Entropy production analysis for mechanism reduction

Mahdi Kooshkbaghi, Christos E. Frouzakis *, Konstantinos Boulouchos, Ilya V. Karlin

Aerothermochemistry and Combustion Systems Laboratory, Swiss Federal Institute of Technology, Zurich CH-8092, Switzerland

ABSTRACT

A systematic approach based on the relative contribution of each elementary reaction to the total entropy production is developed for eliminating species from detailed reaction mechanisms in order to generate skeletal schemes. The approach is applied to a database of solutions for homogeneous constant pressure auto-ignition of *n*-heptane to construct two skeletal schemes for different threshold values defining the important reactions contributing to the total entropy production. The accuracy of the skeletal mechanisms is evaluated in spatially homogeneous systems for ignition delay time, a single-zone engine model, and a perfectly stirred reactor in a wide range of thermodynamic conditions. High accuracy is also demonstrated for the speed and structure of spatially-varying premixed laminar flames.

© 2013 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

1. Introduction

Detailed reaction mechanisms of practical fuels provide accurate predictions of the combustion process over wide ranges of temperature, pressure and compositions. For large hydrocarbons, the detailed description typically includes hundreds of species participating in thousands of elementary chemical reactions. Incorporating such a detailed reaction mechanism into multidimensional simulations is practically impossible. In addition to the large number of variables, discretization of the spatial terms and the disparate time scales result in excessively large systems of stiff nonlinear ordinary differential equations (ODEs). Reactive flow simulations using detailed reaction mechanisms have demonstrated that a significant part of the total computational cost is spent in solving the stiff ODEs for species with negligible concentration [1]. Different methods for reducing the computational cost have been proposed in the literature. A brief overview of the reduction approaches is presented below while more detailed descriptions can be found in recent reviews [2–4].

The solution storage/retrieval approaches are based on the tabulation of frequently visited states during the simulation. The quantities are stored only for the accessible regions of the chemically admissible space. The in situ Adaptive Tabulation (ISAT) [5], Piecewise Reusable Implementation (PRISM) [6] and orthogonal polynomials storage method [7] belong to this category.

Other methods are based on the decomposition of motion in phase space into fast and slow. Various methods are used to find

an accurate description of the slow subsystem which dominates the long-time behavior. The group of species associated with the fast timescales can then be represented (usually implicitly) as functions of the species associated with the slow subspace. The Quasi Steady State Approximation (QSSA) and the Partial Equilibrium Assumption (PEA) are two well known classical methods for this purpose [8]. The Computational Singular Perturbation (CSP) [9], Intrinsic Low Dimensional Manifold (ILDM) [10] and Method of Invariant Manifold (MIM) [11] were proposed based on the dynamical systems point of view for model reduction which stems from the attractive low dimensional Slow Invariant Manifold (SIM) concept. In the resulting reduced schemes the differential equations for the fast-evolving species are replaced by systems of algebraic equations or tables, and the reduced system is significantly less stiff than the original set of equations. Although simplified models obtained by reduction techniques can reduce the computational cost, retaining maximum fidelity to the underlying non-linear dynamical system is not possible when the fast and slow time scales are not sufficiently decoupled. For example, in the case of oscillatory dynamics, reduced model based on QSSA have been shown to miss the bifurcation type (sub- vs. supercritical) and significantly modify the amplitude of the limit cycle [12]. In addition, there can still be a significant computational cost associated with the solution of the typically non-linear system of algebraic equations and/or the retrieval of information from the tables. For large reaction mechanisms, unimportant species and reactions should therefore be eliminated prior to using reduction methods based on time scale analysis [13].

The third group of methods introduces skeletal reduction techniques. The skeletal mechanism can be generated by eliminating reactions and/or species [1,14]. Elimination of unimportant reactions can be performed using, for example, sensitivity analysis

* Corresponding author. Address: Aerothermochemistry and Combustion Systems Laboratory, Swiss Federal Institute of Technology (ETH), Sonnegstrasse 3, Zurich CH-8092, Switzerland.

E-mail address: frouzakis@lav.mavt.ethz.ch (C.E. Frouzakis).

[15], the importance index of CSP [16], Principal Component Analysis (PCA) [17] or optimization-based methods [18,19]. Due to their nonlinear coupling, the direct elimination of species is more challenging. CSP [16,20–23], Directed Relation Graph (DRG) [13,24–27], DRG with Error Propagation (DRGEP) [28,29], DRG-Aided Sensitivity Analysis (DRGASA) [30,31], Transport Flux-Based DRG (TFBDRG) [32], Path Flux Analysis (PFA) [33,34] and necessity analysis [35] have been employed for species elimination. In addition, species with similar thermal and transport properties and diffusivities can be lumped together to further reduce the size of the skeletal mechanism [36–38]. Selecting important species during the simulation (on the fly model reduction) is also possible as proposed for example by the Dynamic Adaptive Chemistry (DAC) reduction method [39,40]. The aforementioned methods can be combined with storage/retrieval approaches [41].

For large mechanisms, approaches which select species based on the slow/fast decomposition bear heavy computational cost because of the timescale analysis of the Jacobian matrix of the associated large system of ODEs. On the other hand, QSSA, PEA and sensitivity analysis require additionally mechanism-dependent knowledge. The methods which are based on the graph structure relation between species sometimes need a careful a priori choice of the group of target species [39].

In addition to timescale analysis, thermodynamic properties of the system have been used to determine low dimensional manifolds. The Rate Controlled Constrained Equilibrium (RCCE) is based on the second law and assumes that the system state evolves through a sequence of constrained-equilibrium (or quasi-equilibrium) states, which are obtained by maximizing entropy subject to a small number of constraints imposed by certain classes of rate-controlling reactions [42,43]. It has been shown that in some cases the RCCE manifold results in large errors in the evolution of the reduced system in comparison with the detailed description, particularly for species with small concentration [44]. Entropy production has also been used for the slow/fast timescale decomposition of dynamics and construction of the SIM. In particular, the closest to the equilibrium trajectory known as Minimal Entropy Production Trajectory (MEPT) was considered as the SIM [45]. As it was shown in [46], however, low dimensional manifolds resulting from methods employing classical thermodynamic functions can only approximate the actual SIM. Nevertheless, in the scope of chemical kinetics, important reactions in different regions of composition space can be characterized by the local entropy production [47,48].

In the present study, the relative contribution of elementary reactions in the total entropy production is proposed as a criterion for the construction of accurate skeletal reaction mechanisms. The important reactions are identified based on their relative contribution to the total entropy production being larger than a user-specified threshold. This criterion leads to a procedure that is easy to implement without any prior knowledge about the detailed mechanism. Skeletal mechanisms of different sizes can be obtained by choosing the threshold based on desired deviation from the results obtained with the detailed reaction mechanism.

A significant reduction in the number of species as well as the stiffness of the system is reported here for the case of a detailed mechanism for n-heptane. The skeletal mechanisms are shown to provide very accurate results at a fraction of the computational cost in comparison to the detailed mechanism for various cases over a wide range of thermodynamic conditions. Compared to the other methods such as [13,23], the same level of reduction can be achieved with the much simpler entropy production analysis.

The paper is organized as follows. In Section 2, the basic notion of the entropy production for chemical kinetics is briefly reviewed. The features and algorithm of the method for skeletal mechanism reduction are presented in Section 3. In Section 4, the algorithm is applied on a database generated using a detailed n-heptane mechanism and two skeletal mechanisms are validated in terms of ignition delay time, in a homogeneous engine model, a perfectly stirred reactor and laminar premixed flame. Conclusions are drawn in Section 5. Finally, instructions on the numerical procedure of the entropy production analysis are presented in the appendix.

2. Entropy production for chemical kinetics

For the sake of completeness, the notion of the entropy production is briefly reviewed in this section following the formalism of [49]. For a detailed discussion of the entropy and entropy production concepts for chemical kinetics and other systems the reader is also referred to [50,43].

The changes in the entropy for a system at local equilibrium is expressed as

$$dS = d^{ex}S + d^{in}S \tag{1}$$

where superscripts 'in' and 'ex' denote the change of the system entropy due to interactions inside the domain and with its environment [49].

Chemical reactions describe the change in the number of moles of the n_s reactants represented by the vector $\underline{N} = (N_1, \ldots, N_{n_s})^T$. The change in the chemical composition of the species is the result of n_r reversible reactions,

$$\sum_{i=1}^{n_s} v'_{ik} N_i \rightleftharpoons \sum_{i=1}^{n_s} v''_{ik} N_i, \quad k = 1, \ldots, n_r \tag{2}$$

where, the v'_{ik} and v''_{ik} are the stoichiometric coefficients of the ith species in the kth reaction for the reactants and products, respectively. The rate of progress q_k of the kth reaction is given by the difference of the forward and reverse reaction rates

$$q_k = q_{f_k} - q_{r_k} = k_{f_k} \prod_{i=1}^{n_s} [N_i]^{v'_{ik}} - k_{r_k} \prod_{i=1}^{n_s} [N_i]^{v''_{ik}}, \quad k = 1, \ldots, n_r \tag{3}$$

where $[N_i]$ denotes the molar concentration of the ith species and k_{f_k} and k_{r_k} are the forward and reverse rate constants of the kth reaction having the Arrhenius form

$$k_{f_k} = A_k T^{\beta_k} \exp\left(\frac{-E_k}{R_c T}\right) \tag{4}$$

with A_k, β_k, E_k and R_c being the pre-exponential factor, temperature exponent, activation energy and ideal gas constant, respectively. The reverse and forward rate constants are related via the equilibrium constant, K_{C_k}

$$k_{r_k} = \frac{k_{f_k}}{K_{C_k}} \tag{5}$$

where

$$K_{C_k} = \exp\left(\frac{\Delta S_k^0}{R} - \frac{\Delta H_k^0}{R_c T}\right) \left(\frac{p_{atm}}{R_c T}\right)^{\Sigma_{i=1}^{ns}(v''_{ik} - v'_{ik})} \tag{6}$$

$p_{atm} = 1$ bar, and $\Delta S_k^0, \Delta H_k^0$ are the entropy and enthalpy changes for reaction k.

For a closed homogeneous system, the rate of change of the concentration of the ith species is given by

$$\frac{d[N_i]}{dt} = [\dot{N}_i] = \sum_{k=1}^{r} (v''_{ik} - v'_{ik}) q_k, \quad i = 1, \ldots, n_s \tag{7}$$

Using the reactor volume V, we can rewrite (7) in vector form as

$$\frac{d\underline{N}}{dt} = V[\underline{\dot{N}}] = \underline{f}(\underline{N}) \tag{8}$$