem, that is, the processes (i) driving the solution towards the slow manifold and constraining it there, and (ii) moving the solution along the manifold, can be singled out and included in the skeletal mechanism. For example, the importance of reactions which have relatively small and slow rates (and affect the slow evolution of a certain species) will surface as soon as the reactions that have large and fast rates (and affect only its fast evolution) are removed by means of the fast/slow decomposition of the phase space.

3. The simplification algorithm

The procedure for the simplification of a detailed kinetic mechanism is organized as follows.

First, a solution of the combustion problem of interest is computed. A CSP analysis of this solution producing all relevant CSP data (fast/slow importance indices, CSP radicals, etc.) is then performed. The CSP data at each time t_n ($n = 1, L$) (and/or space location x_n) are stored as an entry record, r_n, of a database.

The simplification algorithm takes this database as input and proceeds with the identification of a self-consistent subset S of the original species 'relevant' to a pre-specified kernel set of species S_0, typically consisting of a major reactant and a major product (e.g. in methane combustion S_0 = [CH_4, CO_2] or S_0 = [CH_4, NO]).

At each record r_n, the identification of S is iterative. The i-th guess of S, $S^{[i]}(r_n)$, is identified as the set of species occurring in all reactions possessing importance indices relative to the set $S^{[i-1]}(r_n)$ greater than a user specified tolerance, say *tol*, where $S^{[0]}(r_n) = S_0$. The iterations are stopped when $S^{[i]}(r_n) = S^{[i-1]}(r_n) = S^*(r_n)$; this procedure is repeated at each record r_n ($n = 1, L$) in the database. Taking the union of all $S^*(r_n)$, $S = S^*(r_1) \cup \ldots \cup S^*(r_L)$, yields the subset of species to be included in the desired skeletal mechanism. The ensuing skeletal reaction pathway interconnecting the set S is then derived from the original detailed mechanism by selecting all the elementary reactions involving the species in S.

4. Results

The algorithm was first used to simplify the 325 reactions, 53 species GRI-Mech 3.0 mechanism [15] for the homogeneous self-ignition of methane in air. A reference solution was obtained, using the detailed mechanism, for a stoichiometric ($\Phi = 1.0$) mixture at $p = 1$ atm, and an initial temperature of $T = 1000$ K.

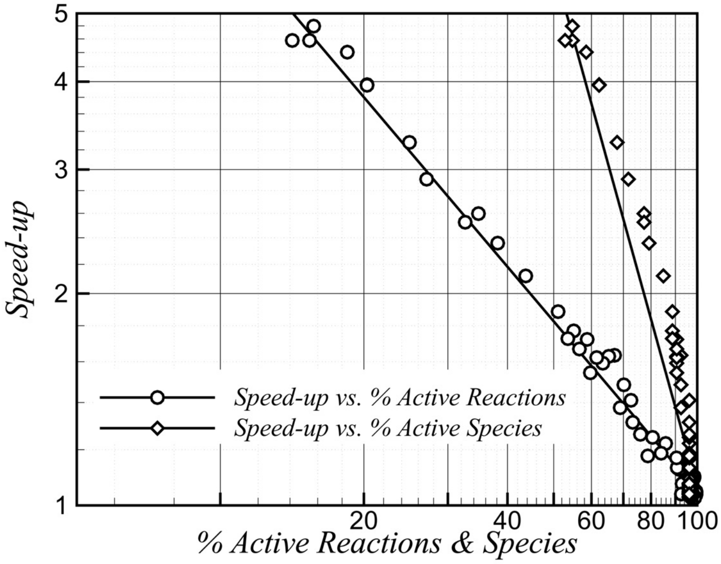

Fig. 1. Log-log plots of speed-up vs. % of active species and reactions in skeletal mechanisms. Straight lines represent fits of the kind $\log y = \log x^A + B$. When x represents % of active species $A \approx -2.45$, when x represents % of active reactions $A \approx -0.8$.

The related CSP database was then constructed and a number of skeletal mechanisms were generated with $S_0 = [CH_4, NO]$ and for a wide range of values of *tol*. NO was chosen in order to test the capability of skeletal mechanisms to accurately reproduce the pollutant formation subprocesses.

The accuracy of the skeletal mechanisms has been tested by comparing the related solution with the reference one. A CPU speed-up factor F was defined as the ratio between the CPU time required to integrate the skeletal and the detailed mechanisms, respectively. Fig. 1 shows the speed-up factor against the percentage of species and elementary reactions retained in the skeletal mechanisms (referred to as active species and active reactions). The speed-up was indeed found to have an approximately quadratic dependence on the active species and an approximately linear one on the active reactions.

The root mean square relative percent error in NO mole fraction, $E(X_{NO})$, evaluated along the whole solution trajectory, was also computed and plotted in Fig. 2 as a function of the speed-up, this being a measure of the workload reduction induced by the skeletal mechanism. The results of Fig. 2 show that the error $E(X_{NO})$ scales with the speed-up as $E(X_{NO}) \sim F^6$. As expected, a compromise between computational efficiency and accuracy needs to be found. Note that a three-fold speed-up is achievable at the cost of a $\approx 5\%$ rms error in NO.

The algorithm was then tested on the GRI-Mech 1.2 mechanism [16] for methane/air premixed laminar flames at $p = 1$ atm. Several CSP databases were constructed, each corresponding to a different equivalence ratio in the range ($\Phi \in [0.7, 1.3]$). The simplification algorithm was run using all of these databases as input so as to obtain a series of comprehensive, in the sense introduced in [3], skeletal mechanisms. Figure 3 shows that laminar flame speeds are correctly reproduced for each Φ up to the 19 species, 77 reactions skeletal mechanism for which a three-fold speed-up in CPU time is achieved.

5. Conclusions

A CSP-based algorithm for the simplification of chemical kinetics mechanisms was introduced and tested. Skeletal mechanisms were obtained for the homogeneous combustion and the premixed laminar flame problems, both involving methane and air mixtures. Validation proved that a three-fold speed-up in CPU time can be obtained at the expense of a moderate loss of accuracy (overall error $<5\%$). Standard reduction techniques, such as QSSA, may indeed be performed directly on the simplified mechanism thus combining the advantages of both reduction techniques.

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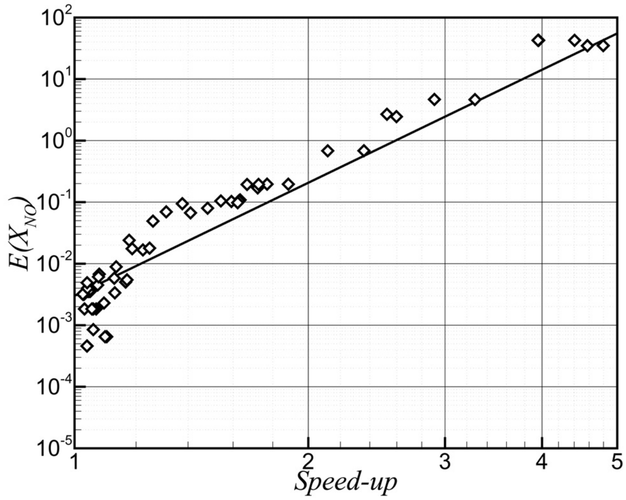

Fig. 2. Log-log plot of rms percent error $E(X_{\mathrm{NO}})$ vs. speed-up F for each simplified mechanism.

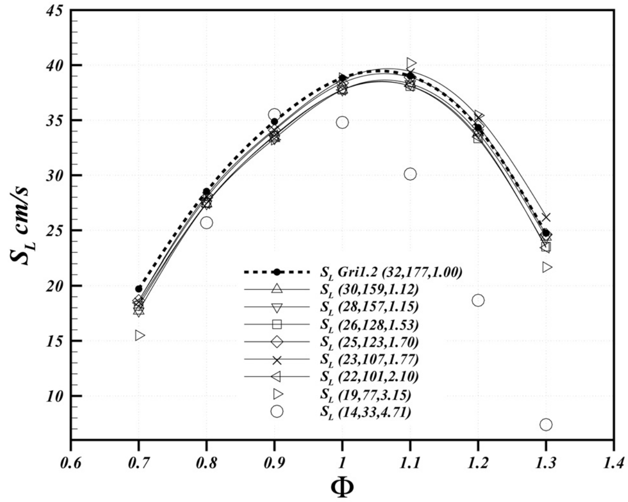

Fig. 3. Premixed laminar flame speeds S_L (cm/s) resulting from the detailed GRI Mech 1.2 mechanism (dashed line) and from the comprehensive simplified mechanisms. The first number in brackets is the number of active species in the mechanism tested, the second is the number of reactions and the third number is the average speed-up factor with respect to the detailed mechanism.

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