Calculation of Slow Invariant Manifolds for Reactive Systems

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Introduction

Motivation and background

- Detailed kinetics are essential for accurate modeling of real systems.
- Reactive flow systems admit multi-scale solutions.
- Severe stiffness arises in detailed gas-phase kinetics modeling.
- Computational cost for reactive flow simulations increases with the spatio-temporal scales’ range, the number of species, and the number of reactions.
- Manifold methods provide a potential for computational saving.
Partial review of manifold construction in reactive systems

• ILDM, CSP, and ICE-PIC are approximations of the system’s slow invariant manifold.

• MEPT, RCCE, and similar methods are based on minimizing a thermodynamic potential function.

• Iterative methods may not converge.

• Davis and Skodje, 1999, present a technique to construct the 1-D SIM based on global phase analysis.

• Creta et al. and Giona et al., 2006, extend the technique to slightly higher dimensional reactive systems.
Long-term objective

Create an efficient algorithm that reduces the computational cost for simulating reactive flows based on a reduction in the stiffness and dimension of the composition phase space.

Immediate objective

Construct 1-D SIMs for dynamical system arising from modeling unsteady spatially homogenous closed reactive systems.
Slow Invariant Manifold (SIM)

- The composition phase space for closed spatially homogeneous reactive system:

\[
\frac{dz}{dt} = f(z), \quad z \in \mathbb{R}^3.
\]
• An invariant manifold is defined as a subset \( S \subset \mathbb{R}^{N-L-Q} \) if for any solution \( z(t), z(t_0) \in S \), implies that for any \( t_f > t_0 \), \( z(t) \in S \) for all \( t \in [t_0, t_f] \).

• Not all invariant manifolds are attracting.

• SIMs describe the asymptotic structure of the invariant attracting trajectories.

• Attractiveness of a SIM increases as the system’s stiffness increases.

• On a SIM, only slow modes are active.

• SIMs can be constructed by identifying all critical points, finite and infinite, and connecting relevant ones via heteroclinic orbits.
Mathematical Model

For a mixture of mass \( m \) confined in volume \( V \) containing \( N \) species composed of \( L \) elements that undergo \( J \) reversible reactions,

\[
\frac{dn_i}{dt} = V \dot{\omega}_i, \quad i = 1, \ldots, N,
\]

where,

\[
\dot{\omega}_i = \sum_{j=1}^{J} \nu_{ij} k_j \left( \prod_{i=1}^{N} \left( \frac{n_i}{V} \right)^{\nu'_{ij}} - \frac{1}{K_{cj}^c} \prod_{i=1}^{N} \left( \frac{n_i}{V} \right)^{\nu''_{ij}} \right), \quad i = 1, \ldots, N,
\]

\[
k_j = A_j T^{\beta_j} \exp \left( \frac{-E_j}{\mathcal{R}T} \right), \quad j = 1, \ldots, J,
\]

\[
K_{cj}^c = \left( \frac{p^o}{\mathcal{R}T} \right)^{\sum_{i=1}^{N} \nu_{ij}} \exp \left( -\frac{\sum_{i=1}^{N} \bar{\mu}_i^o \nu_{ij}}{\mathcal{R}T} \right), \quad j = 1, \ldots, J.
\]
System reduction

- In chemical reactions, the total number of moles of each element is conserved,

\[
\sum_{i=1}^{N} \phi_i n_i^* = \sum_{i=1}^{N} \phi_i n_i, \quad l = 1, \ldots, L.
\]

- Additional \( Q \) constraints can arise in special cases.

- The reactive system is recast as an autonomous dynamical system,

\[
\frac{dz_i}{dt} = f_i (z_1, \ldots, z_{N-L-Q}), \quad i = 1, \ldots, N - L - Q,
\]

where,

\[
z = \mathcal{L} (n) \mid \mathcal{L} : (\mathbb{R}^N \to \mathbb{R}^{N-L-Q}).
\]
Method of Construction

- For isothermal reactive systems, reaction speeds depend on combinations of polynomials of $z$.
- The set of equilibria of the full reaction network is complex:
  \[ \{ z^e \in \mathbb{C}^{N-L-Q} \mid f(z^e) = 0 \} \].
- The set consists of several different dimensional components and contains finite and infinite equilibria.
- A 1-D SIM has a maximum of two branches that connect the unique physical critical point (a sink) to two equilibria.
- These equilibria are identified by their special dynamical character: their eigenvalue spectrum typically contains only one unstable direction.
Projective space

- One-to-one mapping of the composition space, $\mathbb{R}^{N-L-Q} \rightarrow \mathbb{R}^{N-L-Q}$,

\[
Z_k = \frac{1}{z_k}, \quad k \in \{1, \ldots, N-L-Q\},
\]
\[
Z_i = \frac{z_i}{z_k}, \quad i \neq k, \quad i = 1, \ldots, N-L-Q.
\]

- This maps equilibria located at infinity into a finite domain.

- To deal with the time singularity, we add the transformation

\[
\frac{dt}{d\tau} = (Z_k)^{d-1},
\]

where $d$ is the highest polynomial degree of $\mathbf{f}(\mathbf{z})$. 
Computational strategy

- We use the Bertini software (based on a homotopy continuation numerical technique) to compute the system’s equilibria up to any desired accuracy.

- Thermodynamic data is obtained from Chemkin-II.

- The SIM heteroclinic orbits are obtained by numerical integration of the species evolution equations using a computationally inexpensive scheme.

- Computation time is typically less than 1 minute on a 2.16 GHz Mac Pro machine.
Simple Hydrogen-Oxygen Mechanism


- The mechanism consists of $J = 8$ bimolecular elementary reactions involving $N = 6$ species $\{H, H_2, O, O_2, OH, H_2O\}$ and $L = 2$ elements $\{H, O\}$. In addition, since the total number of moles is constant, $Q = 1$. Subsequently, $z \in \mathbb{R}^3$.

- The system is spatially homogenous with isothermal and iso-choric conditions, $T = 1200 \, K$, $V = 10^3 \, cm^3$.

- Selected species are $i = \{1, 2, 3\} = \{H_2, O, O_2\}$.

- Initial number of moles of all species are $n_i^* = 10^{-3} \, mol$. 
Reactive system evolution

$n_i/m \times 10^{-3}$

$[\text{mol/g}]

n_i/m$ vs $t$ [s]

- H
- H$_2$O
- O$_2$
- O
- H$_2$
- OH

$t = 10^{-10} - 10^{4}$
Dynamical system

\[
\begin{align*}
\frac{dz_1}{dt} &= 3.45 \times 10^4 - 1.68 \times 10^{11} z_1 - 3.47 \times 10^{16} z_1^2 \\
&\quad - 1.35 \times 10^{10} z_2 + 6.27 \times 10^{16} z_1 z_2 + 1.40 \times 10^{10} z_3 \\
&\quad + 1.11 \times 10^{17} z_1 z_3 - 1.35 \times 10^{16} z_2 z_3 - 2.04 \times 10^{16} z_3^2,
\end{align*}
\]

\[
\begin{align*}
\frac{dz_2}{dt} &= 7.69 \times 10^5 + 2.66 \times 10^{11} z_1 + 2.25 \times 10^{16} z_1^2 \\
&\quad - 1.29 \times 10^{12} z_2 - 2.47 \times 10^{17} z_1 z_2 \\
&\quad + 3.91 \times 10^{17} z_2^2 - 8.66 \times 10^{11} z_3 - 1.51 \times 10^{17} z_1 z_3 \\
&\quad + 7.49 \times 10^{17} z_2 z_3 + 2.46 \times 10^{17} z_3^2,
\end{align*}
\]

\[
\begin{align*}
\frac{dz_3}{dt} &= 6.84 \times 10^{11} z_2 + 1.37 \times 10^{17} z_1 z_2 - 2.74 \times 10^{17} z_2^2 \\
&\quad - 4.10 \times 10^{17} z_2 z_3 - 2.24 \times 10^{15} z_3 \left(10^{-6} - z_1 + z_3\right),
\end{align*}
\]

\[\equiv \mathbf{f}(\mathbf{z}).\]
Finite equilibria

\[ R_1 \equiv (z_1^e, z_2^e, z_3^e) = (-5.84 \times 10^{-2}, 6.85 \times 10^{-4}, -3.52 \times 10^{-4}) \text{ mol/g}, \]
\[ (\lambda_1, \lambda_2, \lambda_3) = (5.93 \times 10^6 \pm i5.10 \times 10^5, -1.18 \times 10^6) \text{ 1/s}, \]

\[ R_2 \equiv (z_1^e, z_2^e, z_3^e) = (4.65 \times 10^{-2}, 0, 3.49 \times 10^{-2}) \text{ mol/g}, \]
\[ (\lambda_1, \lambda_2, \lambda_3) = (-1.01 \times 10^7, -3.35 \times 10^6, 7.93 \times 10^5) \text{ 1/s}, \]

\[ R_3 \equiv (z_1^e, z_2^e, z_3^e) = (3.73 \times 10^{-3}, 6.32 \times 10^{-3}, 1.61 \times 10^{-2}) \text{ mol/g}, \]
\[ (\lambda_1, \lambda_2, \lambda_3) = (-1.02 \times 10^7, -1.23 \times 10^6, -4.30 \times 10^5) \text{ 1/s}, \]

\[ R_4 \equiv (z_1^e, z_2^e, z_3^e) = (6.33 \times 10^{-3}, -1.86 \times 10^{-3}, 2.49 \times 10^{-2}) \text{ mol/g}, \]
\[ (\lambda_1, \lambda_2, \lambda_3) = (6.88 \times 10^6, 3.51 \times 10^6, 1.57 \times 10^6) \text{ 1/s}, \]

\[ R_5 \equiv (z_1^e, z_2^e, z_3^e) = (1.28 \times 10^{-3}, -5.98 \times 10^{-2}, 6.00 \times 10^{-2}) \text{ mol/g}, \]
\[ (\lambda_1, \lambda_2, \lambda_3) = (5.65 \times 10^7, 3.56 \times 10^6, -1.06 \times 10^4) \text{ 1/s}, \]

\[ R_6 \equiv (z_1^e, z_2^e, z_3^e) = (1.43 \times 10^{-3}, -7.58 \times 10^{-2}, 7.08 \times 10^{-2}) \text{ mol/g}, \]
\[ (\lambda_1, \lambda_2, \lambda_3) = (7.19 \times 10^7, 4.47 \times 10^6, 1.05 \times 10^4) \text{ 1/s}. \]
Infinite equilibria

• Employ the projective space mapping with $d = 2$ and $k = 2$:

$$\frac{d}{d\tau} \begin{pmatrix} t \\ Z_1 \\ Z_2 \\ Z_3 \end{pmatrix} = Z_2^2 \cdot \begin{pmatrix} Z_2^{-1} \\ f_1 (Z_1, Z_2, Z_3) - Z_1 f_2 (Z_1, Z_2, Z_3) \\ -Z_2 f_2 (Z_1, Z_2, Z_3) \\ f_3 (Z_1, Z_2, Z_3) - Z_3 f_2 (Z_1, Z_2, Z_3) \end{pmatrix} \equiv F(Z),$$

$I_1 \equiv (Z^e_1, Z^e_2, Z^e_3) = (-9.77, 0, -4.59),$ 
$(\lambda_1, \lambda_2, \lambda_3) = (-5.74 \times 10^{12} \pm i7.83 \times 10^{12}, 6.10 \times 10^{12}),$

$I_2 \equiv (Z^e_1, Z^e_2, Z^e_3) = (0.60, 0, -0.48),$ 
$(\lambda_1, \lambda_2, \lambda_3) = (-1.19 \times 10^{13}, 7.35 \times 10^{11}, 6.32 \times 10^{11}),$

$I_3 \equiv (Z^e_1, Z^e_2, Z^e_3) = (-0.01, 0, -0.67),$ 
$(\lambda_1, \lambda_2, \lambda_3) = (-1.12 \times 10^{13}, -6.50 \times 10^{11}, 7.62 \times 10^9).$
The system’s 1-D SIM

\[ R_2 \]

\[ R_3 \]

\[ I_3 \]
Detailed Hydrogen-Air Mechanism


- The mechanism consists of $J = 19$ reversible reactions involving $N = 9$ species, $L = 3$ elements, and $Q = 0$, so that $z \in \mathbb{R}^6$.

- Closed and spatially homogenous system with isothermal and isochoric conditions at $T = 1500$ K, and $p^* = 10^7$ dyne/cm$^2$.

- Stoichiometric mixture $2H_2 + (O_2 + 3.76N_2)$.

- Selected species are

$$i = \{1, 2, 3, 4, 5, 6\} = \{H_2, O_2, H, O, OH, H_2O\}.$$
Reactive system evolution

\[ z_i \text{ [mol/g]} \]

\[ t \text{ [s]} \]

\[ \begin{align*}
\text{H}_2 & \\
\text{O}_2 & \\
\text{O} & \\
\text{OH} & \\
\text{H} & \\
\text{H}_2\text{O} & \\
\end{align*} \]
System’s equilibria

- The system has 284 finite and 42 infinite equilibria.
- The set of finite equilibria contains 90 real and 186 complex 0-$D$, one 1-$D$, one 2-$D$, and six 3-$D$ equilibria.
- The set of infinite equilibria contains 18 real and 18 complex 0-$D$, and six 1-$D$ equilibria.
- Only 14 critical points have an eigenvalue spectrum that contains only one unstable direction.
- Inside the physical domain there is a unique equilibrium:

$$R_{19} = \left( 1.98 \times 10^{-6}, 9.00 \times 10^{-7}, 1.72 \times 10^{-9}, 
2.67 \times 10^{-10}, 3.66 \times 10^{-7}, 1.44 \times 10^{-2} \right) \text{ mol/g.}$$
3-D projection of the system’s SIM
Summary and Conclusions

- Once the difficult task of identifying all equilibria is complete, constructing the actual SIM is computationally efficient and algorithmically easy; thus, there is no need to identify it only approximately.

- Identifying all critical points, finite and infinite, plays a major role in the construction of the SIM.

- The construction procedure can be systematically extended to construct higher-dimensional SIMs.
Simple Reactive System

\[ A + A \rightleftharpoons B \quad k_f^A = 1, \quad k_b^A = 10^{-5}. \]
\[ B \rightleftharpoons C \quad k_f^B = 10, \quad k_b^B = 10^{-5}. \]

- Model consists of \( J = 2 \) reversible reactions involving \( N = 3 \) species \( \{c_A, c_B, c_C\} \)
- Conservation of mass, \( c_A + c_B + c_C = 1 \), so that \( z \in \mathbb{R}^2 \).
- Major species are \( i = \{1, 2\} = \{A, B\} \),
The system’s global phase space

The projective space.

Projection from Poincaré’s sphere.
The 1-D SIM vs. MEPT
Idealized Hydrogen-Oxygen

- Kinetic model adopted from Ren et al.\textsuperscript{a}

- Model consists of $J = 6$ reversible reactions involving $N = 6$ species $\{H_2, O, H_2O, H, OH, N_2\}$ and $L = 3$ elements $\{H, O, N\}$, with $Q = 0$, so that $z \in \mathbb{R}^3$.

- Spatially homogenous with isothermal and isobaric conditions with $T = 3000 \text{ K}, p_o = 1 \text{ atm}$.

- Major species are $i = \{1, 2, 3\} = \{H_2, O, H_2O\}$.

- Initial conditions satisfying the element conservation constraints are identical to those presented by Ren et al.

The system’s 1-D SIM

![Diagram showing a 3D graph with axes labeled $z_1$, $z_2$, and $z_3$, with points $R_6$ and $R_7$ and a path labeled SIM.]
The system’s 1-D SIM