Geometric criteria for model reduction in chemical kinetics via optimization of trajectories

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Abstract— In previous work we proposed an approach for the approximation of slow invariant manifolds by computing trajectories as solutions of an optimization problem with respect to their initial values. The objective functional of the optimization problem is supposed to represent the extent of relaxation of chemical forces. Following these ideas we discuss this approach on the basis of results for three example models of chemical reaction mechanisms.

I. INTRODUCTION

The need for reduced chemical kinetics is motivated by the fact that the computational effort for a full simulation of reactive flows, e.g. of fluid transport involving combustion processes, is computationally extremely expensive.

For getting useful approximations of the full mechanism, we are convinced, that global information on phase space dynamics should be used to determine the reduced kinetics. As reaction kinetics are usually modeled by ordinary differential equations (ODE), trajectories in phase space that are solutions of these ODE bear global information of the system dynamics. This information can be exploited within a trajectory optimization framework for identifying suitable reaction trajectories approximating slow attracting manifolds, where – after a short initial time – the system dynamics take place.

A suitable formulation of the computation of reduced models as an optimization problem assures the existence of a solution irrespective of assumptions on the time scale structure and sophisticated optimization software can be used for the numerical solution of these problems.

The optimization criterion for the identification of suitable trajectories should represent the assumption that chemical forces are maximally relaxed along these trajectories. Various approaches for the formulation of optimization criteria are conceiveable.

II. METHODOLOGY

A. General Problem Formulation

In our approach the general trajectory-based optimization problem can be written as

$$\min_{c} \int_{0}^{t_{\rm f}} \Phi\left(c(t)\right) \, \mathrm{d}t \tag{1a}$$

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subject to

$$\frac{\mathrm{d}c(t)}{\mathrm{d}t} = f\left(c(t)\right) \tag{1b}$$

$$0 = g\left(c(0)\right) \tag{1c}$$

$$c_k(0) = c_k^0, \qquad k \in I_{\text{fixed}}.$$
 (1d)

Here the nonlinear function f describes the chemical reaction kinetics for the chemical species vector c(t). The element mass conservation is collected in g. I_{fixed} is the index set of reaction progress variables chosen for parameterization of the reduced model. These can in principle be selected without restriction from the list of all species and are fixed at t = 0 in (1d). All other species concentrations at t = 0 are free variables and subject to optimization. Thus the solution of the optimization problem is equivalent to species reconstruction. The computed full composition should represent a point on the slow invariant manifold. The final time $t_{\rm f}$ is chosen as large as necessary for approximately reaching the chemical equilibrium point. The central issue to be addressed is how to choose the objective function Φ in (1a). This will be discussed in the following.

B. Entropy-Based Criteria

In previous work (including the first workshop on model reduction in reacting flows, Rome 2007) the entropy production rate was suggested as an optimization criterion. Entropy production is related to the relaxation of chemical forces and the development of partial equilibria [1].

The formula for the entropy production rate with the forward and backward reaction rates $R_{j,\rightarrow}$ and $R_{j,\leftarrow}$, respectively, is

$$\frac{\mathrm{d}S_{j}}{\mathrm{d}t} = R\left(R_{j,\rightarrow} - R_{j,\leftarrow}\right)\log\left(\frac{R_{j,\rightarrow}}{R_{j,\leftarrow}}\right) \tag{2}$$

for the *j*-th elementary reaction in the kinetic mechanism. Here R is the gas constant. With (2) a relaxation criterion for the objective function (1a) can be formulated

$$\Phi(c(t)) = \sum_{j=1}^{m} \frac{\mathrm{d}S_j}{\mathrm{d}t}.$$
(3)

This criterion was studied in [1] and [2]. The results and the concept of the approach look promising but do not provide a sufficiently accurate approximation of the slow attracting manifold, in particular far from equilibrium. In the following, alternative criteria have been investigated.

C. Geometric Criteria

As stated above, a suitable reduction criterion $\Phi(c(t))$ should characterize the relaxation of "chemical forces". From a physical point of view, curvature (in the sense of the rate of change in velocity) is closely related to the geometric interpretation of force. The aim of [3], [4], [5], [6] was to make an attempt to transfer that relation to the field of reaction kinetics in a way suitable to model reduction via problem formulations such as in (1).

In chemical systems, dissipative forces are active. The different time scales of dynamic modes result in an anisotropic force relaxation in phase space. We consider the tangent (reaction velocity) vectors $\dot{c}(t) = f(c(t))$ of reaction trajectories. The relaxation of chemical forces results in a change of $\dot{c}(t)$ along a trajectory on its way towards chemical equilibrium. This change along the trajectory may be characterized by taking the directional derivative of the tangent vector of the curve c(t) with respect to its own direction $v := \frac{\dot{c}}{\|\dot{c}\|_2}$.

Mathematically that can be formulated as

$$D_v \dot{c}(t) := \frac{\mathrm{d}}{\mathrm{d}\alpha} (\dot{c}(t) + \alpha v) \Big|_{\alpha=0} = J_c f \cdot \frac{f}{\|f\|_2},$$

with $J_c f$ being the Jacobian of the right hand side f evaluated at c(t) and $\|\cdot\|_2$ denoting the Euclidian norm. Hence, we may choose the optimization criterion

$$\Phi(c) = \frac{\|J_c f \cdot f\|_2}{\|f\|_2}.$$
(4)

The natural way for the evaluation of this criterion would be a path integral along the trajectory towards equilibrium

$$\int_{l(0)}^{l(c^{\mathrm{eq}})} \Phi(c(l(t))) \, \mathrm{d}l(t)$$

where l(t) is the length of the curve c(t) at time t given by

$$l(t) = \int_0^t \|\dot{c}(\tau)\|_2 \mathrm{d}\tau.$$

This results in the reparametrization

$$dl(t) = \|\dot{c}(t)\|_2 dt.$$
 (5)

The objective used in (1a) would be

$$\min_{c} \int_{0}^{t_{\rm f}} \|J_c f \cdot f\|_2 \, \mathrm{d}t. \tag{6}$$

However, an alternative norm for the evaluation of $||J_c f \cdot f||$ might be taken into account, which has already been used in [7] and is motivated from thermodynamics. In this norm the criterion adapted from (4) can be written as

$$\frac{\|J_c f \cdot f\|_W}{\|f\|_W} = \frac{(f^{\mathrm{T}} \cdot (J_c f)^{\mathrm{T}} \mathrm{diag}(1/c_i) J_c f \cdot f)^{1/2}}{\|f\|_W}$$
(7)

with $W = \text{diag}(1/c_i)$ being the diagonal matrix with diagonal elements $1/c_i$. This criterion brings thermodynamic considerations into play and represents the Riemannian metric induced by the second differential of Gibbs

free enthalpy G

$$G = \sum_{i=1}^{n} c_i [\ln(c_i/c_i^{eq}) - 1], \quad W = \text{Hess}(G).$$

The corresponding metric has been discussed in the context of an entropic scalar product [8]. The corresponding optimization problem is

$$\min_{c} \int_{0}^{t_{\mathrm{f}}} \|J_{c}f \cdot f\|_{W} \,\mathrm{d}t. \tag{8}$$

In the following results for both criteria (6) and (8) are presented.

D. Numerical Methods

Problem (1) together with a suitable choice of $\Phi(c(t))$ can be numerically solved with an appropriate solver for nonlinear programming problems (NLP) coupled to a numerical integrator. For our results MUSCOD-II [9], [10] is used. This software package is based on a multiple shooting discretization of trajectories and sequential quadratic programming (SQP) for the resulting finite-dimensional NLP. For numerical integration on the multiple shooting intervals DAESOL [11], [12] is used, which is an integrator based on backward differentiation formulae.

The computation of optimal trajectories for neighboring fixed initial values for the reaction progress variables in order to span higher-dimensional manifolds by families of trajectories can be significantly accelerated by the use of continuation methods embedding the problem into a parametric family of optimization problems. Diehl et al. describe an efficient numerical implementation of an initial value embedding strategy in [13]; this stategy is used for the computations presented below.

III. RESULTS

Here we present the application of the method described above for three example problems. First a temperature-independent six species hydrogen combustion process is analyzed, then we study the benchmark Skodje-Davis system and finally we discuss a temperature dependent ozone mechanism involving oxygen as only chemical element.

A. Example Mechanism: Hydrogen Combustion

In this section we consider a small test mechanism taken from [8], that we already used for previous work:



Fig. 1. Solution of (1) with (4) as relaxation criterion for the hydrogen combustion mechanism (9).

with the rate constants

$$\begin{array}{ll} k_1 = 2.0, & k_{-1} = 216.0 \\ k_2 = 1.0, & k_{-2} = 337.5 \\ k_3 = 1.0, & k_{-3} = 1400.0 \\ k_4 = 1000.0, & k_{-4} = 10800.0 \\ k_5 = 1000.0, & k_{-5} = 33750.0 \\ k_6 = 100.0, & k_{-6} = 0.7714. \end{array}$$

Together with the conservation relations

$$2 c_{H_2} + 2 c_{H_2O} + c_H + c_{OH} = C_1$$

$$2 c_{O_2} + c_{H_2O} + c_O + c_{OH} = C_2$$

this mechanism yields a system with four degrees of freedom. For the computations with this mechanism mass relations with $C_1 = 2.0$ and $C_2 = 1.0$ were chosen.

In Fig. 1 the results with the Euclidian norm criterion (6) as objective functional are depicted. We analyze the approximation accuracy of the slow manifold via checking consistency (invariance) by restarting the solution of the optimization problem from a later time point on the earlier computed trajectory. If the slow invariant manifold has been identified correctly, the solution of the second optimization problem should be exactly on the trajectory computed before, a property that we denote consistency. The results are not too bad but can be improved.

The weighted norm proposed in (8) is used as a criterion for the results presented in Fig. 2. The results demonstrate that this criterion can be regarded to be nearly consistent. These results encourage to test the criterion (7) for the Davis-Skodje problem in the next section.

B. Davis-Skodje Problem

The well-known Davis-Skodje mechanism is our second test case.

$$\begin{aligned} \frac{\mathrm{d}y_1}{\mathrm{d}t} &= -y_1\\ \frac{\mathrm{d}y_2}{\mathrm{d}t} &= -\gamma y_2 + \frac{(\gamma - 1)y_1 + \gamma y_1^2}{(1 + y_1)^2} \end{aligned}$$

where $\gamma > 1$ is a measure for the spectral gap or stiffness respectively of the system. Results are shown in Fig. 3. For large values of γ , representing a large gap in time scales between fast and slow modes, the results are acceptable. For small values of γ the approximation is getting worse.



Fig. 2. Solution of (1) with (7) as relaxation criterion for the hydrogen combustion mechanism (9). The results look promising.



Fig. 3. Results for the Davis-Skodje problem with (8) as relaxation criterion. Results for different values of γ are shown. The red curve is the analytically computed SIM (slow invariant manifold). The black dashed curve represents the analytic Maas-Pope-ILDM. The blue curves are trajectories integrated from solution points of our optimization problem.

C. Example Mechanism: Ozone

The last test case is a three component ozone mechanism shown in Table I taken from [14]. It is chosen to demonstrate the performance of our method taking temperature dependence into account. Many approaches based on time scale separation fail when the spectral gap becomes too small. Together with the element conservation

$$c_{\rm O} + 2 c_{\rm O_2} + 3 c_{\rm O_3} = C$$

this mechanism yields a system with two degrees of freedom. We use without loss of generality C = 1.

TABLE I

Ozone decomposition mechanism from [14]. Rate coefficient $k = AT^b \exp(-E_a/RT)$. Collision efficiencies in reactions including M: $f_{\rm O} = 1.14, f_{\rm O_2} = 0.40, f_{\rm O_3} = 0.92$.

Reaction	A (cm, mol, s)	b	$E_{\rm a}\left(\frac{\rm kJ}{\rm mol}\right)$
$O + O + M \rightarrow O_2 + M$	2.90×10^{17}	-1.0	0.0
$O_2 + M \rightarrow O + O + M$	6.81×10^{18}	-1.0	496.0
$O_3 + M \rightarrow O + O_2 + M$	9.50×10^{14}	0.0	95.0
$O + O_2 + M \rightarrow O_3 + M$	3.32×10^{13}	0.0	-4.9
$O + O_3 \rightarrow O_2 + O_2$	5.20×10^{12}	0.0	17.4
$O_2 + O_2 \rightarrow O + O_3$	4.27×10^{12}	0.0	413.9

The results for the Euclidian criterion (4) shown in Fig. 4 appear to become worse in particular for low temperatures. In contrast the weighted criterion (7) gives much better results as illustrated in Fig. 5.



Fig. 4. Solution of (1) with (6) as objective function for the ozone mechanism as in Table I. Here red dots denote the solution for different values of the progress variable c_{O_2} . The blue trajectory can be regarded as relaxed to the one-dimensional SIM after a short integration time.

IV. CONCLUSION

Here we present an extension of the model reduction approach discussed at the first workshop in Rome and in [5]. Various geometric criteria are investigated. In many cases the results demonstrate a good quality of the approximation of the slow attracting manifold. The SIM can even be approximated with sufficient accuracy for the ozone mechanism in the case of low temperatures.

To summarize, this approach looks promising for application to realistic and large-scale detailed combustion mechanisms. Even though a detailed and systematic investigation of the different criteria with a focus on theoretical analysis, approximation accuracy and (numerical) applicability remains a challenging task for our future work.



Fig. 5. Solution of (1) with (7) as relaxation criterion for the ozone mechanism as in Fig. 4. The results look much better even for low temperature.

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