Model reduction in chemical kinetics based on the optimization of trajectories

Mathematics of Model Reduction,

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Contents

Introduction

- **Task:** Automatic model reduction for chemical kinetics modeled by ODEs
- **Most common idea in practical model reduction: ILDM**
  - Fix differential variables
  - Locally determine fast processes by eigenvalues of Jacobian
  - Compute algebraic variables by relaxation of fast processes
- **Problems with ILDM:**
  - Fixed dimension necessary for tabulation, but separation of fast and slow processes depends on boundary conditions
  - ILDM points in lower-temperature domain demand high dimensions
  - only local information is exploited
- **Lebiedz presented novel approach to model reduction in 2004** (reduction to one dimension)
  - Compute trajectories with minimal entropy production subject to one fixed initial value
  - **Here:** Generalize this approach for usage in multiple dimensions

General Problem

General trajectory-based optimization approach for model reduction in chemical kinetics:

$$\min_{c_k} \quad \int_0^T \Phi(c(t))\, \mathrm{d}t$$

subject to

$$\frac{\mathrm{d}c_k}{\mathrm{d}t} = f_k(c), \qquad k = 1, \ldots, m$$

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

$$|c_k(T) - c_k^{\text{eq}}| \leq \varepsilon, \qquad k \in I_{\text{fixed}}$$

and subject to conservation relations.

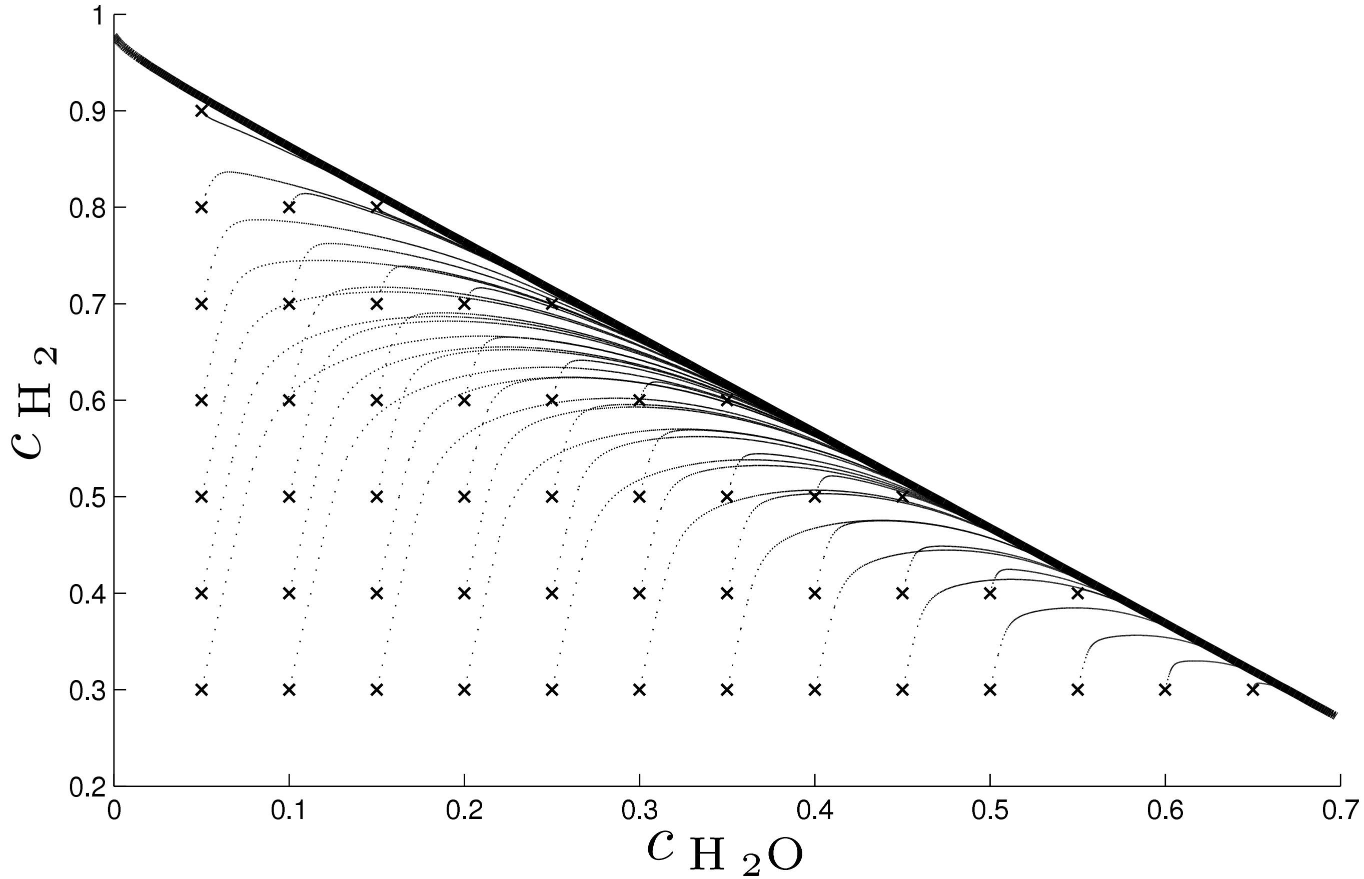
Solution:
This problem is a *variational boundary value problem* - can be solved efficiently using MUSCOD-II (Research group Bock)

Why this approach?

- Trajectories contain **global information** about mechanism
- Optimization approach for "guaranteed" solvability
- Natural realization of progress variables as initial values of trajectories
- Automatic approach

Continution strategy

- “Reduced trajectories” can be efficiently calculated by initial value embedding
- low computational demands for tabulation
- efficient initialization for in-situ computation of reduced descriptions



Generality of approach

Generality of approach allows for adaptation of

- optimization criterion
- integration horizon
- "initial" time (T_0 at which progress variables are set)

Here: Adaptation of optimization criterion.

$$\min_{c_k} \int_0^T \Phi(c(t))\,\mathrm{d}t$$

subject to

$$\frac{\mathrm{d}c_k}{\mathrm{d}t} = f_k(c), \qquad k = 1, \ldots, m$$

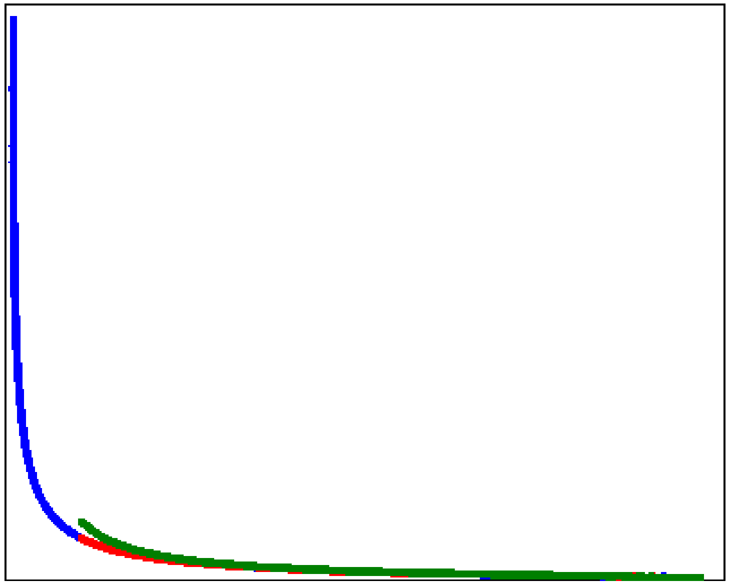
$$c_k(T_0) = c_k^0, \qquad k \in I_{\text{fixed}}$$

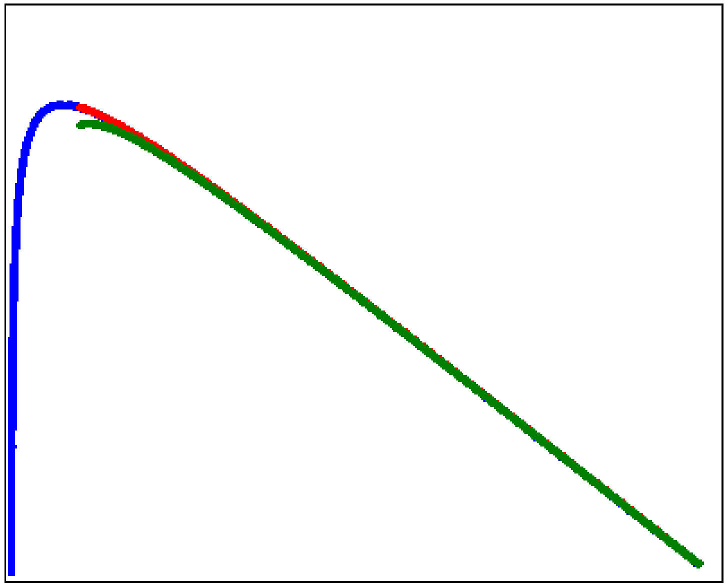
$$|c_k(T) - c_k^{\text{eq}}| \leq \varepsilon, \qquad k \in I_{\text{fixed}}$$

Relaxation Criterion

- Φ should describe extent of relaxation of "chemical forces" along trajectories:
  - should be minimal along a trajectory as close to equilibrium as allowed by the initial constraints
  - should consist of easily accessible data (e.g. reaction rates, chemical source terms and their derivatives)
  - should be continuously differentiable along reaction trajectories.

Desirable, but not necessary: Consistence property (Invariance)





Entropy production rate

Lebiedz [2004]: Minimize entropy production rate along trajectory

$$\frac{\mathrm{d_i} S_k}{\mathrm{d}t} = R\left((R_{k\mathrm{f}} - R_{k\mathrm{r}}) \ln \left(\frac{R_{k\mathrm{f}}}{R_{k\mathrm{r}}} \right) \right) \geq 0.$$

for single reaction step k.

Reduction criterion:

$$\Phi(c(t)) = \sum_{k=1}^{n} \frac{\mathrm{d_i} S_k}{\mathrm{d}t}$$

Note: For isothermal systems (negative) "Gibbs free energy" is the Lyapunov function. However, as

$$\frac{\mathrm{d}G}{\mathrm{d}t} = -T \frac{\mathrm{d_i} S}{\mathrm{d}t},$$

minimization of (negative) Gibbs free energy production = minimization of entropy production.

Relate curvature to relaxation

- Physical principle “Force = Curvature”

Curvature of trajectories?

$$\ddot{c}(t) = \frac{\mathrm{d}^2 c}{\mathrm{d}t^2} = \frac{\mathrm{d}\dot{c}}{\mathrm{d}t} = \frac{\mathrm{d}\dot{c}}{\mathrm{d}c}\frac{\mathrm{d}c}{\mathrm{d}t} = J(\dot{c}(t)) \cdot \dot{c}(t) = J(f(c(t))) \cdot f(c(t)),$$

$J(f)$ ... Jacobian of RHS of ODE $\dot{c}(t) = f(c(t))$.

Curvature of trajectory: $\|J(f)f\|$

- Becomes zero in thermodynamic equilibrium
- Can also be related to stiffness of solutions of ODE

Curvature based Concepts

Minimize curvature of trajectories, i.e.

$$\Phi(c(t)) = \|J(c)f(c)\|$$

Reflects the physical principle ”Force = Curvature” (in a suitable geometry).

Suitable geometry in phase space? Replace euclidian norm

$$\|x\|_2^2 = x^T x \text{ by } \|x\|_A^2 = x^T Ax$$

Norm induced by scalar product - pos. def. symm. bilinear form. Find A, such that scalar product $< x, y >:= x^T Ay$ is positive definite. Choose A diagonal with elements

$$a_{jj} = \sum_{k=1}^{n} \nu_{kj} \frac{\mathrm{d}_i S_k}{\mathrm{d}t}$$

with entropy production rate $\frac{\mathrm{d}_i S_k}{\mathrm{d}t}$ for reaction k.

Example Mechanism: Hydrogen Combustion

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

Together with two conservation relations this six-component mechanism yields a system with four degrees of freedom.

Minimum Entropy-Production Trajectories

Trajectory-based optimization approach for minimal entropy production:

$$\min_{c_k} \quad \int_0^T \sum_{k=1}^{n} \frac{\mathrm{d_i} S_k}{\mathrm{d}t} \, \mathrm{d}t$$

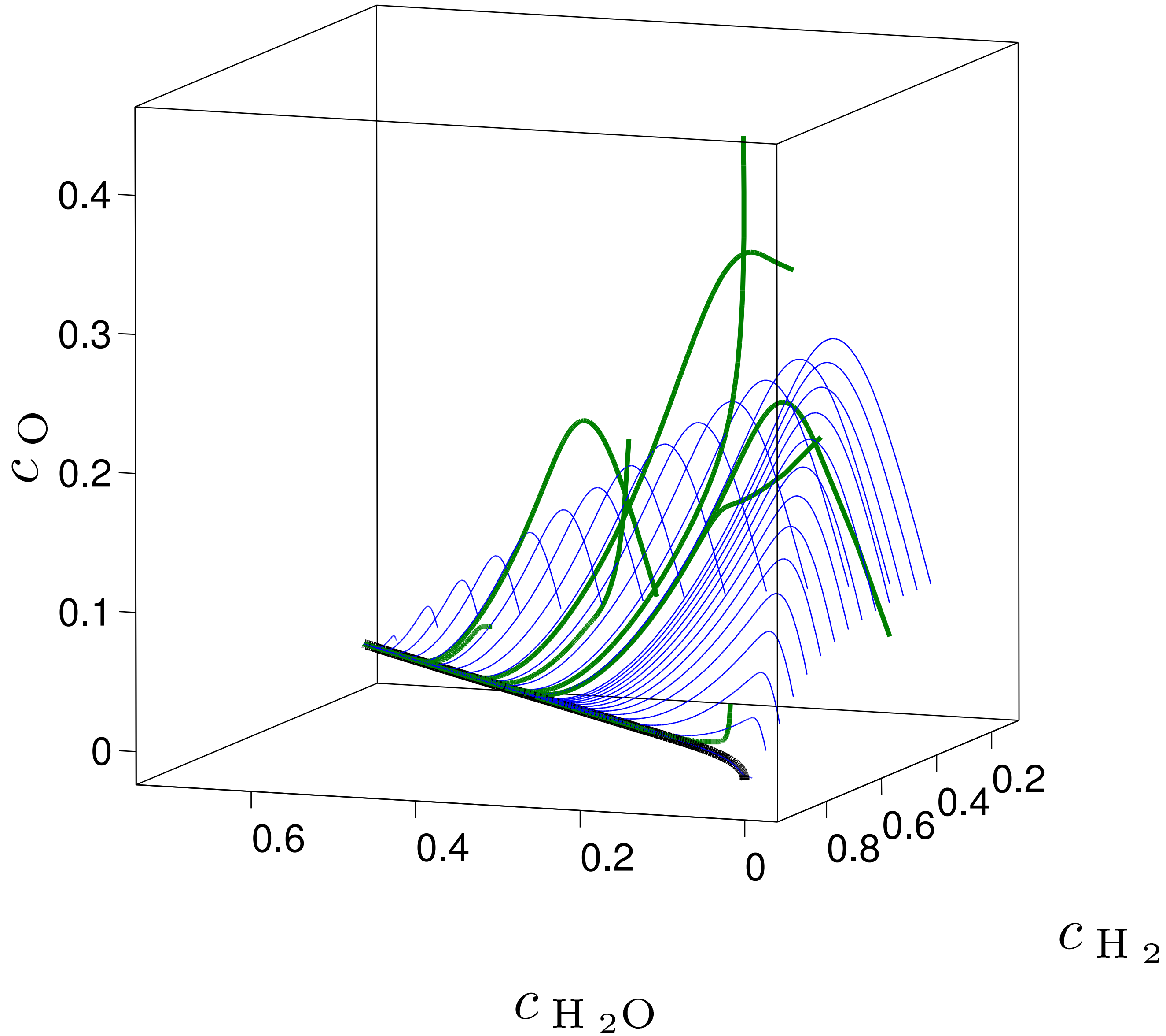
$$\text{subject to} \quad \frac{\mathrm{d}c_k}{\mathrm{d}t} = f_k(c), \qquad k = 1, \ldots, m$$

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

$$T \text{ sufficiently large}$$

and subject to conservation relations.

Entropy production rate



Arclength Parametrization

Resulting MEPTs form smooth manifold, but relax to 2D manifold first.
Possible explanation: time-integral in objective function.
More natural formulation: Path integral from initial value to equilibrium

$$\int_{l(0)}^{l(c^{\mathrm{eq}})} \sum_{j=1}^{n} \frac{\mathrm{d}_i S_j}{\mathrm{d}t} \mathrm{d}l(t),$$

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

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

As $\dot{c}(t) = f(c)$, modified minimal entropy production trajectories can also be written as

$$\min_{c_k(0)} \int_0^T \left(\sum_{j=1}^{n} \frac{\mathrm{d}_i S_j}{\mathrm{d}t} \right) ||f(c)||\mathrm{d}t$$

Minimal Entropy-Production Trajectories

Trajectory-based optimization approach for minimal entropy production in arclength parametrization:

$$\min_{c_k} \quad \int_0^T \sum_{k=1}^{n} \frac{\mathrm{d_i} S_k}{\mathrm{d}t} \|f(c)\| \, \mathrm{d}t$$

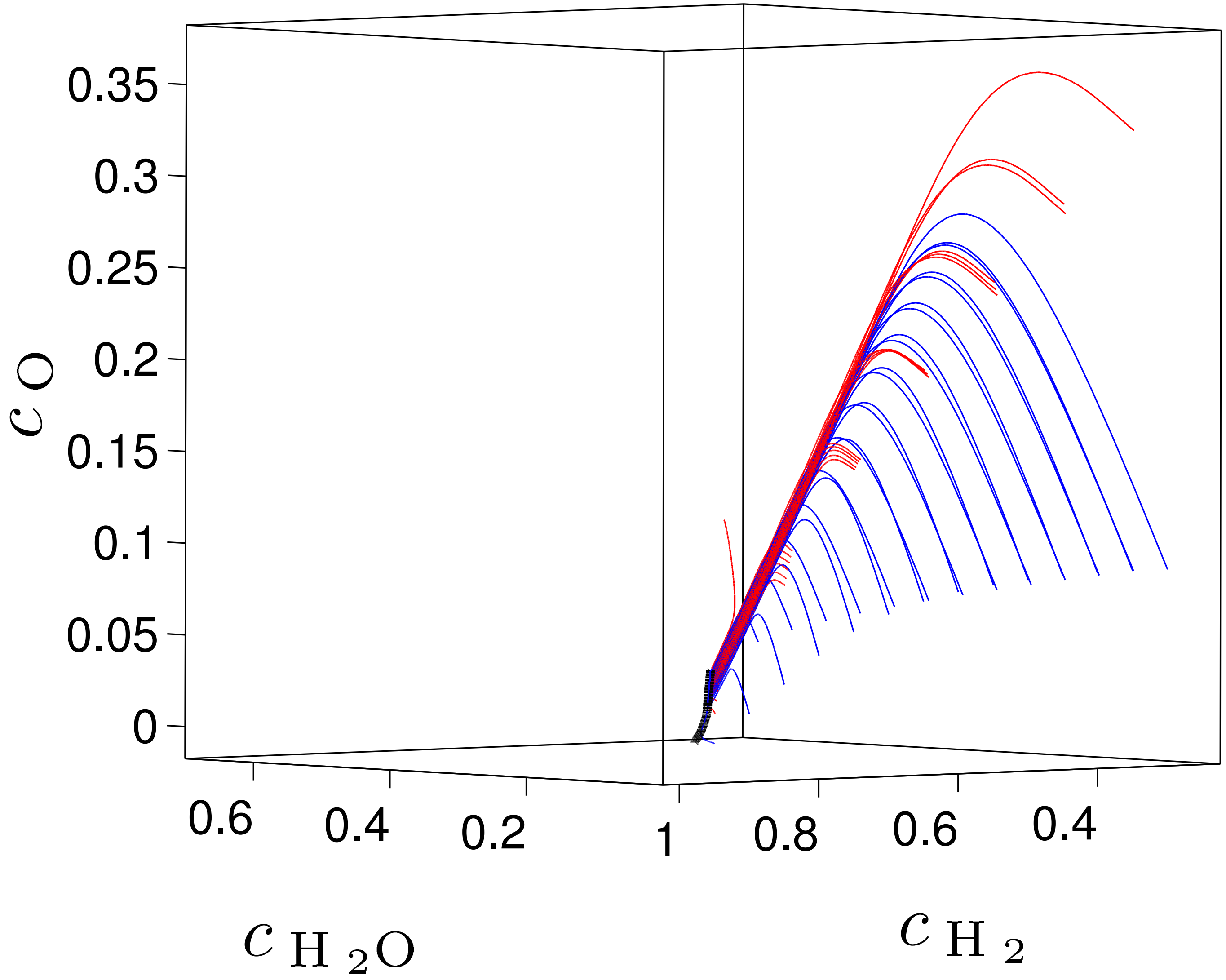
$$\text{subject to} \quad \frac{\mathrm{d}c_k}{\mathrm{d}t} = f_k(c), \qquad k = 1, ..., m$$

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

T sufficiently large

and subject to conservation relations.

Minimal entropy production trajectories



Minimally Curved Trajectories

Trajectory-based optimization approach for minimally curved trajectories:

$$\min_{c_k} \int_0^T \|J(c)f(c)\|_A \,\mathrm{d}t =$$

$$\min_{c_k} \int_0^T f^T J^T \begin{pmatrix} \sum_{j=1}^n \nu_{1j} \frac{\mathrm{d}_i S_1}{\mathrm{d}t} & 0 & \dots & 0 \\ 0 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \vdots \\ 0 & \dots & 0 & \sum_{j=1}^n \nu_{nj} \frac{\mathrm{d}_i S_n}{\mathrm{d}t} \end{pmatrix} J f \mathrm{d}t$$

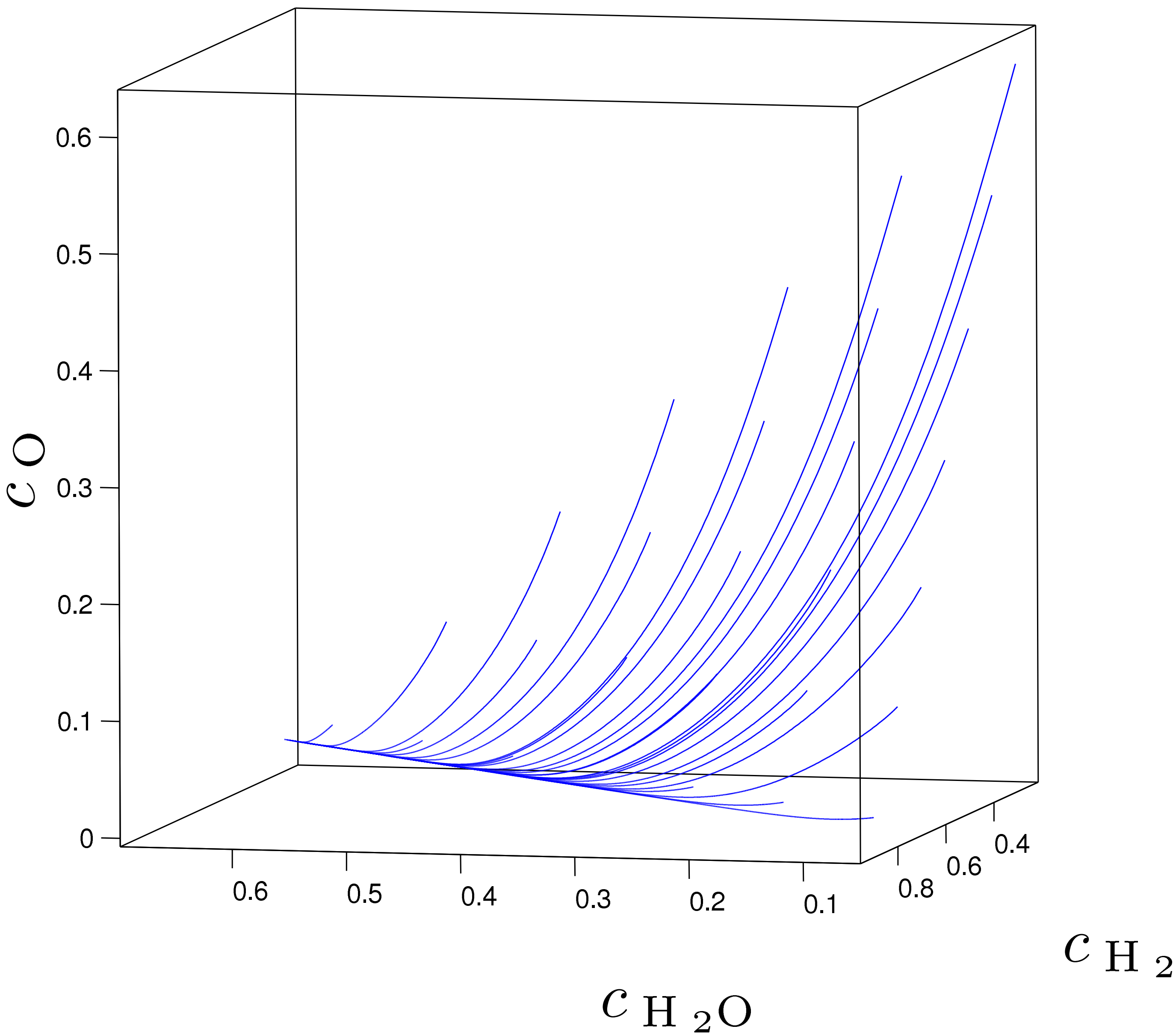
subject to $\dfrac{\mathrm{d}c_k}{\mathrm{d}t} = f_k(c), \qquad k = 1, \dots, m$

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

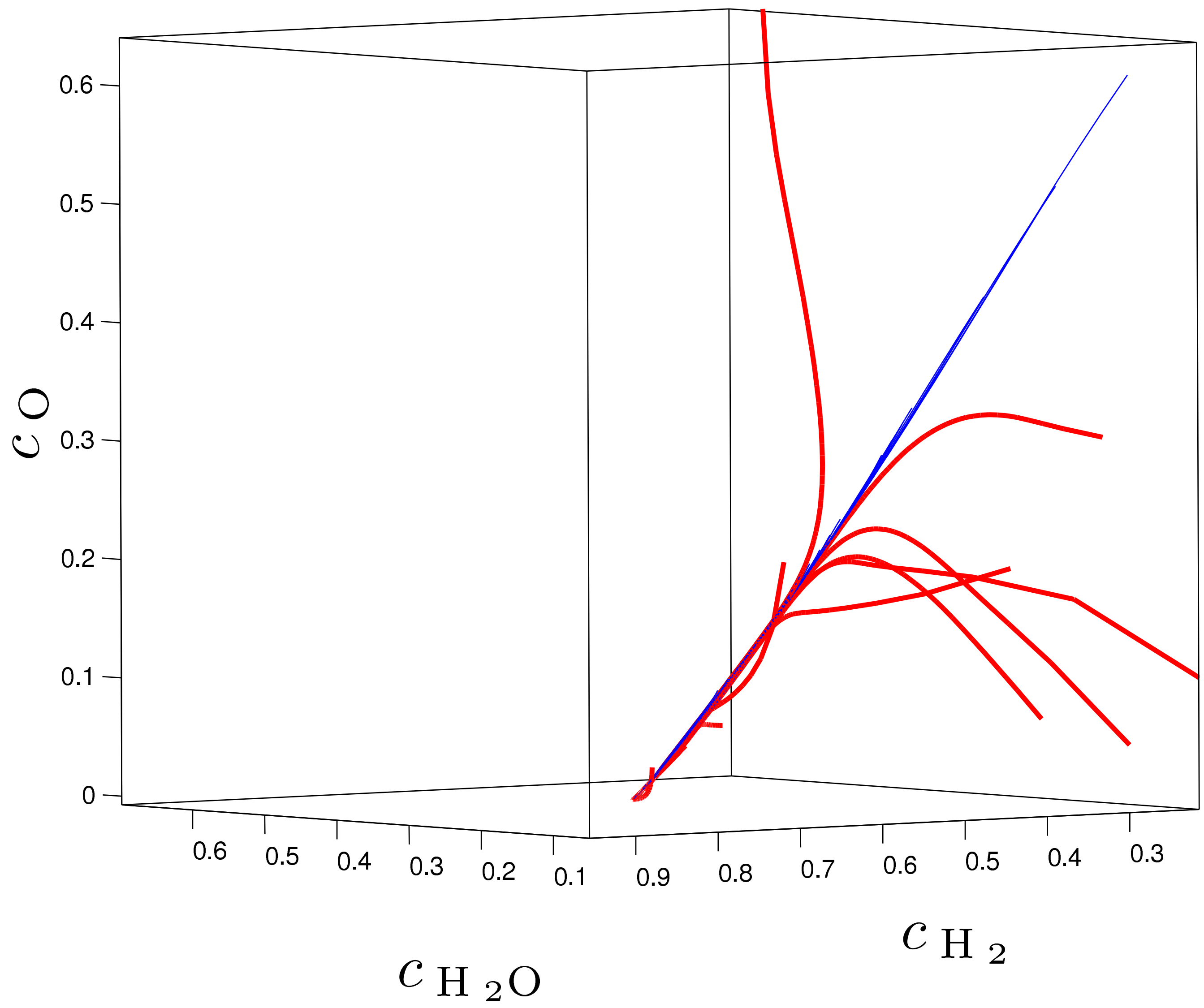
T sufficiently large

and subject to conservation relations.

Curvature minimization



Curvature minimization



Summary and Outlook

Summary:

- Introduced general trajectory-based optimization concept for model reduction
  - arbitrary dimension
  - optimization approach for solvability
  - approach to automatic model reduction
- Application of trajectory-based optimization concept with novel curvature-based relaxation criterion shows promising results

Outlook:

- Alternative Relaxation Criteria ?
- Alternative Solution Strategies ?
- More realistic mechanisms (temperature dependence)

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