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On the applicability of directed relation graphs to the reduction of reaction mechanisms

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Abstract

The conditions for application of the directed relation graph (DRG) method in skeletal reduction of mechanisms with vastly different time scales were systematically analyzed. It was found that the existence of quasi-steady-state species induces no additional restriction on the application of DRG. When there are partial equilibrium reactions, DRG requires reactions with fast forward or backward rates to be reversible and the backward rate to be computed through the equilibrium constant. The effect of loss of significant digits in the evaluation of species relations due to substantial cancellation between the forward and backward rates of partial equilibrium reactions was identified and a criterion for minimum accuracy in sampled reaction states for DRG reduction was identified. The method of DRG was then compared with two methods recently developed for skeletal reduction: one is based on computational singular perturbation (CSP) and another is the directed relation graph with error propagation (DRGEP). Advantages and restrictions of including fast–slow subspace separation in skeletal reduction and the validity of the geometric error propagation model in DRGEP were discussed, with examples in the existence of exhausted fast processes.

Keywords: Directed relation graph; Mechanism reduction; Skeletal reduction

1. Introduction

Application of detailed chemistry in combustion simulations has been widely practiced in the past several decades for accurate and comprehensive description of chemically reactive flows. However, the large typical sizes of detailed mechanisms frequently result in high demand for computation time, and render it necessary to reduce the mechanisms to acceptable sizes before they are applied in large combustion simulations, such as those involving turbulence or complex geometries. Consequently, substantial effort has been devoted toward the development of theoretical and numerical methodologies for systematic mechanism reduction, as reviewed in [1] and recently in [2].

There are two major categories of reduction techniques, namely time scale analysis and skeletal reduction. Time scale analysis is based on the observation that there are frequently highly reactive radicals or fast reactions in detailed chemistry, resulting in vastly different time scales and stiffness in the system, and making the system reducible by replacing some differential equations with algebraic relations through the assumptions of quasi-steady-state (QSS) species and partial equilibrium (PE) reactions [3–8]. More systematic approaches to time scale analysis include

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intrinsic low-dimension manifolds (ILDM) [9] and computational singular perturbation (CSP) [10–18]. Specifically, CSP separates the fast and slow subspaces by a refinement procedure [12], with each iteration resulting in higher order accuracy [17,18]. Since it is typically time-consuming to separate the fast and slow subspaces when the number of species is large, skeletal reduction is frequently performed before time scale analysis to eliminate unimportant species and reactions, so that time scale analysis is faster when it starts from skeletal mechanisms.

Sensitivity analysis is one of the earliest methods for skeletal reduction [1], and other methods have subsequently been developed based on it. For example, principal component analysis decouples different reaction groups [19], and species coupling was studied through Jacobian matrices such that species not strongly coupled to the major ones were eliminated [20]. However, sensitivity-based methods are typically time-consuming when the mechanism is large. An optimization approach to obtaining a minimal set of reactions for given constraints was also developed [21]; such an optimization approach typically involves integer programming, and global optima are typically difficult to find for large systems. Detailed reduction is a faster method based on rate analysis [22], which eliminates reactions with rates lower than some preselected critical values. This method is rather aggressive, considering that a slow reaction is not always unimportant.

In a recent work [23], the method of directed relation graphs (DRG) was developed and applied to reduce several large detailed mechanisms for hydrocarbon fuels of various molecular complexities [23–25]. DRG transforms species couplings into a graph and exploits linear-time graph-searching algorithms to identify the species strongly coupled to the major ones. It features overall-linear reduction time and controllable error in reduced mechanisms and requires minimal user interaction with the reduction process. As such, it is suitable to be exploited as the first step to quickly reduce detailed mechanisms, which may contain thousands of species, to much smaller ones without significant loss of accuracy. The method of DRG with error propagation (DRGEP) was developed in a recent work [26]. Reduction error can be more accurately estimated by considering error propagation in DRG such that smaller skeletal mechanisms can be obtained for the same threshold error. In another recent work [27], species relations were decomposed into components in fast and slow subspaces using CSP, with one species considered important to another if the coupling is strong in either the fast or the slow subspace.

While the method of DRG for skeletal reduction has been successfully applied to detailed mechanisms of ethylene, dimethyl ether, n-heptane, and iso-octane in our previous work [23–25], the restrictions and intrinsic mechanisms for how DRG handles systems with fast dynamics have not been adequately addressed. In the present study, situations under which DRG is applicable were systematically analyzed with several artificially constructed simple mechanisms representing various characteristics of the detailed chemical kinetics. In addition, DRG is compared with DRGEP and the CSP-based method in [27].

2. Background of DRG

DRG was designed to reduce large detailed mechanisms with high efficiency. More specifically, species couplings are mapped to a graph and strongly coupled species are identified by linear-time graph searching. Since species are coupled through reactions, the definition of species relations in DRG starts from the rate expressions of the species and reactions in a detailed mechanism. For example, the production rate R_A of species A in a mechanism with I reversible elementary reactions is expressed as

$$R_A = \sum_{i=1,I} \nu_{A,i}\omega_i, \tag{2.1}$$

$$\omega_i = \omega_{fi} - \omega_{ri}, \tag{2.2a}$$

$$\omega_{fi} = k_{fi} \prod_{j=1}^{K} C_j^{\nu'_{ij}}, \tag{2.2b}$$

$$\omega_{ri} = k_{ri} \prod_{j=1}^{K} C_j^{\nu''_{ij}}, \tag{2.2c}$$

$$k_{fi} = \left[A_i T^{n_i} \exp\left(-\frac{T_{\mathrm{a}i}}{T} \right) \right] F_i, \tag{2.3a}$$

$$k_{ri} = \frac{k_{fi}}{K_{\mathrm{c}i}}, \tag{2.3b}$$

where the subscripts i and j indicate the ith elementary reaction and the jth species, respectively, and the subscripts f and r denote forward and backward directions of a reaction, respectively. Furthermore, ν_A is the net stoichiometric coefficient of species A, ν' and ν'' are the stoichiometric coefficients for the reactants and products, respectively, C the species molar concentration, A, n, and T_{a} are the reaction parameters, and F is a correction term including the third body concentration, fall-off, and other special effects, T the temperature, and K_{c} the equilibrium constant.

To quantify the relation of one species to another, the normalized contribution of species B to the pro-