Calculation of Slow Invariant Manifolds for Reactive Systems

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Outline

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- Method of Construction
- Illustration Using Model Problem
- Application to Hydrogen-Air Reactive System
- Summary

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.

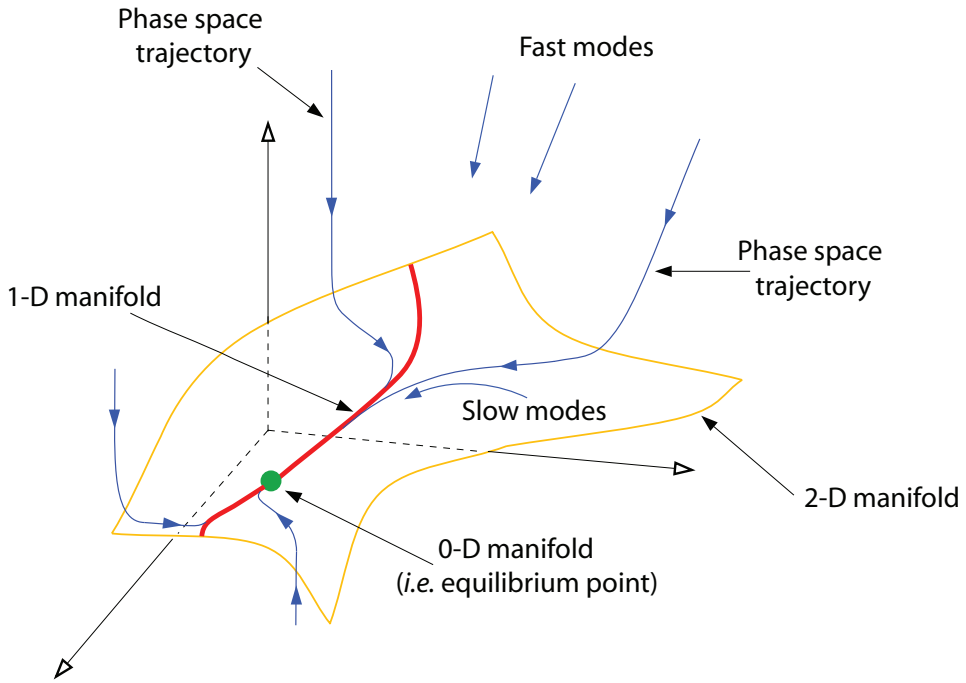
Immediate objective

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:

$$\frac{d\mathbf{z}}{dt} = \mathbf{f}\left(\mathbf{z}\right), \quad \mathbf{z} \in \mathbb{R}^3.$$



- An invariant manifold is defined as a subset $\mathcal{S} \subset \mathbb{R}^{N-L-Q}$ if for any solution $\mathbf{z}(t)$, $\mathbf{z}(t_0) \in \mathcal{S}$, implies that for any $t_f > t_0$, $\mathbf{z}(t) \in \mathcal{S}$ 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,

$$\begin{aligned}
\dot{\omega}_i &= \sum_{j=1}^{J} \nu_{ij} \mathsf{k}_j \left(\prod_{i=1}^{N} \left(\frac{n_i}{V} \right)^{\nu'_{ij}} - \frac{1}{K_j^c} \prod_{i=1}^{N} \left(\frac{n_i}{V} \right)^{\nu''_{ij}} \right), \quad i = 1, \ldots, N, \\
\mathsf{k}_j &= A_j \, T^{\beta_j} \, \exp\left(\frac{-E_j}{\Re T} \right), \quad j = 1, \ldots, J, \\
K_j^c &= \left(\frac{p^o}{\Re T} \right)^{\sum_{i=1}^{N} \nu_{ij}} \exp\left(- \frac{\sum_{i=1}^{N} \bar{\mu}_i^o \nu_{ij}}{\Re T} \right), \quad j = 1, \ldots, J.
\end{aligned}$$

System reduction

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

$$\sum_{i=1}^{N} \phi_{li} n_i^* = \sum_{i=1}^{N} \phi_{li} n_i, \quad l = 1, \ldots, L.$$

- Additional Q constraints can arise in special cases.

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

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

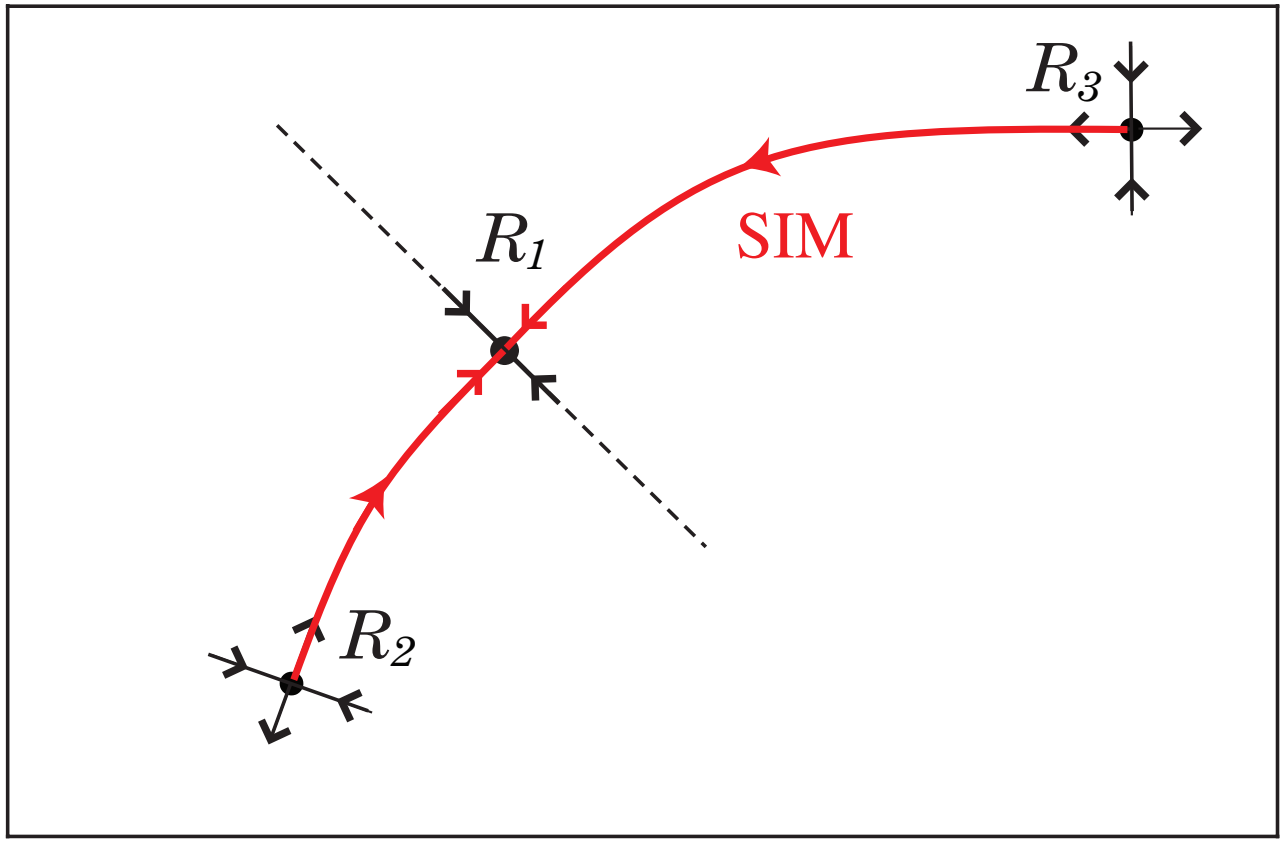
where,

$$\mathbf{z} = \mathcal{L}\left(\mathbf{n}\right) \;\Big|\; \mathcal{L} : \left(\mathbb{R}^N \rightarrow \mathbb{R}^{N-L-Q} \right).$$

Method of Construction

- For isothermal reactive systems, reaction speeds depend on combinations of polynomials of $\mathbf{z}$.
- The set of equilibria of the full reaction network is complex: $\{\mathbf{z}^e \in \mathbb{C}^{N-L-Q} \,|\mathbf{f}\left(\mathbf{z}^e\right) = \mathbf{0}\}$.
- 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.

Sketch of SIM construction



Projective space

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

$$
\begin{aligned}
Z_k &= \frac{1}{z_k}, \quad k \in \{1, \ldots, N-L-Q\}, \\
Z_i &= \frac{z_i}{z_k}, \quad i \neq k, \quad i = 1, \ldots, N-L-Q.
\end{aligned}
$$

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

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

$$
\frac{dt}{d\tau} = (Z_k)^{\mathtt{d}-1},
$$

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

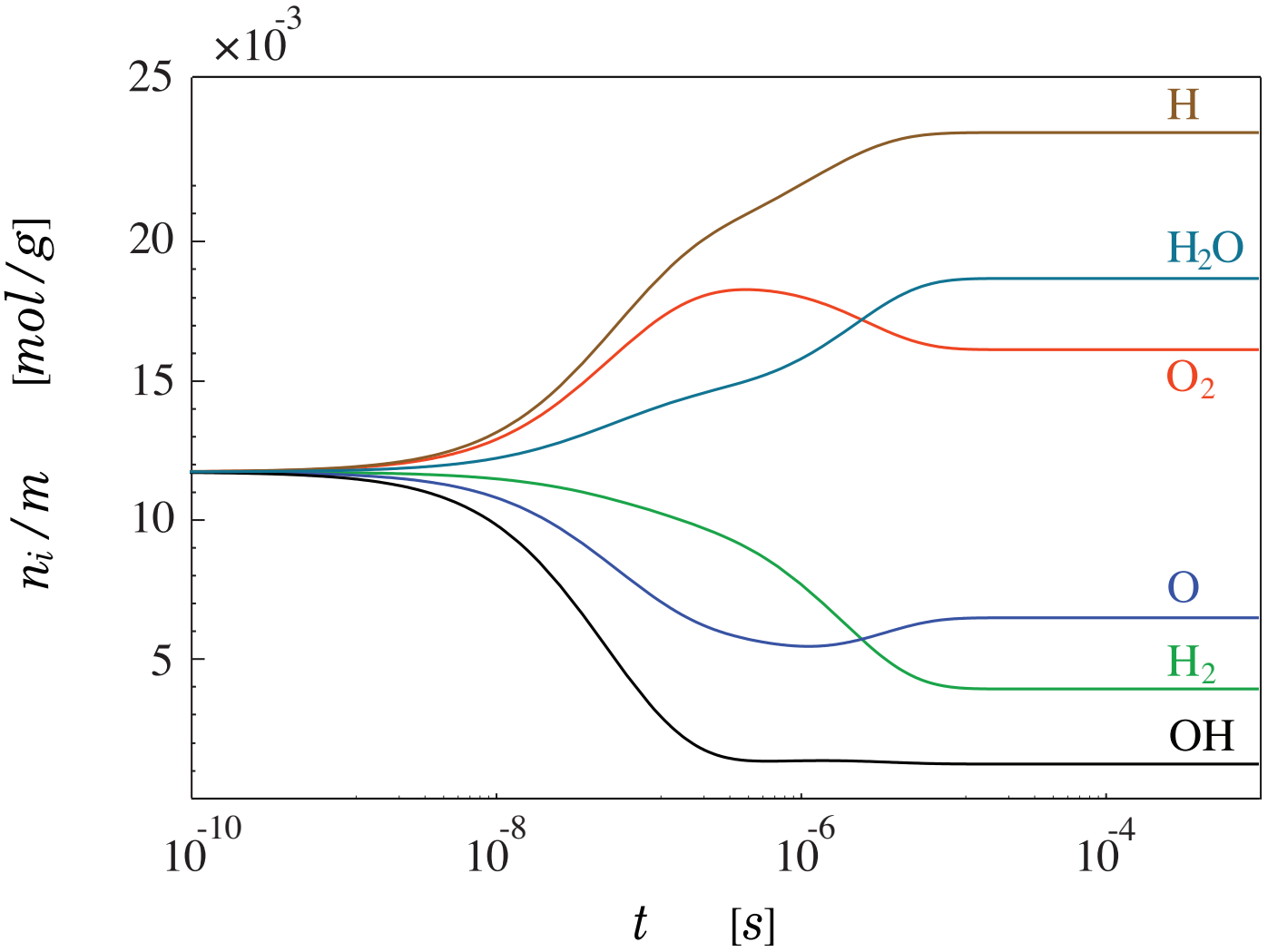
Computational strategy

- 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 kinetic model is adopted from Michael, 1992, *Prog. Energy Combust. Sci.* **18**(4), p. 327.
- 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, $\mathbf{z} \in \mathbb{R}^3$.
- The system is spatially homogenous with isothermal and isochoric 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



Dynamical system

$$
\left.
\begin{aligned}
\frac{dz_1}{dt} &= 3.45\times10^{4} - 1.68\times10^{11} z_1 - 3.47\times10^{16} z_1^2 \\
&\quad -1.35\times10^{10} z_2 + 6.27\times10^{16} z_1 z_2 + 1.40\times10^{10} z_3 \\
&\quad +1.11\times10^{17} z_1 z_3 - 1.35\times10^{16} z_2 z_3 - 2.04\times10^{16} z_3^2, \\
\frac{dz_2}{dt} &= 7.69\times10^{5} + 2.66\times10^{11} z_1 + 2.25\times10^{16} z_1^2 \\
&\quad -1.29\times10^{12} z_2 - 2.47\times10^{17} z_1 z_2 \\
&\quad +3.91\times10^{17} z_2^2 - 8.66\times10^{11} z_3 - 1.51\times10^{17} z_1 z_3 \\
&\quad 7.49\times10^{17} z_2 z_3 + 2.46\times10^{17} z_3^2, \\
\frac{dz_3}{dt} &= 6.84\times10^{11} z_2 + 1.37\times10^{17} z_1 z_2 - 2.74\times10^{17} z_2^2 \\
&\quad -4.10\times10^{17} z_2 z_3 - 2.24\times10^{15} z_3 \left(10^{-6} - z_1 + z_3\right),
\end{aligned}
\right\} \equiv \mathbf{f}(\mathbf{z}).
$$

Finite equilibria

$$
\begin{aligned}
R_1 \equiv (z_1^e, z_2^e, z_3^e) &= \left(-5.84 \times 10^{-2}, 6.85 \times 10^{-4}, -3.52 \times 10^{-4}\right)\ mol/g, \\
(\lambda_1, \lambda_2, \lambda_3) &= (5.93 \times 10^{6} \pm i 5.10 \times 10^{5}, -1.18 \times 10^{6})\ 1/s, \\
R_2 \equiv (z_1^e, z_2^e, z_3^e) &= \left(4.65 \times 10^{-2}, 0, 3.49 \times 10^{-2}\right)\ mol/g, \\
(\lambda_1, \lambda_2, \lambda_3) &= (-1.01 \times 10^{7}, -3.35 \times 10^{6}, 7.93 \times 10^{5})\ 1/s, \\
R_3 \equiv (z_1^e, z_2^e, z_3^e) &= \left(3.73 \times 10^{-3}, 6.32 \times 10^{-3}, 1.61 \times 10^{-2}\right)\ mol/g, \\
(\lambda_1, \lambda_2, \lambda_3) &= (-1.02 \times 10^{7}, -1.23 \times 10^{6}, -4.30 \times 10^{5})\ 1/s, \\
R_4 \equiv (z_1^e, z_2^e, z_3^e) &= \left(6.33 \times 10^{-3}, -1.86 \times 10^{-3}, 2.49 \times 10^{-2}\right)\ mol/g, \\
(\lambda_1, \lambda_2, \lambda_3) &= (6.88 \times 10^{6}, 3.51 \times 10^{6}, 1.57 \times 10^{6})\ 1/s, \\
R_5 \equiv (z_1^e, z_2^e, z_3^e) &= \left(1.28 \times 10^{-3}, -5.98 \times 10^{-2}, 6.00 \times 10^{-2}\right)\ mol/g, \\
(\lambda_1, \lambda_2, \lambda_3) &= (5.65 \times 10^{7}, 3.56 \times 10^{6}, -1.06 \times 10^{4})\ 1/s, \\
R_6 \equiv (z_1^e, z_2^e, z_3^e) &= \left(1.43 \times 10^{-3}, -7.58 \times 10^{-2}, 7.08 \times 10^{-2}\right)\ mol/g, \\
(\lambda_1, \lambda_2, \lambda_3) &= (7.19 \times 10^{7}, 4.47 \times 10^{6}, 1.05 \times 10^{4})\ 1/s.
\end{aligned}
$$

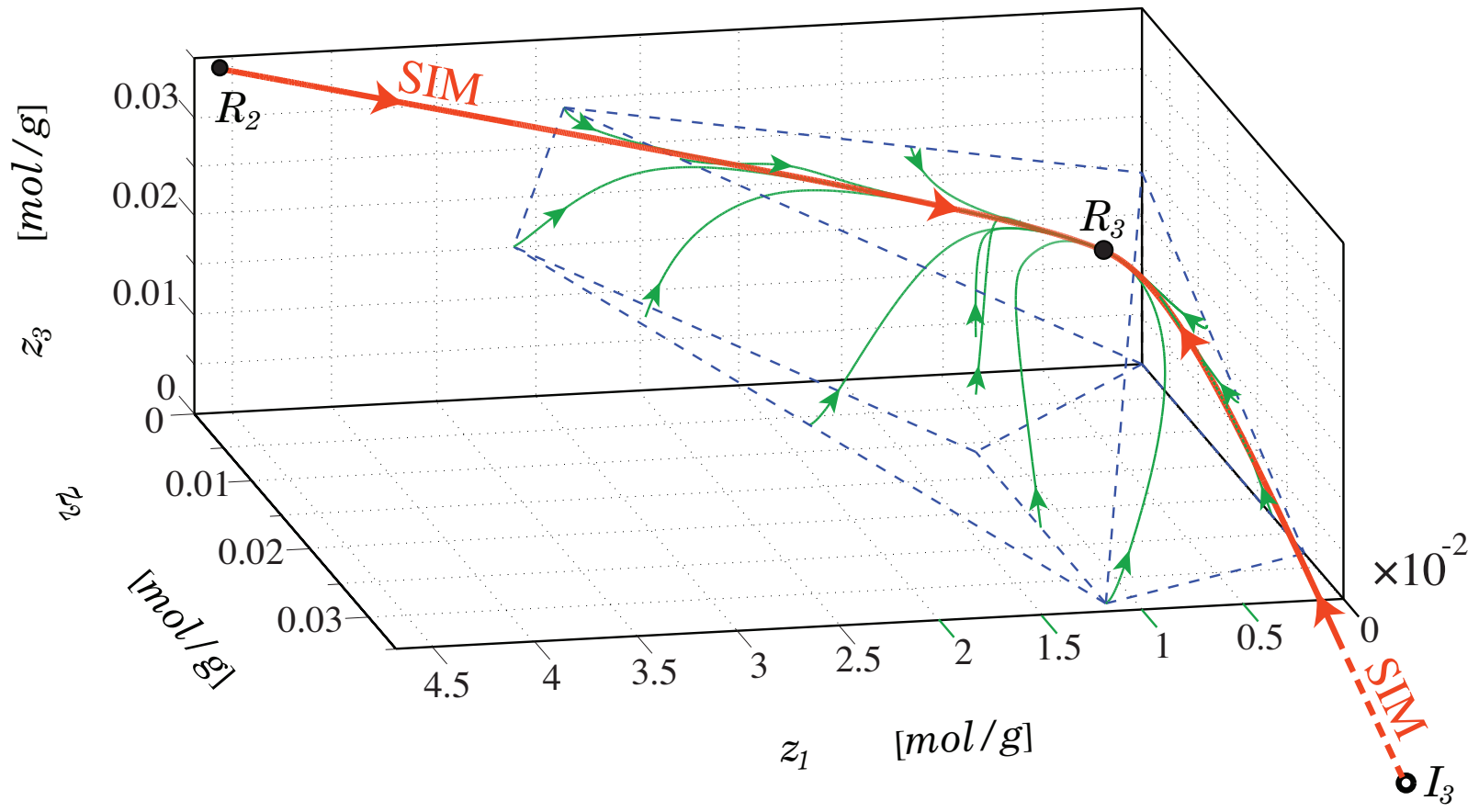
Infinite equilibria

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

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

$$\begin{aligned}
I_1 \equiv (Z_1^e, Z_2^e, Z_3^e) &= (-9.77, 0, -4.59)\,, \\
(\lambda_1, \lambda_2, \lambda_3) &= (-5.74 \times 10^{12} \pm i 7.83 \times 10^{12}, 6.10 \times 10^{12}), \\
I_2 \equiv (Z_1^e, Z_2^e, Z_3^e) &= (0.60, 0, -0.48)\,, \\
(\lambda_1, \lambda_2, \lambda_3) &= (-1.19 \times 10^{13}, 7.35 \times 10^{11}, 6.32 \times 10^{11}), \\
I_3 \equiv (Z_1^e, Z_2^e, Z_3^e) &= (-0.01, 0, -0.67)\,, \\
(\lambda_1, \lambda_2, \lambda_3) &= (-1.12 \times 10^{13}, -6.50 \times 10^{11}, 7.62 \times 10^{9}).
\end{aligned}$$

The system's 1-D SIM

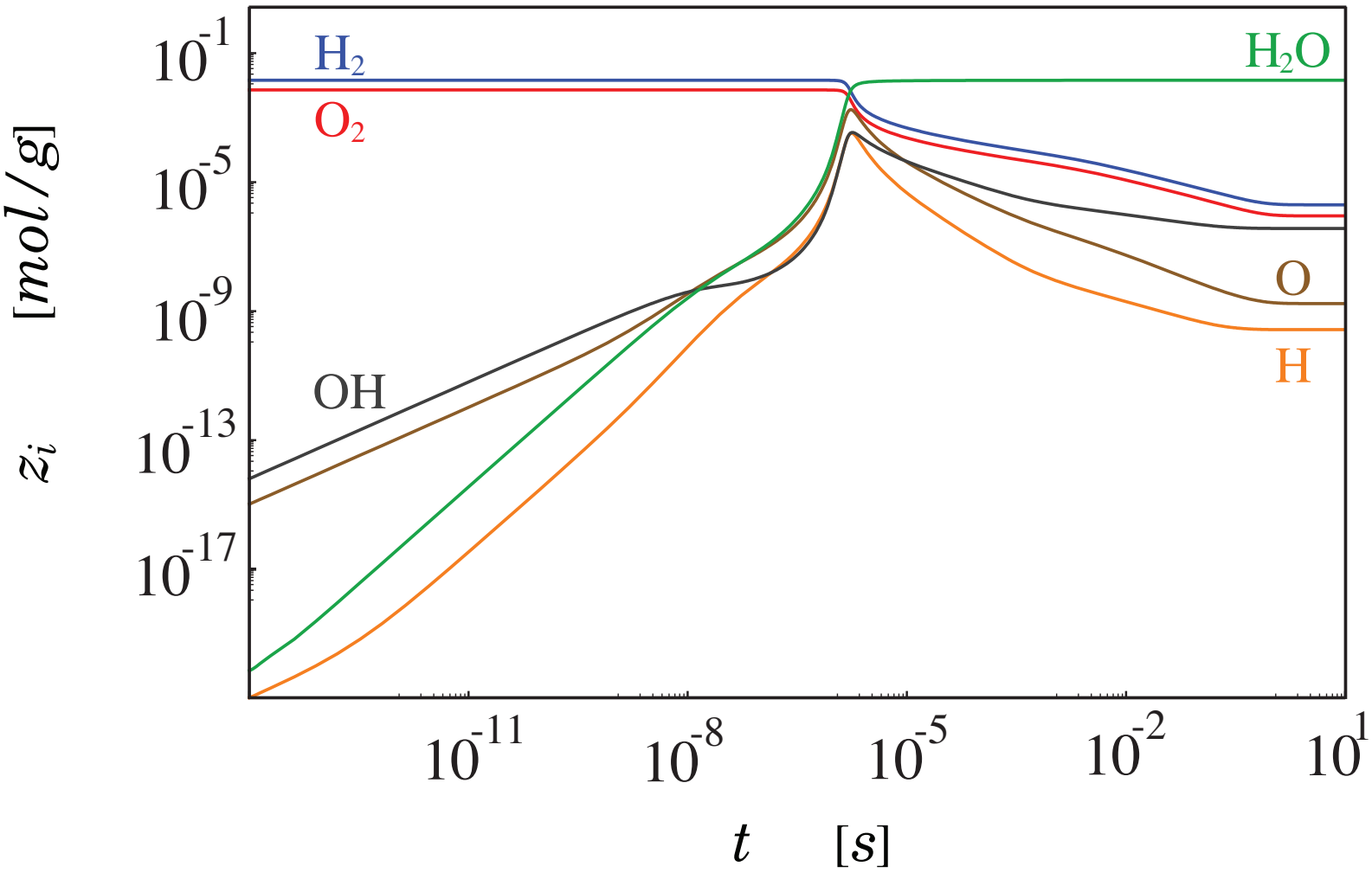


Detailed Hydrogen-Air Mechanism

- A kinetic model is adopted from Miller *et al.*, 1982, *Proc. Combust. Ins.* **19**, p. 181.
- The mechanism consists of $J = 19$ reversible reactions involving $N = 9$ species, $L = 3$ elements, and $Q = 0$, so that $\mathbf{z} \in \mathbb{R}^6$.
- 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

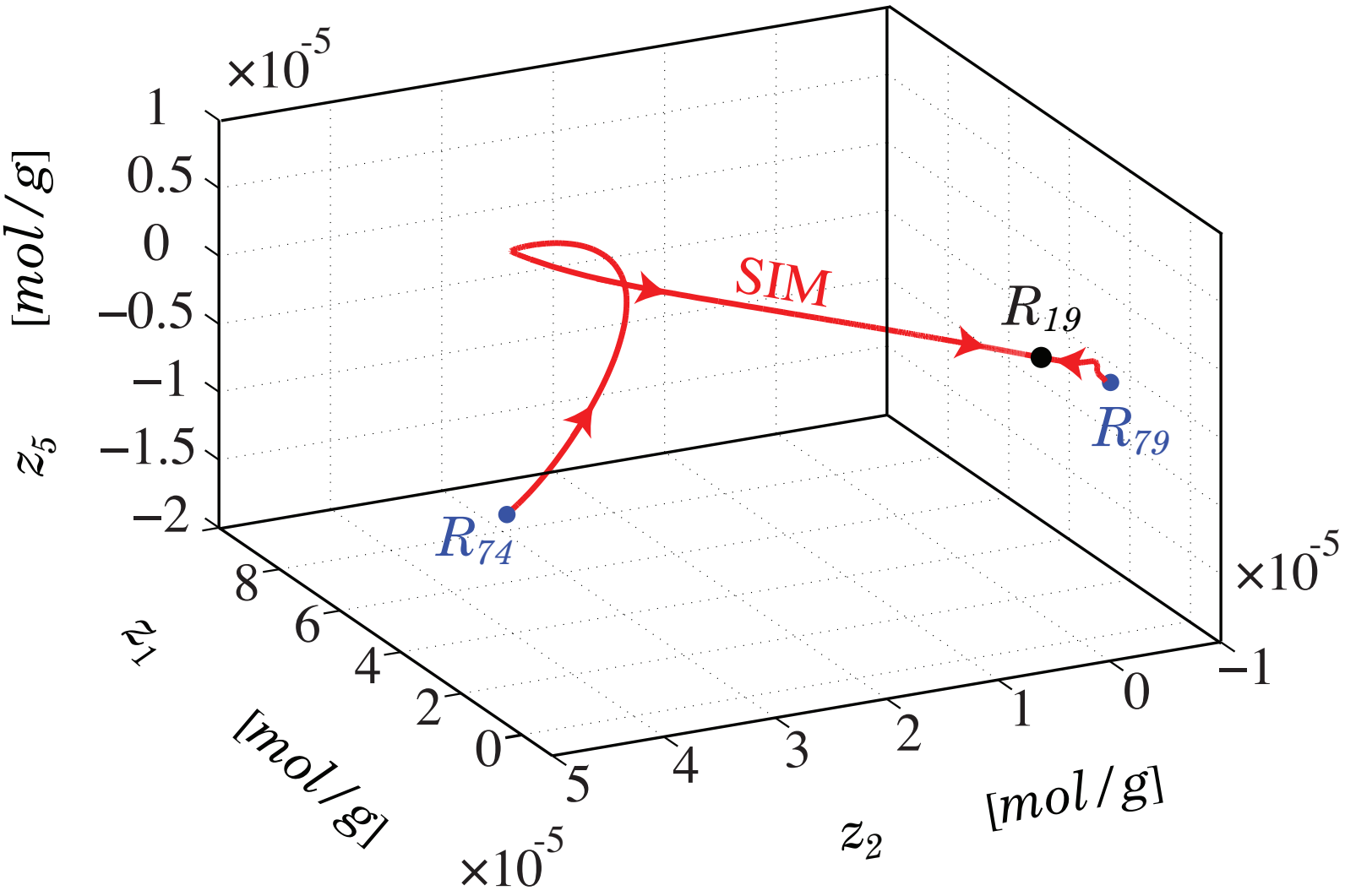


System's equilibria

- 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:

$$R_{19} = \big(1.98 \times 10^{-6}, 9.00 \times 10^{-7}, 1.72 \times 10^{-9},$$
$$2.67 \times 10^{-10}, 3.66 \times 10^{-7}, 1.44 \times 10^{-2}\big)\ mol/g.$$

3-D projection of the system's SIM



Summary and Conclusions

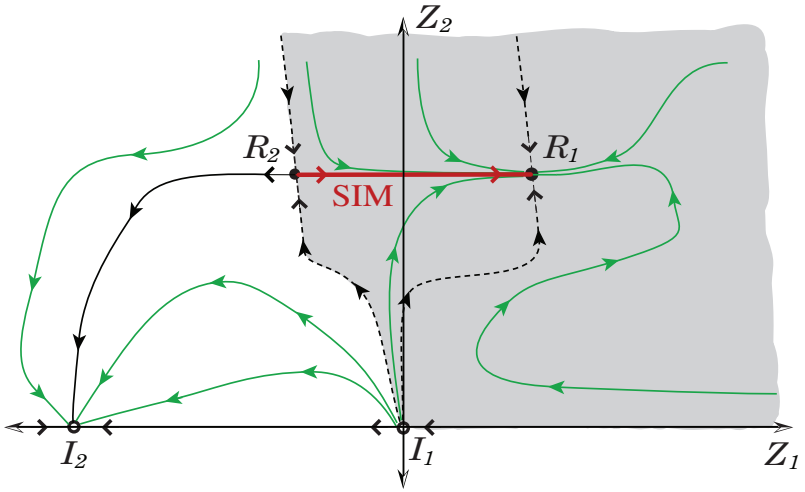
- Once the difficult task of identifying all equilbria is complete, constructing the actual SIM is computationally efficient and algorithmically easy; thus, there is no need to identify it only approximately.
- Identifying all critical points, finite and infinite, plays a major role in the construction of the SIM.
- The construction procedure can be systematically extended to construct higher-dimensional SIMs.

Simple Reactive System

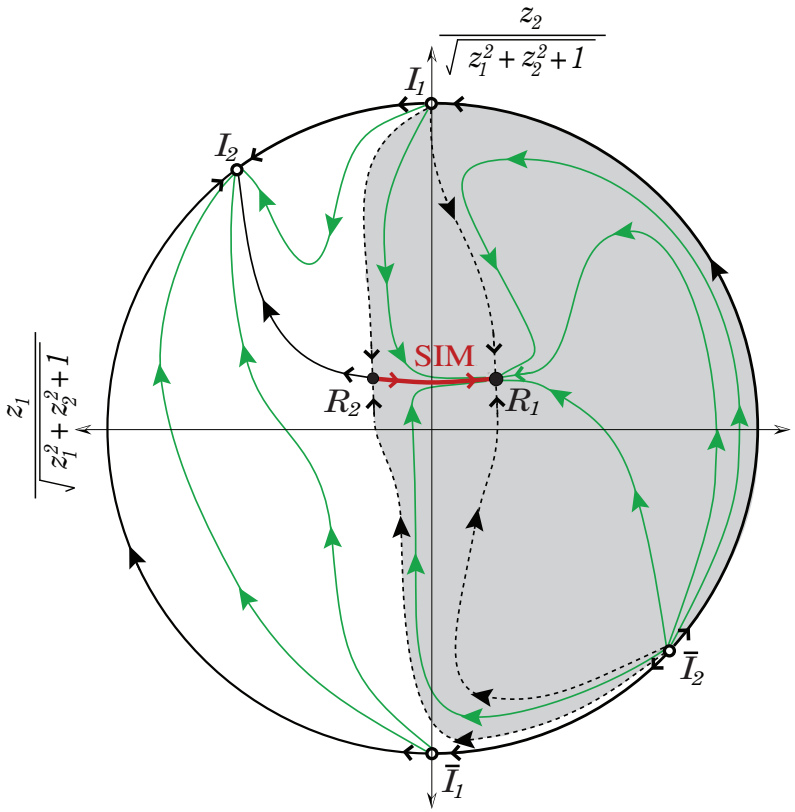
$$\begin{aligned} A + A &\rightleftharpoons B \qquad k^f = 1, k^b = 10^{-5}. \\ B &\rightleftharpoons C \qquad k^f = 10, k^b = 10^{-5}. \end{aligned}$$

- A reactive system adopted from D. Lebiedz, 2004, *J. Chem. Phys.* **120** (15), p. 6890.
- 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 $\mathbf{z} \in \mathbb{R}^2$.
- Major species are $i = \{1, 2\} = \{A, B\}$,

The system's global phase space

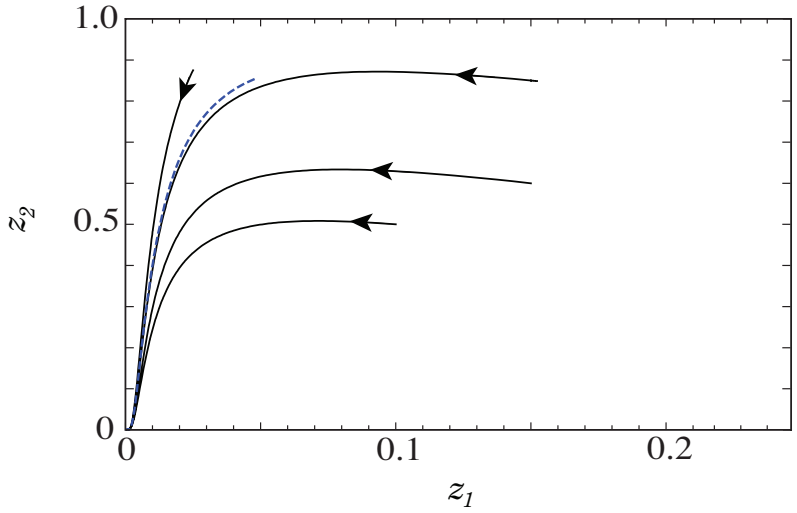


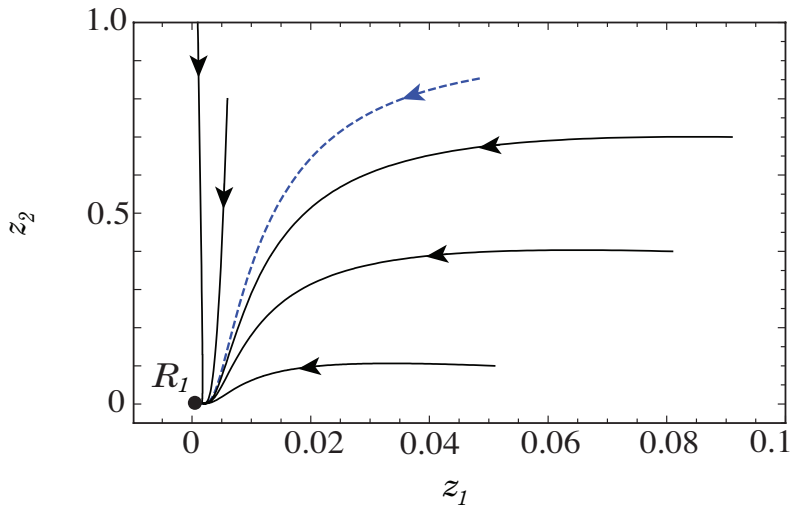
The projective space.

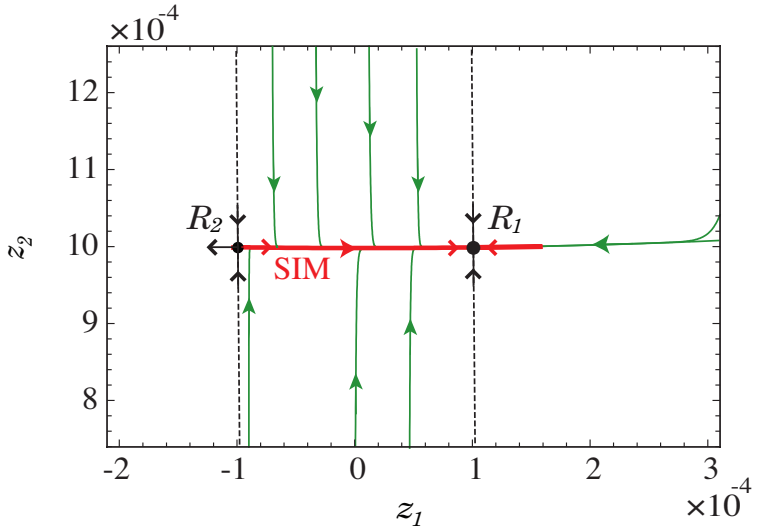


Projection from Poincaré's sphere.

The 1-D SIM *vs.* MEPT





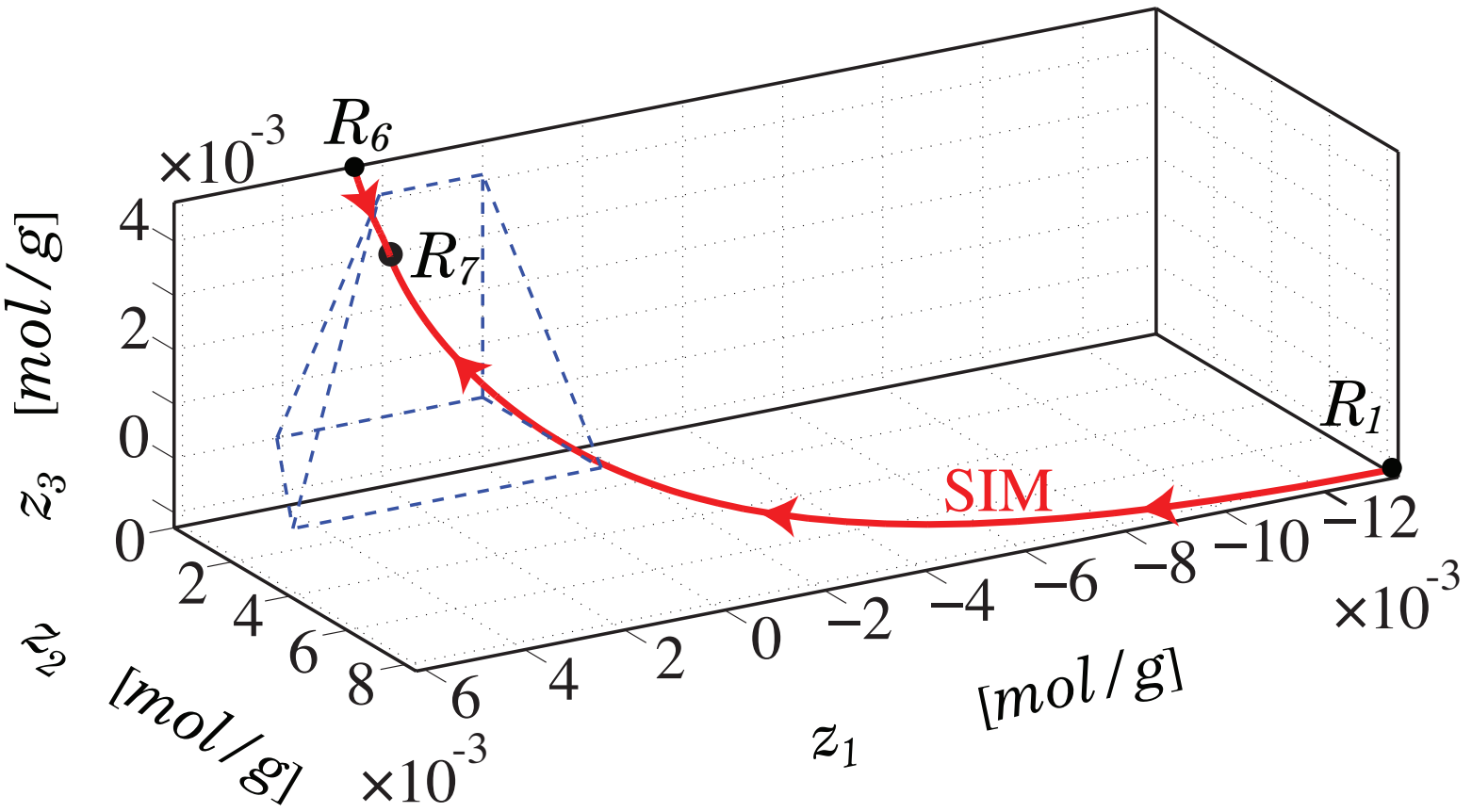


Idealized Hydrogen-Oxygen

- Kinetic model adopted from Ren *et al.*[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 $\mathbf{z} \in \mathbb{R}^3$.
- Spatially homogenous with isothermal and isobaric conditions with $T = 3000\ K, p_o = 1\ atm$.
- 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.*

[a] Z. Ren, S. Pope, A. Vladimirsky, J. Guckenheimer, 2006, *J. Chem. Phys.* **124**, 114111.

The system's 1-D SIM



The system's 1-D SIM