

A Dynamic Approach to the Dimension Reduction of Chemical Kinetic Schemes

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Abstract

The use of both experimental and theoretical techniques has improved our understanding of chemical reaction mechanisms considerably in recent years. As a result, highly detailed chemical reaction mechanisms are being developed that incorporate large numbers of species and elementary reaction steps. However, even with modern high performance computers, it is still difficult to incorporate such large comprehensive schemes within commercial software, such as computational fluid dynamic codes used to simulate industrial processes, due to the computing burden involved. Much research is therefore currently focussed on the development of methods for reducing the dimension of comprehensive schemes whilst retaining the important behavioural features of the original scheme. In this paper, a dynamic approach based on a net rate of production analysis for scheme reduction is proposed. The success of the new approach is illustrated for a CO-H₂ oxidation reaction system in a continuously stirred tank reactor that exhibits complex oscillatory behaviour. The main advantage of the approach is that it does not depend on any training data set, and therefore does not suffer from domain restrictions that limit the applicability of many established reduction methods. Consequently, it can be implemented in any numerical simulation package.

Keywords: chemical kinetics, mechanism reduction, dynamic system, CO oxidation

1. Introduction

A chemical scheme is a reaction network that is derived from theoretical and/or experimental data. As more and more data become available and our understanding of the underlying mechanism of many chemical processes improves, we are capable of building comprehensive schemes which have better predictability within a wider range of experimental conditions than in the past. However, one drawback of these schemes may be that their dimensions are too high, preventing their utilisation in practical applications, especially when computational fluid dynamics codes are involved. This has led to a branch of research which investigates model reduction methods to decrease the dimensions of chemical schemes.

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There are many methods for model reduction. Broadly speaking, they can be classified into several categories. Methods that reduce the full mechanism to a skeletal scheme, involve the permanent removal of so-called redundant species and reactions over a prescribed range of operating conditions. Such methods include sensitivity analysis, principal component analysis (Turanyi, 1990) and mathematical programming methods (Banerjee et al., 2003). These methods are very effective and depending on the application can lead to large reductions in the size and dimension of a given mechanism. However, the removed species, which are redundant in terms of the considered reaction conditions, may be important under other conditions. Therefore the domain in which the reduced scheme works well, may be restrictive. A second category, the lumping approach, combines species which have similar chemical properties to form pseudo-species and thereby reduce the system dimensions. Chemical, empirical and formal lumping methods have been developed, as well as a new hybrid approach (Huang et al., 2004). However, the chemical similarity of lumped species may change significantly over wide ranging reaction conditions and again this may affect the domain of applicability of these methods. A third category covers time-scale analysis methods, and includes approaches such as the use of intrinsic low dimensional manifolds, and the application of quasi steady-state analysis methods (Maas and Pope, 1992; Turányi et al., 1993; Tomlin et al., 1997). Such approaches rely on the assumption that for long reaction times many variables or modes within the system equilibrate with respect to slower processes. A fourth category involves replacing the chemical kinetic equations with more efficient mathematical representations of the chemical change over a time step, and includes tabulation methods (Pope, 1997) as well as repro-modelling which involves the use of fitting methods such as artificial neural networks and polynomial fitting (Tonse et al., 1999; Lowe and Tomlin, 2000)

Generally speaking, the success of most of these methods is related to the data sets which are used to build and evaluate the reduced models. The wider the range of the data set, the better and wider the predictive capability of the reduced model will be. The transferability of reduced models built in this way therefore depends on the ability to describe a wide range of conditions under which the model reduction is carried out. If the reduced model needs to cover all conditions, then many species and reactions may have to be retained. A further issue which complicates the use of training model reduction approaches is that the highly nonlinear nature of chemical dynamics means that a condition which is located between the training sets is not necessarily guaranteed to be successfully predicted by the reduced scheme. Therefore, a general non-training and predicting model reduction approach is worthy of investigation.

2. Methodology

The dilemma of model reduction is that we aim to reduce the number of reactions and/or species of a scheme whilst retaining a wide range of validity of the reduced scheme. Often a balance has to be sought, and the choice is made to adopt a single, relatively large reduced scheme that covers all the conditions of interest. Schwer et al. (2003) proposed an adaptive chemistry approach in order to produce different, smaller reduced schemes for different sets of conditions.

Here, we propose a dynamic reduction approach that can be applied for any simulation conditions. At any point in a simulation, certain species are numerically significant and others are negligible. There are two scenarios in this respect. One is that a scheme which accounts for a wide range of experimental conditions may contain a certain number of species which are permanently insignificant throughout the considered simulation. The other scenario is that a certain number of species in a scheme are numerically significant during certain periods of time, but insignificant during other periods over the considered simulation. Thus, if we could identify which species in which periods of time are insignificant, then computing time will be saved by neglecting them for certain periods of the numerical calculation.

To identify the insignificant species, Schwer et al. (2003) suggested a minimum tolerance threshold on mass fraction. However, in oxidation reactions, for example, some radicals such as H and OH may have very small mass fractions, but they are actively involved in important reactions with other species and therefore cannot be neglected. Here, we suggest a criterion based on the net production rate of a species, since it reflects the combined effect of species mass fraction and the reactivity of the species. At a given time point, we define species i as insignificant if the absolute value of its net production rate $|f_i| < f_{tol}$, where f_{tol} is a given small positive tolerance. If there are m insignificant species among the total number of species n , then a system variable Y with n dimensions can be divided into significant variables Y_I with $(n-m)$ dimensions and insignificant variables Y_{II} with m dimensions. Then the system equations defined by the full scheme

$$\frac{dY}{dt} = f(Y), Y(0) = Y_0 \quad (1)$$

can be split into the following two systems

$$\frac{dY_I}{dt} = f(Y_I) \quad (2)$$

and

$$\frac{dY_{II}}{dt} = f(Y_{II}). \quad (3)$$

Since $|f(Y_{II})|$ is negligible by definition at the given time point, we make the reasonable assumption that in the following short period of time from t_1 to t_2 , $|f(Y_{II})|$ is also negligible. The mass fractions of Y_{II} are therefore kept constant during this time period. Then we have:

$$Y_{I,t_2} = \int_{t_1}^{t_2} f(Y_I) dt + Y_{I,t_1} \quad (4)$$

and

$$Y_{II,t_2} = Y_{II,t_1}. \quad (5)$$

Therefore, we only need to solve the problem of Y_I , which becomes the reduced $(n-m)$ dimensional problem. At the end of each period, we re-evaluate $|f(Y)|$ and obtain the new sets of Y_I and Y_{II} . The process is then repeated until the end of the simulation.

In this paper, we evaluate two procedures for implementing the proposed dynamic reduction approach. The first is to set a fixed number of species. In this we evaluate

$|f(Y)|$ at given time points and only take the fixed number of species which have higher values of reaction rates. The remaining species are taken as insignificant species. This method is similar to the skeletal reduction method in that it leads to a reduced scheme with a fixed dimension. However, the dynamic approach may contain different species during different periods of time in the simulation, whereas other reduction methods that lead to skeletal schemes usually produce a fixed set of species. Given a fixed number of equations, the dynamic approach may be more accurate in reflecting the important species for the local conditions of the considered simulation.

The second method is based on setting a relative threshold on the net production reaction rates. At a given simulation time point, we define

$$f_{sum} = \sum_{i=1}^n |f_i|, \quad (6)$$

where f is the net production rate and i represents one of the n species. If the absolute value of the net production rate of species i ,

$$|f_i| < tol * f_{sum}, \quad (7)$$

where tol is a small positive number as a relative threshold, then species i is an insignificant species since its involvement is insignificant in terms of the total reactivity of the system, otherwise it is a significant species. The threshold tol therefore represents a fraction of the total reaction rate from which we can decide whether a species is significant or not. Once the two categories of species are identified, we can apply the proposed dynamic approach to reduce the dimensions of the system.

3. Results and Discussion

We illustrate the proposed dynamic reduction approach by considering the CO-H₂ oxidation process in a continuously stirred tank reactor, as described previously by Brad et al. (2003). The main reason for choosing this process is that if the proposed approach works well for this very complex oscillatory dynamic system, then it should be easily extended to other less complex systems. The chemical scheme used as the basis of this work was derived (Brad et al., 2003) from the Leeds methane combustion scheme and contains 11 species and 66 reactions.

In this paper, we evaluate the accuracy of different reduction methods by comparing their results with predictions of the full (i.e. 11 species) scheme under one experimental condition. This condition was taken as : a feed composition of 49.5% CO, 50% O₂ and 0.5% H₂ by volume; a pressure of 15 Torr; an ambient temperature of 695 K; a reactor overall heat transfer coefficient (including area, i.e. UA) of $1.6 \times 10^{-4} \text{ Js}^{-1}\text{K}^{-1}$; residence time of 8 s and simulation time of 20 s. Through conventional sensitivity analysis, Brad et al. (2003) identified that HCO is the only redundant species that can be removed from the 11 species scheme if a reasonable degree of accuracy of the reduced scheme is to be maintained. Here, we first show results of the dynamic reduction method using the fixed equation number approach described above. In Figure 1a, the dotted line is the simulation after removing HCO from the full scheme by sensitivity analysis, while the broken line represents the results of the first dynamic reduction method with the species equation number fixed at 10. The broken line is seen to overlap with the solid line

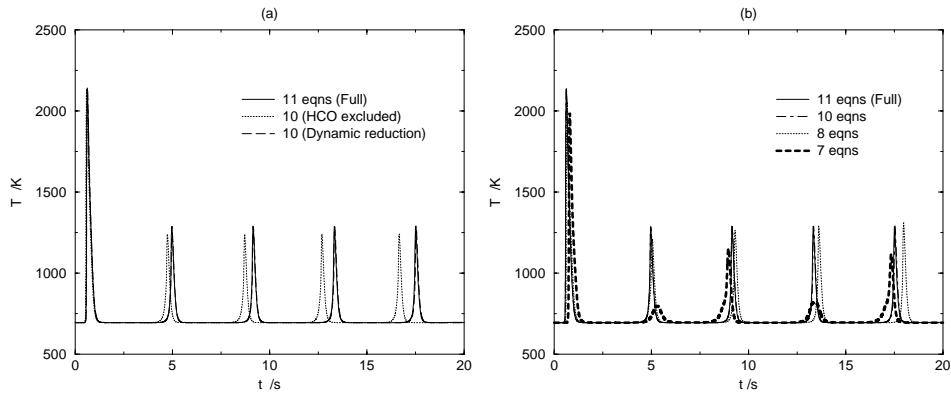


Figure 1. Comparison of results of (a) fixed reduction and dynamic reduction, and (b) dynamic reduction method 1.

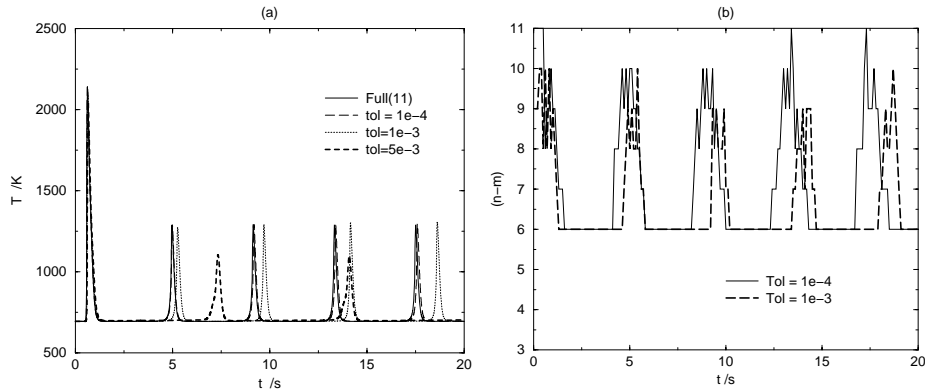


Figure 2. (a) Results of dynamic reduction method 2, and (b) dimensional profiles of two reductions with different tolerances.

which represents the results of the full scheme. Therefore, given the same system dimension, the dynamic approach is better in terms of accuracy when compared to the full scheme. Figure 1b shows that we can even reduce the dimension to 8, which is shown by the dotted line, without losing too much accuracy, but further dimension reduction to 7, shown by the thick dashed line, leads to a different kind of oscillatory dynamic behaviour. Figure 2a shows the results of the tolerance enforced dynamic reduction method. For example, the long dashed line in the figure is the results of $tol = 1 \times 10^{-4}$, which means a species which has a rate of change less than 0.01% of the f_{sum} is an insignificant species and its concentration is constant in the following time period. The dotted line in the figure shows that when the tolerance is increased to 1×10^{-3} the reduced system produces qualitatively the same dynamic behaviour. However, if the tolerance is increased further to 5×10^{-3} , the dynamic behaviour shown by the thick dashed line is unsatisfactory. Figure 2b shows the change of number of significant species ($n-m$) over time under two tolerances. It reveals that we need only 6 species for much of the time horizon, and only during short periods of time do we need 9 species.

The work described is part of an ongoing project, and as such further work remains to be performed to fully explore the computational savings that can be made using the dynamic approach. Nevertheless, for the example considered above, for the fixed equation number approach we save 9% of CPU time by using 8 equations when compared to the full scheme. Using the second method, we save 16% of CPU time by setting a threshold 1×10^{-3} when compared to the full scheme. Greater savings would be expected for larger initial schemes than the 11 species one used here and testing the method on other examples will be a topic of future work.

4. Conclusions

Many studies are currently underway to develop methodologies for reducing the dimensions of mathematical models such as comprehensive chemical reaction schemes. Many of these methods are based on the use of training data. Due to the nonlinearity of chemical dynamics, however, a reduced model produced using training model reduction approaches is not necessarily guaranteed to cover conditions which are not included in the training set. In this paper, a new dynamic model reduction methodology has been proposed, and the success of the proposed method has been illustrated by consideration of a complex oscillatory oxidation process. The main advantage of the new reduction approach is that it does not depend on any training data set, and therefore no domain restrictions apply that may limit the range of applicability of traditional reduction methods. The method proposed can be implemented in any numerical simulation package, and for the particular application considered has been shown to lead to significant reductions in model run times.

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