

**Towards Optimal Criteria for  
Trajectory-Based Model  
Reduction in Chemical Kinetics  
via Numerical Optimization**

submitted by  
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# Acronyms

ALDM	Attracting Low Dimensional Manifold
BDF	Backward Differentiation Formulae
CEM	Constrained Equilibrium Manifold
CE-PIC	Constrained Equilibrium Preimage Curve
CFD	Computational Fluid Dynamics
CSP	Computational Singular Perturbation
DAE	Differential Algebraic Equation
ICE	Invariant Constrained Equilibrium Edge
ILDm	Intrinsic Low Dimensional Manifold
IVP	Initial Value Problem
KKT	Karush-Kuhn-Tucker
LMM	Linear Multistep Method
MEPT	Minimal Entropy Production Trajectory
NLP	Nonlinear Programming
NMPC	Nonlinear Model Predictive Control
ODE	Ordinary Differential Equation
PEA	Partial Equilibrium Assumption
PIM	Preimage Manifold
QP	Quadratic Programming
QSSA	Quasi-Steady-State Assumption
RCCE	Rate-Controlled Constrained-Equilibrium
SQP	Sequential Quadratic Programming



# Chapter 1

## Introduction

The idea of modeling chemical kinetics is to map reality to a mathematical description of the system, i.e. to describe its dynamics by mathematical equations. While reducing reality to equations one has to bear in mind that it is impossible to describe every microscopic detail of the system considered. Rather the essential features which cause the macroscopic behavior to be investigated should be detected and described.

Depending on the task at hand the appropriate degree of accuracy of the system description has to be chosen. For example in a simulation of technical combustion processes not every single molecule has to be modeled on a microscopic level. Instead, usually only a few characteristic macroscopic variables are used to describe the phenomenological system behavior of interest.

Most such processes are multi-scale problems where the gap between atomic properties and thermodynamic variables like species concentrations, temperature, pressure, and energy has to be bridged. The art of modeling now consists in finding an appropriate level of abstraction for describing the aspects which are to be investigated.

There are two general approaches to model multi-scale problems. One of them is the so called *top-down approach*. First a rough model of the system phenomena is set up which then is refined according to experimental observations. In the other approach, called *bottom-up approach*, a system is modeled using first-principle physical and chemical laws, taking into account as much detailed knowledge as available. The latter approach is more precise and describes a system more accurately than the first one. However, the necessary data are not available in every case and it generally leads to large-scale models with huge numbers of vari-

ables. For efficient spatiotemporal simulations these high-dimensional models are inappropriate, in particular if they involve multiple time scales.

This is where model reduction comes into play. The goal of all model reduction techniques in chemical kinetics is to find a low-dimensional approximation of a reaction mechanism which contains all the essential information to still describe the full mechanism accurately under certain restrictions. For a kinetic model set up by the bottom-up approach this is equivalent to identifying the essential degrees of freedom with respect to the system properties of interest. In the case of chemical kinetics those properties of interest are often related to long-term dynamics. To construct low-dimensional approximations, many model reduction techniques therefore make use of intrinsic multiple time scales. The time scale separation is exploited depending on the subject of investigation. If for example the long-term behavior of a system is to be studied, fast transient dynamical modes are assumed to be relaxed within the model approximation.

In the context of chemical reaction systems which can be described by ordinary differential equations, the goal of model reduction is then to replace the original system of differential equations by one of lower dimension without losing too much key information about the system dynamics.

## 1.1 Model Reduction Approaches for Chemical Kinetics

An overview of the most common model reduction techniques and their underlying concepts is given in [OM98, GKZ04].

Most modern model reduction techniques are based on one of the following three general strategies: lumping, sensitivity analysis and time scale analysis.

*Lumping* transforms the original vector of species to a vector of “pseudo-species” which is of lower dimension. This transformation is usually based on physical properties or the reactivity of the components. The resulting differential equation system of lower dimension should be easier to solve and have fewer parameters which need to be determined experimentally than the original problem.

From the mathematical point of view there exist two types of lumping techniques. In continuous lumping techniques one lump is the integral of a set which is defined by a continuous index variable, whereas lumps in discrete lumping as described

e.g. in [LR91, LRT94] are functions of the individual chemical species. The components of a complex mixture are transformed based on their reactivities using matrix operations.

One big drawback of lumping techniques in general is the loss of information about specific reactants and individual reactions which cannot be incorporated in the reduced model. In addition, it is quite difficult to determine appropriate lumping schemes for large nonlinear reaction networks and the lumped model may still contain multiple time scales.

*Sensitivity Analysis* aims at eliminating insignificant species and redundant reactions from the original system based on their impact on designated important species. Turanyi et al. [Tur90] and Rabitz et al. [RKD83] apply this idea for the purpose of model reduction in chemical kinetics.

After identifying the “important species” determined by their relevance for the problem to be investigated, “necessary species” mainly influencing these important ones are determined by analyzing the Jacobian of the system. Redundant reactions are determined through principal component analysis of the rate sensitivity matrix. Reactions can be eliminated if their contributions measured by the singular values are below a desired precision threshold. With increasing number of important species, the extent of model reduction possible by sensitivity analysis decreases. Therefore sensitivity analysis is often coupled with the quasi-steady-state approximation [TPT<sup>+</sup>92] (see also below).

*Time scale analysis* identifies multiple time scales being present in a kinetic system and utilizes the different time scales to reduce the original system by decoupling them explicitly. This is possible since multiple time scales cause a successive bundling of phase space trajectories on low-dimensional manifolds by relaxation of fast processes before thermodynamic equilibrium is reached in isolated chemical reaction systems. Therefore these low-dimensional manifolds describe the long-term dynamics by enslaving the fast (relaxed) processes to the slow ones. These manifolds will be referred to as *attracting slow manifolds* in this work.

One of the first methods using time scale analysis for model reduction was the quasi-steady-state assumption (QSSA) [Bod13, CU13]. In the QSSA approach fast intermediate species, which after an initial transient period can be considered instantaneously reacting compared to the remaining slow ones, are eliminated. The right hand sides of the corresponding differential equations are assumed to be zero. This does not mean that the concentration of the species is constant,

but rather that the rates of change of those species depend on the changes of the other concentrations with time (enslavement). Differential equations for those fast species are replaced by algebraic ones and the result is a system of differential algebraic equations with the number of differential variables being reduced to the number of the slow variables.

In contrast to the QSSA approach where the fast species are eliminated, in the partial equilibrium approximation (PEA) [MM13] fast elementary reaction steps are assumed to be relaxed to equilibrium immediately.

Since the identification of slow and fast modes “by hand” is difficult and time-consuming, especially for large-scale mechanisms, the implementation of automatic methods based on time scale analysis is crucial in practice.

Computational singular perturbation (CSP) methods [HG99, LG94], inertial manifold approaches [YTB<sup>+</sup>95], intrinsic low-dimensional manifolds (ILDm) [MP92, Maa95, Maa98] and ideas from optimization [PZ99, And00] are just some of the most important computational methods which have been developed subsequently for efficient model reduction.

In simulations of technical processes usually all species have to be considered, not only the ones included in the reduced mechanism. Hence the concentrations for the species of the full mechanism need to be automatically calculated as functions of the species of the reduced mechanism. This so-called *automatic species reconstruction* is implemented in most of the model reduction algorithms, independent of the concepts the methods are based on.

One of the most popular techniques for model reduction which came into broad application is the ILDM method developed by Maas and Pope in 1992 [MP92]. The central idea of the ILDM method is to exploit time scale separation in order to locally transform a system of ordinary differential equations (ODE) describing the kinetics of a chemical system into a system of differential algebraic equations (DAE). For an autonomous ODE system, its local time scales can be determined using the eigenvalues of the Jacobian of the right hand side at a reference point. In order to identify these local time scales, a small virtual perturbation of the reference state is considered and its propagation over time is analyzed. This propagation of the perturbation can be described to first order as a variational differential equation involving the Jacobian. For a sufficiently small time horizon in which the system stays close to the reference value, the Jacobian matrix can be considered as constant. In this case the variational differential equation

describing the propagation of the perturbation is a linear differential equation, whose solution is a linear combination of terms depending exponentially on the eigenvalues of the Jacobian.

The characteristic time scales are defined by the real parts of the eigenvalues of the Jacobian. In order to identify and decouple the slow and the fast modes of the system, a coordinate transformation of the original system of ordinary differential equations based on the local eigenvector analysis for the Jacobian at the reference point is performed.

First an orthogonal similarity transformation is applied to the Jacobian resulting in an upper triangular block matrix which has real Schur form and whose diagonal elements then can be arranged according to the order of magnitude of the real parts of the eigenvalues. Thus the diagonal of the resulting matrix consists of two upper-quasi-triangular sub-matrices representing the slow and the fast modes. In a second step the coupling matrix can be eliminated.

The matrix now has diagonal block structure with two entirely decoupled sub-matrices – one representing the slow, the other one representing the fast modes. Applying the coordinate transformation described above to the original ODE system, one can identify “fast” modes and “slow” modes. Once the slow and fast modes are identified, the system is locally projected onto the slow subspace under the assumption that the fast modes are and remain fully relaxed. Assuming the fast modes as relaxed, the ODE system then can be approximated by a DAE system with the number of differential equations corresponding to the number of slow mode variables and the algebraic part “enslaving” the fast modes to the slow ones. The algebraic equation system defines the ILDM.

The ILDM is widely applied in practice, especially in combustion [Maa98]. It can be performed prior to computational fluid dynamics (CFD) simulations involving detailed chemical reaction mechanisms. Chemical source terms of the full mechanism can be stored in a lookup table as functions of the slow variables in the reduced mechanism. Nevertheless it has some major shortcomings. Since it is a local method, the ILDM attracts trajectories only locally. Furthermore it is not invariant, i.e. a system being on the ILDM may leave the manifold again e.g. due to eigenvalue crossing. Another problem is that the implemented numerical algorithm for the solution of the ILDM needs good initial guesses within a continuation approach since the algebraic equation system is nonlinear and usually of high dimension.

Apart from methods making explicit use of time scale separation as e.g. the ILDM method, also geometrical approaches to simplification of kinetics have been investigated [Fra88, RF90, RF91, DS99, SD01]. Attracting low-dimensional manifolds (ALDM) in the phase space of concentrations are used to describe the simplified models. Unlike the ILDM which is only a local attractor, the ALDM represents the exact manifold which globally attracts trajectories. One approach to construct such ALDMs was proposed by Fraser and Roussel [Fra88, RF90, RF91]. Fraser and Roussel consider the attracting slow manifold as a stable fixed point of a functional mapping in phase space. In an iterative scheme to generate the attracting slow manifold time is eliminated from the system of differential equations, resulting in orbit equations in phase space.

For the functional iteration scheme to actually converge to the attracting manifold it is crucial to start the iteration with a good initial guess which is not an actual trajectory, because for actual trajectories the iteration equation is always met. If taking the ILDM as an initial guess, the convergence to the attracting slow manifold is usually guaranteed for the modified version of Fraser's algorithm [DS99, SD01]. In the modified version of Fraser's algorithm the original representation of the manifold through analytic functions is replaced by a more facile numerical representation to enable the application to larger kinetic systems. For the independent variables a grid is adopted upon which the dependent concentrations are numerically computed.

Another approach which is not explicitly based on time scale separation is the rate-controlled constrained-equilibrium (RCCE) method first proposed by Keck and Gillespie [KG71] and later further developed by Hamiroune et al. [HBMK98]. It is based on the thermodynamic principle of maximum entropy.

For this method it is assumed that slow reactions of a complex chemical reaction mechanism impose constraints on its composition which delay relaxation to the final equilibrium. At the same time the fast reactions equilibrate the system subject to those constraints. Thus the relaxation to the complete equilibrium takes place through a sequence of constrained-equilibrium states. The overall rate of change is controlled by the slowly changing or non-changing constraints. Obvious constraints are for example the ones which ensure the conservation of elements. In order to find the constrained-equilibrium composition, either the entropy of the system is maximized (see Section 2.3.2 for a discussion of the thermodynamic significance of entropy) or the Gibbs free energy minimized (see also Section 2.3.2) subject to the constraints using the Lagrange multipliers method.

To describe the original system within a desired accuracy, in most cases it is sufficient to refer to a much smaller number of constraints than the number of species in the system which can result in efficient model reduction.

Ren et al. introduced the invariant constrained equilibrium edge preimage curve (ICE-PIC) method in 2006 [RPVG06]. The ICE-PIC method is based on an invariant constrained equilibrium edge (ICE) manifold (of dimension  $n$ ) which is generated by the reaction trajectories emanating from its  $(n - 1)$ -dimensional edge. On the edge, the composition of the system is in a constrained equilibrium state. Based on the ICE manifold, species can be reconstructed locally from a reduced description without having to generate the whole manifold (as necessary e.g. for global species reconstruction methods as the Fraser Algorithm [Fra88]). For an arbitrarily given reduced composition the corresponding feasible region is defined as the union of compositions in the realizable region (comprising all possible and physically allowed full compositions of the system), which have that specified reduced composition. Starting from any point in the feasible region, one can trace the reaction trajectory backwards in time until it intersects with the boundary of the realizable region. The union of all those trajectories is called the preimage manifold (PIM). If considering an isobaric, isothermal system, the so-called constrained equilibrium manifold (CEM) is the union of all points in the feasible region, at which the Gibbs function has a minimum. In the case of an adiabatic system instead of an isothermal one, the same concept applies, but then based on the maximization of entropy instead of minimizing the Gibbs function. The intersection of the PIM and the CEM is called constrained equilibrium preimage curve (CE-PIC).

For fixed values of the reduced composition one can calculate the corresponding constrained equilibrium point lying on the CEM by using e.g. the constraint potential method [Pop04]. Starting from the feasible end, which is the constrained equilibrium point, the CE-PIC is followed backwards in time to its boundary end which is the intersection of the CEM, the PIM, and the boundary of the realizable region. Then the reaction trajectory is followed forward in time starting at this so called generating boundary point until it intersects the feasible region. The invariant constrained equilibrium edge manifold (ICE manifold), which is the union of all the trajectories emanating from generating boundary points in the edge of the constrained equilibrium manifold, is the resulting description of the attracting low-dimensional manifold and the points on the ICE represent the values of all variables of the full reconstructed composition.

A model reduction approach involving optimization was presented by Petzold and Zhu [PZ99] and later discussed by Androulakis [And00]. Binary variables are introduced to denote the existence/nonexistence of species or reactions in a reduced model. The objective is to choose for given initial conditions a specified number of reactions for the reduced mechanism such that the behavior of the resulting reduced system is as close as possible to the behavior of the original one.

One of the problems of this optimization approach is that the reduced mechanism strongly depends on the initial conditions used during the reduction process. It is not clear what the range of the initial conditions is for which the reduced mechanism is a good approximation of the original system. In addition, the problem to be solved in order to obtain a reduced model is a nonlinear integer programming problem. Such integer optimization problems are difficult to solve and require considerable computational effort.

## 1.2 Model Reduction in Applications

One of the classical areas where model reduction is applied is combustion [WMD06]. To describe important combustion properties like flame propagation, flame structure and pollutant formation accurately, detailed chemical reaction mechanisms are needed for numerical simulation. Such detailed reaction mechanisms often involve hundreds of species and thousands of reactions. Furthermore physical transport also needs to be included in the simulation. Those aspects combined lead to a high-dimensional, non-linear description of reactive flows involving Navier-Stokes partial differential equations of reaction-diffusion-convection type [WMD06].

In most of the chemical systems considered multiple time scales are present, which leads to extremely stiff chemical source terms. Therefore implicit integration methods or extremely small time steps are required in order to numerically solve those equations accurately. For systems containing hundreds of species, the solution is very time consuming and it is impossible to obtain results for these systems in a reasonable simulation time.

Hence in practical applications model reduction methods (as described above) are used to automatically reduce the dimensionality of chemical mechanisms. In most reduction techniques applied chemical systems are described by only a few

degrees of freedom, the so-called reaction progress variables. For those progress variables the Navier-Stokes reactive flow equations are solved using common computational fluid dynamics (CFD) software [WMD06]. For simulation, the CFD programs utilized need information about the chemical source terms depending on all the species concentrations, not only of the concentrations of the reaction progress variables. Therefore the remaining species concentrations are calculated as functions of the progress variables. This is usually done under the assumption that the system dynamics already have relaxed to some low-dimensional manifold. The so defined slow manifold is parametrized by the progress variables and can be computed before starting the CFD calculations.

Species reconstruction needs to be very fast if it is done online during simulation. This is a general problem of all model reduction techniques described above. When using the algorithm developed by Roussel and Fraser [Fra88, RF90, RF91] it is even impossible to locally reconstruct the species. It is only possible to calculate the attracting low-dimensional manifold as a whole. Reconstructing species locally is – in principle – possible with the ILDM method [MP92, Maa95, Maa98], but for this purpose good initial values are required. In practical applications therefore a continuation method is used. Starting near equilibrium, ILDM points are successively calculated using already computed neighboring points as initial values. For the needed range of reaction progress variable concentrations, ILDM points are often calculated and tabulated before starting a CFD simulation. During simulation the CFD program just reads the necessary composition of concentrations from the ILDM table. Using the ICE-PIC method [RPVG06] it is also possible to locally reconstruct species concentrations, but it seems to be computationally highly expensive.

## 1.3 Trajectory-Based Model Reduction via Optimization Approaches

In this work a model reduction approach first introduced by Lebiez [Leb04, LRK06, Leb06] is further developed which can perform local species reconstruction overcoming some of the problems of the ILDM or the Roussel-Fraser algorithm. Similar to the ICE-PIC technique proposed by Ren et al. [RPVG06] our method does not necessarily require good initial values. Even far away from equilibrium species can be reconstructed without necessarily having to use a con-

tinuation strategy starting close to equilibrium or even having to calculate the whole manifold. Although good initial guesses are not required, one can reduce the computational effort considerably by using an initial value embedding (IVE) strategy for solving neighboring problems [Die01]. Thus both tabulation of reduced mechanisms and CFD programs may use the IVE technique for efficient offline or online species reconstruction.

The general concept of our approach is to find special trajectories which account for maximal relaxation of a chemical system under constraints imposed by given arbitrary values of the progress variables. These trajectories are determined by minimizing the “distance” of the chemical system from its attractor – namely thermodynamic equilibrium – in an appropriate sense. A priori some species need to be specified as reaction progress variables with fixed initial concentrations representing the reduced model. Then both a special trajectory – in the following also called *optimal trajectory* – converging towards the equilibrium point in phase space and the initial values of the remaining species are calculated at the same time as the solution of an optimization problem involving ordinary differential equation constraints given by the chemical reaction mechanism.

In the course of this work three different criteria for the characterization of maximal relaxation of chemical systems are investigated and tested for a realistic hydrogen combustion mechanism.

The first criterion is based on the thermodynamic “principle of minimum entropy production” [KP98]. De Donder [dDvR36] first introduced the concept of chemical affinity as the driving force of chemical reactions towards equilibrium. For elementary reaction steps, chemical affinity can be related to the concept of entropy production. Since near thermodynamic equilibrium according to the second law of thermodynamics the entropy production rate is decreasing on the way towards equilibrium, maximal relaxation of a chemical system can be characterized by a minimal total entropy production rate along trajectories.

All chemical systems are dissipative systems whose phase space volume is contracting on the way towards equilibrium due to relaxation of chemical forces (affinities) which drive chemical reactions. Since the change of the phase space volume can be described by the divergence of right hand side of the ODE modeling the chemical system, another possibility to characterize maximally relaxed chemical forces is to minimize the contraction of the phase space volume which is equivalent to minimizing the divergence.

For the third criterion presented, the concept of “force being equal to curvature” already exploited in physics, e.g. in Einstein’s general theory of relativity [Ein16], is transferred to the field of chemical systems. The curvature of trajectories in phase space is considered. Minimal curvature (corresponding to minimal “chemical forces”) of the trajectories can be interpreted on the one hand as a minimal overall “velocity” of the reaction system, or on the other hand as a geodesic minimizing the length of the path between two points on a curved manifold for an appropriate Riemannian metric. If the Riemannian metric applied is modified by introducing entropy production rates as a weighting factor, a very accurate description of the reduced model is obtained by the optimal trajectories as approximations of the slow attracting manifold.

Since many disadvantages in the application of previous model reduction techniques can be overcome with our approach, it has a great potential to become a valuable tool for practical applications.

## 1.4 Outline of this Thesis

In Chapter 2 the theoretical background necessary for the development of our model reduction technique is presented. First a brief introduction to the theory of dynamical systems is given (Section 2.1). Important concepts of thermodynamics are introduced in Section 2.3, especially the concept of minimal entropy production is presented here in detail. To be able to further develop appropriate model reduction criteria, some basic definitions and concepts from differential geometry are presented in Section 2.2. In the last section of Chapter 2 (Section 2.4) mathematical background on nonlinear optimization problems involving ordinary differential equation constraints is given and a powerful approach to solve these problems based on the multiple shooting method combined with an initial value embedding strategy for parametric optimization is presented.

In Chapter 3 the different criteria for our new trajectory-based model reduction approach to find an accurate low-dimensional representation of a large-scale model are investigated and applied to a realistic hydrogen combustion mechanism. First the concept of entropy production in dissipative chemical systems is discussed in Section 3.1. The criterion which is based on minimal contraction of the phase space volume of dissipative systems is discussed in Section 3.2. In Section 3.3 finally the concept of curvature from differential geometry is combined with the

thermodynamic concept of entropy production to yield a very successful criterion for describing the reduced model.

# Chapter 2

## Theoretical Background

### 2.1 Dynamical Systems

Model reduction techniques developed in the course of this work are applied to problems arising from the field of chemical kinetics. In nature, and in particular in the field of chemistry, most processes depend on time. The theory of dynamical systems [Wig96, Ver00] aims at analyzing qualitative properties of mathematical models which describe and predict the behavior of such time-dependent processes. The dynamical systems considered here are chemical reaction mechanisms, which can be described by ordinary differential equations (ODE) of the form

$$\dot{c} := \frac{dc}{dt} = f(c(t)) , \quad (2.1)$$

with  $c(t) \in U \subset \mathbb{R}^n$  and  $t \in \mathbb{R}$ .  $U$  is an open set in  $\mathbb{R}^n$  and the vector function  $f : U \rightarrow \mathbb{R}^n$  is continuous in  $c$ .

A solution of (2.1) is a mapping

$$\begin{aligned} c : I &\rightarrow \mathbb{R}^n \\ t &\mapsto c(t) \end{aligned}$$

from some interval  $I \subset \mathbb{R}$  into  $\mathbb{R}^n$ , such that  $c(t)$  satisfies equation (2.1), i.e.

$$\dot{c}(t) = f(c(t)) .$$

$c$  can be geometrically interpreted as a curve in  $\mathbb{R}^n$  whose tangent vectors at each point of the curve are given by (2.1). Therefore (2.1) can also be referred to as a *vector field*.

**Definition 2.1** (Autonomous Differential Equation)

A differential equation or system of ordinary differential equations  $\dot{c} = f(c, t)$  is said to be **autonomous**, if it does not explicitly depend on time  $t$ , i.e.

$$\dot{c} = f(c), \quad c \in \mathbb{R}^n. \quad (2.2)$$

**Definition 2.2** (Phase Space)

The space of dependent variables  $c(t)$  of ODE (2.2) is called **phase space**.

A solution of (2.2) for a specified initial condition  $c(t_0) = c_0$  is often denoted as  $c(t, c_0)$ . If displaying the initial values is not crucial for the problem at hand, the solution may also be referred to as  $c(t)$ .

**Definition 2.3** (Trajectory)

The solution  $c(t, c_0)$  of (2.2) with initial value  $c_0$  is also called **trajectory** or **phase curve** through the point  $c_0$  at  $t = t_0$ .

**Definition 2.4** (Orbit through  $c_0$ )

For a point  $c_0$  in the phase space of (2.2), the **orbit**  $O(c_0)$  **through**  $c_0$  is defined as the set of points in phase space which lie on a trajectory passing through  $c_0$ . For  $c_0 \in U \subset \mathbb{R}^n$ , the orbit through  $c_0$  is given by

$$O(c_0) = \{c \in \mathbb{R}^n \mid c = c(t, c_0), t \in I\}.$$

By specifying an initial condition, one can distinguish between solutions of the general ODE (2.2).

**Definition 2.5** (Initial Value Problem (IVP))

The ODE system (2.2) together with a specified initial condition

$$\begin{aligned} \dot{c}(t) &= f(c(t)) \\ c(t_0) &= c_0 \end{aligned} \quad (2.3)$$

is called **initial value problem (IVP)**.

If the right hand side  $f$  of an initial value problem satisfies a few simple regularity conditions, it can be shown that it has exactly one solution:

**Theorem 2.6**

Let  $f$  be defined and continuous on the strip  $S := \{(t, c) \mid t_0 \leq t \leq t_f, c \in \mathbb{R}^n\}$  with  $t_0$  and  $t_f$  finite. Let there be a constant  $L < \infty$  such that

$$\|f(c_1(t)) - f(c_2(t))\| \leq L \|c_1(t) - c_2(t)\| \quad (2.4)$$

for all  $t \in [t_0, t_f]$  and all  $c_1, c_2 \in \mathbb{R}^n$  (“Lipschitz condition”).

Then for every  $t \in [t_0, t_f]$  and every  $c_0 \in \mathbb{R}^n$  there exists exactly one function  $c(t)$  such that

1.  $c(t)$  is continuous and continuously differentiable for  $t \in [t_0, t_f]$ ,
2.  $\dot{c}(t) = f(c(t))$  for  $t \in [t_0, t_f]$ ,
3.  $c(t_0) = c_0$ .

*Proof.* See e.g. Henrici [Hen62]. □

A sufficient condition for (2.4) in Theorem 2.6 is continuous differentiability of  $f$  with respect to  $c$ .

When modeling chemical reaction systems, often the problem of *stiffness* is observed. For this phenomenon there is no standardized definition. Curtiss and Hirschfelder [CH52] introduced the term of stiff equations as equations for which implicit methods perform better than explicit ones.

One of the definitions for stiff differential equations commonly used is the following:

**Definition 2.7** (Stiff Differential Equation)

An ordinary differential equation  $\dot{c}(t) = f(c(t))$  is called **stiff** (along a solution  $c(t)$ ), if there are eigenvalues  $\lambda(t)$  of the Jacobian  $\frac{df}{dc}(c(t))$  for which holds

$$\frac{\max_{\operatorname{Re}\lambda(t)<0} |\operatorname{Re}\lambda(t)|}{\min_{\operatorname{Re}\lambda(t)<0} |\operatorname{Re}\lambda(t)|} \gg 1. \quad (2.5)$$

In the context of chemical systems, an ODE system modeling the chemical kinetics is called **stiff**, if both very fast and very slow processes are present in the system. This is the case for the example reaction mechanism considered in the course of this work.

One of the methods used for numerically solving stiff differential equations is the so-called BDF (Backward Differentiation Formulae) method, which will be presented in Section 2.4.3.

**Definition 2.8** (Two-Point Boundary Value Problem)

If not only the initial conditions at  $t = t_0$  are specified, but also conditions at the end point  $t = t_f$ , then the problem

$$\begin{aligned} \dot{c} &= f(c(t)), & t &\in [t_0, t_f] \\ 0 &= r(c(t_0), c(t_f)) \end{aligned} \quad (2.6)$$

is called a **two-point boundary value problem**.

A two-point boundary value problem is a special case of a more general formulation of boundary value problems (see e.g. Stoer [SB96]). For this work, however, only two-point boundary value problems as presented here are of importance.

**Definition 2.9** (Equilibrium Solution)

A solution  $\bar{c} \in \mathbb{R}^n$  of (2.2), which satisfies

$$f(\bar{c}) = 0$$

is called **equilibrium solution**.

An equilibrium solution does not change in time. Therefore, sometimes an equilibrium solution is also referred to as *fixed point*, *critical point* or *steady state*.

For dynamical systems these equilibrium solutions are of particular interest since they can be used to analyze the structure of the system's phase space in their surrounding. An important property is the stability of such an equilibrium solution. One distinguishes between two kinds of stability:

**Definition 2.10** (Lyapunov Stability)

An equilibrium solution  $\bar{c}$  of (2.2) is called **stable** (or **Lyapunov stable**), if for any given  $\varepsilon > 0$  there exists a  $\delta = \delta(\varepsilon) > 0$  such that  $\|\bar{c} - c(t)\| < \varepsilon$  for any other solution  $c(t)$  of (2.2) which satisfies  $\|\bar{c} - c(t_0)\| < \delta$  with  $t > t_0$ ,  $t_0 \in \mathbb{R}$ .

This means that  $\bar{c}$  is *stable* if solutions starting "close" to  $\bar{c}$  at a given time will remain close to  $\bar{c}$  for all later times.

**Definition 2.11** (Asymptotic Stability)

An equilibrium solution  $\bar{c}$  of (2.2) is called **asymptotically stable** if it is Lyapunov stable and if there exists a constant  $b > 0$  such that if  $\|\bar{c} - c(t_0)\| < b$  holds, then  $\lim_{t \rightarrow \infty} \|\bar{c} - c(t)\| = 0$ .

In other words,  $\bar{c}$  is *asymptotically stable* if nearby starting trajectories all actually converge to  $\bar{c}$  as  $t \rightarrow \infty$ .

**Definition 2.12** (Lyapunov Function)

For a dynamical system  $\dot{c} = f(c)$ ,  $c \in \mathbb{R}^n$ , with a fixed point  $\bar{c}$ , a  $C^1$ -function  $V : U \rightarrow \mathbb{R}$  on some neighborhood  $U$  of  $\bar{c}$  is called **Lyapunov function**, if the following properties are satisfied

- $V(\bar{c}) = 0$ ,

- $V(c) > 0$  if  $c \neq \bar{c}$ ,
- $\dot{V}(c) \leq 0$  in  $U \setminus \{\bar{c}\}$ .

**Theorem 2.13**

If for a fixed point  $\bar{c}$  of  $\dot{c} = f(c)$  there exists a Lyapunov function  $V$ , then  $\bar{c}$  is a stable fixed point.  $\bar{c}$  is asymptotically stable, if  $\dot{V}(c) < 0$  in  $U \setminus \{\bar{c}\}$  holds.

*Proof.* See [Wig96]. □

**Definition 2.14** (Invariant Set)

A set  $S \subset \mathbb{R}^n$  is called **invariant** under  $\dot{c} = f(c)$ , if for any  $c_0 \in S$  it holds that  $c(t, c_0) \in S$  for all  $t \in \mathbb{R}$ .

**Definition 2.15** (Invariant Manifold)

An invariant set  $S \subset \mathbb{R}^n$  is said to be a  $C^k$  ( $k \geq 1$ ) **invariant manifold**, if  $S$  has the structure of a  $C^k$  differentiable manifold (see also Section 2.2).

**Definition 2.16** (Attracting Set / Attractor)

A closed and invariant set  $\mathcal{A}$  is called an **attracting set** if there exists an open neighborhood  $U$  of  $\mathcal{A}$  such that all solutions  $c(t)$  with initial solution in  $U$  will eventually enter  $\mathcal{A}$ , i.e.

$$\lim_{t \rightarrow \infty} d(c(t), \mathcal{A}) = 0 \quad (2.7)$$

with a given metric  $d$ .

An **attractor** of (2.2) is an attracting set which contains a dense orbit.

**Example 2.17**

Every asymptotically stable fixed point is an attractor.

**Definition 2.18** (Dissipative/Conservative System)

A dynamical system  $\dot{c} = f(c)$  is called **dissipative**, if the volume of its phase space contracts along a trajectory.

If a dynamical system is volume preserving, it is called **conservative**.

For dissipative systems the generalized divergence is less than zero, i.e.

$$\sum_{i=1}^n \frac{\partial f_i}{\partial c_i} < 0 \quad (2.8)$$

The change of the volume of an element in phase space caused by the flow of an autonomous differential equation (2.2) can be characterized by the following lemma.

**Lemma 2.19**

Consider the equation  $\dot{c} = f(c)$  in  $\mathbb{R}^n$  and a domain  $D(0)$  in  $\mathbb{R}^n$  which is supposed to have a volume  $v(0)$ . The flow defines a mapping  $g$  of  $D(0)$  into  $\mathbb{R}^n$ ,  $g : \mathbb{R}^n \rightarrow \mathbb{R}^n$ ,  $D(t) = g^t D(0)$ . For the volume  $v(t)$  of the domain  $D(t)$  we have

$$\frac{dv}{dt}\Big|_{t=0} = \int_{D(0)} \nabla \cdot f \, dc$$

$$(\nabla \cdot f = \partial f_1 / \partial c_1 + \partial f_2 / \partial c_2 + \cdots + \partial f_n / \partial c_n = \operatorname{div} f)$$

*Proof.* See Verhulst [Ver00].

□

## 2.2 Differential Geometry

In this section first basic concepts from topology are explained as the basis for concepts from differential geometry. At the end of the section, Riemannian manifolds will be defined. With a suitable Riemannian metric, the concept of Riemannian manifolds will be used in Chapter 3 to derive a new approach to model reduction by minimizing the length of a curve on a Riemannian manifold.

**Definition 2.20** (Topological Space)

A **topological space** is a set  $X$  together with a set  $\mathcal{T}$  whose elements are subsets of  $X$ , such that

- $\emptyset \in \mathcal{T}$
- $X \in \mathcal{T}$
- If  $U_j \in \mathcal{T}$  for all  $j \in J$ , then  $\bigcup_{j \in J} U_j \in \mathcal{T}$
- If  $U \in \mathcal{T}$  and  $V \in \mathcal{T}$ , then  $U \cap V \in \mathcal{T}$

The set  $\mathcal{T}$  is called a **topology** on  $X$ .

Elements of  $\mathcal{T}$  are called **open sets** of  $X$ .

A subset  $C \subset X$  is called a **closed set**, if the complement  $X \setminus C$  is an open set.

**Definition 2.21** (Basis of Topology)

A **basis**  $\mathcal{B}$  for a topological space  $X$  with topology  $\mathcal{T}$  is a collection of open sets in  $\mathcal{T}$  such that every open set in  $\mathcal{T}$  can be written as a union of elements of  $\mathcal{B}$ .

**Definition 2.22** (Locally Euclidean)

A topological space  $X$  is called **locally Euclidean**, if for every point  $x \in X$  there is a neighborhood  $U \subseteq X$ , a subset  $V \subseteq \mathbb{R}^n$ , and a homeomorphism  $\phi : U \rightarrow V$ .

In other words, a locally Euclidean space  $X$  is a topological space which locally “looks” like  $\mathbb{R}^n$ .

The integer  $n$  is called *dimension* of  $X$  and must be the same for all points  $x \in X$ .

**Definition 2.23** (Hausdorff Space)

A topological space  $X$  is called **Hausdorff space**, if for any given  $x, y \in X$ ,  $x \neq y$ , there exist disjoint open sets  $U$  and  $V$  (that is,  $U \cap V = \emptyset$ ) such that  $x \in U$  and  $y \in V$ .

In other words,  $X$  is a Hausdorff space if any two distinct points of  $X$  can be separated by neighborhoods.

**Definition 2.24** (Second Countable Space)

A topological space  $X$  is said to be **second countable** if it has a countable basis of the topology.

For example the Euclidean space  $\mathbb{R}^n$  with its usual topology is second countable. The usual base of open balls is not countable, but restricted to the set of all open balls with rational radii and whose centers have rational coordinates, the set is countable and still forms a base since  $\mathbb{Q}^n \subset \mathbb{R}^n$  is dense in  $\mathbb{R}^n$ .

**Definition 2.25** (Topological Manifold)

A **topological manifold** is defined to be a locally Euclidean Hausdorff space which is second countable.

**Definition 2.26** (Paracompact)

A topological space  $X$  is said to be **paracompact** if every open cover of  $X$  has a locally finite open refinement.

This means, if  $(U_i)_{i \in I}$  is any family of open subsets of  $X$  such that  $\bigcup_{i \in I} U_i = X$ , then there exists another family  $(V_i)_{i \in I}$  of open sets such that  $\bigcup_{i \in I} V_i = X$ ,  $V_i \subset U_i$  for all  $i \in I$  and any specific  $x \in X$  is in  $V_i$  for only finitely many  $i$ .

**Definition 2.27** (Metrizability)

A topological space  $X$  with topology  $\mathcal{T}$  is said to be **metrizable** if there is a metric

$$d: X \times X \rightarrow [0, \infty)$$

such that the topology induced by  $d$  is  $\mathcal{T}$ .

**Definition 2.28** (Regular Space)

A topological space  $X$  is a **regular space** if for every closed set  $F$  and every point  $x \notin F$  there are two disjoint open sets  $U$  and  $V$  such that  $F \subseteq V$  and  $x \in U$ .

**Theorem 2.29** (Urysohn's Metrization Theorem)

Every second countable, regular Hausdorff space is metrizable.

*Proof.* See e.g. Willard [Wil70]. □

**Remark 2.30**

A manifold is metrizable if and only if it is paracompact.

**Remark 2.31**

It follows from Theorem 2.29 and Definition 2.25 that every topological manifold is metrizable.

Similar to the spherical earth being described by flat maps or charts which are collected in an atlas, a manifold can also be described by mathematical maps, so-called coordinate charts (which by Definition 2.32 are homeomorphisms), collected in a mathematical atlas. In general it is impossible to describe a manifold with just one chart - as it is impossible to describe the earth by just one flat map. Information about the global structure of a manifold being constructed from multiple overlapping charts can be retrieved from the regions where the charts overlap.

**Definition 2.32** (Coordinate Chart)

For any neighborhood  $U$  of a point  $x \in M$  on a topological manifold  $M$ , a homeomorphism  $\phi : U \rightarrow \phi(U) \subset \mathbb{R}^n$  is called a **coordinate chart** on  $U$ .

**Definition 2.33** (Atlas)

An **atlas**  $\mathcal{A}$  is a collection of charts  $\phi : U_\phi \rightarrow \mathbb{R}^n$  whose domains cover the manifold  $M$ , i.e.  $M = \bigcup_{\phi} U_\phi$ .

**Definition 2.34** (Transition Function)

Given two charts  $\phi : U \rightarrow \phi(U) \subset \mathbb{R}^n$  and  $\psi : V \rightarrow \psi(V) \subset \mathbb{R}^n$  with overlapping domains  $U$  and  $V$ , then there is a **transition function** or a **change of coordinates**  $\psi \circ \phi^{-1} : \phi(U \cap V) \rightarrow \mathbb{R}^n$ .

Such a map is a homeomorphism between open subsets of  $\mathbb{R}^n$ .

**Definition 2.35** (Differentiable Manifold / Smooth Manifold)

A **differential manifold** is a topological manifold whose transition functions are all differentiable.

A  $C^k$   **$n$ -manifold** is a topological  $n$ -manifold for which all transition functions are  $C^k(\mathbb{R}^n)$ .

A **smooth manifold**, or  $C^\infty$  **manifold** is a differentiable manifold for which all the transition functions are smooth.

In the remainder of this thesis a manifold will denote a smooth manifold, and a  $n$ -manifold a smooth manifold of dimension  $n$ .

**Example 2.36**

If a  $k$ -dimensional submanifold  $M$  of  $\mathbb{R}^n$  is locally described by  $M = \{x \in \mathbb{R}^n \mid F(x) = 0\}$ , with  $F : \mathbb{R}^n \rightarrow \mathbb{R}^{n-k}$  being a continuously differentiable submersion (i.e. the differential  $DF$  is surjective and  $\text{rank}(DF) = n - k$ ),

then the (implicit) equation  $F(x^1, \dots, x^n) = 0$  can be *locally* rearranged into the explicit form

$$\begin{aligned} x^{k+1} &= x^{k+1}(x^1, \dots, x^n) \\ &\vdots \\ x^n &= x^n(x^1, \dots, x^n) \end{aligned}$$

Then the mapping  $(x^1, \dots, x^k) \mapsto (x^1, \dots, x^k, x^{k+1}, \dots, x^n)$  is a parametrization and the mapping  $(x^1, \dots, x^n) \mapsto (x^1, \dots, x^k)$  is the corresponding chart.

This is exactly the parametrization used for species reconstruction in many model reduction techniques (see Chapters 1 and 3).

**Definition 2.37** (Tangent Space - Definition as Directions of Curves)

Suppose  $M$  is a  $C^k$  manifold ( $k \geq 1$ ) and  $x$  is a point in  $M$ . Pick a chart  $\phi : U \rightarrow \mathbb{R}^n$  where  $U$  is an open subset of  $M$  and  $x \in U$ . Suppose two curves  $\gamma_1 : (-1, 1) \rightarrow M$  and  $\gamma_2 : (-1, 1) \rightarrow M$  with  $\gamma_1(0) = \gamma_2(0) = x$  are given such that  $\phi \circ \gamma_1$  and  $\phi \circ \gamma_2$  are both differentiable at 0. Then  $\gamma_1$  and  $\gamma_2$  are called **tangent** at 0 if  $(\phi \circ \gamma_1)'(0) = (\phi \circ \gamma_2)'(0)$ .

This defines an equivalence relation on the set of such curves, and the equivalence classes are called the **tangent vectors** of  $M$  at  $x$ . The equivalence class of the curve  $\gamma$  is written as  $\gamma'(0)$ . The **tangent space** of  $M$  at  $x$ , denoted by  $T_x M$ , is defined as the set of all tangent vectors at  $x$ ; it does not depend on the choice of chart  $\phi$ .

Apart from this geometric definition of the tangent space, there also exist an algebraic definition via derivations and a physical definition. Since all the definitions are isomorphic and only the geometric one is needed in this work, for the other definitions we refer to e.g. Kühnel [Küh06].

To define vector space operations on  $T_x M$ , we use a chart  $\phi : U \rightarrow \mathbb{R}^n$  and define the map  $(d\phi)_x : T_x M \rightarrow \mathbb{R}^n$  by  $(d\phi)_x(\gamma'(0)) = (\phi \circ \gamma)'(0)$ . It turns out that this map is bijective and can thus be used to transfer the vector space operations from  $\mathbb{R}^n$  over to  $T_x M$ , turning the latter into an  $n$ -dimensional real vector space. One can show that this construction does not depend on the particular chart  $\phi$  chosen.

**Definition 2.38** (Tangent Bundle)

Let  $M$  be a differentiable manifold. The **tangent bundle**  $TM$  of  $M$  is (as a set)

defined as the disjoint union of all the tangent spaces to  $M$ ,

$$TM = \coprod_{x \in M} T_x M . \quad (2.9)$$

This means the tangent bundle of  $M$  can be described as the set of pairs  $\{(x, v) \mid x \in M, v \in T_x M\}$  and there exists a natural projection  $\pi : TM \rightarrow M$  which maps  $(x, v)$  to the base point  $x$ .

**Definition 2.39** (Vector Bundle)

A **real vector bundle** is given by

- a topological space  $X$  (the “base space”) and a topological space  $E$  (the “total space”),
- a continuous surjective map  $\pi : E \rightarrow X$  (the “projection”),
- and the structure of a real vector space on the so-called fiber  $\pi^{-1}(x)$  for all  $x \in X$ ,

which satisfy the following compatibility condition:

For every point  $x \in X$  there exists an open neighborhood  $U$ , a natural number  $n$ , and a homeomorphism  $\phi : U \times \mathbb{R}^n \rightarrow \pi^{-1}(U) \subseteq E$  such that for every point  $x \in U$  holds:

- $(\pi \circ \phi)(x, v) = x$  for all vectors  $v \in \mathbb{R}^n$ ,
- and the map  $v \mapsto \phi(x, v)$  yields an isomorphism between the vector spaces  $\mathbb{R}^n$  and  $\pi^{-1}(x)$ .

In other words, a vector bundle is a geometrical construct where to every point of a topological space (for example a manifold) a vector space is “attached” in a compatible way such that all those vector spaces “glued together” form another topological space.

A typical example of a vector bundle is the tangent bundle of a differential manifold: to every point of the manifold the tangent space of the manifold at that point is “attached”.

**Definition 2.40** (Sections)

Given a vector bundle  $\pi : E \rightarrow X$  and an open subset  $U$  of  $X$ , we can consider **sections** of  $\pi$  on  $U$ , i.e. continuous functions  $s : U \rightarrow E$  with  $\pi \circ s = id_U$ .

Essentially, a section assigns to every point of  $U$  a vector from the attached vector space in a continuous manner.

For example sections of the tangent bundle of a differential manifold are vector fields on that manifold.

**Definition 2.41** (Riemannian Manifold and Riemannian Metric)

A **smooth Riemannian manifold** is a pair  $(M, g)$ , where  $M$  is a smooth manifold and  $g$  a **Riemannian metric**, i.e. a smooth section of the positive-definite quadratic forms on the tangent bundle, meaning a mapping

$$g_x : T_x M \times T_x M \rightarrow \mathbb{R}$$

which depends smoothly on  $x$  and defines in every point  $x \in M$  an inner product with the following properties:

1.  $g_x(X, Y) = g_x(Y, X)$  for all  $X, Y$  (i.e.  $g_x$  is symmetric),
2.  $g_x(X, X) > 0$  for all  $X \neq 0$ , (i.e.  $g_x$  is positive definite).

This allows the definition of various geometric notions such as angles, lengths of curves, volumes, and curvature on a manifold.

**Definition 2.42** (Parametric Curve)

For  $n \in \mathbb{N}$ ,  $k \in \mathbb{N} \cup \{\infty\}$  and  $t \in I = [a, b]$  ( $a, b \in \mathbb{R}, a < b$ ), a vector valued function  $\gamma : I \rightarrow \mathbb{R}^n$  of class  $C^k$  is called a **parametric curve of class  $C^k$**  or a  $C^k$  **parametrization** of the curve  $\gamma$ .

$t$  is called the **parameter** of the curve  $\gamma$ .

$\gamma(I)$  is called the **image** of the curve.

The parameter  $t$  is often thought of as representing time, and the curve  $\gamma(t)$  as the trajectory of a moving point in phase space.

**Definition 2.43** (Reparametrization)

Two parametric curves of class  $C^k$ ,  $\gamma_1 : I_1 \rightarrow \mathbb{R}^n$  and  $\gamma_2 : I_2 \rightarrow \mathbb{R}^n$ , are said to be **equivalent** if there exists a bijective  $C^k$  map  $\phi : I_1 \rightarrow I_2$  such that  $\phi'(t) \neq 0$ , ( $t \in I_1$ ), and  $\gamma_2(\phi(t)) = \gamma_1(t)$ , ( $t \in I_1$ ).

$\gamma_2$  is said to be a **reparametrization** of  $\gamma_1$ . This reparametrization of  $\gamma_1$  defines an equivalence relation on the set of all parametric  $C^k$  curves. The equivalence class is called a  $C^k$  **curve**.

**Definition 2.44** (Length and Natural Parametrization)

The **length**  $L$  of a smooth curve  $\gamma : [a, b] \rightarrow \mathbb{R}^n$  can be defined as

$$L(\gamma) = \int_a^b \|\gamma'(t)\| dt \tag{2.10}$$

The length of a curve is invariant under reparametrization and therefore a differential geometric property of the curve.

For each regular  $C^k$  curve  $\gamma : [a, b] \rightarrow \mathbb{R}^n$  we can define a function

$$s(t) = \int_a^t \|\gamma'(\tau)\| \, d\tau .$$

Writing  $\gamma(t) = \bar{\gamma}(s(t))$ , we get a reparametrization  $\bar{\gamma}$  of  $\gamma$  which is called **natural, arc-length** or **unit speed parametrization**.

$s(t)$  is called the **natural parameter** of  $\gamma$ .

Often the natural parametrization is preferred because the natural parameter  $s(t)$  traverses the image of  $\gamma$  at unit speed such that  $\|\bar{\gamma}'(s(t))\| = 1$ , ( $t \in [a, b]$ ).

In practice it is often very difficult to explicitly calculate the natural parametrization of a curve, but it is useful for theoretical arguments. For a given parametrized curve  $\gamma(t)$  the natural parametrization is unique up to shift of parameter.

A Riemannian metric  $g$  on  $M$  itself is not a distance metric on  $M$ . However, on a connected manifold every Riemannian metric on  $M$  induces a distance metric on  $M$ , given by

$$d(x, y) = \inf \{ L(\gamma) \mid \gamma : [0, 1] \rightarrow M, \gamma(0) = x, \gamma(1) = y \} . \quad (2.11)$$

where  $\gamma$  is a continuously differentiable curve joining  $x$  and  $y$ , and  $L(\gamma)$  is the length of the curve  $\gamma$  defined as

$$L(\gamma) = \int_0^1 \sqrt{g_{\gamma(t)}(\dot{\gamma}(t), \dot{\gamma}(t))} \, dt , \quad (2.12)$$

and  $\dot{\gamma}$  is the derivative of the curve  $\gamma$  with respect to  $t$ , i.e. its tangent vector.

Here in (2.12) the Euclidean norm used in Definition 2.44 (equation (2.10)) is replaced by a different norm involving the Riemannian metric  $g$ .

**Definition 2.45** (Geodesic)

A **geodesic** is a locally length-minimizing curve.

In the plane, geodesics are straight lines. The geodesics in a curved space depend on the Riemannian metric, which affects the notions of distance.

On a Riemannian manifold  $M$  a geodesic is a curve  $\gamma(t)$  which minimizes the length of the curve (2.12).

## 2.3 Fundamentals of Physical Chemistry

### 2.3.1 Chemical Kinetics

The behavior of chemical systems over time can be modeled by ordinary differential equations. For this purpose complex chemical reaction systems are decomposed into single elementary reaction steps. In order to illustrate how the differential equations describing the chemical kinetics are derived from the reaction mechanism, a bimolecular elementary reaction step



is considered in this section.

A reaction between the substances A and B only can take place, if molecules of A and B collide with sufficient energy. The frequency of collision is proportional both to the concentration of A and to the concentration of B. Since the reaction rate is proportional to the frequency of successful collisions, the reaction rate  $R_{\rightarrow}$  of the forward reaction in (2.13) can be expressed as

$$R_{\rightarrow} = k_1 c_A c_B \quad (2.14)$$

with  $c_A$  and  $c_B$  being the concentrations of A and B, and  $k_1$  being the constant of proportionality (*reaction rate coefficient*).

For the reaction rate coefficients  $k_1$  of the forward and  $k_2$  of the backward reaction, and for the concentrations  $c_A$ ,  $c_B$ ,  $c_C$ , and  $c_D$  of the substances A, B, C and D, the following ordinary differential equations hold:

$$\begin{aligned} \frac{dc_A}{dt} = \frac{dc_B}{dt} &= -k_1 c_A c_B + k_2 c_C c_D \\ \frac{dc_C}{dt} = \frac{dc_D}{dt} &= +k_1 c_A c_B - k_2 c_C c_D \end{aligned}$$

In thermodynamic equilibrium forward and backward reaction rates are equal, i.e.

$$k_1 c_A c_B = R_{\rightarrow} = R_{\leftarrow} = k_2 c_C c_D, \quad (2.15)$$

which is equivalent to the relation

$$\frac{c_C c_D}{c_A c_B} = \frac{k_1}{k_2} =: K, \quad (2.16)$$

the so-called *law of mass action* proposed by C.M. Guldberg and P. Waage in 1864 with equilibrium constant  $K$ .

In general,  $k_1$  and  $k_2$  depend on the temperature  $T$  via the so-called *Arrhenius law* [AP06]. However, in this work the temperature is assumed to be constant at all times.

In the general case, based on similar assumptions, one can demonstrate that the right hand side of an ODE system modeling chemical kinetics has polynomial form and therefore is of class  $C^\infty$ . Hence, the corresponding autonomous IVP has a unique solution according to Theorem 2.6 (see Section 2.1).

### 2.3.2 Thermodynamics

In thermodynamics (from the Greek *thermos* meaning heat and *dynamics* meaning power) the effects on a system by changes in its surroundings such as e.g. temperature, pressure, or volume are studied at a macroscopic scale.

**Definition 2.46** (Isolated / Closed / Open System)

*Isolated systems* exchange neither energy nor matter with their exterior.

*Closed systems* exchange energy with their exterior but not matter.

*Open systems* exchange both energy and matter with their exterior.

In most thermodynamic considerations, the fundamental laws of thermodynamics play an important role.

#### The Fundamental Laws of Thermodynamics

The first law postulates the conservation of energy.

**Theorem 2.47** (First Law of Thermodynamics)

*In an isolated system the internal energy is conserved in any thermodynamic process.*

Theorem 2.47 states that the change in the internal energy of a closed thermodynamic system is equal to the sum of the amount of heat energy supplied to the system and the work done on the system, i.e. different forms of energy can be converted into each other, but no energy is lost.

In mathematical terms the First Law of Thermodynamics can be formulated with differentials as follows:

$$dU = \delta Q + \delta W, \quad (2.17)$$

where  $dU$  can be interpreted as an infinitesimal increase in the internal energy of the system,  $\delta Q$  as an infinitesimal amount of heat added to the system, and  $\delta W$  as an infinitesimal amount of work done on the system.

Since the first law does not yield any information about the spontaneity and directionality of chemical reaction systems, the Second Law of Thermodynamics needs to be consulted additionally.

**Theorem 2.48** (Second Law of Thermodynamics)

*“It is impossible that, at the end of a cycle of changes, heat has been transferred from a colder to a hotter body without at the same time converting a certain amount of work into heat.” Clausius (1822 - 1888)*

*“A perpetual motion machine of the second kind is impossible.” Max Planck (1858 - 1947)*

Using the state function entropy  $S$  defined in (2.19), the Second Law of Thermodynamics can also be formulated as

**Theorem 2.49** (Second Law of Thermodynamics (in terms of entropy))

*The entropy  $S$  of an isolated system not at equilibrium will tend to increase over time, approaching a maximum value at equilibrium.*

Another state function, the Gibbs free energy  $G$ , can be used to investigate the spontaneity and directionality of chemical reactions.

**Definition 2.50** (Gibbs Free Energy)

*For closed systems, the **Gibbs free energy**  $G$  is defined as*

$$G := H - T S \quad (2.18)$$

*with the enthalpy  $H = U + pV$  ( $U$  being the internal energy of the system,  $p$  the pressure, and  $V$  the volume), temperature  $T$  and entropy  $S$ .*

**Theorem 2.51** (Second Law of Thermodynamics (in terms of Gibbs free energy))

*The Gibbs free energy of a system under constant pressure and constant temperature will tend to decrease over time, approaching a minimum value at equilibrium.*

Or as Clausius stated the Second Law of Thermodynamics in 1865 in general:

*“For any process the sum of all entropy changes occurring as a result of the process is greater than zero and approaches zero in the limit as the process becomes reversible.”*

Details on the significance of the Laws of Thermodynamics can be found in [AP06].

## Entropy and Entropy Production

The *entropy*  $S$  can be interpreted as a measure of energy dissipation in a system. It is a thermodynamic *state function* which only depends on the initial and final states of a process, and does not depend on the way the states were reached.

Rudolf Clausius (1822 - 1888) defined the change of entropy  $dS$  of a thermodynamic system during a reversible process as

$$dS = \frac{dQ_{\text{rev}}}{T}, \quad (2.19)$$

where  $dQ_{\text{rev}}$  is the amount of heat reversibly introduced to the system, and  $T$  is the absolute temperature.

The total change in entropy of a system in nonequilibrium thermodynamics can also be expressed as

$$dS = dS_i + dS_e. \quad (2.20)$$

$dS_e$  is the change of a system's entropy due to exchange of energy and matter with its environment. In an isolated system  $dS_e$  is zero.  $dS_i$  is the change of entropy due to irreversible processes within the system.

In the following,  $dS_e$  is also referred to as *entropy flow* and  $dS_i$  as *entropy production*.

If in a system the change of mole numbers  $dN_k = d_i N_k + d_e N_k$  (with  $d_i N_k$  being the change due to irreversible chemical reactions and  $d_e N_k$  being the change due to the exchange of matter with the exterior, which is zero in a closed system) is due to irreversible chemical reactions, then the resulting entropy production  $dS_i$  can be written as

$$dS_i = - \frac{\sum_{k=1}^n \mu_k d_i N_k}{T}, \quad (2.21)$$

where  $\mu_k$  is the chemical potential of species  $k$  defined as the Gibbs free energy per mole number (see e.g. Atkins [AP06] for a more precise definition and inter-

pretation).

In the following only isolated systems with  $dS_e = 0$  are considered.

According to the Second Law of Thermodynamics it holds that

$$dS_i \geq 0 \quad (2.22)$$

for any spontaneous process [GP71].

De Donder [Don27, dDvR36] was the first one to introduce the concept of *affinity* of a chemical reaction, which enables us to express the entropy production  $dS_i$  as a product of a thermodynamic force and a thermodynamic flow. The affinity

$$A = \sum_{k=1}^n \nu_k \mu_k \quad (2.23)$$

with the stoichiometric coefficients  $\nu_k$  and the chemical potentials  $\mu_k$  of the participating species is the driving force for chemical reactions. If in a system the affinity is not equal to zero, this system is not in thermodynamic equilibrium and chemical reactions will occur driving the system towards equilibrium until the affinity vanishes.

This concept of affinity can be related to the concept of entropy production by reformulating equation (2.21). The rate of change of entropy  $dS_i/dt$  can be written in terms of affinity  $A$ :

$$\frac{dS_i}{dt} = \left( \frac{A}{T} \right) \frac{d\xi}{dt} \geq 0. \quad (2.24)$$

One can see that the entropy production rate here is a product of the thermodynamic force  $A/T$  and the corresponding thermodynamic flow  $d\xi/dt$  generated by the force  $A/T$ .

Considering the elementary reaction step (2.13) with forward reaction rate  $R_{\rightarrow} = k_1 c_A c_B$  and backward reaction rate  $R_{\leftarrow} = k_2 c_C c_D$ , the velocity of the reaction is

$$\frac{1}{V} \frac{d\xi}{dt} = R_{\rightarrow} - R_{\leftarrow} = k_1 c_A c_B - k_2 c_C c_D. \quad (2.25)$$

with  $V$  being the volume of the system considered. In the course of this work, the volume of the systems considered is assumed to be constant.

According to [KP98], the affinity of (2.13) can be expressed as

$$A = R T \ln \left( \frac{R_{\rightarrow}}{R_{\leftarrow}} \right). \quad (2.26)$$

The entropy production rate per unit volume is then

$$\frac{1}{V} \frac{dS_i}{dt} = \frac{1}{V} \frac{A}{T} \frac{d\xi}{dt} = R (R_{\rightarrow} - R_{\leftarrow}) \ln \left( \frac{R_{\rightarrow}}{R_{\leftarrow}} \right), \quad (2.27)$$

where  $R$  is the gas constant.

For several elementary reaction steps, affinities are additive. Therefore the total entropy production rate of a chemical reaction system can be calculated explicitly, if all the kinetic data is available and all the  $n$  elementary reaction steps of the system are known:

$$\frac{1}{V} \frac{dS_i}{dt} = \frac{1}{V} \sum_{k=1}^n \frac{A_k}{T} \frac{d\xi_k}{dt} = \sum_{k=1}^n R (R_{k \rightarrow} - R_{k \leftarrow}) \ln \left( \frac{R_{k \rightarrow}}{R_{k \leftarrow}} \right). \quad (2.28)$$

A detailed derivation of (2.27) and (2.28) can be found in [KP98].

## 2.4 Optimization

In this section the theoretical basis will be presented which is necessary to understand the mathematical concepts from optimization theory used in this work. The general structure of optimization problems involving ODE constraints is stated and a direct solution approach is explained. For the numerical solution of our optimization problems, the originally infinite dimensional problem is parametrized using the direct multiple shooting approach originally developed by Bock and Plitt [Pli81, BP84, Boc87] and extended by Leineweber [Lei99]. The resulting problem is a finite dimensional nonlinear programming (NLP) problem which can be solved using e.g. the Sequential Quadratic Programming (SQP) algorithm developed by Han and Powell [Han76, Pow78].

In the software package MUSCOD-II [Lei95, Lei99] originally developed for solving large scale optimal control problems for nonlinear dynamical systems, the direct multiple shooting approach is implemented and combined with the SQP algorithm to solve the optimization problem. For the example applications presented in this work, MUSCOD-II is used to solve optimization problems with ODE constraints.

### 2.4.1 Problem Formulation

The chemical reaction systems considered in this work can be described by ODE models of the form:

$$\dot{x}(t) = f(x(t), p) \quad (2.29)$$

$x \in \mathbb{R}^{n_x}$  denotes the differential state vector,  $t \in \mathbb{R}$  the time, and  $p \in \mathbb{R}^{n_p}$  is a vector of constant system parameters such as for example reaction coefficients in chemical kinetics.

#### Objective Functional

The objective of an ODE-constrained optimization problem in general is to minimize overall “costs”. Those costs are usually defined by a general Bolza-type objective functional on a time horizon  $[t_0, t_f]$  with start time  $t_0$  and final time  $t_f$  as

$$\int_{t_0}^{t_f} L(x(t), p) dt + E(x(t_f), p) . \quad (2.30)$$

$L(x(t), p)$  is called the *Lagrange term* and  $E(x(t_f), p)$  the *Mayer term* of the objective function.

In this work, we only consider Lagrange-type objective functionals since our problem formulations do not involve extra final state costs that should be minimized.

### Path Constraints and Boundary Conditions

On the time horizon of interest, the state trajectories  $x(t)$  often have to satisfy so-called *path constraints*

$$g(x(t), p) \geq 0, \quad \forall t \in [t_0, t_f]. \quad (2.31)$$

In the case of a chemical system those constraints may for example be positivity of chemical species concentrations.

Often there are also boundary conditions, which for the purpose needed in this work can be written in the general form

$$r_0(x(t_0), p) + r_f(x(t_f), p) = 0. \quad (2.32)$$

These constraints may include conservation equations (of mass) or can be used e.g. to fix concentrations of specific species at the initial or at the final time.

### Problem Formulation

Now the ODE-constrained optimization problem needed for the applications in this work can be formulated as

$$\min_{x(\cdot), (T)} \int_0^T L(x(t), p) dt \quad (2.33a)$$

subject to

$$\dot{x}(t) - f(x(t), p) = 0, \quad \forall t \in [0, T] \quad (2.33b)$$

$$g(x(t), p) \geq 0, \quad \forall t \in [0, T] \quad (2.33c)$$

$$r_0(x(0), p) + r_f(x(T), p) = 0 \quad (2.33d)$$

for the initial time  $t_0 = 0$  and the final time  $t_f = T$ .

The functions  $L$ ,  $r_0$ ,  $r_f$ , and  $g$  are assumed to be continuously differentiable and for  $f$  the usual assumptions (see Theorem 2.6) shall hold which ensure local

existence and uniqueness of the solution  $x$  for given initial values  $x(0) = x_0$ . The length  $T$  of the time interval can either be fixed or also be an additional degree of freedom subject to optimization.

## 2.4.2 Direct Multiple Shooting Discretization

To numerically solve an infinite dimensional optimization problem of the type (2.33), algorithms based on the *direct* solution approach have turned out to be particularly successful. In the direct approach the originally infinite dimensional problem has to be transformed into a finite dimensional nonlinear programming problem (NLP) which then in turn can be solved using standard NLP solution techniques.

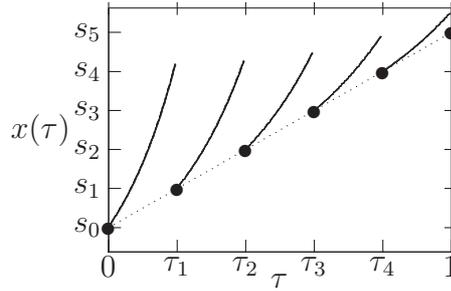
Strategies for formulating the finite-dimensional NLP can be divided into *sequential* and *simultaneous* approaches.

In the *sequential approach* a simulation of the dynamic model equations is performed to eliminate the state trajectories. Simulation and optimization calculations are performed sequentially – one after the other. A significant drawback of this method however is that poor initial guesses may cause a strong nonlinearity of the resulting NLP and a poor convergence behavior – especially for unstable systems.

This difficulty is avoided by the *simultaneous approach*. In the simultaneous approach first the state trajectory is discretized, then the dynamic model equations and the optimization problem are solved simultaneously in a large constrained NLP. The discretized state variables become part of the optimization variables. Thus nonlinearity and instability can be better controlled.

For all calculations carried out in this work the *direct multiple shooting* method is applied to solve optimization problems. It was first presented by Plitt in 1981 [Pli81]. The optimization interval is divided into several subintervals (see Figure 2.1). On each subinterval an independent initial value problem is solved. Continuity of the state trajectory from one subinterval to the next is guaranteed by imposing matching conditions which enter the optimization problem as additional equality constraints.

The direct multiple shooting approach originally developed by Bock [Boc87, BP84] is implemented in the software package MUSCOD-II by Leineweber [Lei95, Lei99].



**Figure 2.1:** State parametrization ( $N = 5$ ).

For discretizing the state variables (see Figure 2.1), a multiple shooting grid with multiple shooting nodes at time points  $\tau_0, \dots, \tau_N$ ,

$$0 = \tau_0 < \tau_1 < \dots < \tau_N = T$$

is introduced. Then the problem is decomposed into several initial value problems (IVP). On each interval  $[\tau_i, \tau_{i+1}]$ , ( $i = 0, \dots, N - 1$ ) the IVP

$$\begin{aligned} \dot{x}_i(\tau) &= f(x_i(\tau), p) \\ x_i(\tau_i) &= s_i \end{aligned} \quad (2.34)$$

has to be solved. Those IVPs can be solved simultaneously, since their solution trajectories  $x_i(\tau)$  on  $[\tau_i, \tau_{i+1}]$  only depend on the parameters  $s_i$ .

To enforce continuity of the differential state trajectory, the *matching conditions*

$$s_{i+1} = x_i(\tau_{i+1}; s_i), \quad i = 0, \dots, N - 1 \quad (2.35)$$

have to be met. They require the differential node value  $s_{i+1}$  to be equal to the final value of the previous trajectory  $x_i(\tau_{i+1})$ . Likewise the value of the first differential node  $s_0$  should be equal to the initial value  $x_0$  of the original problem,

$$s_0 = x_0. \quad (2.36)$$

Equations (2.35) and (2.36) remove the additional degrees of freedom introduced to the problem by adding the parameters  $s_i$  ( $i = 0, \dots, N$ ) at the multiple shooting nodes.

Using the same multiple shooting grid  $\tau_0, \dots, \tau_N$ , the infinite dimensional path constraints are also transformed into  $N + 1$  vector inequality constraints

$$g(s_i, p) \geq 0, \quad i = 0, 1, \dots, N, \quad (2.37)$$

and the boundary conditions are transformed into

$$r_0(s_0, p) + r_f(s_N, p) = 0 . \quad (2.38)$$

When substituting the independent trajectories  $x_i(\tau)$  into the Lagrange term  $L$  in (2.30)

$$\sum_{i=0}^{N-1} \int_{\tau_i}^{\tau_{i+1}} L(x_i(\tau), p) \, d\tau , \quad (2.39)$$

the objective contributions  $L_i(s_i) = \int_{\tau_i}^{\tau_{i+1}} L(x_i(\tau), p) \, d\tau$  can be calculated simultaneously in analogy to the solution of the independent IVPs in (2.34) by integration.

The resulting finite dimensional NLP can now be reformulated as

$$\min_{s_0, \dots, s_N} \sum_{i=0}^{N-1} \int_{\tau_i}^{\tau_{i+1}} L(x_i(\tau), p) \, d\tau \quad (2.40a)$$

$$\text{subject to} \quad 0 = x_i(\tau_{i+1}; s_i) - s_{i+1}, \quad i = 0, \dots, N-1 \quad (2.40b)$$

$$0 = x_0 - s_0 \quad (2.40c)$$

$$0 \leq g(s_i, p), \quad i = 0, \dots, N, \quad \tau \in [\tau_i, \tau_{i+1}] \quad (2.40d)$$

$$0 = r_0(s_0, p) + r_f(s_N, p) \quad (2.40e)$$

Because of the multiple shooting parametrization, NLP (2.40) has more variables and more equality constraints than the original formulation (2.33). But due to the decoupled structure of the problem a condensing algorithm can be used [Boc87]. The resulting condensed problem is numerically only slightly more expensive to solve than solving the original problem e.g. with the single shooting method.

### 2.4.3 Backward Differentiation Formulae

For the numerical solution of the initial value problems (2.34) the implicit DAE solver DAESOL [Bau99, BBS99, Alb05] is integrated in the software package MUSCOD-II [Lei95, Lei99]. Solving stiff differential equations with explicit methods to a desired degree of accuracy would force the step size to be too small. Therefore implicit integration algorithms are necessary to efficiently solve stiff differential equations such as e.g. chemical kinetics with multiple time scales present. In particular multistep BDF (backward differentiation formulae) methods which are implemented in DAESOL have beneficial stability properties (see e.g. [DB02]).

**Definition 2.52** (Linear Multistep Method (LMM))

In a general **linear multistep method (LMM)** for the numerical solution of an initial value problem (2.34) an approximate value  $\eta_{m+k}$  of  $x(t_{m+k})$  is computed from  $k$  ( $k \geq 2$ ) given approximate values  $\eta_j$  of  $x(t_j)$ ,  $j = m, m+1, \dots, m+k-1$ , at equidistant points  $t_j = t_0 + jh$  by the following general formula

$$\sum_{l=0}^k \alpha_l \eta_{m+l} = h \sum_{l=0}^k \beta_l f(\eta_{m+l}), \quad m = 0, \dots, N-k \quad (2.41)$$

with  $\alpha_l, \beta_l \in \mathbb{R}$ ,  $\alpha_k \neq 0$  and  $|\alpha_0| + |\beta_0| \neq 0$ .

If  $\beta_k = 0$  this is an explicit method, if  $\beta_k \neq 0$  the method is implicit.

BDF methods are linear multistep methods whose idea consists in finding a polynomial which interpolates the  $(k+1)$  values  $\eta_m, \dots, \eta_{m+k}$  and satisfies the differential equation at  $t = t_{m+k}$ .

**Definition 2.53** (BDF method)

The  **$k$ -step BDF method** is defined by the  $k$  starting values  $\eta_m, \dots, \eta_{m+k-1}$  specified and the formula

$$\sum_{l=0}^k \alpha_l \eta_{m+l} = h f(\eta_{m+l}), \quad m = 0, \dots, N-k \quad (2.42)$$

with  $\alpha_l \in \mathbb{R}$ , and  $\alpha_0, \alpha_k \neq 0$ .

For a more detailed introduction to BDF methods and an extensive analysis of stability of multistep methods we refer to [HNW93, HW96].

## 2.4.4 Local Optimality Conditions

Problem (2.40) is a special formulation of a general NLP problem of the form

$$\begin{aligned} & \min_{\omega \in \mathbb{R}^{n_\omega}} F(\omega) \\ \text{subject to} & \quad G(\omega) = 0 \\ & \quad H(\omega) \geq 0 \end{aligned} \quad (2.43)$$

where the functions  $F : \mathbb{R}^{n_\omega} \rightarrow \mathbb{R}$ ,  $G : \mathbb{R}^{n_\omega} \rightarrow \mathbb{R}^{n_G}$  and  $H : \mathbb{R}^{n_\omega} \rightarrow \mathbb{R}^{n_H}$  are assumed to be twice continuously differentiable.

The gradient of a scalar function  $F$  is defined to be a column vector, and the

gradient of a vector function  $G$  is defined here as the transpose of the Jacobian matrix

$$\nabla_{\omega} G(\omega) := \left( \frac{\partial G}{\partial \omega}(\omega) \right)^T \quad (2.44)$$

**Definition 2.54** (Feasibility and Optimality)

The set  $S := \{ \omega \mid G(\omega) = 0, H(\omega) \geq 0 \}$  is called **feasible set**, and  $\omega^* \in S$  is called **feasible point**.

A feasible point  $\omega^*$  is called a **local minimizer** of NLP (2.43) if there exists a neighborhood  $U_{\varepsilon}(\omega^*)$  of  $\omega^*$  such that  $F(\omega^*) \leq F(\omega)$  for all  $\omega \in U_{\varepsilon}(\omega^*) \cap S$ .

The constraint  $H_i(\omega) \geq 0$  is called **active**, if  $H_i(\omega) = 0$ .

All active inequality constraints at the feasible point  $\omega$  are denoted by  $H^{\text{act}}(\omega)$ .

A feasible point  $\omega$  is called a **regular point**, if the Jacobian of the active constraints,  $\nabla \tilde{G}(\omega)^T$ , has full rank (with  $\tilde{G}(\omega) := \begin{pmatrix} G(\omega) \\ H^{\text{act}}(\omega) \end{pmatrix}$ ).

To formulate the first order necessary and second order sufficient optimality conditions for (2.43), the **Lagrangian function**  $\mathcal{L}$  is defined as

$$\mathcal{L}(\omega, \lambda, \mu) := F(\omega) - \lambda^T G(\omega) - \mu^T H(\omega). \quad (2.45)$$

**Theorem 2.55** (Karush-Kuhn-Tucker Necessary Conditions)

Suppose that  $\omega^*$  is a local minimizer of (2.43) and a regular point. Then there exist Lagrange multiplier vectors  $\lambda^* \in \mathbb{R}^{n_G}$  and  $\mu^* \in \mathbb{R}^{n_H}$  such that  $(\omega^*, \lambda^*, \mu^*)$  satisfy the following necessary conditions:

$$\nabla_{\omega} \mathcal{L}(\omega^*, \lambda^*, \mu^*) = 0 \quad (2.46a)$$

$$G(\omega^*) = 0 \quad (2.46b)$$

$$H(\omega^*) \geq 0 \quad (2.46c)$$

$$\mu^* \geq 0 \quad (2.46d)$$

$$\mu_j^* H_j(\omega^*) = 0, \quad j = 1, \dots, n_H \quad (2.46e)$$

*Proof.* See e.g. Nocedal and Wright [NW99]. □

**Definition 2.56** (Karush-Kuhn-Tucker Point)

A triple  $(\omega^*, \lambda^*, \mu^*)$  which satisfies the necessary Karush-Kuhn-Tucker conditions (2.46) is called a **stationary point** or **KKT point**.

The active set vector function  $H^{act}(\omega^*)$  at a KKT point  $(\omega^*, \lambda^*, \mu^*)$  can be divided into *strongly* active parts (with positive multipliers) and *weakly* active parts (with zero multipliers):

$$H^{act}(\omega^*) =: \begin{pmatrix} H^{s.act} \\ H^{w.act} \end{pmatrix}(\omega^*).$$

**Theorem 2.57** (Strong Second Order Sufficient Conditions)

For a point  $\omega^* \in \mathbb{R}^{n_\omega}$  to be a local minimizer of (2.43), the following sufficient conditions have to be met:

- $\omega^*$  is a regular point,
- there exist Lagrange multiplier vectors  $\lambda^* \in \mathbb{R}^{n_G}$  and  $\mu^* \in \mathbb{R}^{n_H}$  such that the KKT conditions (2.46) are satisfied, and
- the Hessian matrix  $\nabla_\omega^2 \mathcal{L}(\omega^*, \lambda^*, \mu^*) := \frac{\partial^2 \mathcal{L}}{\partial \omega^2}(\omega^*, \lambda^*, \mu^*)$  is positive definite on the null space  $\mathcal{N}^s := \{ \Delta\omega \in \mathbb{R}^{n_\omega} \mid \nabla_\omega \tilde{G}^s(\omega^*)^T \Delta\omega = 0 \}$  of the linearized strongly active constraints

$$\tilde{G}^s(\omega^*) := \begin{pmatrix} G \\ H^{s.act} \end{pmatrix}(\omega^*),$$

i.e. for every non-zero vector  $\Delta\omega \in \mathcal{N}^s$  it holds that

$$\Delta\omega^T \nabla_\omega^2 \mathcal{L}(\omega^*, \lambda^*, \mu^*) \Delta\omega > 0.$$

For a more detailed introduction to (nonlinear) optimization see e.g. Nocedal and Wright [NW99].

### 2.4.5 Sequential Quadratic Programming

One of the most effective methods to solve nonlinearly constrained optimization problems is the sequential quadratic programming (SQP) approach. If a NLP problem as stated in (2.43) is highly nonlinear and difficult to solve, the KKT point  $(\omega^*, \lambda^*, \mu^*)$  of the NLP can be found by iteratively solving quadratic programming (QP) problems.

At each iterate  $y_k = (\omega_k, \lambda_k, \mu_k)$  the original problem is approximated by a quadratic programming subproblem whose minimizer is used to define a new iterate  $y_{k+1}$ .

For every iterate  $y_k$  the following quadratic subproblem is solved:

$$\begin{aligned} \min_p \quad & \frac{1}{2} p^T W_k p + \nabla_{\omega} F(\omega_k)^T p \\ \text{subject to} \quad & G(\omega_k) + \nabla_{\omega} G(\omega_k)^T p = 0 \\ & H(\omega_k) + \nabla_{\omega} H(\omega_k)^T p \geq 0 \end{aligned} \tag{2.47}$$

The solution  $(p_k, \tilde{\lambda}_k, \tilde{\mu}_k)$  of (2.47) yields the new iterate

$$y_{k+1} = y_k + \alpha_k \Delta y_k \tag{2.48}$$

where  $\alpha_k \in (0, 1]$  is a relaxation factor that can be determined by a line search procedure, and

$$\Delta y_k = \begin{pmatrix} p_k \\ \Delta \lambda_k \\ \Delta \mu_k \end{pmatrix} := \begin{pmatrix} p_k \\ \tilde{\lambda}_k - \lambda_k \\ \tilde{\mu}_k - \mu_k \end{pmatrix}$$

is the search direction.

If the solution of the subproblem yields  $p_k = 0$ , the new iterate  $y_{k+1}$  cannot be improved. In this case the current iterate  $y_k$  is a KKT point of the original problem which meets the first order necessary conditions (2.46). However, since in numerical optimization  $p_k = 0$  will never be exactly fulfilled, one requires  $p_k$  only to be smaller than the so called KKT tolerance,  $p_k \leq TOL$ .

Formally equivalent to solving a NLP using the SQP method is applying Newton's method to the KKT conditions (2.46) of the original problem (2.43).

There are many variants of the SQP method. They all differ by the choice of the step length  $\alpha_k$  and the choice of the so called Hessian matrix  $W_k$ . Only one of them is explicitly mentioned here because of its good theoretical properties as local quadratic convergence and its application in parametric optimization (see Section 2.4.6): the *full step exact Hessian SQP method*. It was introduced by Wilson [Wil63] and is exploited e.g. in Diehl's real-time iteration approach to nonlinear model predictive control (NMPC) problems [Die01]. In Chapter 3 Diehl's iteration approach is applied to example applications for model reduction in a modified form.

As the name already suggests, in the full step exact Hessian SQP method  $\alpha_k := 1$ , and  $W_k := \nabla_{\omega}^2 \mathcal{L}(\omega^*, \lambda^*, \mu^*)$  is the exact Hessian of the Lagrangian function. In practice, however, usually update formulas are used to approximate the Hessian matrix since calculating the exact Hessian is often numerically expensive.

### 2.4.6 Initial Value Embedding Strategy

In [Die01] and [DBS<sup>+</sup>02] an initial value embedding (IVE) strategy is described for the case of a real-time optimal control problem. Combined with the direct multiple shooting approach (see Section 2.4.2) the initial value embedding strategy is a powerful tool to minimize the online computational effort for those problems. Subsequent problems to be solved only differ in one parameter, which can be included in the problem formulation as an additional NLP-variable and which is fixed by a trivial equality constraint. In the SQP framework therefore derivatives with respect to that parameter are computed. Formally based on a prediction from the previous problem solution, an excellent initial guess is provided for the current problem. That way precalculated information (e.g. Hessians, gradients and QP presolves for iterated reference trajectories) is used to minimize computational costs.

The initial value embedding strategy was implemented in the first version of the online direct multiple shooting method by Diehl [Die98].

The same initial value embedding strategy is employed in this work to solve a sequence of neighboring optimization problems. For the applications presented in Chapter 3, consecutive problems need to be solved which only differ slightly in the initial value  $x_0$ .

We consider the NLP formulation (2.40) as an embedded problem formulation of the form

$$\min_{s_0 \in \mathbb{R}^{n_x}, \tilde{\omega} \in \mathbb{R}^{(n_\omega - n_x)}} F(s_0, \tilde{\omega}) \quad (2.49a)$$

$$\text{subject to } s_0 - x_0 = 0 \quad (2.49b)$$

$$\tilde{G}(s_0, \tilde{\omega}) = 0 \quad (2.49c)$$

$$\tilde{H}(s_0, \tilde{\omega}) \geq 0 \quad (2.49d)$$

with  $\omega = (s_0, \tilde{\omega})$ . The actual value of the parameter which distinguishes between the different problems – the initial value – is fixed by a trivial equality constraint. Thus derivatives with respect to the initial value are present in the SQP framework.

If the solution  $y^*(x_0) = (\omega^*(x_0), \lambda^*(x_0), \mu^*(x_0))$  to the problem with initial value  $x_0$  has already been found, the neighboring problem with initial value  $x_0 + \varepsilon$  can be initialized with the solution  $y^*(x_0)$ .

If the results of the previous iteration are used without any changes to initialize

the current iteration, this technique is called *warm start strategy*. An initial violation of constraint (2.49b) is accepted since due to the linearity of the constraint the violation is immediately corrected after the first (full) SQP iteration. When using a full step exact Hessian SQP algorithm one can show that already the first iterate provides an excellent (first order) approximation of the solution  $y^*(x_0 + \varepsilon)$  (see Theorem 3.6 in [Die01]).

# Chapter 3

## Results

In this work, a novel model reduction approach for chemical kinetics first proposed by Lebiez [Leb04, LRK06, Leb06] is further developed and extended. Its conceptual idea is based on finding criteria related to maximal relaxation of chemical forces along phase space trajectories under given constraints. This idea is exploited by formulating optimization problems for the numerical computation of such trajectories as a representation of a reduced model. In the course of this chapter we will track a systematic search for appropriate optimization criteria characterizing slow, invariant attracting manifolds and their numerical implementation. We will finally lead the way to a very successful choice and present promising results for the reduction of a realistic test case reaction mechanism describing hydrogen combustion. Our most successful criterion unites ideas from and shares a deep connection to both differential geometry concepts related to the curvature of trajectories and slow long-term dynamics enslaving fast modes in a multiple time-scale kinetic system.

Petzold and Zhu first presented an optimization approach to model reduction in chemical kinetics [PZ99]. The underlying ideas have already been described in the introduction (see Section 1.1). However, their implementation requires to solve a computationally extremely expensive nonlinear integer programming problem, whereas our approach can be formulated as a standard nonlinear programming (NLP) problem which can be solved by a standard NLP solver.

As the Roussel-Fraser (RF) algorithm [Fra88, RF01] and the ICE-PIC method [RPVG06] described in the introduction (see Section 1.1), our optimization approach is trajectory-based and therefore yields invariant manifolds and can be interpreted as the computation of special trajectories which are “as close as pos-

sible” to their attractor – the thermodynamic equilibrium – in an adequate sense concretized by the optimization criterion.

An important practical issue of model reduction in chemical kinetics is the a priori choice of some species as so-called *reaction progress variables* which serve as representatives of the reduced model in terms of a parametrization. In our context this finds a fully natural realization in terms of initial conditions of trajectories. For fixed initial values of those progress variables both a special trajectory converging towards the equilibrium point in phase space – in the following also called *optimal trajectory* – and the a priori unknown initial values of the remaining species are calculated at the same time as a solution of the optimization problem. Mapping the progress variables to the full phase space is called species reconstruction and has already been described in the introduction (see Section 1.1). As in the ICE-PIC but in contrast to the RF method, in our approach species reconstruction is possible locally – meaning without the computation of the whole low-dimensional manifold representing the reduced model – which is an important advantage. The interpretation of our species reconstruction procedure as the maximal relaxation of thermodynamic forces or dynamic modes of a chemical system under the constraints of fixed progress variables can be pointed out in different ways. In three subsequent sections of this chapter a thermodynamic criterion, namely minimal entropy production, a criterion based on dissipative contraction of phase space volume and a concept from differential geometry will be discussed in more detail and compared to each other.

From a mathematical point of view, all the methods presented here can be formulated as either initial value optimization problems or closely related boundary value problems for ordinary differential equation systems:

$$\min_{c_k, k \in I_{\text{free}}} \int_0^T \Phi(c(t)) dt \quad (3.1a)$$

$$\text{subject to } \frac{dc_k}{dt} = f_k(c), \quad k \in I_{\text{fixed}} \cup I_{\text{free}} \quad (3.1b)$$

$$c_k(0) = c_k^0, \quad k \in I_{\text{fixed}} \quad (3.1c)$$

$$|c_k(T) - c_{k_{\text{eq}}}| \leq \varepsilon, \quad k \in I_{\text{fixed}} \quad (3.1d)$$

and subject to chemical conservation relations as e.g. mass conservation.

$I_{\text{fixed}}$  and  $I_{\text{free}}$  are index sets which contain the indices of variables with fixed initial values (the reaction progress variables) and free initial values (all other species) respectively ( $I_{\text{fixed}} \cup I_{\text{free}} = \{1, \dots, m\}$  with  $m$  being the number of chemical species). The system dynamics are described by (3.1b) and the initial concen-

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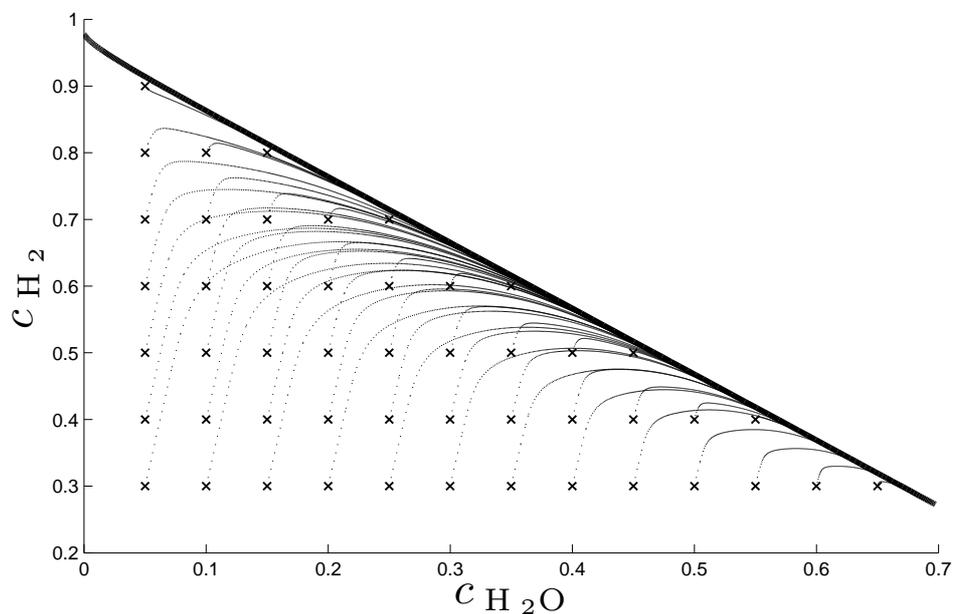
trations of the reaction progress variables are fixed in (3.1c). When approaching the equilibrium point  $c_{\text{eq}}$ , system dynamics become infinitely slow. Therefore the equilibrium point is approximated in (3.1d) within a surrounding of radius  $\varepsilon$  for the reaction progress variables. A priori the end time  $T$  is free and is determined within the optimization such that (3.1d) is fulfilled. Alternatively the time  $T$  can be fixed such that the final state of the system is very close to the chemical equilibrium point. The objective functional  $\Phi(c(t))$  describes the optimization criterion related to the degree of relaxation of chemical forces. Appropriate choices and their motivation will be discussed in the next sections.

For the numerical solution of the boundary value problem stated in (3.1), elaborate mathematical optimization techniques exist. In the example applications presented in the following sections, the software package MUSCOD-II [BP84, Lei95, Lei99] originally developed for solving large scale optimal control problems for nonlinear dynamical systems is used for the numerical solution of problem (3.1). In MUSCOD-II the direct multiple shooting method, which is described in detail in Section 2.4.2, is implemented. By discretizing the state variables, the originally infinite dimensional problem is transformed into a finite dimensional nonlinear programming problem (NLP), which then can be solved by a sequential quadratic programming (SQP) method. The state trajectories are numerically integrated only on small subintervals of the full time horizon, which are initially decoupled, using a BDF-type (backward differentiation formulae) stiff integrator [BFD<sup>+</sup>97] (see Section 2.4.3). As a result, for each multiple shooting interval an initial value problem has to be solved instead of just one for the whole time horizon. Although the resulting NLP is much larger than the one resulting from the single shooting approach, the mathematical structure of the multiple shooting discretization can be exploited such that the related optimization problem can be solved with approximately the same effort as in the single shooting approach [LBBS03]. However, compared to single shooting, multiple shooting is much more robust. Furthermore even for systems with dynamical instabilities, e.g. strongly diverging state trajectories, the computation of derivative information which is required for the SQP optimization is much more stable and in some cases even possible at all.

A significant advantage of the multiple shooting approach is that neighboring problems can be initialized very efficiently from the previous optimal trajectory. In the so called *initial value embedding* strategy (see Section 2.4.6) formally a

linear extrapolation prediction of the previous solution is used to calculate an initial guess for the new solution if the same problem needs to be solved with just slightly modified initial values [BDLS00, Die01]. The incorporation of a priori information about the optimal solution (trajectory) by setting initial conditions for the state variables at the multiple shooting nodes generally results in highly improved and fast convergence to the new solution which actually makes the solution of parametrized optimization problems efficient. This is an important issue since reduced models often need to be computed and tabulated for a whole range of reaction progress variables.

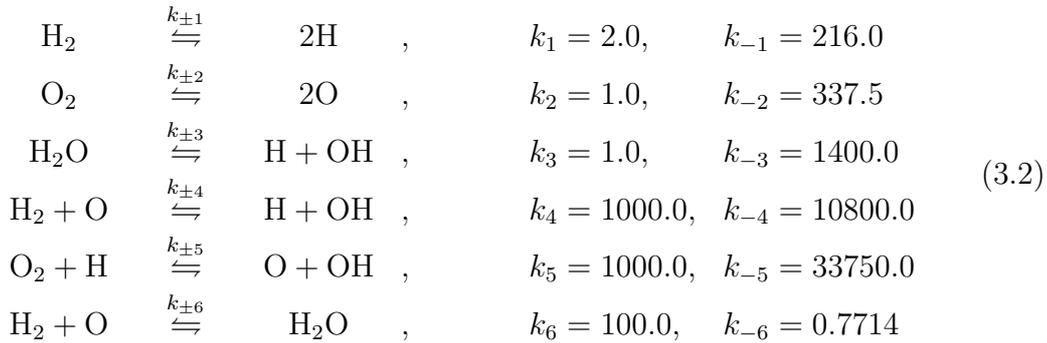
The initial value embedding strategy is implemented and successfully exploited for reasons of practical applicability of a model reduction approach for the first time in this work. Both for the offline tabulation and for the online use in CFD simulations (see Section 1.2) whole families of optimal trajectories need to be calculated. For a specified range of the reaction progress variables, these optimal trajectories have to be calculated on a discrete grid, where neighboring grid points only slightly differ in the values of the progress variables (see Figure 3.1). These



**Figure 3.1:** Application of the initial value embedding strategy to the calculation of families of optimal trajectories illustrated for the hydrogen combustion mechanism (3.2): For a discrete grid of initial values of the reaction progress variables  $\text{H}_2$  and  $\text{H}_2\text{O}$  (depicted as cruxes), optimal trajectories spanning a two-dimensional manifold are calculated (dotted lines).

ideas cannot only be used to calculate families of optimal trajectories spanning two-dimensional manifolds as demonstrated in this work, but can also easily be extended to large-scale mechanisms and the calculation of optimal trajectories spanning higher-dimensional manifolds. For most common model reduction techniques the calculation of higher-dimensional manifolds is hardly practicable due to the immense computational effort necessary. Using MUSCOD-II together with the initial value embedding strategy to solve the optimization problem set up in our model reduction approach results in drastically reduced computing times due to the accelerated convergence of the optimization problem. Therefore it should even be applicable to large-scale mechanisms for which reduced models often need to be represented by higher-dimensional manifolds.

In the following various criteria for our model reduction approach described in (3.1) will be derived. As a test case example system to illustrate the performance of the techniques, a semi-quantitative six component hydrogen combustion mechanism is considered throughout this work:



The parameters  $k_j$  and  $k_{-j}$ ,  $j = 1, \dots, n = 6$  represent the reaction rate coefficients for forward and backward reactions respectively (the number of reactions is  $n = 6$ ), and  $c_k$  the concentrations of the chemical species  $k$  (the number of species is  $m = 6$ ).

Together with the two conservation equations

$$\begin{aligned}
 2 c_{\text{H}_2} + 2 c_{\text{H}_2\text{O}} + c_{\text{H}} + c_{\text{OH}} &= C_1 \\
 2 c_{\text{O}_2} + c_{\text{H}_2\text{O}} + c_{\text{O}} + c_{\text{OH}} &= C_2
 \end{aligned} \tag{3.3}$$

the kinetic model of this six-component mechanism described by the following

ordinary differential equations

$$\begin{aligned}
\frac{dc_{\text{H}_2}}{dt} &= -k_1 c_{\text{H}_2} + k_{-1} c_{\text{H}_2}^2 - k_4 c_{\text{H}_2} c_{\text{O}} + k_{-4} c_{\text{H}} c_{\text{OH}} \\
&\quad - k_6 c_{\text{H}_2} c_{\text{O}} + k_{-6} c_{\text{H}_2\text{O}} \\
\frac{dc_{\text{H}}}{dt} &= 2 k_1 c_{\text{H}_2} - 2 k_{-1} c_{\text{H}_2}^2 + k_3 c_{\text{H}_2\text{O}} - k_{-3} c_{\text{H}} c_{\text{OH}} \\
&\quad + k_4 c_{\text{H}_2} c_{\text{O}} - k_{-4} c_{\text{H}} c_{\text{OH}} - k_5 c_{\text{O}_2} c_{\text{H}} + k_{-5} c_{\text{O}} c_{\text{OH}} \\
\frac{dc_{\text{O}_2}}{dt} &= -k_2 c_{\text{O}_2} + 2 k_{-2} c_{\text{O}}^2 - k_5 c_{\text{H}} c_{\text{O}_2} + k_{-5} c_{\text{O}} c_{\text{OH}} \\
\frac{dc_{\text{O}}}{dt} &= 2 k_2 c_{\text{O}_2} - 2 k_{-2} c_{\text{O}}^2 - k_4 c_{\text{H}_2} c_{\text{O}} + k_{-4} c_{\text{H}} c_{\text{OH}} \\
&\quad + k_5 c_{\text{H}} c_{\text{O}_2} - k_{-5} c_{\text{O}} c_{\text{OH}} - k_6 c_{\text{H}_2} c_{\text{O}} + k_{-6} c_{\text{H}_2\text{O}} \\
\frac{dc_{\text{H}_2\text{O}}}{dt} &= -k_3 c_{\text{H}_2\text{O}} + k_{-3} c_{\text{H}} c_{\text{OH}} + k_6 c_{\text{H}_2} c_{\text{O}} - k_{-6} c_{\text{H}_2\text{O}} \\
\frac{dc_{\text{OH}}}{dt} &= k_3 c_{\text{H}_2\text{O}} - k_{-3} c_{\text{H}} c_{\text{OH}} + k_4 c_{\text{H}_2} c_{\text{O}} - k_{-4} c_{\text{H}} c_{\text{OH}} \\
&\quad + k_5 c_{\text{H}} c_{\text{O}_2} - k_{-5} c_{\text{O}} c_{\text{OH}}
\end{aligned} \tag{3.4}$$

yields a system with four degrees of freedom.

### 3.1 Minimal Entropy Production Trajectories

In order to derive a thermodynamic criterion which describes maximal relaxation of chemical forces along phase space trajectories, a generalized concept for the distance of a chemical system from its attractor is considered. Under isolated conditions the attractor of a chemical system is given by the thermodynamic equilibrium. In our model reduction approach based on a thermodynamic concept, a special trajectory (called **Minimal Entropy Production Trajectory** (MEPT) in the following) converging towards equilibrium is calculated such that the sum of affinities of the single reaction steps is minimized [Leb04, LRK06, Leb06]. The concept of chemical affinity was first introduced by de Donder [dDvR36] as the driving force of chemical reactions. For an elementary reaction step  $j$  with the reaction rates  $R_{j\rightarrow}$  and  $R_{j\leftarrow}$ , the concept of chemical affinity can be related to the concept of entropy production by the following relation [KP98] (see also Section 2.3.2):

$$\frac{dS_{i,j}}{dt} = R (R_{j\rightarrow} - R_{j\leftarrow}) \ln \left( \frac{R_{j\rightarrow}}{R_{j\leftarrow}} \right), \tag{3.5}$$

where  $dS_{i,j}/dt$  is the entropy production rate for reaction  $j$  and  $R$  is the gas constant. Entropy production rates are additive for several elementary reaction steps. Therefore the total entropy production rate (being the sum of the entropy production rates of all  $n$  elementary reaction steps) can be computed for an arbitrary reaction system, if kinetic data are available and a detailed elementary reaction step mechanism is known.

If the concept of local equilibrium is valid, the total entropy production rate is even well-defined for nonequilibrium systems [GP71]. The concept of local equilibrium assumes that a system can be described by the same macroscopic variables which are known from equilibrium thermodynamics. But now these variables are functions of time and/or space.

Assuming the equilibrium to be stable, the Second Law of Thermodynamics (see Theorem 2.49 in Section 2.3.2) states that the entropy production rate of a spontaneous process near equilibrium is always positive, monotonously decreasing and approaching zero in thermodynamic equilibrium [GP71, KP98]. A function with those properties is called a Lyapunov function (see Definition 2.12 in Section 2.1). Entropy production can therefore be used to provide a measure for the distance of the system from equilibrium because it formally plays the role of a gradient of a “kinetic potential” being the driving force towards equilibrium. The larger the entropy production rate  $dS_{i,j}/dt$  in (3.5), the farther away from equilibrium the corresponding reaction step is considered. Relaxation of thermodynamic forces can be described by a decrease of the entropy production rate over time.

In the linear regime near equilibrium (linear nonequilibrium thermodynamics) the Lyapunov properties of the entropy production rate also remain valid for open systems, which can exchange energy and matter with the surrounding. However, in this work we only consider isolated systems. The Lyapunov properties are directly related to the “principle of minimum entropy production” proven by Prigogine (see e.g. [KP98]). A measure for the relaxation of single reaction steps can be formulated exploiting the Lyapunov properties of the entropy production rate.

In order to calculate a minimal entropy production trajectory (MEPT), the sum of the deviations of the entropy production rate from zero in each reaction step is minimized. Substituting the minimization of the total entropy production rate for the objective functional in the general problem formulation (3.1) yields:

$$\min_{c_k, k \in I_{\text{free}}} \int_0^T \sum_{j=1}^n \frac{dS_{i,j}}{dt} dt \quad (3.6a)$$

$$\text{subject to } \frac{dc_k}{dt} = f_k(c), \quad k \in I_{\text{fixed}} \cup I_{\text{free}} \quad (3.6b)$$

$$c_k(0) = c_k^0, \quad k \in I_{\text{fixed}} \quad (3.6c)$$

$$|c_k(T) - c_{k_{\text{eq}}}| \leq \varepsilon, \quad k \in I_{\text{fixed}} \quad (3.6d)$$

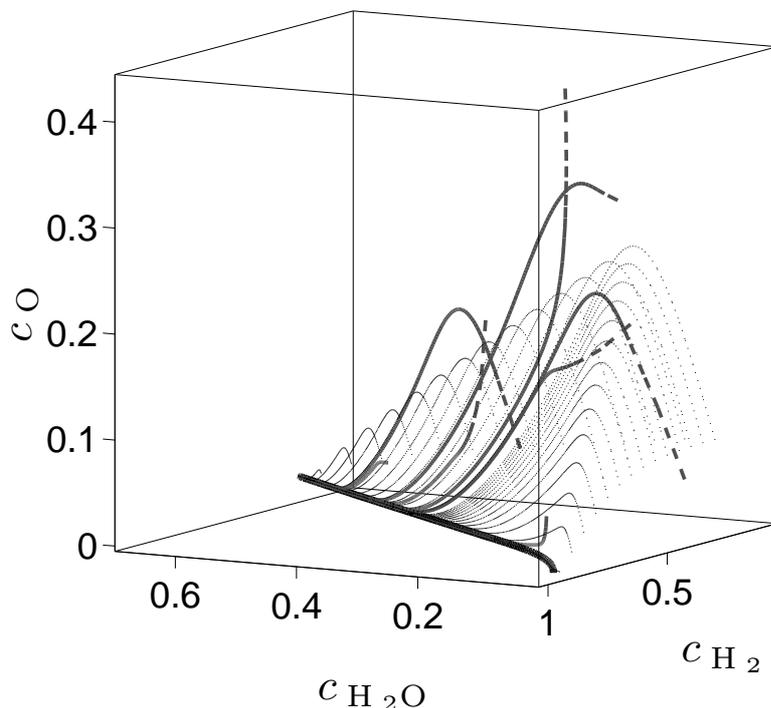
$$C_1 = 2 c_{\text{H}_2} + 2 c_{\text{H}_2\text{O}} + c_{\text{H}} + c_{\text{OH}} \quad (3.6e)$$

$$C_2 = 2 c_{\text{O}_2} + c_{\text{H}_2\text{O}} + c_{\text{O}} + c_{\text{OH}} \quad (3.6f)$$

An intuitive justification for the minimization of the total entropy production rate (3.6a) in the optimization problem (3.6) is provided by relation (3.5). In partial equilibrium the entropy production rate  $dS_{i,j}/dt$  of a single elementary reaction step is zero, since in partial equilibrium forward and backward reaction rates are equal. This is equivalent to the thermodynamic driving force being fully relaxed, which in turn is an equivalent of the assumption of model reduction techniques based on time scale separation. There it is assumed that fast reaction modes relax into partial equilibrium or quasi-steady-states and the whole system can be satisfactorily described by the slow modes only. But unlike the methods explicitly based on time scale separation it is not necessary in our MEPT approach to actually identify and analyze the dynamical modes by e.g. numerically expensive eigenvalue decomposition. A configuration with as many elementary reaction steps as possible being close to quasi-equilibrium in a chemical sense is determined automatically by the optimization algorithm. The logarithmic ratio of forward and backward reaction rates in (3.5) has the meaning of a reaction affinity [KP98]. It is weighted by the absolute difference between the rates for forward and backward reactions. Thus fast processes produce more entropy than slow ones and the fast reactions have a stronger weighting factor in the optimization problem (3.6), which is fully natural.

A significant advantage of our approach is the possibility to compute low-dimensional approximations even for systems whose gap in intrinsic time scale is not large enough for computational time scale separation and mode decomposition as used in many common model reduction techniques [MP92, LG94, HG99].

In this work we thoroughly investigate and extend the first MEPT approach proposed by Lebiedz [Leb04, LRK06, Leb06] for a realistic mechanism for hydrogen combustion. We present results for the computation of one-dimensional attract-



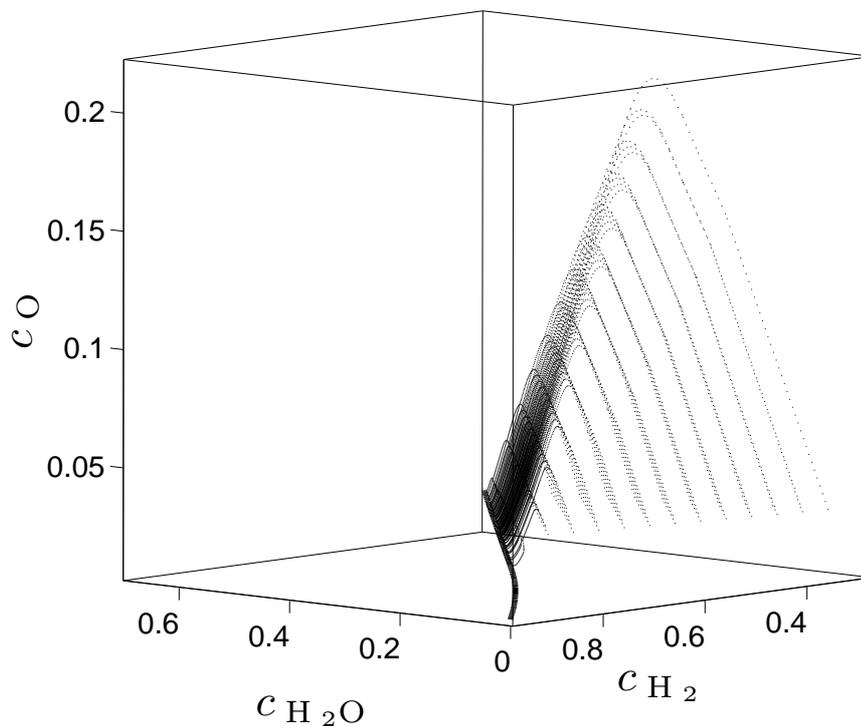
**Figure 3.2:** Minimal Entropy Production Trajectories computed for reaction mechanism (3.2) as solution of problem (3.6): dotted lines represent MEPTs with  $\text{H}_2\text{O}$  and  $\text{H}_2$  as reaction progress variables, which span a two-dimensional attracting manifold; the thick black line represents MEPT with only  $\text{H}_2\text{O}$  as reaction progress variable; dashed lines are arbitrary trajectories bundling on the MEPT manifolds.

ing slow manifolds and demonstrate an extension to two-dimensional manifolds, which are efficiently computed as families of MEPTs exploiting initial value embedding for parametric optimization (see Section 2.4.6). To illustrate the MEPT method described above the hydrogen combustion mechanism (3.2) is considered. By choosing only one reaction progress variable and fixing its initial concentration, a single trajectory with “maximally relaxed chemical forces” (meaning a minimal total entropy production rate) can be computed. In Figure 3.2 the MEPT for a fixed initial concentration of  $\text{H}_2\text{O}$ ,  $c_{\text{H}_2\text{O}}(0) = 10^{-4}$ , and the constants  $C_1 = 2.0$ ,  $C_2 = 1.0$  in the conservation equations is depicted as a bold black line. The equilibrium value is  $(c_{\text{H}_2}, c_{\text{H}}, c_{\text{O}_2}, c_{\text{O}}, c_{\text{H}_2\text{O}}, c_{\text{OH}}) = (0.27, 0.05, 0.135, 0.02, 0.7, 0.01)$ .

As long as there is at least one degree of freedom left in the system, the problem formulation (3.6) permits the choice of more reaction progress variables. To

illustrate how the MEPT method can be applied for model reduction to higher dimensions than one, families of MEPTs are calculated using  $\text{H}_2\text{O}$  and  $\text{H}_2$  as reaction progress variables.

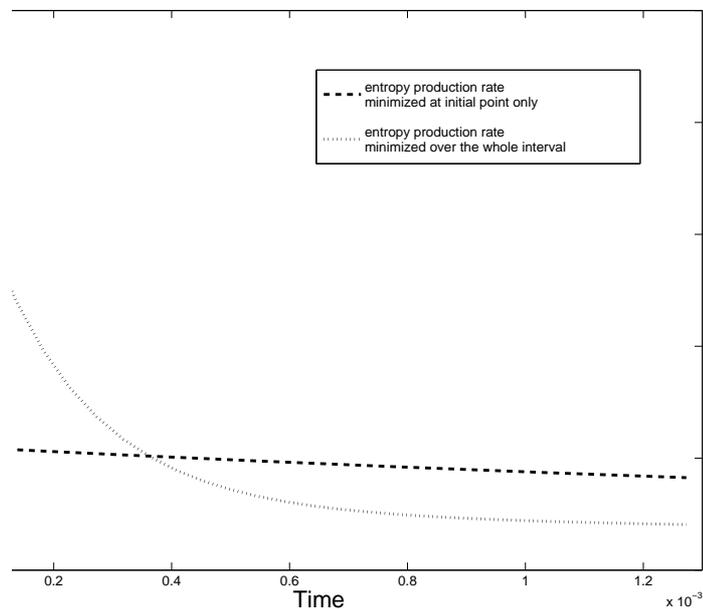
First the initial concentration of  $\text{H}_2$  is varied from 0.3 to 0.95 with the initial concentration of  $\text{H}_2\text{O}$  set to  $10^{-4}$ . Then the initial concentration of  $\text{H}_2$  is set to 0.3 and the initial concentration of  $\text{H}_2\text{O}$  is varied from 0.05 to 0.65. In Figure 3.2 the trajectories belonging to the family of MEPTs calculated with two reaction progress variables are depicted as dotted lines. One can see that those MEPTs span a two-dimensional manifold. All of them relax to an attracting trajectory, the MEPT calculated with just  $\text{H}_2\text{O}$  as reaction progress variable and  $c_{\text{H}_2\text{O}}(0) = 10^{-4}$ . Trajectories with arbitrary initial concentrations (plotted in Figure 3.2 as thick, dashed lines) all first relax to a part of the spanned two-dimensional manifold, then to the one-dimensional attracting MEPT and finally to equilibrium illustrating the bundling behavior of trajectories on the computed MEPT manifolds.



**Figure 3.3:** The dotted lines represent MEPTs with  $\text{H}_2\text{O}$  and  $\text{H}_2$  as reaction progress variables. The MEPTs themselves relax to the two-dimensional attracting slow manifold before relaxing to equilibrium.

When looking at the MEPTs calculated with two reaction progress variables  $\text{H}_2\text{O}$  and  $\text{H}_2$  and the manifold they are spanning, one can see in Figure 3.3 that the MEPTs themselves first seem to relax fast to some two-dimensional slow manifold before relaxing to the one-dimensional attracting MEPT and finally to equilibrium.

A more detailed look at the development of the total entropy production rate over time in Figure 3.4 shows that when minimizing the entropy production rate over the whole interval  $t \in [0, T]$ , the total entropy production rate is high at the beginning of the interval, however decreases fast.



**Figure 3.4:** Comparison of the total entropy production rate over time. Dotted line: total entropy production rate at time  $t = 0$  minimized. Dashed line: total entropy production rate minimized over the whole interval

This leads to a smaller total entropy production rate over the whole interval compared to the entropy production rate when minimizing just the entropy production rate at the initial point ( $t = 0$ ). In Figure 3.4 the dotted line depicts a MEPT calculated by solving problem (3.6) with the initial concentrations of  $\text{H}_2$  and  $\text{H}_2\text{O}$  fixed, i.e. by minimizing the total entropy production rate over the whole time horizon  $[0, T]$ . The dashed line shows the trajectory which results from pointwise minimization of the entropy production rate at  $t = 0$ . Initial concentrations for  $\text{H}_2$  and  $\text{H}_2\text{O}$  are chosen as for the MEPT, all other concentrations

are determined such that the total entropy production rate

$$\frac{dS_i}{dt}(0) = \sum_{j=1}^n \frac{dS_{i,j}}{dt}(0)$$

at the initial point of the trajectory is minimal.

The effect of the MEPTs themselves relaxing onto a two-dimensional manifold is obviously caused by the large entropy production rate at the beginning of the considered interval causing a fast relaxation there.

We have shown here that by calculating families of MEPTs one- and two-dimensional attracting manifolds can be determined. However, the MEPTs themselves seem to relax to the real two-dimensional slow manifold first. Therefore in the first part these trajectories do not describe the attracting slow manifold accurately enough. An alternative approach of minimizing pointwise the total entropy production rate at the initial time doesn't yield satisfactory results either. For a more accurate description of the attracting slow manifold the phenomenon of the optimal trajectories themselves relaxing to a manifold needs to be investigated further. It seems necessary to consider other criteria characterizing maximal relaxation of chemical forces in order to determine the real attracting slow manifold. However, in Section 3.3 we will refer back to the minimal entropy production rate criterion presented here, modified and extended to ideas from differential geometry.

## 3.2 Minimal Contraction of Phase Space Volume

By definition, the divergence of a vector field describes the change of an infinitesimal volume element transported by the phase flow. This relation is formulated mathematically e.g. in Lemma (2.19) (see Section 2.1).

The volume in phase space enclosed by neighboring trajectories is constant with time for conservative systems (Liouville's Theorem, see e.g. [Ver00]). For dissipative chemical reaction systems, which we are considering here in this work, however, phase space volume is contracting due to relaxation of chemical forces (affinities) which drive chemical reactions. Thus the divergence of a vector field of ordinary differential equations describing the kinetics of a chemical reaction system is a local measure for the dissipation of chemical energy. Therefore it

seems to correlate with the strength of the chemical forces being active. Their total strength in the course of a reaction can be determined by integrating the divergence along reaction trajectories. This motivates another approach of characterizing maximal relaxation of thermodynamic forces.

For arbitrary initial concentrations any trajectory eventually relaxes to the equilibrium point in phase space. In thermodynamic equilibrium all forces are and stay relaxed, and therefore no contraction of the phase space volume occurs. The “farther away” from the equilibrium point (in a chemical sense) a trajectory starts, the greater the contraction of the phase space volume is on the way towards equilibrium. And likewise starting “close to” equilibrium means just a small contraction of the phase space volume.

Finding trajectories which are as close to equilibrium as possible in the sense that all forces are maximally relaxed might therefore be expressed by finding trajectories along which the local contraction of the phase space volume is minimal.

Since for dissipative systems  $\dot{c} = f(c)$  as the ones considered here the divergence is always negative,  $\text{div } f < 0$ ,  $(\text{div } f)^2$  is minimized in the problem formulation (3.1):

$$\min_{c_k, k \in I_{\text{free}}} \int_0^{\hat{T}} \left( \sum_{k=1}^n \frac{\partial f_k}{\partial c_k} \right)^2 dt \quad (3.7a)$$

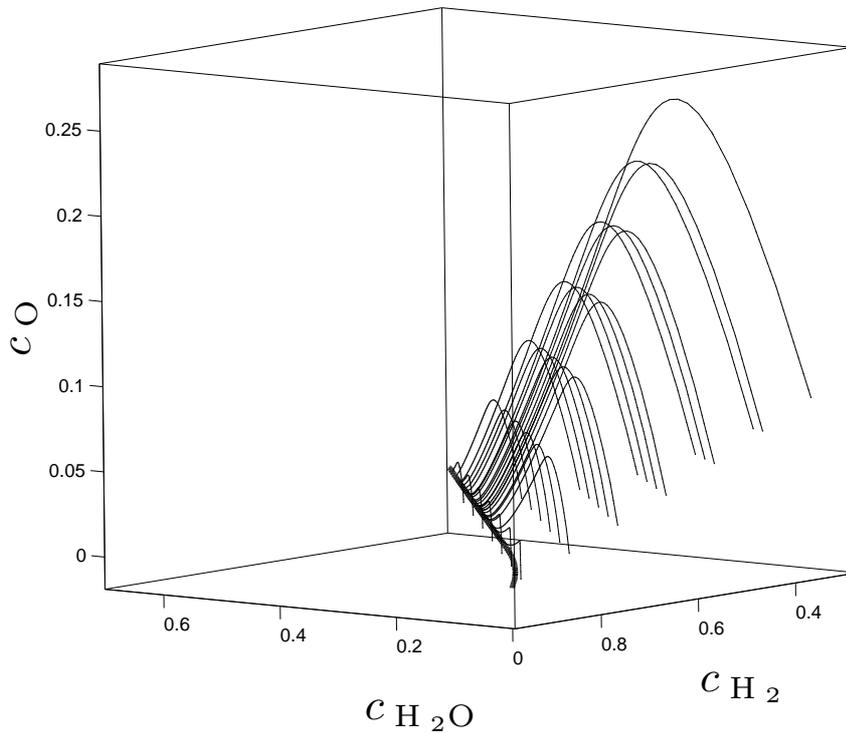
$$\text{subject to } \frac{dc_k}{dt} = f_k(c), \quad k \in I_{\text{fixed}} \cup I_{\text{free}} \quad (3.7b)$$

$$c_k(\hat{T}) = \hat{c}_k, \quad k \in I_{\text{fixed}} \quad (3.7c)$$

$$C_1 = 2 c_{\text{H}_2} + 2 c_{\text{H}_2\text{O}} + c_{\text{H}} + c_{\text{OH}} \quad (3.7d)$$

$$C_2 = 2 c_{\text{O}_2} + c_{\text{H}_2\text{O}} + c_{\text{O}} + c_{\text{OH}} \quad (3.7e)$$

Here a slightly different problem formulation is used. Instead of fixing the initial values of the reaction progress variables and integrating the system until reaching equilibrium as in (3.1), a small interval  $[0, \hat{T}]$  is chosen and the final concentrations of the reaction progress variables are fixed at time  $\hat{T}$ . The idea of this approach (called *reverse approach* in the following) is to find a trajectory which reaches a point in phase space specified by the fixed concentrations of the reaction progress variables already under minimal contraction of the phase space volume. The end point of the optimal trajectory now is the initial value for the trajectory representing the reduced model we are actually interested in and which can be obtained by pure integration.



**Figure 3.5:** Trajectories calculated with the reverse approach as solutions of problem (3.7).

In Figure 3.5 the resulting trajectories are shown, which have been calculated by integrating the trajectory from the final value of the optimal trajectory of problem (3.7) into equilibrium. Problem (3.7) is solved for the concentration of  $H_2$  varying from 0.3 to 0.9 and the concentration of  $H_2O$  varying from 0.05 to 0.65 using the initial value embedding strategy described in Section 2.4.6 such that the conservation equations are met for the constants  $C_1 = 2.0$  and  $C_2 = 1.0$ . The time horizon considered is  $[0, \hat{T}] = [0, 0.0001]$ .

It can be seen that these optimal trajectories also span a two-dimensional manifold. However, similar to the results of the MEPT formulation (see Figure 3.3 in Section 3.1) the trajectories themselves seem to relax to a two-dimensional slow manifold first before relaxing to equilibrium.

Both the MEPTs and the trajectories calculated on the basis of the concept of minimal contraction of phase space volume only partly describe the actual attracting slow manifold.

In the next section concepts from differential geometry are exploited and com-

bined with the thermodynamic concept of entropy production to yield a criterion which describes the attracting slow manifold much more accurately.

### 3.3 Minimal Curvature and Geodesics

As we have seen in the previous sections, both the criterion of a minimal total entropy production rate and the criterion of minimal contraction of the phase space volume yield families of trajectories spanning two-dimensional manifolds for the example application (3.2). However, for both criteria the optimal trajectories calculated themselves still relax to a two-dimensional manifold and therefore do not represent the true attracting slow manifold accurately enough in all parts.

In this section we want to derive another criterion for the characterization of maximal relaxation of thermodynamic forces based on the concept of curvature of trajectories in phase space. This criterion can overcome the problems of the criteria described previously and yields an improved and very accurate description of the real attracting slow manifold.

From a physical point of view curvature is closely related to the concept of force. One of the most popular examples is Einstein’s general theory of relativity [Ein16] which proposes the idea that gravitational force is replaced by a “geometric picture”. Einstein’s general theory of relativity relates the special theory of relativity and Newton’s law of universal gravitation with the insight that gravitation can be described by curvature of space-time. Space-time is treated as a 4-dimensional manifold whose curvature is due to the presence of mass, energy, and momentum.

But even long before Einstein, the concept of curvature has already been related to the concept of force in physics. In 1687 Sir Isaac Newton published the laws of motion in his work “Philosophiae Naturalis Principia Mathematica”. In a differential formulation Newton’s second law can be stated as

$$F = m \cdot a ,$$

where  $m$  is mass,  $a$  is acceleration and  $F$  is force. Since the acceleration  $a$  is the second derivative of the state variable  $x(t)$  with respect to time,  $a = \ddot{x}$ , and thus contains information about the curvature of  $x$ , in Newton’s law for the first time force is related to curvature.

In this context it is important to remark that equations of motion in classical

mechanics can also be described by a variational principle, the principle of least action or principle of stationary action. In Lagrangian mechanics, the trajectory of an object is determined such that the action (which is defined as the integral of the Lagrangian over time, where the Lagrangian is the difference of kinetic energy and potential energy) is minimal. It can be shown by using the calculus of variations, that Lagrange's equations of motion are equivalent to Hamilton's principle – also called the principle of stationary action [Gol80].

Another well known variational principle is Fermat's principle of optics. It states in its classical form that the actual path between two points taken by a beam of light is minimal.

We now want to transfer the principle of “force = curvature” to the field of chemical systems and look for a corresponding variational principle formally similar to those mentioned above in a physical context.

In chemical systems dissipative forces are present. Slow and fast dynamic modes result in an anisotropic force relaxation behavior in phase space. To formally being able to describe this anisotropy for a chemical system whose dynamics are described by the ODE  $\dot{c} = f(c)$ , curvature of the trajectories in phase space is considered. The following relations hold:

$$\ddot{c}(t) = \frac{d^2c}{dt^2} = \frac{d\dot{c}}{dt} = \frac{d\dot{c}}{dc} \cdot \frac{dc}{dt} = J(\dot{c}(t)) \cdot \dot{c}(t) = J(f(c(t))) \cdot f(c(t)) \quad (3.8)$$

with  $J(f)$  being the Jacobian of the right hand side of the ODE  $\dot{c}(t) = f(c(t))$ . Hence we may define the curvature of  $c(t)$  as

$$\|\ddot{c}(t)\| = \|J(f(c(t))) \cdot f(c(t))\| . \quad (3.9)$$

Transferring the principle of force being equivalent to curvature, we consider the curvature of trajectories in a kinetic model  $\dot{c} = f(c)$  as the forces driving the chemical system towards equilibrium. Close to thermodynamic equilibrium those chemical forces decrease and at equilibrium the driving forces are zero. In search of a criterion which characterizes maximal relaxation of thermodynamic forces it is tempting to describe the relaxation of the system towards equilibrium by minimal remaining chemical forces, i.e. in our context by minimal total (“integrated”)

curvature of trajectories defined as an optimization problem

$$\min_{c_k, k \in I_{\text{free}}} \int_0^T \|J(f(c)) \cdot f(c)\| dt \quad (3.10a)$$

$$\text{subject to } \frac{dc_k}{dt} = f_k(c), \quad k \in I_{\text{fixed}} \cup I_{\text{free}} \quad (3.10b)$$

$$c_k(0) = c_k^0, \quad k \in I_{\text{fixed}} \quad (3.10c)$$

$$|c_k(T) - c_{k_{\text{eq}}}| \leq \varepsilon, \quad k \in I_{\text{fixed}} \quad (3.10d)$$

$$C_1 = 2 c_{\text{H}_2} + 2 c_{\text{H}_2\text{O}} + c_{\text{H}} + c_{\text{OH}} \quad (3.10e)$$

$$C_2 = 2 c_{\text{O}_2} + c_{\text{H}_2\text{O}} + c_{\text{O}} + c_{\text{OH}} \quad (3.10f)$$

As the curvature – being the norm of a second derivative – is some kind of “acceleration”, the integral over the curvature in the objective function (3.10a) can be interpreted as some term with the physical dimension of velocity. It correlates to the time scales present in the chemical system described by (3.10b). Minimizing the velocity term is related to minimizing the “overall” velocity of the reactions. In the optimal solution then the fast modes are relaxed as much as possible subject to constraints (3.10b) - (3.10f), and the system is “as close to equilibrium as possible” in a certain sense.

From a different point of view the objective function (3.10a) can also be interpreted as minimizing the length of a trajectory in a suitable Riemannian metric. For any continuously differentiable curve  $\gamma$  in a Riemannian manifold (see Section 2.2), the length  $L$  of  $\gamma$  is defined as

$$L(\gamma) = \int_{\gamma} \sqrt{g(\dot{\gamma}(t), \dot{\gamma}(t))} dt . \quad (3.11)$$

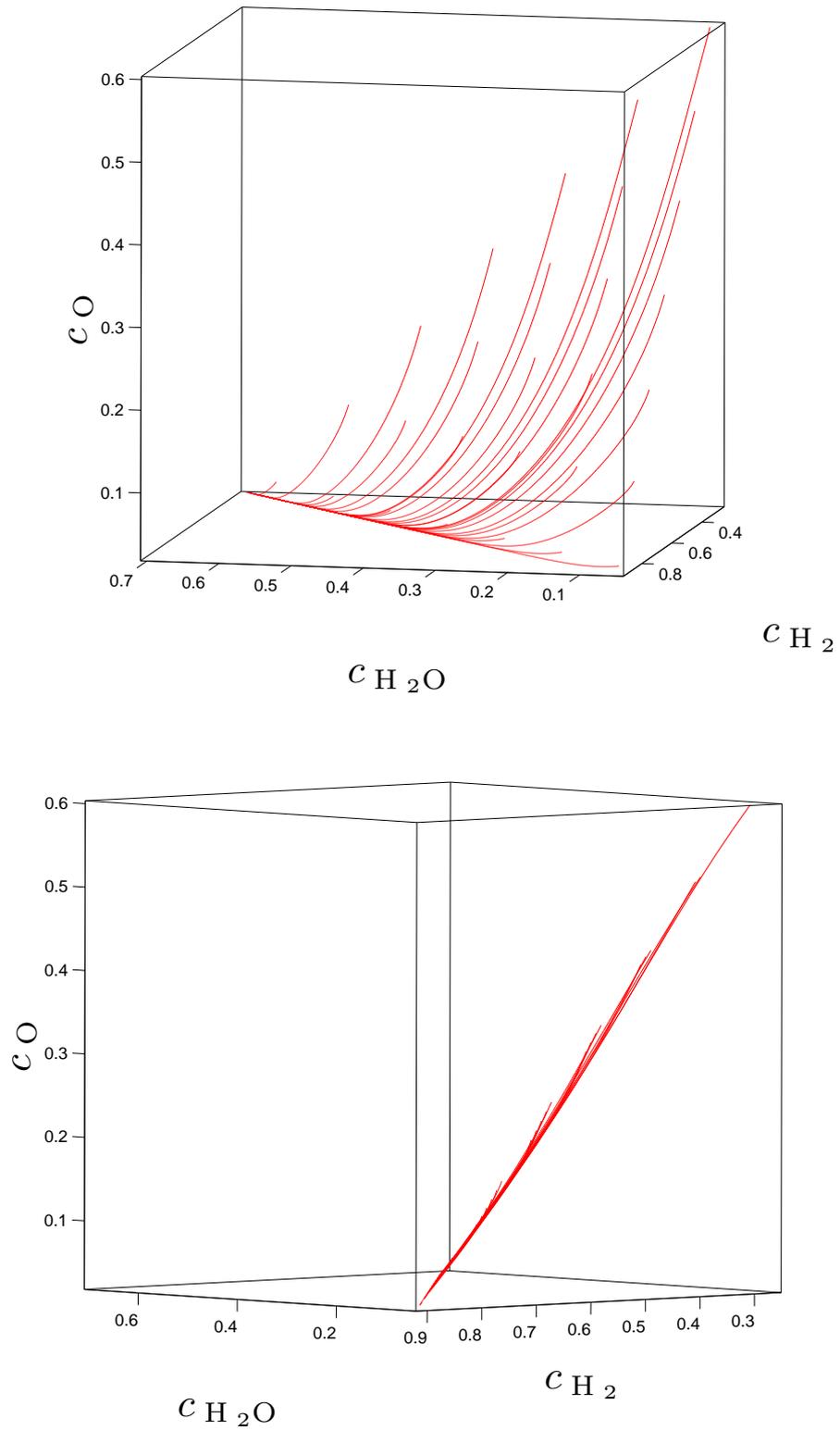
If the Riemannian metric  $g$  is chosen as

$$g(f, f) := f^T \underbrace{J^T J}_{\text{positive definite}} f = \|J f\|^2 \quad (3.12)$$

the length-minimizing objective functional equivalent to (3.10a) is now

$$\min \int_0^T \sqrt{g(\dot{c}(t), \dot{c}(t))} dt . \quad (3.13)$$

The solution trajectory of this problem can be interpreted as a geodesic (see Section 2.2), i.e. the curve which minimizes the length of the path between two points in a curved space. Hence the “distance from equilibrium in a chemical sense” can be formulated here in an explicit mathematical form based on concepts from differential geometry.



**Figure 3.6:** Two different views of trajectories calculated as solutions of problem (3.10)

As an example application again the hydrogen combustion mechanism (3.2) is considered. As in the previous sections  $\text{H}_2$  and  $\text{H}_2\text{O}$  are chosen as reaction progress variables. A family of trajectories is calculated solving problem (3.11), varying the fixed initial concentration of  $\text{H}_2$  between 0.3 and 0.9, and the initial concentration of  $\text{H}_2\text{O}$  between 0.05 and 0.65.

In Figure 3.6 one can see that the resulting trajectories span a two-dimensional manifold, which is much more accurately approximating the two-dimensional attracting slow manifold than the manifold spanned e.g. by the MEPTs discussed in Section 3.1 (Figure 3.2) or the trajectories calculated minimizing the contraction of the phase space volume in Section 3.2 (Figure 3.5). But in the second plot of Figure 3.6 still a rudimentary relaxation of the trajectories towards the attracting manifold can be observed.

Since the goal of this work is to describe the low-dimensional attracting slow manifold by trajectories as accurate as possible using optimization criteria, we tried to diminish the relaxation of the optimal trajectories towards the low-dimensional manifold even more. Therefore in the following we will investigate a further modification of the metric defined by (3.12).

To describe the distance of a chemical system from its thermodynamic equilibrium in an even more specific way, now the following Riemannian metric is considered

$$\hat{g}(f, f) := f^T \underbrace{J^T \cdot A \cdot J}_{\text{positive definite}} f = \|Jf\|_A^2, \quad (3.14)$$

where  $A$  is a diagonal matrix with the entries

$$a_{kk} = \sum_{j=1}^n \nu_{kj} \frac{dS_{i,j}}{dt} \quad (k = 1, \dots, m), \quad (3.15)$$

and zero in non-diagonal entries.

Here  $n$  is the number of reactions,  $\nu_{kj}$  are the stoichiometric coefficients describing the degree to which the chemical species  $k$  participates in reaction  $j$ , and  $dS_{i,j}/dt$  is the entropy production rate of reaction  $j$ .  $a_{kk}$  is the sum of the entropy production rates of all elementary reactions in which species  $k$  takes part.  $A$  is positive definite since according to the Second Law of Thermodynamics (see Theorem 2.49 in Section 2.3.2)  $dS_{i,j}/dt > 0$  holds for all spontaneous processes, and therefore  $a_{kk} > 0$  for all  $k = 1, \dots, m$ .

By including  $A$  into metric (3.12) a sort of anisotropic “kinetic weighting” is added to the measure of the distance from thermodynamical equilibrium.

Problem (3.10) reformulated with the modified Riemannian metric (3.14) yields the optimization problem

$$\min_{c_k, k \in I_{\text{free}}} \int_0^T \sqrt{(J(f(c)) \cdot f(c))^T \cdot A \cdot (J(f(c)) \cdot f(c))} dt \quad (3.16a)$$

$$\text{subject to } \frac{dc_k}{dt} = f_k(c), \quad k \in I_{\text{fixed}} \cup I_{\text{free}} \quad (3.16b)$$

$$c_k(0) = c_k^0, \quad k \in I_{\text{fixed}} \quad (3.16c)$$

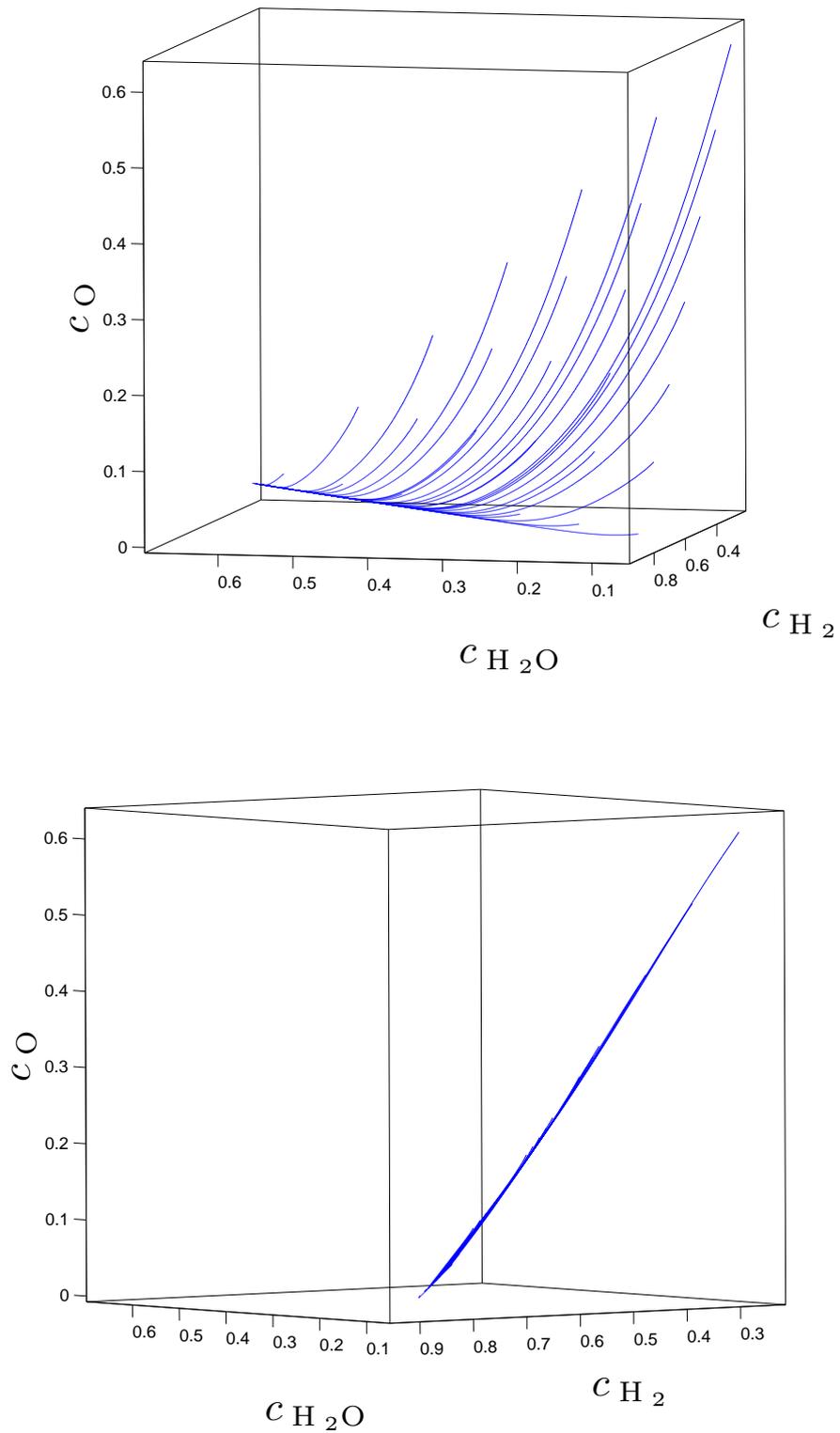
$$|c_k(T) - c_{k_{\text{eq}}}| \leq \varepsilon, \quad k \in I_{\text{fixed}} \quad (3.16d)$$

$$C_1 = 2 c_{\text{H}_2} + 2 c_{\text{H}_2\text{O}} + c_{\text{H}} + c_{\text{OH}} \quad (3.16e)$$

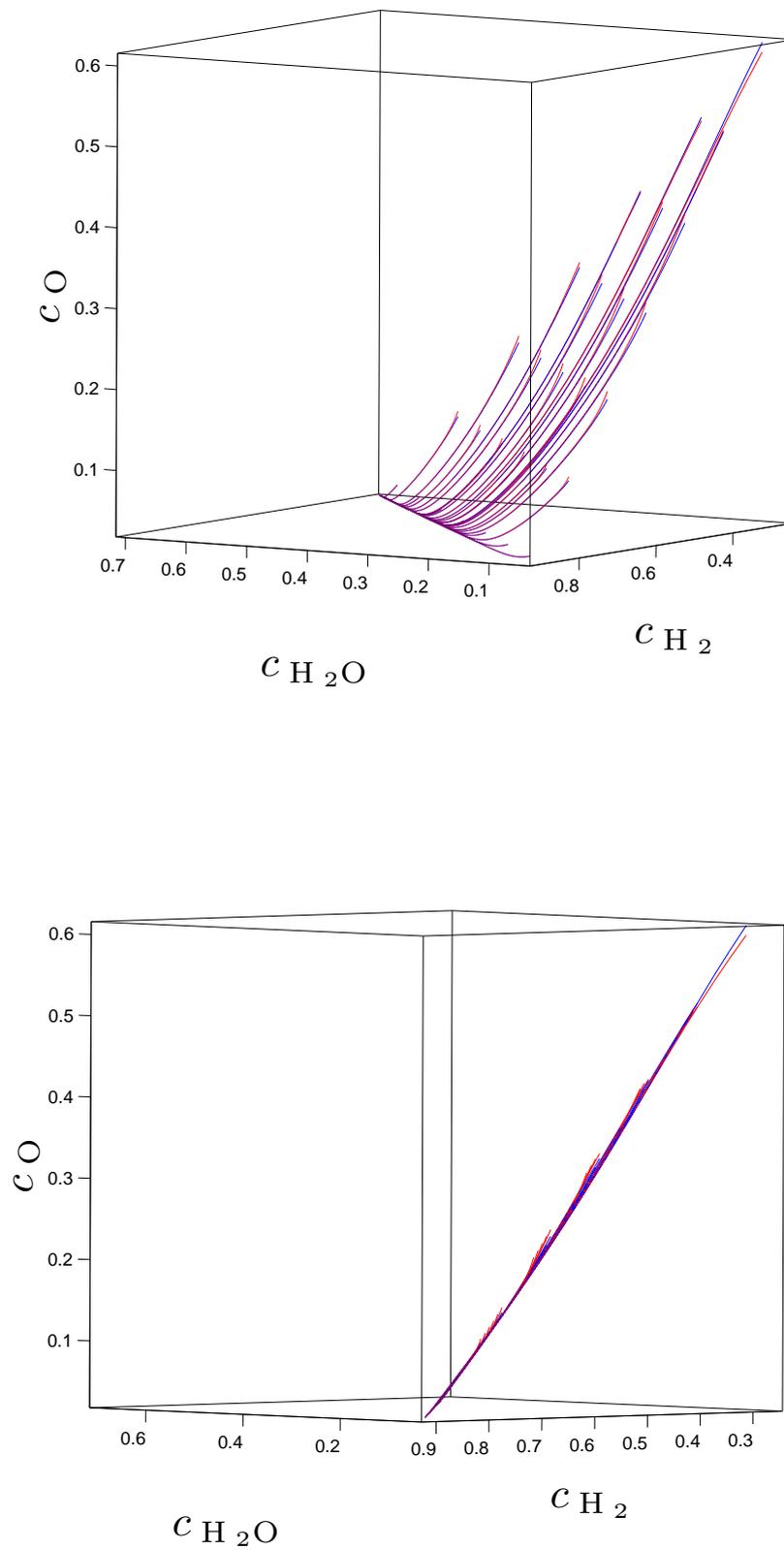
$$C_2 = 2 c_{\text{O}_2} + c_{\text{H}_2\text{O}} + c_{\text{O}} + c_{\text{OH}} \quad (3.16f)$$

In Figure 3.7 the optimal trajectories are depicted. As in the previous problem formulations the fixed initial concentration of  $\text{H}_2$  is varied between 0.3 and 0.9, and the initial concentration of  $\text{H}_2\text{O}$  is varied between 0.05 and 0.65. As in Figure 3.6 the optimal trajectories span a two-dimensional manifold, but in contrast to Figure 3.6, now the relaxation of the optimal trajectories towards the attracting slow manifold has almost completely vanished.

A direct comparison of the families of trajectories calculated by solving problem (3.10) and (3.16) respectively is shown in Figure 3.8.



**Figure 3.7:** Two different views of trajectories calculated as solutions of problem (3.16).



**Figure 3.8:** Two different views of trajectories calculated as solutions of problem (3.16) which are depicted in blue, and trajectories calculated as solutions of problem (3.10) which are depicted in red.

## 3.4 Conclusions

In search of a criterion which accurately describes the attracting slow manifold representing the reduced model of an originally high dimensional chemical reaction system, different approaches have been investigated. The first criterion is based on the “principle of minimum entropy production” ([KP98]) and the aim of the problem formulation is to calculate trajectories which minimize the weighted sum of deviations of the entropy production rate from zero in each reaction step. In another approach, dissipative contraction of the phase space volume is minimized. Both criteria – total minimal entropy production rate and minimal contraction of the phase space volume – yield families of trajectories, which to some extent approximate the two-dimensional attracting slow manifold. However, the description is not accurate enough since the optimal trajectories themselves relax to the attracting manifold in the first part. Therefore another criterion has been developed which unites ideas from differential geometry related to the curvature of curves and the thermodynamic concept of entropy production. For an appropriately chosen Riemannian metric involving entropy production rates as a weighting factor, optimal trajectories can be calculated by minimizing their length with respect to the chosen metric. This chosen metric can also be motivated by the deep physical concept of relating force to curvature of trajectories or manifolds which is transferred to chemical kinetics here. The computed family of optimal trajectories describes very accurately the two-dimensional attracting slow manifold and presents a promising perspective for general applications.



# Chapter 4

## Summary and Outlook

Since reaction mechanisms describing chemical systems continually become more detailed, model reduction techniques gain in importance. The general idea of model reduction techniques is to replace a high-dimensional detailed kinetic model described by ordinary differential equations by a reduced model of lower dimension approximating the original system.

For the purpose of this work, only isolated chemical systems are considered. They are dissipative systems approaching a stable attractor – thermodynamic equilibrium. For dissipative systems, the phase space volume is contracting along trajectories. Since usually different time-scale are present in a chemical system and therefore some processes are relaxing faster than others, the contraction of the phase space volume is not isotropic. Due to the anisotropic contraction, phase space trajectories bundle after a transient time and form low-dimensional attracting slow manifolds which can be exploited for model reduction by computing the long-term dynamics on these manifolds with a model of lower dimension.

In this work a new trajectory-based method for automatic model reduction of chemical systems is investigated whose basic idea is to find criteria related to maximal relaxation of chemical forces along phase space trajectories under given constraints. These trajectories are supposed to approximate attracting low-dimensional manifolds.

For the practical application of model reduction of chemical kinetics, a priori some species are generally chosen as so-called reaction progress variables which serve as representatives of the reduced model in terms of a parametrization. In our approach the initial concentrations of these progress variables are fixed and

both a special trajectory converging towards the equilibrium point in phase space and the a priori unknown initial values of the remaining species are calculated at the same time as a solution of an optimization problem. The reduced model then can be represented by the optimal trajectories being “as close as possible” in some sense to their attractor – thermodynamic equilibrium.

For the characterization of the maximal relaxation of chemical forces, different optimization criteria are developed and compared. The first criterion is based on the thermodynamic concept of a minimal total entropy production rate since entropy production is decreasing while the system approaches its attractor.

As for dissipative chemical systems the phase space volume is contracting, another criterion for a trajectory being “maximally relaxed” can be described by minimal contraction of the phase space volume. The criterion can be formulated as minimizing the divergence of the ODE describing the system dynamics.

For a third criterion, the general concept of curvature from differential geometry is exploited and the principle of “force being equal to curvature” in a suitable geometric picture is transferred from physics to the field of chemical systems. Minimal remaining chemical forces close to equilibrium can be characterized by minimal curvature of trajectories in phase space in a suitable geometry. Most promising results are obtained when an alternative metric is defined which is related to the concept of entropy production. The resulting optimal trajectories can be considered as geodesics describing “minimal distance” from equilibrium on a curved manifold equipped with a suitable metric.

In an application of our model reduction approach to a realistic six component hydrogen combustion mechanism all three criteria yield families of trajectories spanning two-dimensional manifolds. For the minimal total entropy production rate criterion and the criterion of minimal contraction of the phase space volume the resulting manifolds do not describe the low-dimensional attracting slow manifold accurately enough since the optimal trajectories themselves still relax to the slow manifold. The third criterion of minimal curvature, however, yields a very good approximation of the low-dimensional attracting slow manifold and provides a promising basis for a novel model reduction approach which may be very useful in practical applications.

For the numerical solution of the optimization problem of minimizing one of the criteria discussed above subject to the system dynamics, fixed initial values of the reaction progress variables and some conservation equations, the software

package MUSCOD-II is used. The multiple shooting approach implemented in MUSCOD-II combined with an initial value embedding strategy for the solution of neighboring optimization problems yields a fast convergence to the optimal solutions and considerably reduces the computational effort needed when computing higher-dimensional manifolds as families of neighboring trajectories. In this work the initial value embedding strategy is applied to model reduction for the first time and allows the efficient calculation of not only one-dimensional but also two- or higher-dimensional attracting slow manifolds.

In ongoing and future research, the extension of our method to large-scale realistic reaction mechanisms will be tested. Another future aim is to implement our method into simulations of spatially distributed systems, e.g. in CFD applications. In addition, the realization of the full calculation and tabulation of the reduced model needs to be investigated.



# Bibliography

- [Alb05] J. Albersmeyer. Effiziente Ableitungserzeugung in einem adaptiven BDF-Verfahren. Master's thesis, University of Heidelberg, 2005.
- [And00] I. P. Androulakis. Kinetic mechanism reduction based on an integer programming approach. *AIChE Journal*, 46:361 – 371, 2000.
- [AP06] P. Atkins and J. de Paula. *Atkins' Physical Chemistry*. Oxford University Press, 8th edition, 2006.
- [Bau99] I. Bauer. *Numerische Verfahren zur Lösung von Anfangswertaufgaben und zur Generierung erster und zweiter Ableitungen mit Anwendungen bei Optimierungsaufgaben in Chemie und Verfahrenstechnik*. PhD thesis, University of Heidelberg, 1999.
- [BBS99] I. Bauer, H. G. Bock, and J. P. Schlöder. DAESOL – a BDF-code for the numerical solution of differential algebraic equations. Internal report, IWR, SFB 359, University of Heidelberg, 1999.
- [BDLS00] H. G. Bock, M. M. Diehl, D. B. Leineweber, and J. P. Schlöder. A direct multiple shooting method for real-time optimization of nonlinear DAE processes. In F. Allgöwer and A. Zheng, editors, *Nonlinear Model Predictive Control*, volume 26 of *Progress in Systems Theory*, pages 245 – 267, Basel, 2000. Birkhäuser.
- [BFD<sup>+</sup>97] I. Bauer, F. Finocchi, W. J. Duschl, H.-P. Gail, and J. P. Schlöder. Simulation of chemical reactions and dust destruction in protoplanetary accretion discs. *Astron. Astrophys.*, 317:273 – 289, 1997.
- [Boc87] H. G. Bock. *Randwertproblemmethoden zur Parameteridentifizierung in Systemen nichtlinearer Differentialgleichungen*, volume 183 of *Bonner Mathematische Schriften*. Universität Bonn, 1987.

- [Bod13] M. Bodenstein. Zur Kinetik des Chlorknallgases. *Z. Phys. Chem.*, 85:329–397, 1913.
- [BP84] H. G. Bock and K. J. Plitt. A multiple shooting algorithm for direct solution of optimal control problems. In *Proc. 9th IFAC World Congress Budapest*. Pergamon Press, 1984.
- [CH52] C. F. Curtiss and J. O. Hirschfelder. Integration of stiff equations. *Proc. Nat. Acad. Sci. USA*, 38:235 – 243, 1952.
- [CU13] D. Chapman and L. Underhill. The interaction of chlorine and hydrogen. The influence of mass. *J. Chem. Soc. Trans.*, 103:496–508, 1913.
- [DB02] P. Deuffhard and F. Bornemann. *Scientific Computing with Ordinary Differential Equations*, volume 42 of *Texts in Applied Mathematics*. Springer, New York, 2002.
- [DBS<sup>+</sup>02] M. Diehl, H. G. Bock, J. P. Schlöder, R. Findeisen, Z. Nagy, and F. Allgöwer. Real-time optimization and nonlinear model predictive control of processes governed by differential-algebraic equations. *J. of Process Contr.*, 12:577 – 585, 2002.
- [dDvR36] T. de Donder and P. van Rysselberghe. *Thermodynamic Theory of Affinity: A Book of Principles*. Stanford University Press, Menlo Park CA, 1936.
- [Die98] M. M. Diehl. A direct multiple shooting method for the optimization and control of chemical processes. Master’s thesis, University of Heidelberg, 1998.
- [Die01] M. M. Diehl. *Real-Time Optimization for Large Scale Nonlinear Processes*. PhD thesis, University of Heidelberg, 2001.
- [Don27] T. de Donder. *L’Affinité*. Gauthiers-Villars, Paris, 1927.
- [DS99] M. J. Davis and R. T. Skodje. Geometric investigation of low-dimensional manifolds in systems approaching equilibrium. *J. Chem. Phys.*, 111:859 – 874, 1999.
- [Ein16] A. Einstein. Die Grundlage der allgemeinen Relativitätstheorie. *Ann. Phys.*, 49:769–822, 1916.

- [Fra88] S. J. Fraser. The steady state and equilibrium approximations: A geometrical picture. *J. Chem. Phys.*, 88:4732 – 4738, 1988.
- [GKZ04] A. N. Gorban, I. V. Karlin, and A. Y. Zinovyev. Constructive methods of invariant manifolds for kinetic problems. *Phys. Rep.*, 396:197 – 403, 2004.
- [Gol80] H. Goldstein. *Classical mechanics*. Addison-Wesley, Reading, Mass., 2nd edition, 1980.
- [GP71] P. Glansdorff and I. Prigogine. *Thermodynamic Theory of Structure, Stability and Fluctuations*. Wiley, New York, 1971.
- [Han76] S. P. Han. Superlinearly convergent variable-metric algorithms for general nonlinear programming problems. *Math. Program.*, 11:263 – 282, 1976.
- [HBMK98] D. Hamiroune, P. Bishnu, M. Metghalchi, and J. C. Keck. Rate-controlled constraint-equilibrium method using constraint potentials. *Combust. Theor. Model.*, 2:81 – 94, 1998.
- [Hen62] P. Henrici. *Discrete Variable Methods in Ordinary Differential Equations*. Wiley, New York, 1962.
- [HG99] M. Hadjinicolaou and D. A. Goussis. Asymptotic solutions of stiff PDEs with the CSP method: the reaction diffusion equation. *SIAM J. Sci. Comput.*, 20:781 – 810, 1999.
- [HNW93] E. Hairer, S. P. Nørset, and G. Wanner. *Solving Ordinary Differential Equations I - Nonstiff Problems*, volume 8 of *Springer Series in Computational Mathematics*. Springer, Berlin, 2nd edition, 1993.
- [HW96] E. Hairer and G. Wanner. *Solving Ordinary Differential Equations II – Stiff and Differential-Algebraic Problems*, volume 14 of *Springer Series in Computational Mathematics*. Springer, Berlin, 2nd edition, 1996.
- [KG71] J. C. Keck and D. Gillespie. Rate-controlled partial-equilibrium method for treating reacting gas mixtures. *Combust. Flame*, 17:237 – 241, 1971.

- [KP98] D. Kondepudi and I. Prigogine. *Modern thermodynamics*. WILEY-VCH Verlag GmbH, Weinheim, 1998.
- [Küh06] W. Kühnel. *Differential Geometry*. American Mathematical Society, Providence, RI, 2006.
- [LBBS03] D. B. Leineweber, I. Bauer, H. G. Bock, and J. P. Schlöder. An efficient multiple shooting based reduced SQP strategy for large-scale dynamic process optimization - part I: Theoretical aspects. *Comput. Chem. Eng.*, 27:157 – 166, 2003.
- [Leb04] D. Lebiedz. Computing minimal entropy production trajectories: An approach to model reduction in chemical kinetics. *J. Chem. Phys.*, 120:6890 – 6897, 2004.
- [Leb06] D. Lebiedz. Optimal control, model- and complexity-reduction of self-organized chemical and biochemical systems: A scientific computing approach. Habilitation Thesis Physical Chemistry, University of Heidelberg, 2006.
- [Lei95] D. B. Leineweber. The theory of MUSCOD in a nutshell. Master's thesis, University of Heidelberg, 1995.
- [Lei99] D. B. Leineweber. *Efficient reduced SQP methods for the optimization of chemical processes described by large sparse DAE models*. VDI Verlag, Düsseldorf, 1999.
- [LG94] S. H. Lam and D. A. Goussis. The CSP method for simplifying kinetics. *Int. J. Chem. Kinet.*, 26:461 – 486, 1994.
- [LR91] G. Li and H. Rabitz. New approaches to determination of constrained lumping schemes for a reaction system in the whole composition space. *Chem. Eng. Sci.*, 46:95 – 111, 1991.
- [LRK06] D. Lebiedz, V. Reinhardt, and J. Kammerer. Novel trajectory based concepts for model and complexity reduction in (bio)chemical kinetics. In A. Gorban et al., editor, *Model reduction and coarse-graining approaches for multi-scale phenomena*, pages 343 – 364. Springer, Heidelberg, 2006.
- [LRT94] G. Li, H. Rabitz, and H. Toth. A general analysis of exact nonlinear lumping in chemical kinetics. *Chem. Eng. Sci.*, 49:343 – 361, 1994.

- [Maa95] U. Maas. Coupling of chemical reaction with flow and molecular transport. *Appl. Math.*, 40:249 – 266, 1995.
- [Maa98] U. Maas. Efficient calculation of intrinsic low-dimensional manifolds for the simplification of chemical kinetics. *Computing and Visualization in Science*, 1:69 – 81, 1998.
- [MM13] L. Michaelis and M. L. Menten. Die Kinetik der Invertinwirkung. *Biochem. Z.*, 49:333–369, 1913.
- [MP92] U. Maas and S. B. Pope. Simplifying chemical kinetics: Intrinsic low-dimensional manifolds in composition space. *Combust. Flame*, 88:239 – 264, 1992.
- [NW99] J. Nocedal and S. M. Wright. *Numerical Optimization*. Springer Verlag, New York, 1999.
- [OM98] M. S. Okino and M. L. Mavrouniotis. Simplification of mathematical models of chemical reaction systems. *Chem. Rev.*, 98:391–408, 1998.
- [Pli81] K. J. Plitt. Ein superlinear konvergentes Mehrzielverfahren zur direkten Berechnung beschränkter optimaler Steuerungen. Master's thesis, University of Bonn, 1981.
- [Pop04] S. B. Pope. Gibbs function continuation for the stable computation of chemical equilibrium. *Combust. Flame*, 139:222 – 226, 2004.
- [Pow78] M. J. D. Powell. A fast algorithm for nonlinearly constrained optimization calculations. In G. A. Watson, editor, *Numerical Analysis, Dundee 1977*, volume 630 of *Lecture Notes in Mathematics*, Berlin, 1978. Springer.
- [PZ99] L. Petzold and W. Zhu. Model reduction for chemical kinetics: An optimization approach. *AIChE Journal*, 45:869 – 886, 1999.
- [RF90] M. R. Roussel and S. J. Fraser. Geometry of the steady-state approximation: Perturbation and accelerated convergence methods. *J. Chem. Phys.*, 93:1072 – 1081, 1990.

- [RF91] M. R. Roussel and S. J. Fraser. Accurate steady-state approximations: Implications for kinetics experiments and mechanism. *J. Phys. Chem.*, 95:8762 – 8770, 1991.
- [RF01] M. R. Roussel and S. J. Fraser. Invariant manifold methods for metabolic model reduction. *Chaos*, 11:196 – 206, 2001.
- [RKD83] H. Rabitz, M. Kramer, and D. Dacol. Sensitivity analysis in chemical kinetics. *Annu. Rev. Phys. Chem.*, 34:419 – 461, 1983.
- [RPVG06] Z. Ren, S. B. Pope, A. Vladimirov, and J. M. Guckenheimer. The invariant constrained equilibrium edge preimage curve method for the dimension reduction of chemical kinetics. *J. Chem. Phys.*, 124:114111, 2006.
- [SB96] J. Stoer and R. Bulirsch. *Introduction to numerical analysis*. Springer, New York, 1996.
- [SD01] R. T. Skodje and M. J. Davis. Geometrical simplification of complex kinetic systems. *J. Phys. Chem.*, 105(45):10356 – 10365, 2001.
- [TPT<sup>+</sup>92] A. S. Tomlin, M. J. Pilling, T. Turanyi, J. H. Merkin, and J. Brindley. Mechanism reduction for the oscillatory oxidation of hydrogen: Sensitivity and quasi-steady-state analyses. *Combust. Flame*, 91:107 – 130, 1992.
- [Tur90] T. Turányi. Sensitivity analysis of complex kinetic systems: Tools and applications. *J. Math. Chem.*, 5:203 – 248, 1990.
- [Ver00] F. Verhulst. *Nonlinear Differential Equations and Dynamical Systems*. Springer-Verlag, Berlin, Heidelberg, 2000.
- [Wig96] S. Wiggins. *Introduction to Applied Nonlinear Dynamical Systems and Chaos*. Springer, New York, Berlin, Heidelberg, 1996.
- [Wil63] R. B. Wilson. *A Simplicial Algorithm for Concave Programming*. PhD thesis, Harvard University, 1963.
- [Wil70] S. Willard. *General Topology*. Addison-Wesley, 1970.
- [WMD06] J. Warnatz, U. Maas, and R. W. Dibble. *Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation*. Springer, Berlin, 2006.

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- [YTB<sup>+</sup>95] A. N. Yannacopoulos, A. S. Tomlin, J. Brindley, J. H. Merkin, and M. J. Pilling. The use of algebraic sets in the approximation of inertial manifolds and lumping in chemical kinetic systems. *Physica D*, 83:421 – 449, 1995.



## **Erklärung**

Hiermit erkläre ich, dass ich diese Arbeit selbstständig verfasst, keine anderen als die angegebenen Quellen und Hilfsmittel benutzt und alle Stellen, die dem Wortlaut oder Sinne nach anderen Werken entnommen sind, durch Angabe der Quellen als Entlehnung kenntlich gemacht habe.

Heidelberg, January 11, 2007

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(Miriam Winckler)