Towards automatic reduction of kinetic mechanisms by optimization of trajectories

Volkmar Reinhardt[1], Miriam Winckler[1], Jürgen Warnatz[1], Dirk Lebiedz[1]

[1]Interdisciplinary Institute for Scientific Computing, University of Heidelberg,
Im Neuenheimer Feld 368, 69120 Heidelberg, Germany

1 Introduction

In the past, numerous approaches to the reduction of large chemical reaction mechanisms have been presented. Methods performing *species reconstruction*, i.e. the explicit representation of a large number of chemical species in terms of just a small number of chemical species - the so-called reaction progress variables - are of particular interest due to their intuitive handling. However, while many of these approaches directly exploit the time-scale properties of the mechanisms, this procedure can lead to severe problems under conditions where the requirements of clear time-scale separation do not hold. For example the solution of time scale decoupling equations with a fixed dimension may be impeded by low temperatures.
As a result the user of reduced reaction mechanisms may be left with the highly unsatisfactory situation that no reduced chemistry description is available in parts of his CFD computations.

Another problem of some mechanism reduction approaches is the strong numerical dependence on initial values. Due to this dependence, some reduction approaches only make sense in the framework of a continuation method where good initial values can always be guaranteed. Usually these approaches are used for a tabulation of chemistry, allowing in-situ utilization only via path-following strategies.
However, local species reconstruction - i.e. the genuine in-situ computation of reduced chemistry descriptions at any local species composition - is favourable at least if the desired dimension of the reduced description is too high for an efficient tabulation.

2 Model reduction based on optimization criteria

A promising alternative to explicitly time-scale separation based model reduction approaches are model reduction approaches that are based on optimization criteria determining the maximal relaxation of chemical forces along trajectories.

Generally such an approach allows to compute at least optimally reduced - with respect to the given criterion - solutions even under conditions where approaches directly based on time-scale decoupling fail and even with poor initial guesses.

In [1], Lebiedz first introduced such a concept based on the minimization of entropy production $\frac{\mathrm{d}S}{\mathrm{d}t}$ along trajectories with fixed initial concentrations of a given number of variables.
While these variables parametrize the reduced model and can be interpreted as reaction progress variables as in case of other model reduction approaches, all other initial concentrations and the whole trajectories are computed as a solution of an optimization problem.

Correspondence to : lebiedz@iwr.uni-heidelberg.de

The optimization of trajectories with respect to this criterion has been demonstrated for a simple three-species model mechanism, resulting in trajectories which can be interpreted as one-dimensional manifolds along which chemical forces are maximally relaxed [1].

Mathematically this problem can be described as a variational boundary value problem for an ordinary differential equation system:

Problem 1

$$\min_{c_i, i\in I_{\text{free}}} \quad \int_0^T \Phi(c(t))\,\mathrm{d}t \tag{1a}$$

$$\text{subject to} \quad \frac{\mathrm{d}c_i}{\mathrm{d}t} = f_i(c), \qquad i = 1, ..., n \tag{1b}$$

$$c_i(0) = c_i^0, \qquad i \in I_{\text{fixed}} \tag{1c}$$

$$|c_i(T) - c_i^{\text{eq}}| \leq \varepsilon, \qquad i \in I_{\text{fixed}} \tag{1d}$$

and subject to conservation equations.
Here I_{fixed} is the index set containing the indices of the reaction progress variables which are fixed at the initial point of the trajectory by (1c) and I_{free} is the index set of all variables with free initial values (all variables except the progress variables). The final point, i.e. equilibrium is approximated in (1d) within a surrounding radius ε and the system dynamics are described by the ODE system (1b), where the chemical source term of the i-th species is represented by $f_i(c)$. The integration time T is automatically determined during the optimization by the demand of the final point being close to equilibrium (1d).

For the sake of generality, the objective functional has been written as $\Phi(c(t))$, with $\Phi(c(t)) = \frac{\mathrm{d}S}{\mathrm{d}t}$ - i.e. entropy production - being the choice used in [1].

This formulation leaves the freedom to choose an arbitrary number of species as reaction progress variables and in [2, 3], the principal extension of the MEPT method for constructing manifolds of higher dimension has been demonstrated for the mechanism given in Example 2.

Example 2

$$\begin{array}{ccccll}
\mathrm{H_2} & \overset{k_1,k_{-1}}{\longleftrightarrow} & 2\mathrm{H} & , & k_1 = 2.0, & k_{-1} = 216.0 \\
\mathrm{O_2} & \overset{k_2,k_{-2}}{\longleftrightarrow} & 2\mathrm{O} & , & k_2 = 1.0, & k_{-2} = 337.5 \\
\mathrm{H_2O} & \overset{k_3,k_{-3}}{\longleftrightarrow} & \mathrm{H} + \mathrm{OH} & , & k_3 = 1.0, & k_{-3} = 1400.0 \\
\mathrm{H_2} + \mathrm{O} & \overset{k_4,k_{-4}}{\longleftrightarrow} & \mathrm{H} + \mathrm{OH} & , & k_4 = 1000.0, & k_{-4} = 10800.0 \\
\mathrm{O_2} + \mathrm{H} & \overset{k_5,k_{-5}}{\longleftrightarrow} & \mathrm{O} + \mathrm{OH} & , & k_5 = 1000.0, & k_{-5} = 33750.0 \\
\mathrm{H_2} + \mathrm{O} & \overset{k_6,k_{-6}}{\longleftrightarrow} & \mathrm{H_2O} & , & k_6 = 100.0, & k_{-6} = 0.7714
\end{array} \tag{2}$$

This mechanism consists of six species and six reactions. Together with two conservation equations due to element conservation, the mechanism forms a system with four degrees of freedom, which allows for up to three progress variables to be set.

Varying two (for reasons of visuability) progress variables over the region of interest, a bundle of optimal trajectories can be computed, that spans a two-dimensional manifold as an approximation of the slow attracting manifold. A bundle of trajectories generated by minizing entropy production is depicted in the phase space plot in figure 1. There first a one-dimensional manifold has been computed by setting the initial concentration of H_2O to 10^{-4} (depicted with triangles in figure 1 and then H_2O and H_2 have been used as reaction progress variables. Therefore, for a fixed initial concentration of H_2O (10^{-4}), the initial concentration of H_2 has been varied from 0.3 to 0.95 and likewise the initial concentration of H_2O has been varied from 0.05 to 0.3 for the initial concentration of H_2 fixed to 0.3.

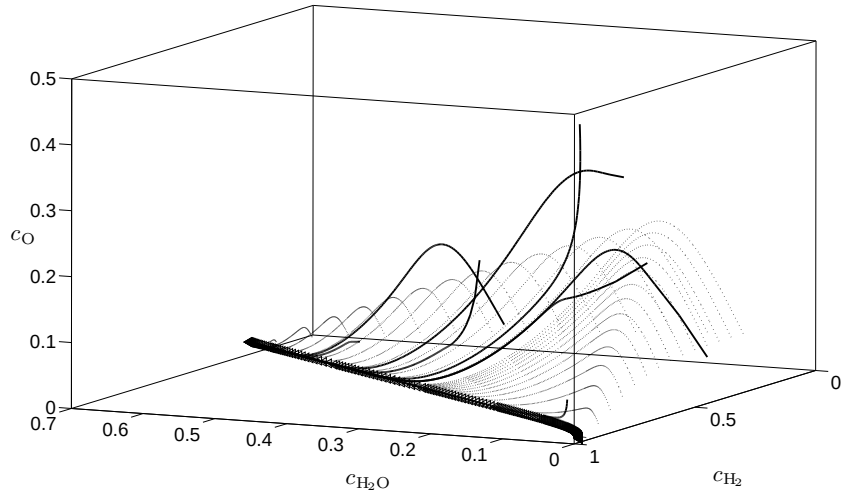

Figure 1: Bundle of optimal trajectories forming a two-dimensional manifold

3 Higher-dimensional manifolds - computational issues

For the successful application of a model reduction approach based on the optimization of trajectories, efficient solution strategies are crucial. Problem 1 is be solved using the optimization software MUSCOD-II [4]

The computation of a single trajectory according to problem 1 is not too strongly dependent on good initial values - as for example the ILDM method is - hence this method can be used locally.

However, an efficient continuation strategy based on initial value embedding can significantly speed up computations in practical purposes like the generation of tables of reduced chemistry or in-situ species reconstruction.

In [5], Winckler successfully applied an initial value embedding strategy originally developed for nonlinear model-predictive control by Diehl [6] to compute trajectory bundles over a given range of progress variables. This procedure, which formally utilizes a linear extrapolation prediction of the previous solution, allows for very fast convergence to a solution for a slightly different combination of progress variables.

4 Towards automatic reduction based on optimal trajectories

The procedures described above and the results achieved with this procedure have promise to bring a method based on the optimization of trajectories into application as a species reconstruction model reduction method. However, on the way towards an automatic method there are some degrees of freedom that lie in the generality of problem 1.

We adress for example the question whether the computation on a fixed integration horizon $[0, T]$ is more favourable for an automatic reduction method than integrating until (1d) is fulfilled. This opens the possibility of integrating on small integration horizons and hence of reducing computiational time.

Another question is whether a small time interval before the setting of the progress variables can improve the accuracy of the method. This interval could be interpreted as a relaxation time.

We present investigations of these questions on the basis of the mechanism from example 2 and promising results of reduced mechanisms, depicted as phase-space plots as seen in figure 1.

For broad application in model reduction, we also present efficient computational strategies for species reconstruction with a trajectory-based optimization approach. These methods are based on the aforementioned initial value embedding strategy by Diehl [6].

References

[1] Lebiedz D (2004). Computing minimal entropy production trajectories: An approach to model reduction in chemical kinetics. J. Chem. Phys. 120:15

[2] Lebiedz D et al. (2006). Novel trajectory based concepts for model and complexity reduction in (bio)chemical kinetics. In: Gorban et al. (eds) Model Reduction and Coarse-Graining Approaches for Multiscale Phenomena

[3] Lebiedz D (2006). Optimal control, model- and complexity-reduction of self-organized chemical and biochemical systems: A scientific computing approach. Habilitation thesis, Ruprecht-Karls-Universität Heidelberg.

[4] Leineweber D B et al. (2003). An efficient multiple shooting based reduced sqp strategy for large-scale dynamic process optimization. In: Computers and Chemical Engineering 27:157 174

[5] Winckler M (2007). Towards optimal criteria for trajectory-based model reduction in chemical kinetics via numerical optimization. Diploma thesis (in preparation)

[6] Diehl M M et al. (2002). Real-Time optimization and nonlinear model predictive control of processes governed by differential-algebraic equations. In: J. Process Contr., 12:577–585