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.

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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 com-

plex 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 mech-

anisms 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

$$R_A = \sum_{i=1,I} \nu_{A,i} \omega_i, \qquad (2.1)$$

$$\omega_i = \omega_{fi} - \omega_{ri}, \qquad (2.2a)$$

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

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

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

$$k_{ri} = \frac{k_{fi}}{K_{ci}}, \qquad (2.3b)$$

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-

duction rate of species A, namely r_{AB}, was defined as follows:

$$r_{AB} \equiv \frac{\sum_{i=1,I} |\nu_{A,i} \omega_i \delta_{Bi}|}{\sum_{i=1,I} |\nu_{A,i} \omega_i|}, \tag{2.4a}$$

$$\delta_{Bi} = \begin{cases} 1, & \text{if the } i\text{th elementary reaction} \\ & \text{involves species } B, \\ 0, & \text{otherwise}. \end{cases} \tag{2.4b}$$

Thus r_{AB} roughly measures the relative error induced in species A due to the removal of species B, and consequently all the reactions involving B, from the detailed mechanism. As such, r_{AB} can be considered as the dependence of species A on B as well. Relations of species are then mapped to a graph, each vertex of which indicates a species, and there is a directed edge $A \rightarrow B$ if and only if $r_{AB} > \varepsilon$, where ε is a user-specified small-threshold relative error. Starting from the major species, such as the fuel, species strongly coupled to the major ones can be identified by a depth-first search such that all the species retained in the skeletal reduction can be computed with small errors of $O(\varepsilon)$. Furthermore, it is noted that the DRG reduction using Eq. (2.4), based on a single reaction state, is only valid locally, and the local skeletal mechanisms derived under different situations can be combined into a global mechanism that is valid over a larger parameter range. More detailed discussions on DRG searching and global mechanism development are provided in [23,25].

There are two immediate alternate definitions of Eq. (2.4a): one is obtained by replacing the denominator with the absolute value of the net production rate of species A, and the other is to treat the forward and backward directions of each reversible reaction as two different reactions. The definitions of r_{AB} for the two alternate definitions are expressed as follows:

$$r_{AB} \equiv \frac{\sum_{i=1,I} |\nu_{A,i} \omega_i \delta_{Bi}|}{|R_A|} \tag{2.5}$$

and

$$r_{AB} \equiv \frac{\sum_{i=1,I} (|\nu_{A,i} \omega_{fi}| + |\nu_{A,i} \omega_{ri}|) \delta_{Bi}}{\sum_{i=1,I} |\nu_{A,i} \omega_{fi}| + \sum_{i=1,I} |\nu_{A,i} \omega_{ri}|}. \tag{2.6}$$

While the definitions of r_{AB} in (2.5) and (2.6) seem only slightly different from that in (2.4a), and could be unintentionally adopted by users in many practical reductions, they may significantly affect the extent of the reduction and the validity of DRG in the existence of QSS species and PE reactions, which are frequently observed in chemical kinetics. The detailed discussions of this subtle issue are presented in the following sections.

3. DRG with QSS problems

A QSS species typically features small or moderate creation rate and short destruction time scale, such that the creation rate is quickly balanced by the destruction rate after a transient period, resulting in a net production rate for the QSS species much smaller than either the creation or destruction rate and a concentration of the QSS species that can be approximated as a function of those of the major species. The net production rate R_A of a QSS species A is highly sensitive to the perturbation, or numerical error, in the concentration of A due to the short destruction time scale, and R_A typically should not be directly evaluated by Eq. (2.1) using sampled reaction states. Instead, the production rates of QSS species can be evaluated using the equation

$$\frac{d\mathbf{c}_Q}{dt} = \frac{d\mathbf{c}_Q}{d\mathbf{c}_{NQ}} \frac{d\mathbf{c}_{NQ}}{dt}, \tag{3.1}$$

where $\mathbf{c}$ is the concentration vector, and the subscripts Q and NQ indicate QSS and the major species, respectively. The $d\mathbf{c}_Q/d\mathbf{c}_{NQ}$ term can be obtained from the algebraic equation, $\mathbf{f}(\mathbf{c}_Q, \mathbf{c}_{NQ}) = 0$, given by the QSS assumptions.

Based on the above discussions on QSS species, the definitions in Eqs. (2.4a) and (2.5) are compared. First, the maximum value of r_{AB} defined in Eq. (2.5) is not normalized to unity, and may consequently result in difficulties in the selection of the threshold value ε. Second, since time scale analysis is not involved, the QSS species set, and consequently the function $\mathbf{f}$, is not available in DRG reduction, so that Eq. (3.1) cannot be employed in DRG, rendering it difficult to accurately evaluate r_{AB} in Eq. (2.5) if A is a QSS species. Third, even if the sampling error is sufficiently low, such that R_A in Eq. (2.1) can be accurately computed, the dependence of species A on B may be significantly overestimated using the definition of Eq. (2.5), in that $R_A \rightarrow 0$ when the destruction time scale of A approaches zero, i.e., when A is an ideal QSS species. In such cases, the value of r_{AB} in Eq. (2.5) may be large even if the reactions coupling species A and B are slow and unimportant. As a result, unimportant species might be misclassified as being important with Eq. (2.5) and the extent of the DRG reduction is thereby compromised. On the other hand, in Eq. (2.4), DRG compares the contribution of species B to A with the creation and destruction rates of A and retains an accurate function $\mathbf{f}$ in the reduction, since all the major terms constituting $\mathbf{f}$, for both the creation and destruction of A, are retained. Correct production rates of QSS species after a transient period are therefore enforced by Eq. (3.1) in the application of the resulting skeletal mechanisms. This

point will be elaborated below with examples and derivations.

To demonstrate the DRG method in existence of QSS species, an artificial reaction mechanism with three reactions is constructed as follows:

Mech 1:

(R1) $F \to R$, $\omega_1 = 1 \cdot F$,

(R2) $R \to P$, $\omega_2 = 10^3 \cdot R$,

(R3) $R \to P'$, $\omega_3 = 1 \cdot R$,
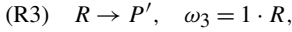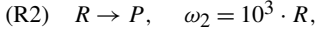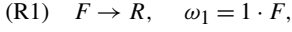
where F, R, P, and P' indicate fuel, radical, and two products, respectively. The reverse reactions are chosen to be much slower than the forward ones and are neglected in this example for simplicity. It is readily seen that R is a good QSS species. Suppose that F is the species of interest. To find all the species required directly or indirectly by F, the species relations are computed from Eq. (2.4). While the reaction rates can be evaluated using sampled reaction states after a transient period, in the present study, the species concentrations are obtained by a CSP analysis, assuming the fast modes are exhausted, to mimic the sample reaction states with negligible sampling error.

The production rates of the species in Mech 1 can be expressed as follows:

$$\frac{d}{dt}\begin{pmatrix} F \\ R \\ P \\ P' \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 1 & -10^3 - 1 & 0 & 0 \\ 0 & 10^3 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}\begin{pmatrix} F \\ R \\ P \\ P' \end{pmatrix}.$$

(3.2)

Since the Jacobian of the above ODEs is constant, CSP degenerates into an eigenvalue analysis. The eigenvalues of the above ODE are $\lambda_1 = -1001$, $\lambda_2 = -1$, and $\lambda_3 = \lambda_4 = 0$. Therefore, if the controlling time scale is $O(1)$, there is only one fast mode, expressed as

$$f_1 = \frac{dF/dt}{-10^3} + dR/dt \approx 0,$$

(3.3a)

which consequently gives

$$R \approx \frac{F}{10^3}.$$

(3.3b)

The rates of the reactions can then be evaluated as

$$\omega_2 \approx \omega_1,$$

(3.4a)

$$\omega_3 = \frac{\omega_2}{10^3},$$

(3.4b)

and the species relations are

$$r_{RF} = \frac{\omega_1}{\omega_1 + \omega_2 + \omega_3} \approx 0.5,$$

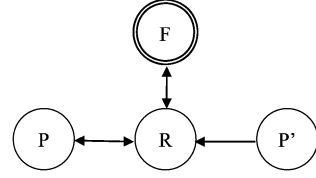(3.5a)

$$r_{FR} = \frac{\omega_1}{\omega_1} = 1,$$

(3.5b)

Fig. 1. A DRG of a sample mechanism (Mech 1) with QSS species.

$$r_{RP} = \frac{\omega_2}{\omega_1 + \omega_2 + \omega_3} \approx 0.5,$$

(3.5c)

$$r_{PR} = \frac{\omega_2}{\omega_2} = 1,$$

(3.5d)

$$r_{RP'} = \frac{\omega_3}{\omega_1 + \omega_2 + \omega_3} \approx \frac{10^{-3}}{2},$$

(3.5e)

$$r_{P'R} = \frac{\omega_3}{\omega_3} = 1.$$

(3.5f)

Fig. 1 shows the resulting species relation graph, in which each directed edge represents a direct dependence of one species on another, measured by Eqs. (2.4) and (3.5). The species relations smaller than a critical value $\varepsilon = 0.1$ are neglected in Fig. 1 as well as in the following sections. Both the species, R and P, reachable from the starting one, F, are retained, while P' is eliminated since it is not important to any other species.

It is further seen that the rates of fast reactions, such as R2, which are responsible for the short time scale of the QSS species, such as R, are limited by the controlling rates, and the contribution of the fast reactions to the QSS species is balanced by that of the rate-limiting reactions. Therefore, the fast reactions involving a QSS species will not dominate the controlling rates in evaluating the species relations, and therefore all the important reactions are retained in the above example.

We next show that DRG with the species relation defined in Eq. (2.5) fails to identify the unimportant species P' in the above example. It is seen that although reaction R3 is not important, its rate is comparable to the net production rate of species R, since

$$\frac{dR}{dt} \approx \frac{dR}{dF}\frac{dF}{dt} = 10^{-3}F,$$

(3.6)

and

$$\omega_3 = \frac{\omega_2}{10^3} \approx \frac{\omega_1}{10^3} = 10^{-3}F = \frac{dR}{dt}.$$

(3.7)

Consequently, $r_{RP'} \approx 1$ using the definition in Eq. (2.5), and the importance of reaction R3, as well as species P', is overestimated, resulting in a skeletal mechanism with unnecessary species and reactions.

It is further noted that the leading-order approximation in the CSP solution, i.e., the classical QSS

assumption,

$$\frac{dR}{dt} = F + (-10^3 - 1)R \approx 0 \qquad (3.8a)$$

or

$$R \approx \frac{F}{-10^3 - 1}, \qquad (3.8b)$$

is sufficiently accurate in calculating the species relations, r_{RF}, r_{RP}, and $r_{RP'}$, since the species relations defined in Eq. (2.4) are not sensitive to small errors in the QSS species concentrations. This property of QSS-type problems is significantly different from that of PE problems, which will be discussed in the following sections.

The DRG method having been demonstrated with the QSS problem in the above example, for a QSS species A in general cases, the production rate of A in Eq. (2.1) can be rewritten as

$$R_A = \sum_{i=1,I} \nu_{A,i}\omega_i = \omega_{A,\text{con}} - \omega_{A,\text{des}}, \qquad (3.9)$$

where the subscripts con and des indicate the creation and destruction rates, respectively. Since A is in QSS,

$$|R_A| \ll \min(\omega_{A,\text{con}}, \omega_{A,\text{des}}) \qquad (3.10)$$

or

$$\omega_{A,\text{con}} \approx \omega_{A,\text{des}}, \qquad (3.11)$$

and if the contribution of species B to A is small, i.e.,

$$\sum_{i=1,I} |\nu_{A,i}\omega_i\delta_{Bi}| \ll \sum_{i=1,I} |\nu_{A,i}\omega_i| \\ \approx 2\omega_{A,\text{con}} \approx 2\omega_{A,\text{des}}, \qquad (3.12)$$

species B can be considered unimportant to the QSS species A, since r_{AB} roughly measures the relative error induced to the creation or destruction rates, and consequently the concentration, by Eq. (3.1), of A due to the elimination of B.

Based on the above analysis, we can conclude that the species relation defined in Eq. (2.4) works correctly and is advantageous over that in Eq. (2.5) for QSS problems, and a larger extent of reduction may be achieved with Eq. (2.4). It is further noted that while the same correct skeletal mechanism is obtained using either Eq. (2.6) or Eq. (2.4), because there is no reverse reaction in Mech 1, applying Eq. (2.6) may leads to wrong results when fast reversible reactions exist. This point is demonstrated in the next section.

## 4. DRG with partial equilibrium problems

While a QSS problem is typically caused by a species being rapidly depleted and hence choking a

reaction pathway, a PE problem typically involves fast reactions canceling one another without such a choking species. The forward and backward rates of a PE reaction can be much larger than the net reaction rate or the system-controlling rate. Two major issues need to be considered in applying DRG to PE problems: First, if forward and backward reactions are considered as different reactions, as in Eq. (2.6), the large forward and backward rates of the PE reactions may dominate the system-controlling rate, the importance of which may therefore be underestimated. Second, there can be a severe loss of significant digits in the evaluation of the net reaction rates with Eq. (2.2) for PE reactions when the forward and reverse reaction rates almost cancel each other. These two issues are addressed below.

4.1. Necessity of combining forward and reverse reactions

To demonstrate the first issue, a sample PE problem with two reversible reactions, R1 and R2, and three species, F, R, and P, is listed:

Mech 2:

(R1) $F \leftrightarrow R$, $\omega_1 = 10^3 \cdot (F - R)$,

(R2) $R \leftrightarrow P$, $\omega_2 = 1 \cdot (R - P)$.
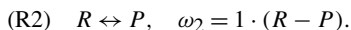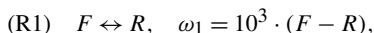
The two reversible reactions have dramatically different rate constants. Thus R1 quickly approaches equilibrium after a transient period, after which R2 becomes rate-limiting. Again, a CSP analysis is performed on the corresponding equations. The column vector $\mathbf{g}$ for the species production rates in Mech 2 is written as follows:

$$\mathbf{g} \equiv \frac{d}{dt}\begin{pmatrix} F \\ R \\ P \end{pmatrix} = \begin{pmatrix} -10^3 & 10^3 & 0 \\ 10^3 & -10^3 - 1 & 1 \\ 0 & 1 & -1 \end{pmatrix}\begin{pmatrix} F \\ R \\ P \end{pmatrix}. \qquad (4.1)$$

The three eigenvalues of the Jacobian and the corresponding basis $\boldsymbol{b}_i$ are

$$\lambda_1 = -2000, \quad \boldsymbol{b}_1 = [0.7069\ -0.7073\ 0.0004],$$
$$\lambda_2 = -1.5, \quad \boldsymbol{b}_2 = [0.4086\ 0.4079\ -0.8165],$$
$$\lambda_3 = 0, \quad \boldsymbol{b}_3 = [-0.5774\ -0.5774\ -0.5774]. \qquad (4.2)$$

Suppose the time scale of interest is $O(1)$; there is only one fast mode, f_1, associated with λ_1. The second mode f_2 is rate-controlling, and the third mode f_3 is invariant and indicates element conservation. The exhausted fast mode f_1 gives

$$f_1 = \mathbf{b}_1 \cdot \mathbf{g} \approx 0. \qquad (4.3)$$

Before proceeding to compare the definitions in Eqs. (2.4a) and (2.6), we digress to show a major difference between PE and QSS problems in the applicability of their leading-order solutions in DRG. It is seen that the leading-order solution of Eq. (4.3), which neglects the third entry in $\mathbf{b}_1$, is the classical PE assumption

$$\frac{dF}{dt} \approx \frac{dR}{dt} \tag{4.4a}$$

or

$$\omega_{f1} \approx \omega_{r1}. \tag{4.4b}$$

While this leading-order solution, or the classical PE assumption, provides an algebraic equation relating F and R, the resulting net reaction rate of R1 is trivial, and thereby should never be applied in the evaluation of the species relations in Eq. (2.4). It is noted that there is no such restriction in applying the leading-order solution of a QSS problem in DRG, as discussed in Section 3. Therefore, for the PE problem, a higher than leading-order solution, given by the exhausted fast mode in Eq. (4.3), has to be employed to correctly compute the net production rates of the PE reaction. That is, without neglecting the third entry in $\mathbf{b}_1$ in Eq. (4.2), we have

$$\omega_1 \approx \frac{1}{2}\omega_2, \tag{4.5}$$

which indicates that the net production rate of the fast reaction R1 follows that of R2.

Having clarified the above difference in PE and QSS problems, we resume the discussion on the definitions in Eqs. (2.4a) and (2.6) by first demonstrating that the definition in Eq. (2.4a) can correctly handle PE problems. Suppose that R is the species of interest. The species relations in DRG can be computed with Eqs. (4.5) and (2.4),

$$r_{RF} = \frac{\omega_1}{\omega_1 + \omega_2} \approx \frac{1}{3},$$
$$r_{RP} = \frac{\omega_2}{\omega_1 + \omega_2} \approx \frac{2}{3}, \tag{4.6}$$

which shows that both F and P are important to R, and should both be retained in the skeletal mechanism, although species F and R involve a PE reaction R1 with much larger forward and backward rates than those of the rate-controlling reaction R2. On the other hand, using Eq. (2.6), the species relations become

$$r_{RF} = \frac{\omega_{f1} + \omega_{r1}}{\omega_{f1} + \omega_{r1} + \omega_{f2} + \omega_{r2}} \approx 1,$$
$$r_{RP} = \frac{\omega_{f2} + \omega_{r2}}{\omega_{f1} + \omega_{r1} + \omega_{f2} + \omega_{r2}} \sim 10^{-3}. \tag{4.7}$$

This result is incorrect because the importance of P is underestimated, and the reason for the incorrect result is because the fast forward and backward rates of R1 dominate those of the rate-controlling reaction R2 using the definition of (2.6); i.e., $\omega_{f1}, \omega_{r1} \gg \omega_{f2}, \omega_{r2}$. Therefore, Eq. (2.4) rather than (2.6) should be applied when PE reactions exist, and the forward and reverse reaction rates must be combined for DRG.

To further show that Eq. (2.4) is applicable for general PE problems with an arbitrary number of fast reactions, the forward or backward rate of which is much larger than the controlling rate, for mechanisms in elementary form expressed in Eqs. (2.1)–(2.3), we shall prove next that the forward rate of each fast reaction is balanced by its backward rate, so that the net reaction rates of the fast reactions are not asymptotically larger than the controlling rate.

In a mechanism with I reactions, let the forward rates of the first J reactions, without loss of generality, be much larger than the controlling rate g_c, which can be defined as the norm of the species production rate vector after the fast modes are exhausted; i.e., $g_c \equiv \|\mathbf{g}\|$. The species production rate in Eq. (2.1) can then be expressed as

$$\mathbf{g} = \sum_{i=1}^{J} \mathbf{S}_i \omega_i + \sum_{i=J+1}^{I} \mathbf{S}_i \omega_i, \tag{4.8a}$$

where

$$\omega_i \gg g_c, \quad i = 1, \ldots, J, \tag{4.8b}$$

and

$$\omega_i \sim o(g_c), \quad i = J+1, \ldots, I, \tag{4.8c}$$

where $\mathbf{S}_i$ is a column vector for the stoichiometric coefficients of the ith reaction. It is noted that $\|\mathbf{S}_i\| \sim O(1)$. Equation (4.8) can then be rewritten as

$$\sum_{i=1}^{J} \mathbf{S}_i \omega_i = \mathbf{h}, \tag{4.9a}$$

where

$$\mathbf{h} = \mathbf{g} - \sum_{i=J+1}^{I} \mathbf{S}_i \omega_i \sim \mathbf{O}(g_c).$$

Suppose, without loss of generality, that the first N of the J stoichiometric vectors are linearly independent and span the vector space consisting of $\mathbf{S}_i$, $i = 1, \ldots, J$. $\mathbf{h}$ can be decomposed to the basis set

$$\mathbf{h} = \sum_{i=1}^{N} \alpha_i \mathbf{S}_i, \tag{4.9b}$$

and

$$\alpha_i \sim O(g_c) \tag{4.9c}$$

and Eq. (4.9) can be rewritten as

$$\sum_{i=1}^{N} \mathbf{S}_i \left(\sum_{j=1}^{J} Q_{ij}(\omega_{fj} - \omega_{rj}) - \alpha_i \right) = \mathbf{0}, \qquad (4.10)$$

with the projection matrix $\mathbf{Q} = (\mathbf{S}_B^T \mathbf{S}_B)^{-1} \mathbf{S}_B^T \mathbf{S}$, $\mathbf{S}_B = (\mathbf{S}_1, \ldots, \mathbf{S}_N)$, and $\mathbf{S} = (\mathbf{S}_1, \ldots, \mathbf{S}_J)$.

Since $\mathbf{S}_1$ to $\mathbf{S}_N$ are linearly independent, we have

$$\sum_{j=1}^{J} Q_{ij}(\omega_{fj} - \omega_{rj}) = \alpha_i \sim O(g_c),$$
$$i = 1, 2, \ldots, N. \qquad (4.11)$$

In the limit that the forward rates of the fast reactions are much larger than the controlling rate, i.e., $g_c/\omega_{fi} \to 0$, $i = 1, \ldots, J$, the leading-order solution of (4.11), together with (2.3), is unique, given by chemical equilibrium of the mechanism consisting of the J fast reactions, i.e., $\omega_{fi} = \omega_{ri}$, $i = 1, \ldots, J$, and the first-order solution gives

$$\omega_{fi} - \omega_{ri} = O(g_c), \quad i = 1, \ldots, J. \qquad (4.12)$$

However, if the reactions are not in the elementary form of Eq. (2.3), the solution in (4.12) is not guaranteed, and the net reaction rates of the fast reactions may dominate the controlling rate. For example, for systems with externally forced reactions, such as those activated by laser irradiation, the forward and backward reaction rates do not follow Eq. (2.3); the net production rates depend on the strength of the external forcing term and can be arbitrarily large. Consequently DRG in its current form is not applicable in such cases.

4.2. Loss of significant digits

While it has been shown above that, theoretically, DRG can handle reactions with fast forward and backward rates in mechanisms of the elementary form of Eq. (2.3), the existence of fast reversible reactions may result in a difficulty in practical applications of DRG due to the loss of significant digits by rate cancellation using Eq. (2.2), which is subsequently employed in the evaluation of r_{AB} in Eq. (2.4). If there are fewer than sufficient, say two, significant digits in a computed net production rate ω, the resulting species relations involving ω may not be trustable. More specifically, when a fast reversible reaction approaches PE, the forward and reverse reaction rates can be much larger than the net production rate; i.e.

$$\frac{\max(\omega_f, \omega_r)}{|\omega|} \gg 1, \qquad (4.13)$$

and the number of significant digits lost due to rate cancellation is estimated by

$$n \approx \log \left(\frac{\max(\omega_f, \omega_r)}{|\omega|} \right). \qquad (4.14)$$

For a specific sampling process with a given relative error tolerance value e, the number of significant digits in the forward and reverse reaction rates is approximately

$$n_0 = -\log_{10}(e). \qquad (4.15)$$

Therefore, a sampled reaction state is suitable for DRG reduction only if it satisfies the criterion

$$n - n_0 > n_c, \qquad (4.16)$$

where n_c is the minimum number of significant digits in net reaction rates required by DRG. Severe loss of significant digits may occur for two situations: when there are PE reactions and when the system approaches equilibrium. For the first situation, sufficiently small error tolerance in the sampling process should be applied so that (4.16) is satisfied. For the second situation, or in the limit of chemical equilibrium, loss of significant digits n approaches infinity since all the net production rates ω approaches zero; as such, the computed values of the species relations are not trustable. In this case, the species relations computed with Eq. (2.4) are not trustable even with extremely small machine error, and DRG is consequently inapplicable. Therefore, the sampling process for DRG should stop sufficiently far away from the equilibrium state. Since the maximum residence time for the sampling process is limited by the error tolerance, a smaller error tolerance can always be applied if a longer residence time is of interest. A moderate error tolerance value of $e \sim 10^{-8}$ was found to be adequate for the reduction of most hydrocarbon mechanisms for many practical applications.

5. DRG with dormant modes

Having discussed the several issues of DRG related to the exhausted fast modes in the above two sections, we shall discuss here the effect of dormant and invariant modes on DRG. Invariant modes induced through element conservation typically have to be strictly enforced in combustion simulations, and it is readily seen that skeletal mechanisms honor element conservation, since each reaction in the skeletal mechanism conserves elements. Modes with time scales much longer than the controlling time scale are dormant [11]. Some of the dormant modes may be responsible for the slow drifting of the system over extended time. Such slow modes might be difficult

to detect by local DRG reduction, since the dormant modes are frequently dominated by the active modes. An example of slow modes is given in the following mechanism with a controlling and a slow reaction:

Mech 3:

(R1) $A \leftrightarrow B$, $\omega_1 = 1 \cdot (A - B)$,

(R2) $B \leftrightarrow C$, $\omega_2 = 10^{-3} \cdot (B - C)$.
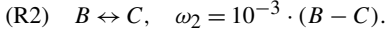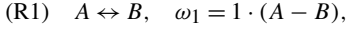
Suppose that A is the species of interest, $A = 1$, $B = 2$, $C = 1$ at the sampled reaction state, and the controlling time scale is $\sim O(1)$. It is seen that there is no fast mode in the current system. The eigenvalues of the Jacobian matrix are $\lambda_1 = -2$, $\lambda_2 = -1.5 \times 10^{-3}$, and $\lambda_3 = 0$, corresponding to the controlling, dormant, and invariant modes, respectively. The dormant mode can be expressed as

$$f_2 = \frac{d}{dt}(A + B - C) = -2 \times 10^{-3}(B - C) \ll 1,$$
(5.1)

which indicates that the species group $A + B$ converts slowly to C. Species relations computed with a local DRG are

$$r_{AB} = \frac{|\omega_1|}{|\omega_1|} = 1 \quad \text{and} \quad r_{BC} = \frac{|\omega_2|}{|\omega_1| + |\omega_2|} \approx 0.$$
(5.2)

Consequently the skeletal mechanism identified by DRG includes only species A and B and reaction R1. While eliminating species C induces only slight error in the production rate of A and B within a residence time of $O(1)$, the concentrations of A and B in the skeletal mechanism drift away from those in Mech 3 after a long time, say $t = 10^3$. The computed profiles of species concentrations for detailed and skeletal mechanisms are shown in Fig. 2. It is seen that the concentrations of A and B for the skeletal mechanism agree well with the detailed one for residence times smaller than 100, after which both A and B show significantly increased error. Therefore skeletal mechanisms reduced by DRG with only a single reaction state are expected to be valid within only a small range of residence times, and the conservation relations implied by the slow modes with much longer time scales than the controlling one may not be detected or preserved.

To derive skeletal mechanisms that correctly preserve a slow mode, the sample space should include reaction states sampled at a sufficiently long residence time for the slow mode to become active. The union of the species sets of the skeletal mechanisms at different residence times then constitutes the species set of a global skeletal mechanism that is valid over an extensive range of residence times [23,25]. For example, with a sampled reaction state ($A = 1.370536$, $B =$
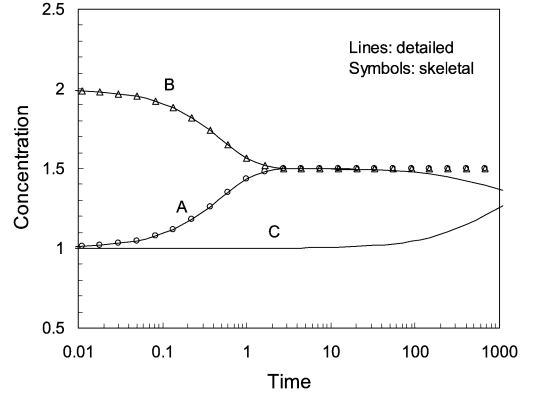

Fig. 2. Calculated species concentrations as functions of time for detailed and skeletal mechanism of an artificial system with two reactions, (1) $A \leftrightarrow B$, $\omega_1 = 1 \cdot (A - B)$ and (2) $B \leftrightarrow C$, $\omega_2 = 10^{-3} \cdot (B - C)$, and species concentrations $A = 1$, $B = 2$, and $C = 1$ at $t = 0$.

1.370480, $C = 1.258985$) at $t = 1000$, the species relations can be computed as: $r_{AB} = 1$ and $r_{BC} \approx 0.67$, such that species C is important to B and all the species have to be retained in the global mechanism.

6. Comparison with CSP

In a recent work [27] of skeletal reduction with CSP through the importance index, species coupling was studied through reaction rates projected to fast and slow subspaces by the reasoning that both fast and slow dynamics should be retained in the skeletal mechanism. More specifically, with the CSP refinement procedure [12], a set of basis vector pairs, $\boldsymbol{a}^i$ and $\boldsymbol{b}_i$, $i = 1, 2, \ldots, K$, can be obtained, where K is the number of species. The first M pairs of basis vectors are for the M fast modes that constitute the fast subspace and the remaining $K - M$ pairs are for slow modes. In [27], the components of the species production rate vector $\mathbf{g}$ can be decomposed into two components in fast and slow subspaces, respectively,

$$\mathbf{g} = \mathbf{SR} = \mathbf{S}_f \mathbf{R} + \mathbf{S}_s \mathbf{R},$$
(6.1)

$$\mathbf{S}_f = \left(\sum_{i=1}^{M} \boldsymbol{a}^i \boldsymbol{b}_i \right) \mathbf{S},$$
(6.2a)

$$\mathbf{S}_s = \left(\sum_{i=M+1}^{K} \boldsymbol{a}^i \boldsymbol{b}_i \right) \mathbf{S},$$
(6.2b)

where $\mathbf{S}$ is the stoichiometric coefficient matrix, $\mathbf{S}_f$ and $\mathbf{S}_s$ are the components of the stoichiometric vectors in the fast and slow subspace, respectively, and $\mathbf{R}$ is a column vector of reaction rates with forward and backward directions treated as different reactions.

The contribution of the components of each reaction in fast and slow subspaces is measured by the "fast" and "slow" importance indices, respectively defined as

$$(I_k^i)_f = \frac{(S_i^k)_f R_k}{\sum_{j=1}^{I} |(S_i^j)_f R_j|}, \quad (6.3a)$$

$$(I_k^i)_s = \frac{(S_i^k)_s R_k}{\sum_{j=1}^{I} |(S_i^j)_s R_j|}, \quad (6.3b)$$

where the subscripts f and s, respectively indicate the fast and slow subspace, I_k^i is the importance index of the kth reaction to the ith species, S_i^j is the stoichiometric coefficient of the ith species in the jth reaction, and R_j is the rate of the jth reaction. It is noted that an additional term associated with error tolerance could be included in the denominator of (6.3) [11], while it is not included in [27] or the current discussion, for simplicity.

A reaction k is considered important to a species i if I_k^i is not small in either the fast or the slow subspace, and a species j is considered important to species i if they appear in the same reaction k, which is important to species i. That is, species j is considered important to species i if they are coupled through an important reaction in either fast or slow subspace. An iterative procedure is applied to find all species strongly coupled to the major ones. It is noted again that forward and backward reactions are treated as different reactions in this method.

It can be seen that DRG and the above method based on CSP share a similar strategy in measuring the importance of one species to another, and the major difference is that the CSP-based method considers species coupling in fast and slow subspaces, respectively, while DRG does not perform a time-scale separation. Consequently, the CSP-based method is expected to be more time-consuming than DRG due to the required Jacobian evaluation and CSP refinement.

A benefit from the fast–slow separation was claimed in [27]: that is, the forward and backward directions of a reaction are considered as different reactions, and as such the reduction method can be applied in a more general system. For example, given an artificial mechanism

Mech 4:
(R1) $D \rightarrow A$, $k = 1$,

(R2) $A \rightarrow B$, $k = 10^3$,

(R3) $B \rightarrow C$, $k = 10^3$,

(R4) $C \rightarrow A$, $k = 10^3$,
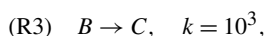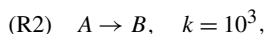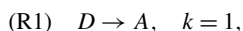
in which the fast reactions form a cycle that equilibrates species A, B, and C quickly, suppose all

species have concentrations of $\sim O(1)$, species A is of interest, and the controlling time scale is $O(1)$. DRG is not applicable to this problem because the reaction rates in Mech 4 are not in the form of Eq. (2.3), or more specifically, because the reverse rates of the fast reactions R2, R3, and R4 are not computed from the equilibrium constants. It can be readily verified that it does not identify the importance of species D to A in Mech 4 with Eq. (2.4), in that there is no backward rate to balance the fast forward rate of R2, and the contribution of reaction R1 to A is dominated by that of R2. On the other hand, it was found with the CSP-based method that species B, C, and D are all important to A, since A is strongly coupled with D in the slow space, and with B and C in the fast space. Therefore, there are mechanisms not in the elementary form of Eq. (2.3), and hence to which DRG is not applicable, that can be successfully reduced with the facilitation from a slow–fast separation. To further compare these two methods, we next discuss two issues induced by the slow–fast separation.

First, since not all fast modes are important to the evolution of a system, the importance of a species might be overestimated due to the slow–fast separation, and thereby the extent of the reduction might be compromised. This problem can be demonstrated by the example below,
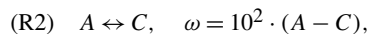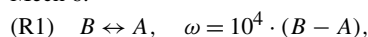
Mech 5:
(R1) $F \rightarrow P$, $\omega_f = 1 \cdot F$,

(R2) $F \rightarrow R$, $\omega_f = 10^{-2} \cdot F$,

(R3) $R \rightarrow P$, $\omega_f = 10^2 \cdot R$,
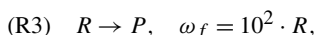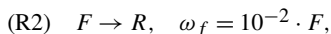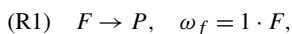
where F is the species of interest, F and P have concentrations $\sim O(1)$, the QSS species R has a concentration of $\sim 10^{-4}$, which is readily solved from the steady state relation, and the controlling time scale is $O(1)$. It is seen that there are two reaction pathways for the consumption of F: $F \rightarrow P$, with a rate of $\omega = 1 \cdot F$, and $F \rightarrow R \rightarrow P$, with an effective rate of $\omega = 10^{-2} \cdot F$. The second pathway is therefore negligible for the F consumption compared with the first pathway, and can be eliminated with a small threshold error, $\sim O(10^{-2})$. DRG correctly identifies that R is not important to F or P with a graph constructed using the threshold value $\varepsilon = 0.1$, as shown in Fig. 3. The resulting skeletal mechanism therefore only contains F and P. It is noted that, in contrast to Mech 4, DRG works correctly for Mech 5, although the reactions are irreversible. This is because Mech 5 may be a realistic mechanism honoring Eq. (2.3), except that all the reverse reaction rates are small and neglected. This is possible when the species free energy decreases dramatically in the order of F, R, and P such that all the equilibrium constants are much larger than unity for R1, R2, and R3.

On the other hand, using the method with slow–fast separation, it is readily seen that $(I^F_{R1})_s \approx 1$, $(I^P_{R3})_f \approx 0.5$, which indicates that no species can be eliminated, in that P is strongly coupled to F through R1 in slow subspace, and R is strongly coupled to P, and hence indirectly coupled to F, through R3 in fast subspace. Therefore, the skeletal mechanism obtained with the CSP-based method may be larger than that from DRG with the same accuracy requirement.

Second, while the slow–fast separation can prevent a fast reaction from dominating the controlling one if they are projected to different subspaces, as shown in Mech 4, there can still be problems when reactions with dramatically different rates are projected to the same subspace. To demonstrate this point, let us consider the following example,

Mech 6:

(R1) $B \leftrightarrow A$, $\omega = 10^4 \cdot (B - A)$,

(R2) $A \leftrightarrow C$, $\omega = 10^2 \cdot (A - C)$,

(R3) $D \rightarrow A$, $\omega = 1 \cdot D$,

in which all three reactions have drastically different rates. Suppose all species concentrations and controlling time scales are $\sim O(1)$, and A is of interest. It is seen that R1 and R2 are fast reactions which become PE after a transient period, after which R3 is rate-controlling. The evolution of this system is rather simple: species A, B, and C form a near-equilibrated species pool, and their concentrations are almost equal. Species D provides elements to the pool through the rate-controlling reaction R3. Therefore, D is important to the system, since it is the source, and B and C are important to A since they equally share the incoming mass flux with A. Consequently, no species can be eliminated in this example.

Using DRG with $\varepsilon = 0.1$, the graph for the species relations is constructed in Fig. 4, in which every
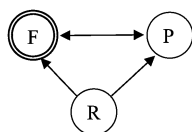

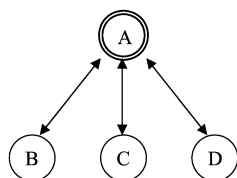Fig. 3. DRG for Mech 5, which consists of an unimportant fast reaction.

Fig. 4. DRG for an example mechanism in which all reactions have drastically different rates.

species is directly required by A, which is consistent with the above analysis. On the other hand, by applying the CSP-based method to Mech 6, it was found that only species B and D are important to A. This is because R1 and R2 are projected to the same subspace, and the forward and backward rates of R2 are dominated by those of R1, although their net reaction rates are comparable. Hence, the importance of the coupling between A and C through reaction R2 is underestimated.

Based on the above discussions, it can be seen that the CSP-based method with fast–slow separation might be applied to reduce certain mechanisms not in the elementary form of Eq. (2.3), to which DRG is not applicable; the fast–slow separation may result in decreased extent of reduction. Furthermore, binary time-scale splitting is shown not to be sufficient to prevent important reactions from being dominated by PE reactions, projected into the same subspace, which have much larger forward and backward rates. In such cases, the simple strategy of combining the forward and reverse reactions, if applicable, is effective and efficient in obtaining correct skeletal mechanisms.

7. Error propagation in DRG

In another recent work [26], the method of directed relation graphs with error propagation (DRGEP) was studied. DRGEP extends DRG by considering error damping along the graph searching path, based on the argument that the error induced to a species A due to the elimination of a species B was damped geometrically while the number of edges increased in graph searching. For example, in the sample DRG shown in Fig. 5, which consists of three species and two edges, the relation of A and C is treated as $R_{AC} = r_{AB} \cdot r_{BC}$, which indicates that the error induced to A by the removal of species C, through the coupling with B, should be smaller than the immediate errors r_{AB} and r_{BC}. The benefit of considering error propagation in DRG reduction is that more species can be eliminated with the same threshold error by using a more accurate estimate of the induced error, rather than its upper bound.

While DRGEP is a promising extension of the current DRG method aiming at obtaining smaller skeletal mechanisms, one of the major issues in DRGEP is how to accurately estimate the error propagation. The reason is clear: underestimation of errors may result in the elimination of important species. In this sense,
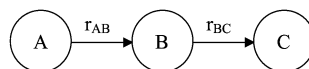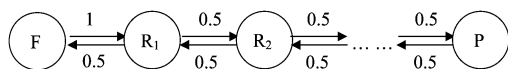

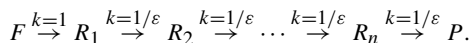Fig. 5. An example DRG with error propagation.

Fig. 6. A DRG with chained fast reactions.

the assumption of geometric error damping in DRG might be risky, as shown in the following example:

Mech 7:

$$F \overset{k=1}{\to} R_1 \overset{k=1/\varepsilon}{\to} R_2 \overset{k=1/\varepsilon}{\to} \cdots \overset{k=1/\varepsilon}{\to} R_n \overset{k=1/\varepsilon}{\to} P.$$

It is seen that the first reaction in Mech 7 is slow and rate-controlling, and all the subsequent reactions are fast reactions choked by the QSS species R_1 to R_n, such that the rates of all the reactions in Mech 7 are approximately equal. The species relations can then be computed with Eq. (2.4):

$$r_{FR_1} = 1, \qquad r_{R_1 F} = 0.5,$$

$$r_{R_i R_{i+1}} \approx r_{R_{i+1} R_i} \approx 0.5, \quad i = 1, 2, \ldots, n-1,$$

$$r_{R_n P} \approx r_{P R_n} \approx 0.5. \tag{7.1}$$

The DRG of this system is shown in Fig. 6.

Suppose species P is of interest; then the species relation of P on F computed with the assumption of geometric error damping is

$$R_{PF} = r_{P R_n} \cdot r_{R_n R_{n-1}} \cdot \cdots \cdot r_{R_2 R_1} \cdot r_{R_1 F} \approx 0.5^{n+1}.$$

It is readily seen that $R_{PF} \to 0$ when n is large, and the importance of species F to P is underestimated since F is the only source generating P through a chain of QSS species $R_1, R_2, \ldots, R_n$.

The breakdown of geometric error propagation assumption in the above example is due to the existence of fast modes, which provides a set of algebraic functions relating the involved species after a transient period. The error propagation inside the species coupled with such algebraic equations can be estimated in the same manner as in Eq. (3.1), which consequently requires the separation of fast and slow subspaces. Therefore, in such cases, the combination of DRGEP and the slow–fast separation might provide more accurate error estimation to DRG reduction. This issue merits further investigation.

8. Conclusions

The effect of fast processes in detailed chemical kinetics on the application of DRG was discussed, with examples as well as systematic derivations. Several restrictions on the applicability of DRG were identified and discussed. It was found that DRG performs correctly in mechanisms that may involve both QSS and PE problems, provided that the reactions are reversible, with the backward reactions computed from the equilibrium constants. Net production rates of the reactions, rather than the separate forward and backward rates, should be employed in computing species relations for valid DRG reduction in existence of PE reactions, which feature much larger forward and backward reaction rates than the system-controlling rate. It was shown that for mechanisms in which reactions are reversible and backward rates are computed through equilibrium constants, the net production rates of fast reactions are not of the same order as the controlling rate, so that the partial equilibrium reactions do not dominate the controlling ones in evaluation of species relations in DRG.

It was further found that the slow processes, which may become important over a long residence time, might not be detected in a local DRG reduction for a residence time much shorter than the time scale of the slow processes. Therefore the skeletal mechanism developed from a single reaction state is only expected to be valid locally within a certain time interval. To develop global skeletal mechanisms valid over an extended range of residence times, a global species set can be obtained by combining the species in local skeletal mechanisms developed for various residence times.

The effect of loss in significant digits due to major cancellations in computing species relations was discussed in two cases: when the fast reactions approach PE, and when the system approaches chemical equilibrium. A criterion for the required sampling accuracy was provided to ensure that the evaluated species relations are valid.

The method of DRG was compared with two recently developed methods for skeletal reduction, based on CSP and on DRG with error propagation, respectively. It was found that while the method based on CSP with slow–fast separation can be employed to reduce certain mechanisms with irreversible fast reactions, the resulting skeletal mechanism might be larger than that reduced by DRG. Furthermore, the reduction based on binary time splitting might not be valid when reactions with vastly different rates are projected to the same subspace.

The error propagation in DRG was found to be quite involved in the presence of fast processes, since the error induced for a species may directly affect other species through couplings by fast dynamics, in which case the geometric error damping assumption may be invalid.

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