Commun. Comput. Phys.
doi: 10.4208/cicp.030709.210110a

Vol. **8**, No. 4, pp. 701-734
October 2010

The Role of Thermodynamics in Model Reduction when Using Invariant Grids

Eliodoro Chiavazzo[1], Iliya V. Karlin[1,2,*] and Alexander N. Gorban[3]

[1] *Aerothermochemistry and Combustion Systems Lab, ETH Zurich, 8092 Zurich, Switzerland.*
[2] *School of Engineering Sciences, University of Southampton, SO17 1BJ Southampton, United Kingdom.*
[3] *Department of Mathematics, University of Leicester, LE1 7RH Leicester, United Kingdom.*

Received 3 July 2009; Accepted (in revised version) 21 January 2010

Available online 17 May 2010

Abstract. In the present work, we develop in detail the process leading to reduction of models in chemical kinetics when using the Method of Invariant Grids (MIG). To this end, reduced models (invariant grids) are obtained by refining initial approximations of slow invariant manifolds, and used for integrating smaller and less stiff systems of equations capable to recover the detailed description with high accuracy. Moreover, we clarify the role played by thermodynamics in model reduction, and carry out a comparison between detailed and reduced solutions for a model hydrogen oxidation reaction.

AMS subject classifications: 52B10, 65D18, 68U05, 68U07

Key words: Chemical kinetics, model reduction, invariant manifold, entropy.

1 Introduction and motivation

The numerical solution of the full set of governing equations, as dictated by modeling of reactive flows with detailed chemical kinetics, remains a challenging task. The reason is, on one side, a large number of kinetic equations needs to be solved in order to keep track of each chemical species. On the other side, a detailed reaction mechanism typically contains many different chemical processes occurring on timescales that range over several orders of magnitude, from seconds down to nanoseconds. It is this feature that gives rise to the stiffness of the governing equations for the chemical reactions. Moreover, the fluid mechanics of chemically reactive flows usually occurs at a narrower range on the

*Corresponding author. *Email addresses:* eliodoro.chiavazzo@gmail.com (E. Chiavazzo), karlin@lav.mavt.ethz.ch (I. V. Karlin), ag153@leicester.ac.uk (A. N. Gorban)

order of milliseconds to microsecond. The stiffness drastically affects the implementation of numerical solvers, where reducing the time step becomes necessary in order to both avoid numerical instabilities (e.g., in the case of explicit schemes) and to keep a satisfactory accuracy. As a result, the smallest time scales need to be resolved even when one is interested only in the slow dynamics. In addition, the larger the number of elementary reactions involved in the detailed mechanism, the more significant becomes the computational effort due to the evaluation of reaction rates. These issues make computations of even simple reacting mixtures time consuming.

On the other hand, some reduction is often possible by simply setting up a criterion for eliminating unimportant reactions (or species) from the detailed reaction mechanism (see, e.g., the sensitivity analysis [1,2], the comparative analysis of entropy production [3,4], and the reaction path analysis [5]). However, in the present study we exploit a more sophisticated concept of time-scale separation in order to construct a reduced description of the detailed kinetic model. In fact, as mentioned above, there are many chemical processes that are much faster than the fluid dynamic phenomena, so if we are only interested in computing the system behavior on the scale of the fluid mechanics, some chemical processes will be already self-equilibrated. The timescale-based reduction techniques are all based on decoupling the fast equilibrating chemical processes from the slower dynamics, and are implemented by seeking a *low dimensional manifold* of slow motions in the solution space of the detailed system.

In this work, we focus on closed isothermal chemical reactors with a unique steady state (equilibrium point). However, notice that applications of reduced models attained by the suggested methodology to open reactive systems, under non-isothermal conditions, have been shown recently [20,21].

The idea that a low dimensional manifold provides a reduced description of a complex system stems from the representation of its numerical solutions in the phase-space (concentration space). The dynamics of such a complex reactive system is often characterized by a short initial transient during which the solution trajectories approach low-dimensional manifolds in the concentration space, known as the slow invariant manifolds (SIM). The remaining dynamics lasts much longer and evolves along the SIM towards the steady state. Thus, it turns out that constructing the SIM enables to establish a simplified description of a complex system by extracting only the slow dynamics and neglecting the fast. As a result, the detailed large set of equations can be reduced to a much smaller system without a significant loss of accuracy.

Therefore, much effort has been devoted to setting up automated model reduction procedures based (explicitly or implicitly) on the notion of SIM: The method of invariant grids (MIG) [6,7], the computational singular perturbation (CSP) method [29–31], the intrinsic low dimensional manifold (ILDM) [27,28], the invariant constrained equilibrium edge preimage curve method (ICE-PIC) [32], the equation-free approaches [33], the method of minimal entropy production trajectories (MEPT) [35] and minimum curvature [36], the constrained runs algorithm in [34] and the finite-time Lyapunov analysis in [37] are some representative examples.