Model reduction in chemical kinetics based on the optimization of trajectories

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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:

\[ \begin{align*}
\min_{c_k} \quad & \int_0^T \Phi(c(t)) \, dt \\
\text{subject to} \quad & \frac{dc_k}{dt} = f_k(c), \quad k = 1, \ldots, m \\
& c_k(0) = c_0^k, \quad k \in I_{\text{fixed}} \\
& |c_k(T) - c_{k}^{eq}| \leq \varepsilon, \quad k \in I_{\text{fixed}}
\end{align*} \]

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
Continuation 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 allows for adaptation of
- optimization criterion
- integration horizon
- “initial” time ($T_0$ at which progress variables are set)

Here: Adaptation of optimization criterion.

$$\min_{c_k} \int_0^T \Phi(c(t)) \, dt$$
subject to
$$\frac{dc_k}{dt} = f_k(c), \quad k = 1, \ldots, m$$
$$c_k(T_0) = c_k^0, \quad k \in I_{\text{fixed}}$$
$$|c_k(T) - c_k^{\text{eq}}| \leq \varepsilon, \quad k \in I_{\text{fixed}}$$
Relaxation Criterion

- $\Phi$ 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

\[ \frac{d_i S_k}{dt} = R \left( (R_{kf} - R_{kr}) \ln \left( \frac{R_{kf}}{R_{kr}} \right) \right) \geq 0. \]

for single reaction step \( k \).

Reduction criterion:

\[ \Phi(c(t)) = \sum_{k=1}^{n} \frac{d_i S_k}{dt} \]

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

\[ \frac{dG}{dt} = -T \frac{d_i S}{dt}, \]

minimization of (negative) Gibbs free energy production = minimization of entropy production.
Relate curvature to relaxation

- Physical principle “Force = Curvature”

Curvature of trajectories?

\[
\ddot{c}(t) = \frac{d^2 c}{dt^2} = \frac{d\dot{c}}{dt} = \frac{d\dot{c}}{dc} \frac{dc}{dt} = J(\dot{c}(t)) \cdot \dot{c}(t) = J(f(c(t))) \cdot f(c(t)),
\]

\( J(f) \) ... 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

\[ \| x \|_2^2 = x^T x \text{ by } \| x \|_A^2 = x^T A x \]

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

\[ a_{jj} = \sum_{k=1}^{n} \nu_{kj} \frac{d_i S_k}{dt} \]

with entropy production rate \( \frac{d_i S_k}{dt} \) for reaction \( k \).
Example Mechanism: Hydrogen Combustion

\begin{align*}
\text{H}_2 & \xrightleftharpoons[\kappa_{-1}]{\kappa_{1}} 2\text{H} \quad , \quad \kappa_1 = 2.0, \quad \kappa_{-1} = 216.0 \\
\text{O}_2 & \xrightleftharpoons[\kappa_{-2}]{\kappa_{2}} 2\text{O} \quad , \quad \kappa_2 = 1.0, \quad \kappa_{-2} = 337.5 \\
\text{H}_2\text{O} & \xrightleftharpoons[\kappa_{-3}]{\kappa_{3}} \text{H} + \text{OH} \quad , \quad \kappa_3 = 1.0, \quad \kappa_{-3} = 1400.0 \\
\text{H}_2 + \text{O} & \xrightleftharpoons[\kappa_{-4}]{\kappa_{4}} \text{H} + \text{OH} \quad , \quad \kappa_4 = 1000.0, \quad \kappa_{-4} = 10800.0 \\
\text{O}_2 + \text{H} & \xrightleftharpoons[\kappa_{-5}]{\kappa_{5}} \text{O} + \text{OH} \quad , \quad \kappa_5 = 1000.0, \quad \kappa_{-5} = 33750.0 \\
\text{H}_2 + \text{O} & \xrightleftharpoons[\kappa_{-6}]{\kappa_{6}} \text{H}_2\text{O} \quad , \quad \kappa_6 = 100.0, \quad \kappa_{-6} = 0.7714
\end{align*}

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:

\[ \min_{c_k} \int_0^T \sum_{k=1}^n d_i S_k \frac{d}{dt} dt \]

subject to

\[ \frac{dc_k}{dt} = f_k(c), \quad k = 1, \ldots, m \]

\[ c_k(0) = c_0^k, \quad k \in I_{\text{fixed}} \]

\( T \) 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

\[
\int_{l(0)}^{l(c_{eq})} \sum_{j=1}^{n} \frac{d_i S_j}{dt} dl(t),
\]

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

\[
l(t) = \int_{0}^{t} ||\dot{c}(\tau)|| d\tau. \Rightarrow dl(t) = ||\dot{c}(t)|| dt.
\]

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

\[
\min_{c_k(0)} \int_{0}^{T} \left( \sum_{j=1}^{n} \frac{d_i S_j}{dt} \right) ||f(c)|| dt
\]
Minimal Entropy-Production Trajectories

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

\[
\begin{align*}
\min_{c_k} & \int_0^T \sum_{k=1}^n \frac{d_l S_k}{dt} \|f(c)\| \, dt \\
\text{subject to} & \quad \frac{dc_k}{dt} = f_k(c), \\
& \quad c_k(0) = c_k^0, \\
& \quad k = 1, \ldots, m \\
& \quad k \in I_{\text{fixed}} \\
& \quad T \text{ sufficiently large}
\end{align*}
\]

and subject to conservation relations.
Minimal entropy production trajectories
Minimally Curved Trajectories

Trajectory-based optimization approach for minimally curved trajectories:

\[
\min_{c_k} \int_0^T \| J(c) f(c) \|_A \, dt = \min_{c_k} \int_0^T f^T J^T \begin{pmatrix}
\sum_{j=1}^n \nu_{1j} \frac{d_i S_1}{d t} & 0 & \ldots & 0 \\
0 & \ddots & \ddots & \vdots \\
\vdots & \ddots & \ddots & \vdots \\
0 & \ldots & 0 & \sum_{j=1}^n \nu_{nj} \frac{d_i S_n}{d t}
\end{pmatrix} J f \, dt
\]

subject to

\[
\frac{dc_k}{dt} = f_k(c), \quad k = 1, \ldots, m
\]

\[
c_k(0) = c_k^0, \quad k \in I_{\text{fixed}}
\]

and subject to conservation relations.
Curvature minimization

- $\text{H}_2$ Mechanism
- Entropy production
- Curvature
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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