

Simplifying Chemical Kinetic Systems under Uncertainty using Markov Chains

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Abstract—We describe a novel method to obtain skeletal reduction of chemical mechanisms. The reduction method maps the system of equations that describe the evolution of the chemical mixture into a set of memoryless Markov processes, one for each chemical element. Each Markov process “tracks” an atom through its chemical evolution, i.e., each state in the Markov process corresponds to a chemical species and the transition probability between two states models the probability that an atom is transferred between molecules. We show that this methodology provides an inexpensive estimate of the species elimination error in stirred reactor problems.

I. INTRODUCTION

In the last decade, the sizes of chemical mechanisms used in combustion modeling have grown by orders of magnitude [1], increasing from 20–30 species for methane combustion to more than 1000 in some recent detailed mechanisms [2]. For this reason, the numerical solution of multidimensional reacting flow still constitutes a great challenge that approaches the limit of the world’s largest computational facilities [3].

A way to bridge the gap between computational fluid dynamics and complex chemistry is to replace the full set of chemical species and reactions by a simpler one. The new smaller model is optimized for a given problem and can thus generate results of the same accuracy at a much smaller computational cost.

We focus our attention on *skeletal reduction*, i.e., on the elimination of unimportant species from the mechanism. A number of techniques are available in the literature to perform this simplification: sensitivity analysis [4], CSP simplification [5], directed relation graph (DRG) reduction [6], which evolved into an array of derived techniques [7], [8], [9], path flux analysis [10], and error minimization [11].

All these methods can be subdivided in two groups:

- 1) *Intrusive* methods, which extract information from the detailed mechanism and use this information to estimate the error generated by the elimination of species;
- 2) *Inspective* methods, which directly test a set of candidate reduced mechanisms and thus generate the skeletal mechanism in a trial-and-error fashion.

The inspective approach typically results in a much smaller skeletal mechanism but is more computationally expensive. Furthermore, there is a link between intrusive and inspective

methods; the error estimate provided by an intrusive method can be used to “guide” an inspective method in the adaptive generation of a skeletal mechanism. For example, the DRG (intrusive) method naturally evolved to the DRGASA (inspective) method.

The present contribution shows that Markov processes can be used to generate a computationally inexpensive estimate of the elimination error.

II. DEFINITION OF THE MARKOV PROCESSES

We consider stirred reactor problem, i.e., a non-equilibrium steady-state chemical mixture, defined by a vector of mass fractions Y_i , $i = 1, \dots, N$ and a temperature T . The steady-state condition is provided by a set of reactions \mathcal{R} characterized by the reaction rates r_α , $\alpha = 1, \dots, M$ and a stoichiometric matrix $\nu_{i\alpha}$. Furthermore, we consider the set of chemical elements \mathcal{E} (for a typical combustion problem, \mathcal{E} includes hydrogen, nitrogen, oxygen and carbon) and the composition matrix n_{iK} , whose entries represent the number of atoms of element K in molecule i .

In a stirred reactor, the mass fraction vector is calculated as the steady-state condition of a stiff system of differential equations, which is computationally expensive to solve. For this reason, we introduce an alternative probabilistic representation of the problem, in which atoms are tracked while they move from one chemical species to another. In particular, a Markov process will be defined for each of the chemical elements.

Any given atom of element K can be part of one of the molecules in set \mathcal{S} (or at least any molecule for which the composition matrix entry $n_{iK} > 0$). Thus we can say that an atom of type K can assume different *states* in \mathcal{S} . Chemical reactions can cause a change of state of the atom since molecule i could be “transformed” into a different chemical species, which we will indicate with index j . Without resorting to molecular simulations—i.e., in the continuous regime of large species populations, typical for gas-phase combustion—it is possible to compute the probability that atom K will transition from i to j .

Elementary probability theory suggests that the probability of an $i \rightarrow j$ transfer for atom K is given by the sum over all reactions of the probability that reaction α occurs

and that this reaction transfers the atom

$$\mathbb{P}(K; i \rightarrow j) = \frac{\sum_{\alpha} \mathbb{P}(K \text{ transferred} | \text{reaction } \alpha)}{\mathbb{P}(\text{reaction } \alpha)}$$

This probability can be calculated from the reaction rates;

$$P_{i \rightarrow j}^K = \sum_{\alpha \in \mathcal{R}(i)} \frac{n_{Kj} \nu_{\alpha j}^-}{\sum_{\ell \in \mathcal{R}_{\alpha}} n_{K\ell} \nu_{\alpha \ell}^-} \frac{r_{\alpha}^+}{\sum_{\beta \in \mathcal{R}(i)} r_{\beta}} \quad (1)$$

where $\mathcal{R}(i)$ is the set of reactions that involve species i and $P_{i \rightarrow j}^K$ is a compact notation for $\mathbb{P}(K; i \rightarrow j)$.

III. THE ERROR ESTIMATE

In order to obtain an elimination error estimate from (1), we introduce the hypothesis that the chemical process under investigation is qualitatively modeled by a one-step irreversible global reaction. This means that there are a set of species—the global products (typically CO_2 and H_2O)—whose transition probabilities are well approximated by $P_{i \rightarrow j}^K = \delta_{ij}$ and that act as *absorbing states* in the Markov process. Conversely, the global reactants provide initial conditions, meaning that we postulate that the initial distribution of the Markov process concentrates the probability of each atom K on the global reactants. Under this approximation the transition probability (1) models the evolution of microstates from reactants to products.

For a given set $\mathcal{S}_r \subset \mathcal{S}$ of potentially unimportant species that could be removed, we define the error estimate as

$$E(\mathcal{S}_r) = \mathbb{P}(\text{reaching } \mathcal{S}_r \text{ before a global product}) \quad (2)$$

which can be efficiently calculated from the transition probability (1).

IV. RESULTS

We consider a stirred reactor with an inlet temperature of 300K, in which a stoichiometric mixture of methane and oxygen is injected along with 90% nitrogen (by mass). The quantity of interest (QoI) in our study is the extinction timescale; to compute this QoI, we perform a continuation solution, progressively reducing the residence time in the reactor until extinction occurs. Starting from the 53-species GRI mechanism [12] we randomly generate skeletal reduced mechanisms of size 47 to 25. Each mechanism is tested and the error estimate (2) is calculated along with the true error in extinction time. Figure 1 shows that the error estimate correlates very well with the elimination error.

V. CONCLUSION

A novel intrusive approach to skeletal reduction has been presented, which relies on a Markov process description of the chemical state to estimate the error associated with the elimination of a set of species. The error estimate correlates very well with the actual elimination error. Thus it can be used to guide intrusive skeletal reduction algorithms.

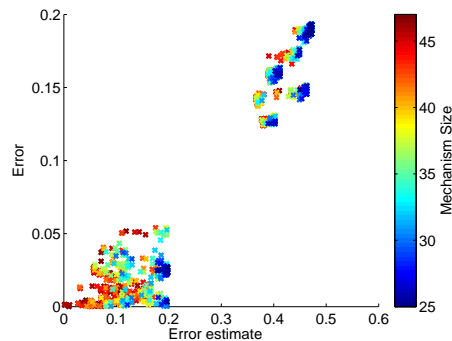


Fig. 1. Scatter plot of error estimates and the true elimination errors for different reduced mechanisms, showing strong correlation.

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