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Chemical model reduction under uncertainty

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ABSTRACT

A general strategy for analysis and reduction of uncertain chemical kinetic models is presented, and its utility is illustrated in the context of ignition of hydrocarbon fuel–air mixtures. The strategy is based on a deterministic analysis and reduction method which employs computational singular perturbation analysis to generate simplified kinetic mechanisms, starting from a detailed reference mechanism. We model uncertain quantities in the reference mechanism, namely the Arrhenius rate parameters, as random variables with prescribed uncertainty factors. We propagate this uncertainty to obtain the probability of inclusion of each reaction in the simplified mechanism. We propose probabilistic error measures to compare predictions from the uncertain reference and simplified models, based on the comparison of the uncertain dynamics of the state variables, where the mixture entropy is chosen as progress variable. We employ the construction for the simplification of an uncertain mechanism in an n-butane–air mixture homogeneous ignition case, where a 176-species, 1111-reactions detailed kinetic model for the oxidation of n-butane is used with uncertainty factors assigned to each Arrhenius rate pre-exponential coefficient. This illustration is employed to highlight the utility of the construction, and the performance of a family of simplified models produced depending on chosen thresholds on importance and marginal probabilities of the reactions.

1. Introduction

Chemical model reduction strategies generally start from a detailed chemical kinetic mechanism as the reference or baseline gold-standard. Given this standard, a specified range of operating conditions or set of state vectors, a select set of Quantities of Interest (QoIs), and a requisite error threshold, a model reduction strategy produces a simplified mechanism of associated size/complexity [1,2].

This strategy, despite its effectiveness, nonetheless relies on the quality of the starting mechanism. Yet, there is typically significant uncertainty in both the structure of available detailed mechanisms for hydrocarbon fuels, and in their thermodynamic and chemical kinetic rate parameters. Therefore, in principle, the analysis/reduction processes that provide simplified mechanisms starting from the detailed mechanism, and the measures of quality of a simplified mechanism relative to the detailed mechanism, need to account for both model and parametric uncertainties in both mechanisms. This is a challenging, yet highly relevant topic. Overconfidence in the detailed mechanism can lead to a misplaced focus on tight error tolerances in the simplified model, relative to a faulty/uncertain baseline. Simplified model errors ought to be handled along with detailed model uncertainties in the same error budget. Any error norm between simplified and detailed models ought to be weighted appropriately with attendant uncertainties. Moreover, the fact that both the detailed and simplified mechanisms are burdened with uncertainty suggests that any measures of distance between their predictions be done in a probabilistic context. This line of reasoning highlights the need for rethinking model analysis/reduction strategies for uncertain chemical kinetic models.

The above is a significant undertaking with a range of technical challenges. There has been some work addressing model reduction under uncertainty in the context of proper orthogonal decomposition (POD) [3], albeit for small degrees of uncertainty. The dynamical analysis of uncertain ordinary differential equation (ODE) systems has also received some attention [4,5], in a full probabilistic setting. Further, from the process control perspective, there has also been work [6,7] addressing dynamical systems reduction under parametric uncertainty, relying on balanced truncation [8,9], singular value decomposition, and sensitivity analysis. We note that this work [6,7] presumes parameter variations in intervals,

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with no probabilistic information. It is not clear, however, how well these methods, traditionally employed for process control in linear or mildly-nonlinear contexts, and, more specifically applied by Sun and Hahn [6,7] for chemical process and isothermal biochemical systems modeling, extend to the strongly nonlinear thermally activated stiff kinetics of hydrocarbon fuels. It is fair to say that the challenge of dynamical analysis and uncertain chemical model simplification in hydrocarbon kinetics of relevance to combustion has yet to receive significant attention.

We lay out in the following a general strategy for analysis and reduction of uncertain chemical kinetic models, and describe its utilization in the context of ignition of hydrocarbon fuel–air mixtures. The construction is fully probabilistic, allowing for an arbitrary uncertainty structure. It is based on an existing analysis and reduction strategy, using computational singular perturbation (CSP) analysis [10,11], that has been used extensively for deterministic models of hydrocarbon fuels [1,2]. We begin in the following with a brief outline of the deterministic simplification strategy, before proceeding to the description of the proposed approach.

2. Deterministic simplification algorithm

In the CSP-based skeletal reduction algorithm, the criterion for selecting the subset of reactions and species to be retained is based on their relevance to the fast or slow dynamics of a prescribed set of “target” species, the concentration of which is desired to be accurately reproduced by the skeletal mechanism. This algorithm relies on the decomposition of the chemical kinetic processes into fast and slow components, using CSP, and on the identification of the processes that produce the most significant contributions in either the fast or slow components [11–14]. As a measure of the degree to which a species contributes to the fast/slow dynamics of the target species, the algorithm adopts the fast/slow CSP Importance Indices, which measure the contribution of each elementary reaction in the detailed mechanism to the fast and slow components of each species production rate [15–17]. Defining as $(I)^i_{k_{\text{slow/fast}}}$ the Importance Index of the kth reaction to the ith species in either the fast or slow subspace and given a user-specified tolerance τ, the kth reaction is included in the simplified mechanism if $(I)^i_{k_{\text{slow/fast}}} > \tau$. The rigorous definition of the Importance Indices and the complete algorithm can be found in [1,2]. This approach is very useful in generating a spectrum of simplified mechanisms of different sizes, each associated with a given degree of fidelity in predicting chosen QoIs specified by a tolerance on the Importance Indices. More details on the simplification algorithm can be found in [1,2,18,19].

3. Simplification strategy under uncertainty

Consider a detailed chemical mechanism $\mathcal{M}^*(\lambda)$, defined by a set of species $\mathcal{S}^* = \{S_1, \ldots, S_N\}$ and elementary reactions $\mathcal{R}^* = \{R_1, \ldots, R_M\}$, where λ is the relevant vector of uncertain parameters, *e.g.* the Arrhenius rate parameters of all reactions. Consider the auto-ignition process of a hydrocarbon fuel–air system in a constant pressure batch-reactor, for a range of initial temperature and stoichiometry, which is used to compute a set of ignition trajectories, providing a database of states $D = \{X^{(1)}, \ldots, X^{(K)}\}$, where $X \in \mathbb{R}^{N+1}$ is the state vector composed of temperature and the N mole fractions. Given that λ is uncertain, let D_λ denote the database computed for a given value of λ.

For any given D_λ, and considering a given set of QoIs – such as the set of target species – and a tolerance τ on Importance Indices [1,2], the CSP-based analysis and simplification strategy provides a simplified mechanism $\mathcal{M}_\tau(\lambda)$, being a subset of the starting mechanism with species $\mathcal{S}_\tau(\lambda)$ and reactions $\mathcal{R}_\tau(\lambda)$. In fact, given the starting model specification, the simplified model can be specified compactly in terms of a vector of M binary indicators $\alpha^\tau(\lambda) = (\alpha^\tau_1(\lambda), \ldots, \alpha^\tau_M(\lambda))^T$, where

$$\alpha^\tau_r(\lambda) = \begin{cases} 1 & \text{for reaction } R_r \in \mathcal{R}_\tau(\lambda) \\ 0 & \text{otherwise.} \end{cases}, \qquad r = 1, \ldots, M \tag{1}$$

In fact, $\alpha^\tau(\lambda)$ is a multi-index that specifies 2^M models. We can view the process of database generation, analysis, and model simplification as an input–output map:

$$f_\tau(\lambda) : \lambda \to \alpha^\tau(\lambda), \tag{2}$$

which provides a convenient abstraction for the use of uncertainty quantification (UQ) methods to account for uncertainty in λ in the process of simplified model selection.

Placing ourselves in a probabilistic UQ setting, uncertain quantities are represented as random variables. Accordingly, λ is defined as a real-valued random vector with a presumed joint Probability Density Function (PDF) $p(\lambda)$. The specification of this PDF is a major challenge in general, requiring recourse to available data on each parameter in the model, and allowing proper accounting for the correlation among different uncertain parameters. We discuss this challenge, as regards chemical mechanisms for combustion, later below in Section 5.

Generating n random samples from $p(\lambda)$, $\{\lambda^{(1)}, \ldots, \lambda^{(n)}\}$, the input–output map of Eq. (2) provides corresponding samples $\{\alpha^{\tau j}\}^n_{j=1}$, where $\alpha^{\tau j} = \alpha^\tau(\lambda^{(j)})$, so that we can estimate, $\forall \alpha = (\alpha_1, \ldots, \alpha_M)$, the joint probabilities,

$$P_\tau(\alpha) \approx \frac{1}{n} \sum_{j=1}^{n} \delta_{\alpha^{\tau j}\alpha} \tag{3}$$

where $\delta_{\alpha^{\tau j}\alpha}$ is the Kronecker delta,

$$\delta_{\alpha^{\tau j}\alpha} = \begin{cases} 1 & \text{if } \alpha = \alpha^{\tau j} \\ 0 & \text{otherwise.} \end{cases} \tag{4}$$

Thus, the contribution of each sample j to the sum for $P_\tau(\alpha)$ in Eq. (3) is 1 if $\alpha^{\tau j} = \alpha$, and 0 otherwise. Further, we have

$$\delta_{\alpha^{\tau j}\alpha} = \prod_{i=1}^{M} \delta_{\alpha_i^{\tau j}\alpha_i}. \tag{5}$$

The joint probabilities provide a wealth of information on the coupling among reactions. For example, marginalizing over $M-2$ reactions, provides the 2-way joint probabilities for any two given reactions (p, q),

$$P_\tau(\alpha_p, \alpha_q) \approx \frac{1}{n} \sum_{j=1}^{n} \delta_{\alpha_p^{\tau j}\alpha_p} \delta_{\alpha_q^{\tau j}\alpha_q}. \tag{6}$$

This provides information on the relevance of two reactions p and q being included/excluded jointly or separately in the model. Similarly, this analysis can be generalized to any subset of reactions forming a pathway of interest. Moreover, extending the scope to a full sub-mechanism, the joint picture provides a statement concerning the probability of any given mechanism that is a subset of the detailed model. Given a reasonable search strategy on α, one can thus select the model with the highest $P(\alpha)$ as the one most supported by the reduction strategy. Alternatively, if multiple models have comparable probability, a Bayesian model averaging [20,21] strategy can be employed to provide a pooled/average prediction.

Given the complexity of the joint-picture, and the need for large numbers of samples to establish multivariate statistics, we confine ourselves here to the marginal probabilities for individual reactions,

$$P_\tau(\alpha_i) \approx \frac{1}{n} \sum_{j=1}^{n} \delta_{\alpha_i^{\tau j}\alpha_i}, \qquad i = 1, \ldots, M. \tag{7}$$