

Article

Entropy-Related Extremum Principles for Model Reduction of Dissipative Dynamical Systems

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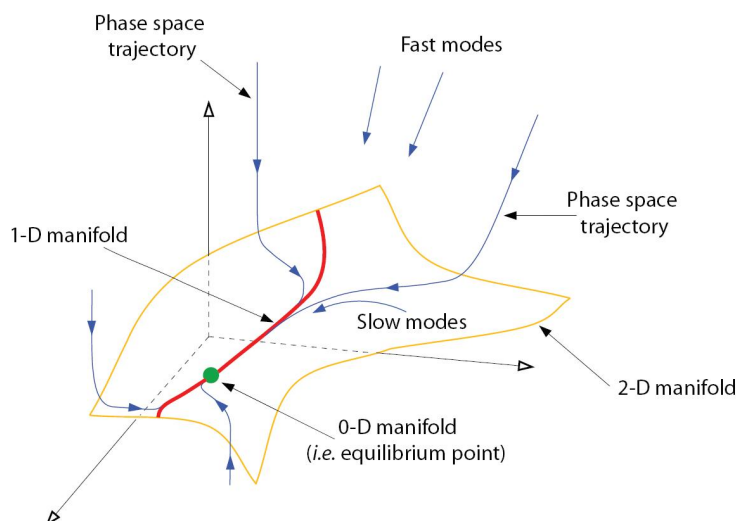
Abstract: Chemical kinetic systems are modeled by dissipative ordinary differential equations involving multiple time scales. These lead to a phase flow generating anisotropic volume contraction. Kinetic model reduction methods generally exploit time scale separation into fast and slow modes, which leads to the occurrence of low-dimensional slow invariant manifolds. The aim of this paper is to review and discuss a computational optimization approach for the numerical approximation of slow attracting manifolds based on entropy-related and geometric extremum principles for reaction trajectories.

Keywords: model reduction; slow invariant manifolds; chemical kinetics; extremum principles; entropy concepts

1. Introduction

Model reduction in chemical kinetics is an important issue in numerical simulations of reactive flows involving high-dimensional detailed reaction mechanisms with multiple time scales [1]. Also, for complexity reduction of chemical reaction mechanisms [2] and biochemical networks [3], insight into the multiple time scale structure is often useful.

Figure 1. Illustration of trajectories relaxing onto a 2-D manifold and successively a 1-D manifold while converging to stable equilibrium point. Figure courtesy of A.N. Al-Khateeb, J.M. Powers, S. Paolucci (private communication).



In dissipative ordinary differential equation (ODE) systems modeling chemical reaction kinetics, different time scales cause anisotropic phase volume contraction along solution trajectories. This leads to a bundling of trajectories near “manifolds of slow motion” of successively lower dimension as time progresses (see Figure 1). Model reduction methods exploit a time scale separation into fast and slow modes by computing a dimension-reduced model via elimination of fast modes enslaving them to the slow ones and projecting the system dynamics from the full state space to a slow manifold.

Prominent numerical techniques are the ILDM-method [4,5], computational singular perturbation (CSP) [6,7], Fraser’s algorithm [8–10], the method of invariant grids [11,35], the zero derivative principle (ZDP) [13,14], the rate-controlled constrained equilibrium (RCCE) method [15], the invariant constrained equilibrium edge pre-image curve (ICE-PIC) method [16,17], flamelet-generated manifolds [18,19] and finite time Lyapunov exponents [20].

Dissipation and the bundling of trajectories on slow manifolds are closely related to the concept of entropy. The term “entropy” is used in various contexts in chemistry, physics and dynamical systems theory, but all definitions follow the same basic idea related to information loss or gain and increase or decrease in complexity. Here, we will refer to the chemical definition of entropy production rate and the general concepts of topological and metric entropy of dynamical systems which measure the increase in dynamical complexity during time evolution. At the core of the thermodynamic point of view of entropy is Gibbs’ variational principle and Boltzmann’s microscopic interpretation of the entropy S as $S = k_B \ln W$ with the thermodynamic probability W measuring the number of microscopic states being consistent with a macroscopic property of a system. Postulating equal *a priori* probabilities of each microstate the thermodynamic probability of a macroscopic state to be implemented in this picture is proportional to the number of microstates being consistent with that macrostate.

Here, we review and discuss the recently proposed use of entropy-related concepts to formulate a variational principle suitable to characterize trajectories on, respectively near, slow invariant manifolds of chemical kinetic systems. In analogy to the classical thermodynamic point of view the slow manifold can be interpreted as a “macroscopic” view of the system and a variational principle is supposed to distinguish this “slow” macrostate from all other possible macrostates being consistent with a chosen parameterization of a low-dimensional manifold.

2. Entropy Concepts

For an elementary reaction step with reaction rates R_j^f and R_j^r for forward and backward reactions the chemical entropy production rate can be calculated from

$$\frac{d_i S_j}{dt} = R(R_j^f - R_j^r) \ln \left(\frac{R_j^f}{R_j^r} \right) \quad (1)$$

where R is the universal gas constant. Since the total entropy production rate is additive for several elementary steps, it can be computed from purely kinetic information for arbitrary reaction systems using (1) if the detailed elementary step mechanism is known and the kinetic rate coefficients are available. For isolated systems with constant internal energy and volume, the entropy is a Lyapunov function of the dynamical system following the *Second Law of Thermodynamics*.

In [21,22], numerical approximations of slow attracting manifolds are obtained by computation of trajectories along which the total (time integral over entropy production rate) entropy production (1) summing over all elementary reaction steps is minimal while chemical equilibrium is approached as time progresses. The approach yields approximations of slow manifolds, however, they lack invariance. Here, we will discuss the extension and improvement of this fundamental idea to more general entropy-related extremum principles tracing trajectories of a dissipative dynamical system **backwards** in time and point out relations to entropy concepts in dynamical systems theory. In the latter context, entropy can generally be interpreted as a measure of the rate of increase in dynamical complexity, e.g., the rate of dissipation. We propose that an extremum principle suitable to characterize trajectories on slow attracting manifolds should incorporate in some sense the idea of minimum dissipativeness (in the sense of “maximum slowness”) of a dynamical system along these trajectories.

In this section, we provide an overview of relevant entropic concepts in dynamical systems theory and in the next section we will try to illustrate how these general concepts qualitatively relate to and provide a motivation for the criteria we choose for the purpose of computing slow attracting manifold by proposing an entropy-related extremum principle for trajectories.

A standard reference for the following definitions and theorems is [23]. Our presentation partially follows that of Young [24].

Definition 1 [Topological entropy] [23] Let X be a compact metric space and $g : X \rightarrow X$, $g(x(t)) = x(t + 1)$ be the time-one map associated with the flow of the dynamical system defined by the vector field $f(x)$ of the ODE $\dot{x} = f(x)$, $f \in C^\infty$. $U \subset X$ is called a (n, ϵ) -separated set, $n \in \mathbb{Z}^+$, $\epsilon > 0$, if

$$\exists i, 0 \leq i < n, \forall x, y \in U : d(g^i(x), g^i(y)) > \epsilon.$$

The topological entropy $h_{top}(g)$ of g is defined as

$$h_{top}(g) := \lim_{\epsilon \rightarrow 0} \left\{ \limsup_{n \rightarrow \infty} \frac{1}{n} N(n, \epsilon) \right\}$$

with $N(n, \epsilon)$ denoting the maximum cardinality of all (n, ϵ) -separated sets.

The illustrative meaning of this entropy concept is the following: ϵ determines the resolution scale above which two points are considered separated. $N(n, \epsilon)$ counts the number of n -orbits (an orbit of “length n ” corresponds to the time- n map g^n) through x, y whose end points $g^n(x), g^n(y)$ are separated in the sense of Definition 1. Thus the limit $\epsilon \rightarrow 0, n \rightarrow \infty$ characterizes the overall divergence of trajectories. According to Definition 1 the number of (on the ϵ -scale) distinguishable orbits grows with n like $\sim e^{nh_{top}}$.

It follows directly from Definition 1 that $h_{top}(g) \in [0, \infty]$ and if g is a differentiable map of a compact d -dimensional manifold $h_{top}(g) \leq d \log \|Dg\|$ with the differential Dg .

Definition 2 [Metric entropy] [23] Let $(X, \mathcal{B}, \mu)$ be a probability space with the σ -algebra $\mathcal{B} \subset \mathcal{P}(X)$, an appropriately chosen probability measure μ such that $g : X \rightarrow X, g(x(t)) = x(t+1)$ is a measure-preserving, i.e. $\mu(A) = \mu(g^{-1}(A))$, time-one map diffeomorphism induced by the flow of the dynamical system defined by $\dot{x} = f(x), f \in C^\infty$. Let $\alpha := \{A_1, \dots, A_k\}$ be a finite partition of X , $g^{-1}(\alpha) := \{g^{-1}(A_1), \dots, g^{-1}(A_k)\}$ and j is called the α -address of $x \in X$ if $x \in A_j$. For two partitions α, β we define $\alpha \vee \beta := \{A \cap B : A \in \alpha, B \in \beta\}$, so that elements of $\bigvee_{i=0}^{n-1} g^{-i}\alpha$ are sets of the form $\{x : x \in A_{i_0}, g^1(x) \in A_{i_1}, \dots, g^{n-1}(x) \in A_{i_{n-1}}\}$ for index tuples $(i_0, \dots, i_{n-1})$ which are called the α -addresses of the n -orbit through x . With $H(\alpha) := -\sum \mu(A_i) \log \mu(A_i)$ the metric (or measure-theoretic) entropy $h_\mu(g)$ is defined as

$$h_\mu(g, \alpha) := \lim_{n \rightarrow \infty} \frac{1}{n} H\left(\bigvee_0^{n-1} g^{-i}\alpha\right), \quad h_\mu(g) := \sup_\alpha h_\mu(g, \alpha).$$

From an illustrative point of view $H(\alpha)$ can be interpreted as a measure of “average uncertainty” in trying to predict the α -addresses of an arbitrary point in phase space. The following variational principle makes the connection between topological and metric entropy.

Theorem 1 [25] Let $g : X \rightarrow X$ be a continuous map of a compact metric space X . Then $h_{top}(g) = \sup_\mu h_\mu(g)$ over all g -invariant probability measures μ .

Metric entropy can also be interpreted as the rate of “loss of information” on the proximity of nearby orbits:

Theorem 2 [24] Let (g, μ) be ergodic. Then for μ -almost every x it holds

$$h_\mu(g) = \lim_{\epsilon \rightarrow 0} \left\{ \limsup_{n \rightarrow \infty} -\frac{1}{n} \log \mu(B(x, n, \epsilon)) \right\}$$

with $B(x, n, \epsilon) := \{y \in X : d(g^i(x), g^i(y)) < \epsilon, 0 \leq i < n\}$.

There is an interesting relation between the above entropy definitions and the concept of Lyapunov exponents characterizing the divergence of trajectories:

Theorem 3 [Ruelle's Inequality] [26] Let $g : M \rightarrow M$ be a C^2 -diffeomorphism of a compact Riemannian manifold M and μ a g -invariant ergodic probability measure. With the r distinct Lyapunov exponents $\lambda_i, i = 1, \dots, r$ of (g, μ) and the linear subspaces U_i corresponding to λ_i with the dimension $\dim U_i$ of the multiplicity of λ_i , it holds

$$h_\mu(g) \leq \sum \lambda_i^+ \dim U_i.$$

Theorem 4 [Pesin's Formula] [27] If μ is equivalent to the Riemannian measure on M it holds

$$h_\mu(g) = \sum \lambda_i^+ \dim U_i.$$

Finally, topological entropy is related to volume growth caused by the phase flow. Let M be a compact m -dimensional C^∞ manifold and $g : M \rightarrow M$ a C^1 -mapping and let $\Sigma(k, l)$ with $k, l \geq 1$ be the set of C^k mappings $\sigma : Q^l \rightarrow M$ with the l -dimensional unit cube Q^l and $\omega(\sigma)$ the l -dimensional volume of the image of σ in M counted with multiplicity (if σ is not a one-to-one mapping and the images of several parts coincide, then the set will be counted as many times as it is covered by the image of σ). For $n = 1, \dots, k \leq \infty, l \leq m$ define

$$V_{l,k}(g) := \sup_{\sigma \in \Sigma(k,l)} \limsup_{n \rightarrow \infty} \frac{1}{n} \log \omega(g^n \circ \sigma), \quad V(g) := \max_l V_{l,\infty}(g)$$

and

$$R(g) := \lim_{n \rightarrow \infty} \frac{1}{n} \log \max_{x \in M} \|Dg^n(x)\|.$$

Theorem 5

a) [28] If g is $C^{1+\epsilon}$, $\epsilon > 0$, then $h_{top}(g) \leq V(g)$

b) [29] For $g \in C^k$, $k = 1, \dots, \infty$ it holds

$$V_{l,k}(g) \leq h_{top}(g) + \frac{2l}{k} R(g).$$

For $g \in C^\infty$ a) and b) imply $h_{top}(g) = V(g)$.

In the case $g \in C^\infty$, $h_{top}(g)$ is related to the rate of growth of volumes of g^n -images of embedded sub-manifolds. Reduced models of chemical kinetics (generally approximating slow attracting invariant manifolds) are represented by such embedded sub-manifolds and intuitively their slowness property should be related to minimum growth of volumes when projected into the tangent bundle of these manifolds. This conceptual point of view will be taken when discussing extremum principles for trajectories supposed to be on, respectively close to, slow invariant manifolds.

3. Extremum Principle for Trajectories Approximating Slow Manifolds

The key of our model reduction approach is based on the goal to exploit non-local phase space information on dissipativeness contained in the behavior of trajectories in time parameterization. This information can be used in a variational problem formulation aimed at a characterization of suitable reaction trajectories approximating slow invariant manifolds (SIM) in terms of an appropriate interpretation of minimum dissipativeness. The formulation of this idea as an ODE-constrained optimization problem allows the use of sophisticated and efficient optimization software for the numerical solution of the problem. The central issue is an objective functional implementing a variational principle for the identification of suitable trajectories which should reflect in a suitable sense minimum dissipation along the slow manifold. We suggest either time-integrated chemical entropy production rate (1) or the norm of velocity change with time (see section 3.1.) as a measure for the degree of dissipation. The latter is conceptually close to the notion of a *slow* manifold.

We consider autonomous ODE systems of the form $\dot{x} = f(x)$, $x(0) = x_0$, $f \in C^\infty$ modeling chemical reaction kinetics that have an asymptotically stable fixed point corresponding to chemical equilibrium. The variational problem can be formulated as

$$\min_{x(t)} \int_{t^0}^{t^f} \Phi(x(t)) \, dt \quad (2a)$$

subject to

$$\frac{dx(t)}{dt} = f(x(t)) \quad (2b)$$

$$0 = g(x(t)), x(t) \geq 0 \quad (2c)$$

$$x_j(t^f) = x_j^{t^f}, \quad j \in I_{\text{rpv}}, \quad t^0 < t^f. \quad (2d)$$

The variable $x = (x_i)_{i=1}^n$ denotes the state vector and I_{rpv} is an index set that contains the indices of state variables (denoted as *reaction progress variables* in chemical kinetics) with (at time t^f) fixed values chosen to parameterize the reduced model, i.e., the slow attracting manifold to be computed. The cardinality of the index set I_{rpv} equals the dimension of the slow manifold to be computed and has to be set a priori by the user. Thus, those state variables representing the actual degrees of freedom within the optimization problem are $x_j(t^f)$, $j \notin I_{\text{rpv}}$. The process of determining $x_j^{t^f}$, $j \notin I_{\text{rpv}}$ from $x_j^{t^f}$, $j \in I_{\text{rpv}}$ is known as *species reconstruction* in model reduction of chemical kinetics and represents a function mapping the reaction progress variables to the full species composition by determining a point on the slow attracting manifold. The system dynamics (e.g., chemical kinetics determined by the reaction mechanism) are described by (2b) and enter the optimization problem as equality constraints. Hence an optimal solution of (2) always satisfies the system dynamics of the full ODE system and therefore represents a solution trajectory of (2b). Additional constraints (e.g. chemical element mass conservation relations in the case of chemical kinetics that have to be obeyed due to the law of mass conservation) are collected in the linear function g in (2). The state variables chosen as parameterization of the SIM are fixed via the equality constraint (2d) at t^f . The function $\Phi(x(t))$ in (2a) characterizes the variational principle that will be discussed in the next section.

The approximated SIM obtained by pointwise solution of problem (2) on a suitable grid of reaction progress variable values can be used as a reduced model of the underlying ODE model, for example

via a look-up table for points on the slow manifold. This reduced model is parameterized by the reaction progress variables (coordinate system of the manifold) chosen to be an arbitrary set of variables that allow a unique parameterization of the manifold. Unfortunately, there is no systematic way to check for global uniqueness, however, in many applications physical insight into the system suggests an appropriate choice. In combustion chemistry, usually reaction products and/or intermediates with monotonic behavior during approach of equilibrium are chosen.

For continuously differentiable Φ it is easy to prove existence of a solution to (2) since the constraints (2b) and (2d) make the problem a finite-dimensional one with the initial values $x(t^0)$ as free optimization variables and the linear constraint $0 = g(x(t))$ together with the inequality constraint $x(t) \geq 0$ define a closed and bounded subset of $\mathbb{R}^n$ for the feasible initial values. Using the standard compactness argument, the existence of a solution follows. In order to prove uniqueness, convexity is required which cannot generally be assured for nonlinear Φ .

3.1. Optimization Criterion

In the original work [21] the entropy production rate (1) has been chosen as a criterion Φ in (2a) and following the fundamental idea to search for an entropy-related extremum principle that characterizes trajectories on or near slow attracting manifolds we discuss geometric criteria in [31]. In Section 4, we show that the latter are superior to the previously used entropy production rate and yield accurate approximations of slow invariant manifolds for an example model of chemical kinetics. We propose an appropriate characterization of maximum “slowness” in terms of an integral over suitably defined curvature (velocity change) of trajectories measured in the Euclidean norm. An attracting SIM is characterized by the property that all trajectories in its neighborhood converge faster (with exponential rates) to the manifold than to the attractor, the chemical equilibrium point. Adrover *et al.* [30] recently argued that this might be expressed as a ratio $r > 1$ of the local stretching (contraction) rate of vectors orthogonal to the manifold compared to those tangent to the manifold. Their local point of view comes close to our reasoning on the basis of a variational principle for trajectories.

The corresponding geometric objective functional (time integral over $\Phi(t)$) to be minimized in (2a) is supposed to incorporate essential characteristics of slow attracting manifolds. The successive relaxation of chemical forces causes curvature in the reaction trajectories (in the sense of velocity change along the trajectory). Therefore, in [31,32]

$$\Phi(x) := \|J_f(x) \cdot f\|_2 \quad (1)$$

is proposed as a suitable criterion in (2a) with $J_f(x)$ being the Jacobian of the right hand side f evaluated at $x(t)$ and $\|\cdot\|_2$ denoting the Euclidean norm.

The term $J_f(x) \cdot f$ represents the rate of change of the reaction velocity vector in its own direction along a trajectory and can be interpreted as a specific definition of curvature in time parameterization of the curve:

$$\ddot{x} = \frac{d\dot{x}}{dt} = \frac{d\dot{x}}{dx} \cdot \frac{dx}{dt} = J_f(x) \cdot f.$$

The minimization of the time integral over Φ in (2a) incorporates the “maximum slowness” respectively “minimum dissipation” issue in terms of an average over suitably measured local curvature (in time parameterization) of a trajectory. The qualitative relation to the entropy concepts in dynamical systems

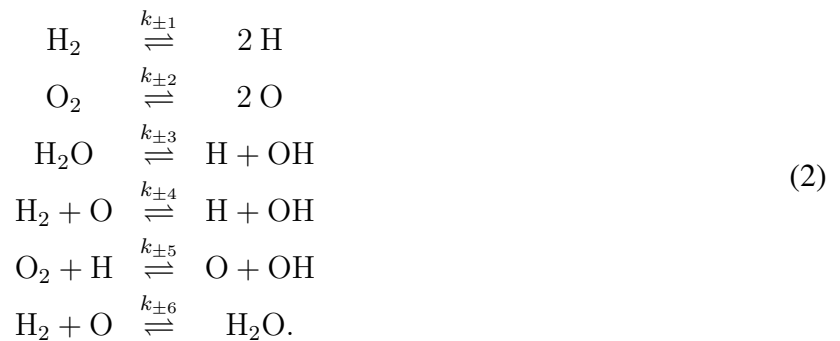
theory reviewed in section 2. becomes obvious when considering the time evolution of two nearby points A and B lying ϵ -close to each other on the same trajectory defined by the optimal solution of (2) with (1) in the objective functional (2a). Imagine now a phase flow field with constant velocity, *i.e.*, $\ddot{x}(t) \equiv 0$, along the trajectory. It follows $f = \text{const}$ and the two points A and B are transported by the phase flow in backward time direction for some time $\Delta t = t^f - t^0$ such that the end points after time Δt have the same distance as the initial points when measured in arc length of the trajectory piece connecting the two points. Increase in that distance between two ϵ -close points A and B under this time- Δt map is obviously related to $\ddot{x}(t)$. Along a trajectory with small $\int_{t^0}^{t^f} \|\ddot{x}(t)\| dt$ (a measure for velocity change in the interval $[t^0, t^f]$) the increase in distance between the two points A and B should be small as well along this particular trajectory. This relates to the ideas contained in the topological and metric entropy Definitions 1 and 2 in section 2. implementing concepts to measure divergence, dissipation or information loss respectively and thus our criterion allows for a minimum entropy interpretation in terms of small distance growth between two points on the optimal trajectory for a given time horizon Δt . A stringent theoretical justification of the curvature criterion and its use for approximating slow attracting manifolds of 2-dimensional linear and nonlinear test models is provided in [38] and beyond the scope of the present paper. Here, we restrict ourselves to the qualitative motivation related to entropy concepts.

3.2. Numerical Methods

Optimization problem (2) can be solved as a standard nonlinear programming problem (NLP), for example via the sequential quadratic programming (SQP) method [33] or interior point methods (e.g., [34]). However, one has to decide how to treat the differential equation constraint and the objective functional. The easiest way is a decoupled iterative approach, a full numerical integration of the ODE model with the current values of the variables subject to optimization. This is called the sequential (or single shooting) approach since it fully decouples simulation of the model and optimization. However, it is often beneficial to have an “all at once” approach that couples simulation and optimization via discretization of the ODE constraint. This simultaneous approach has the advantage of introducing more freedom into the optimization problem since the differential equation model does not have to be solved exactly in each iteration of the optimization. A fully discrete collocation approach and a numerical quadrature formula are appropriate for the treatment of the ODE constraints and the objective functional respectively. On a predefined time grid the collocation method constructs polynomials obeying the differential equation at a certain number of nodes depending on its degree. For the numerical solutions presented in this paper we use a Radau collocation method with linear, quadratic, or cubic polynomials, respectively. The resulting NLP is solved by use of the interior point algorithm implemented in the IPOPT-package [34]. As in [32] we use the invariance defect (see [35,36] and references therein) as a measure of “goodness” of the slow manifolds computed numerically. Restarting the optimization algorithm for parameter values corresponding to a point on a previously computed solution trajectory should yield the same trajectory in the case of invariance of the computed manifold.

4. Results: Application to Model Hydrogen Combustion Reaction Mechanism

In this section we consider a small test mechanism, which has already been used for model reduction purposes in [31,36,37]. It consists of six chemical species involved in six elementary reactions constrained by two element mass conservation relations for hydrogen and oxygen:



With the rate constants

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

and the mass conservation relations

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

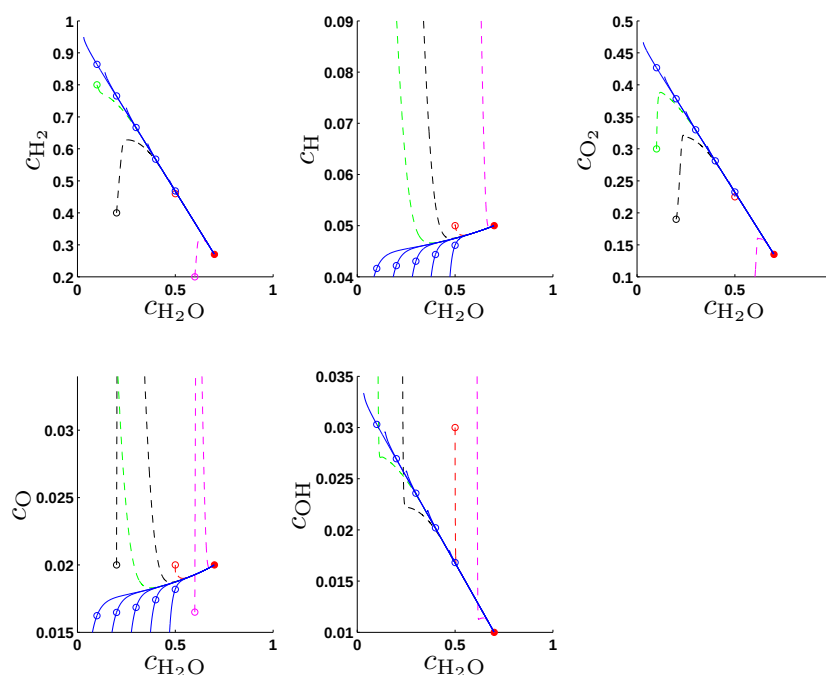
this mechanism yields a system with four degrees of freedom. For our computations $C_1 = 2.0$ and $C_2 = 1.0$ are chosen.

4.1. Computation of One-Dimensional Manifolds

We present results for the computation of one-dimensional manifolds in composition space. The chemical species $c_{\text{H}_2\text{O}}$ is chosen as reaction progress variable. It is varied on a grid between 0.1 and 0.5 with step size 0.1. In Figure 2, the values of the free variables of the optimization problem with the entropy production rate objective functional are plotted versus the value of $c_{\text{H}_2\text{O}}$. Obviously, the manifold generated by the blue circles is a fair approximation of the SIM but lacks invariance.

Figure 3 shows the results for the curvature objective functional. A significant improvement towards invariance is achieved compared to corresponding results for chemical entropy production rate presented in Figure 2.

Figure 2. One-dimensional manifold numerically computed as solution of problem (2) with $\Phi(t) = \sum_{j=1}^6 \frac{d_i S_j}{dt} = R(R_j^f - R_j^r) \ln \left(\frac{R_j^f}{R_j^r} \right)$ (chemical entropy production rate criterion) with reaction rates R_j^f, R_j^r for the six forward and backward reactions of mechanism (2) computed according to mass action kinetics. $c_{\text{H}_2\text{O}}$ is chosen as reaction progress variable and varied between 0.1 and 0.5, $t^0 = -0.03, t^f = 0$. Open blue circles represent the final values at $t^f = 0$ of trajectories (blue lines are their continuations to equilibrium) for $t \in [t^0, t^f]$ computed by solving optimization problem (2), the red dot represents the equilibrium point. Dotted trajectories are started from arbitrary initial values and illustrate the attractiveness of the computed 1-D manifold.



4.2. Computation of Two-Dimensional Manifolds

Since the hydrogen combustion model has four degrees of freedom, also two-dimensional manifolds can be computed. In the presented examples, $c_{\text{H}_2\text{O}}$ and c_{H_2} serve as reaction progress variables. We show three-dimensional plots of the computed two-dimensional manifold and the relaxation of trajectories started from arbitrary initial values onto this 2-D manifold.

The remaining free variables are plotted versus the reaction progress variables in Figures 4 and 5. Trajectories started from arbitrary initial values relax on the 2-D manifold spanned by the computed trajectories before relaxing onto the 1-D manifold.

Computation times for a single point on the 1-D or 2-D manifolds are between 0.5 and 2.5 seconds, dependence on initial values for the iteration of the optimization algorithm is small.

Figure 3. $\Phi(t) = \|J_f(x) \cdot f\|_2^2$ (curvature criterion). $c_{\text{H}_2\text{O}}$ chosen as reaction progress variable and varied between 0.1 and 0.5, $t^0 = -0.03, t^f = 0$, figure components and notations as in Figure 2.

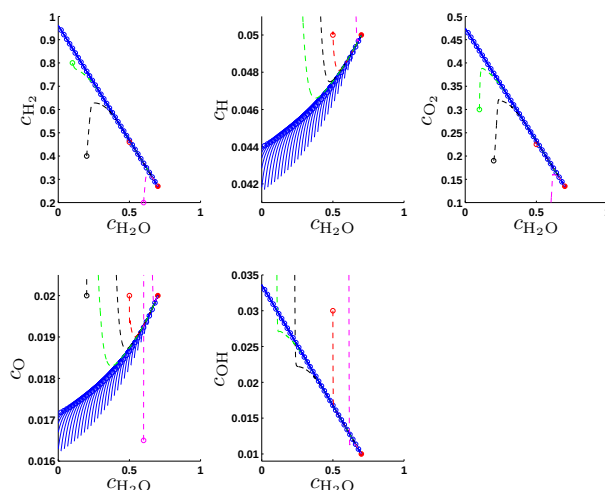


Figure 4. Chemical entropy production rate criterion as in Figure 2, reaction progress variables $c_{\text{H}_2\text{O}}$ and c_{H_2} varied between 0.01 and 0.69, respectively 0.01 and 0.26, $t^0 = -10^{-6}, t^f = 0$. Blue circles represent final values of trajectories (at $t^f = 0$) computed as solutions of optimization problem (2), blue lines the corresponding trajectories starting in these points and converging to equilibrium, colored trajectories are started from arbitrary initial values to illustrate attractiveness of the computed manifold spanned by the blue trajectories.

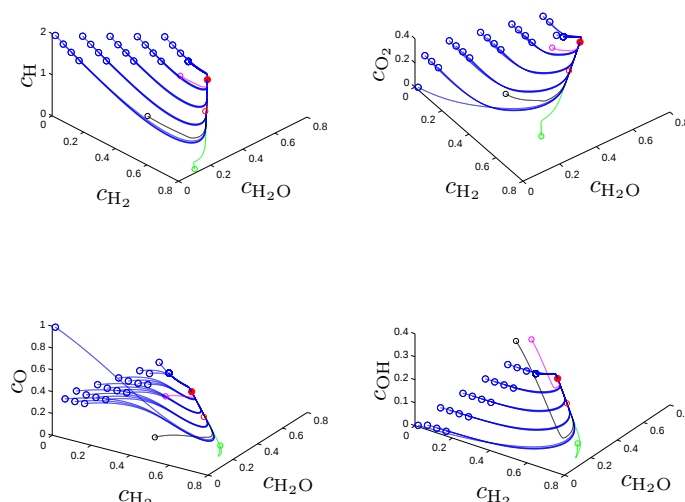
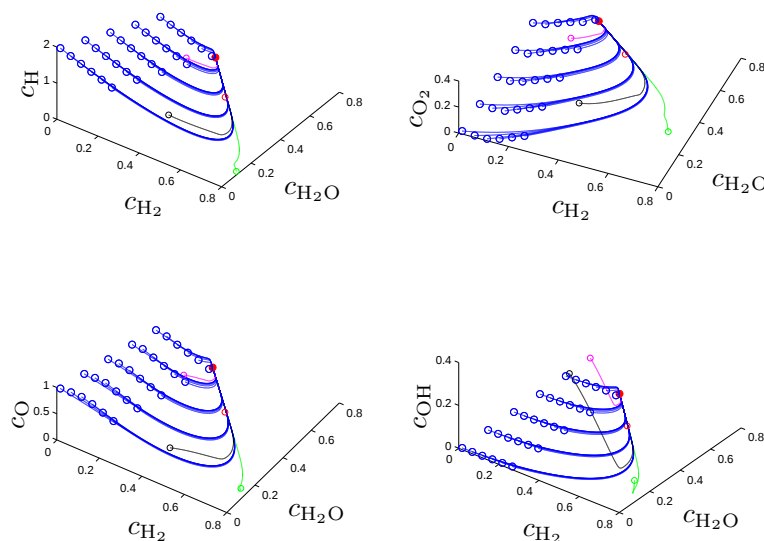


Figure 5. Curvature criterion, conditions, notations and figure components as in Figure 4.



5. Summary and Conclusions

We reviewed and discussed extremum principles related to entropy concepts and their use for numerical approximations of slow invariant manifolds in chemical kinetics by solution of a trajectory optimization problem. The results demonstrate that a geometric curvature-based objective functional related to entropy concepts in dynamical systems theory is superior to the formerly used chemical entropy production rate and yields in a “backward in time”-formulation highly accurate approximations of slow invariant manifolds in application to a six-species reaction mechanism as a test case. In [38] we prove that the curvature-based variational principle yields exact results for the slow invariant manifold in the limiting case of infinite-time horizon $(-\infty, t^f]$ for a linear 2-D dynamical system and the nonlinear Davis-Skodje [8] model widely used for testing model reduction techniques in chemical kinetics.

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