Constructing Slow Invariant Manifolds for Reacting Systems with Detailed Kinetics

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Introduction

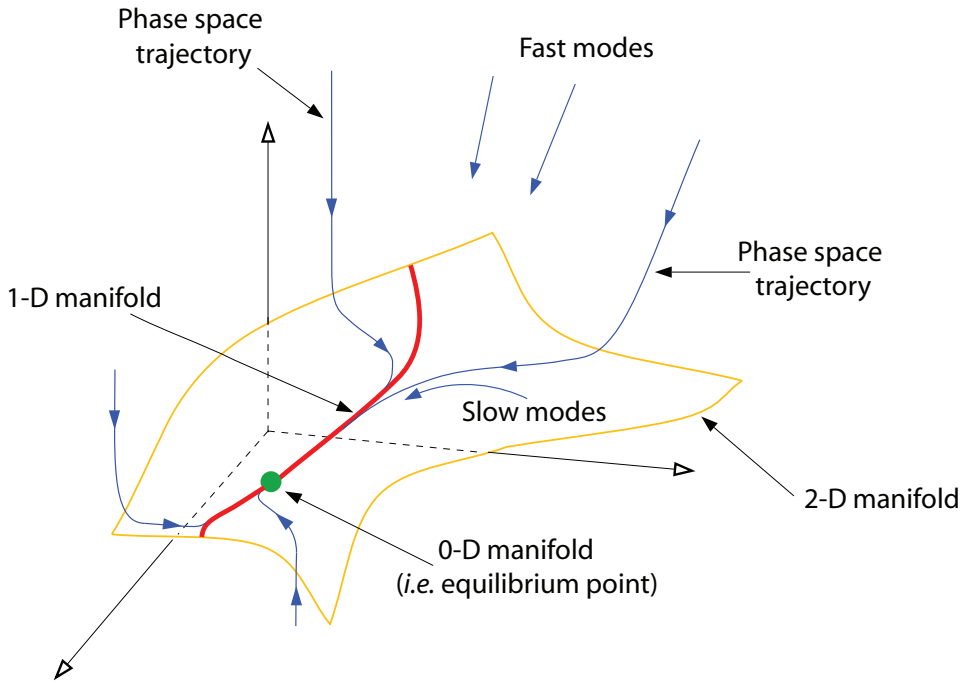
Motivation and background

- Detailed kinetics are essential for accurate modeling of real reactive systems.
- Reactive systems contain many scales and subsequently severe stiffness arises.
- 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 savings.

Slow Invariant Manifold (SIM)

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

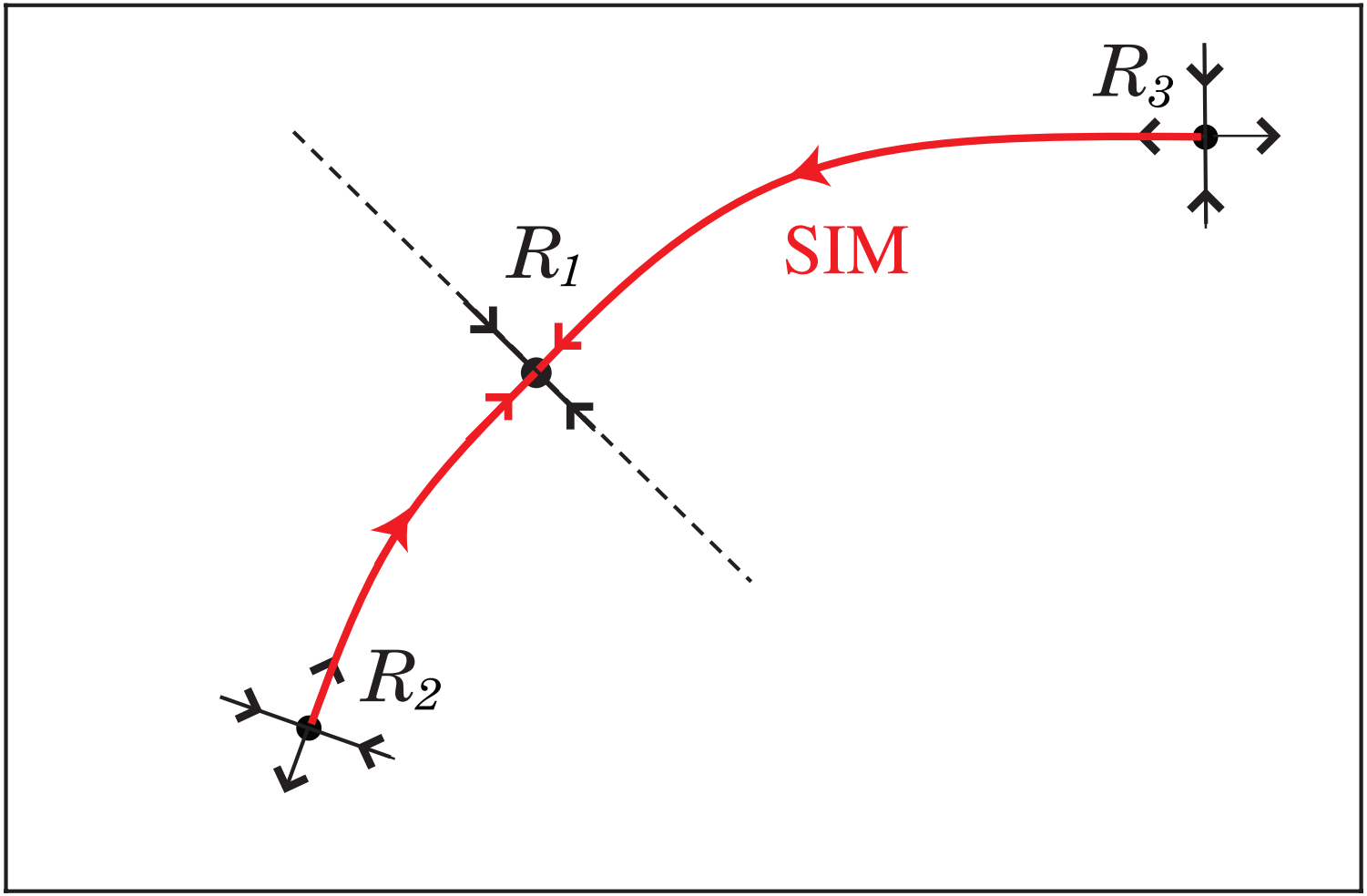
$$\frac{d\mathbf{z}}{dt} = \mathbf{f}\left(\mathbf{z}\right), \quad \mathbf{z} \in \mathbb{R}^{N-L-C}.$$



Method of Construction

- For isothermal reactive systems, reactions speeds depend on combinations of polynomials of species concentrations.
- The set of equilibria of the full reaction network is complex: $\left\{\mathbf{z}^e \in \mathbb{C}^{N-L-C} \left| \mathbf{f}\left(\mathbf{z}^e\right) = \mathbf{0} \right.\right\}$; we focus on real equilibria.
- 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 0-D physical critical point (a sink) to two saddles.
- These saddles are identified by their special dynamical character: their eigenvalue spectrum contains only one unstable direction.

Sketch of SIM Construction



Projective Space for Equilibria at Infinity

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

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

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

- To address the time singularity, we add the following transformation

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

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

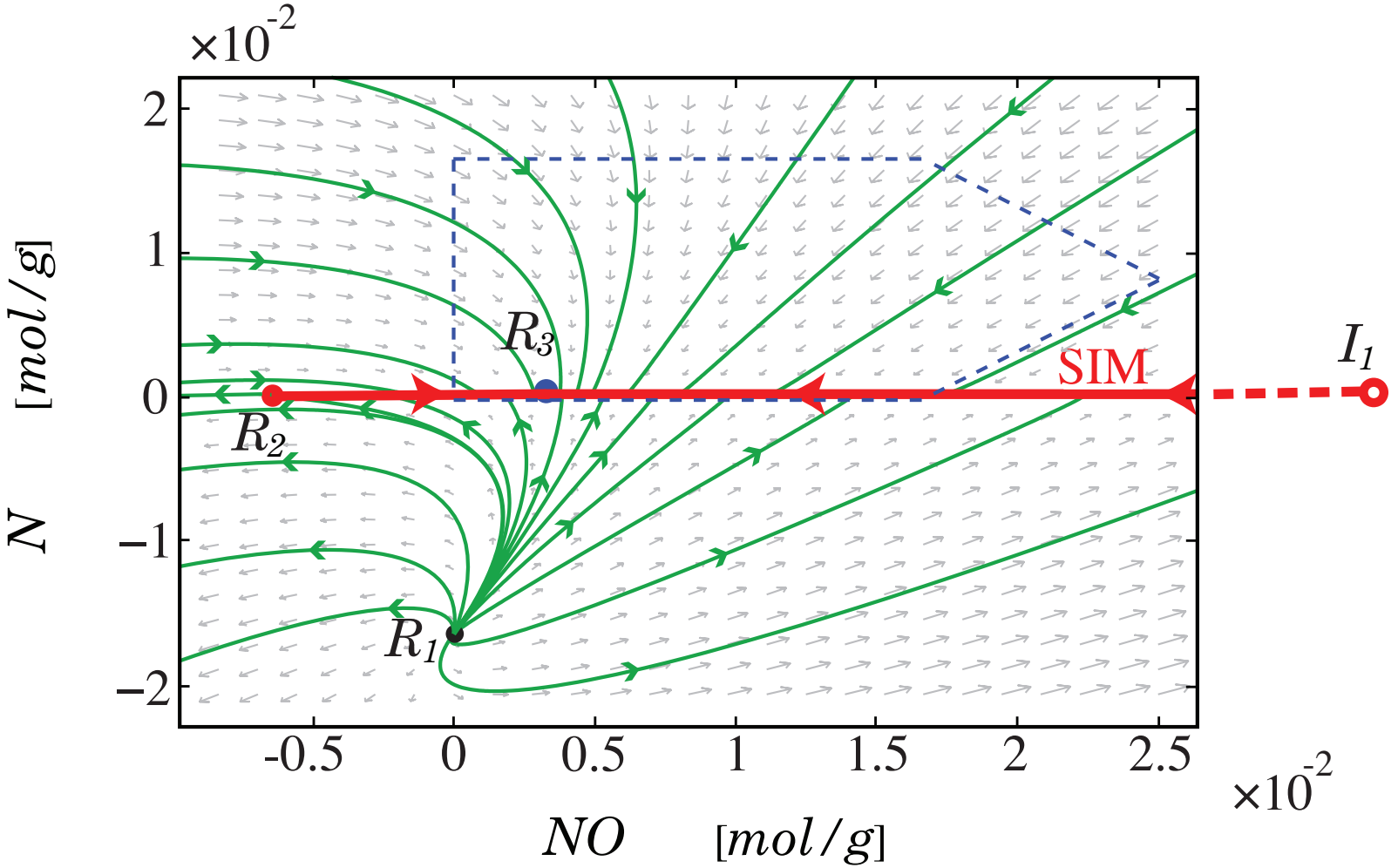
Computational strategy

- 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.

Zel'dovich Mechanism for NO Formation

- The mechanism (see Baulch *et al.*, 2005) consists of $J = 2$ reversible bimolecular reactions involving $N = 5$ species $\{NO, N, O, N_2, O_2\}$ and $L = 2$ elements $\{N, O\}$. In addition, since the total number of moles is constant, $C = 1$. Subsequently, $\mathbf{z} \in \mathbb{R}^2$.
- Spatially homogenous with isothermal and isochoric conditions, $T = 4000\ K, p_0 = 1.65\ atm$.
- We find three 0-D finite equilibria (R_1: source, R_2: saddle, R_3: sink, *physical*) and three 0-D infinite equilibria (I_1: saddle-node, I_2: source, I_3: source)

The system's 1-D SIM



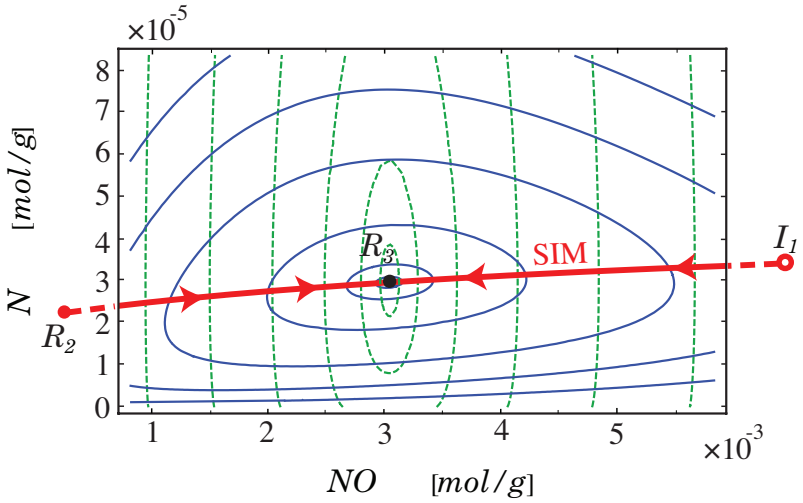
Equilibrium Thermodynamics and SIM

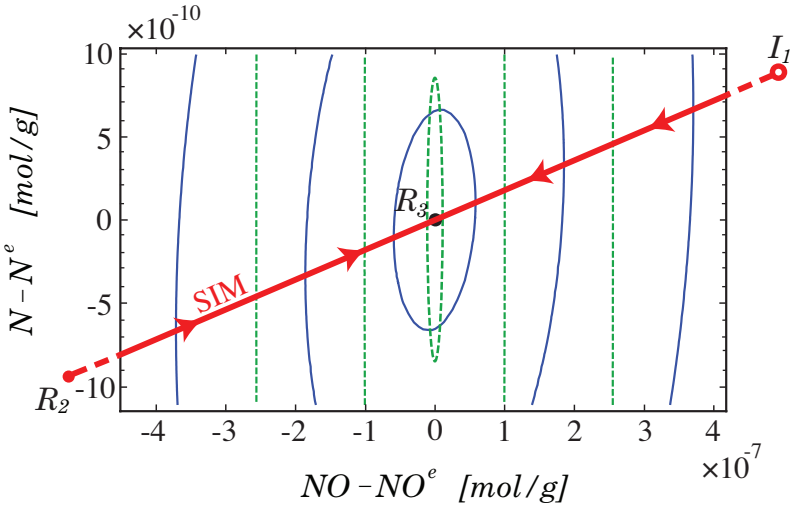
Within the physically accessible domain,

$$\sigma = -\frac{1}{T}\left(\nabla G \cdot \mathbf{f}\right) \geq 0,$$

at equilibrium

$$\mathbf{H}_\sigma = -\frac{2}{T}\left(\mathbf{H}_G \cdot \mathbf{J}_\mathbf{f}\right).$$



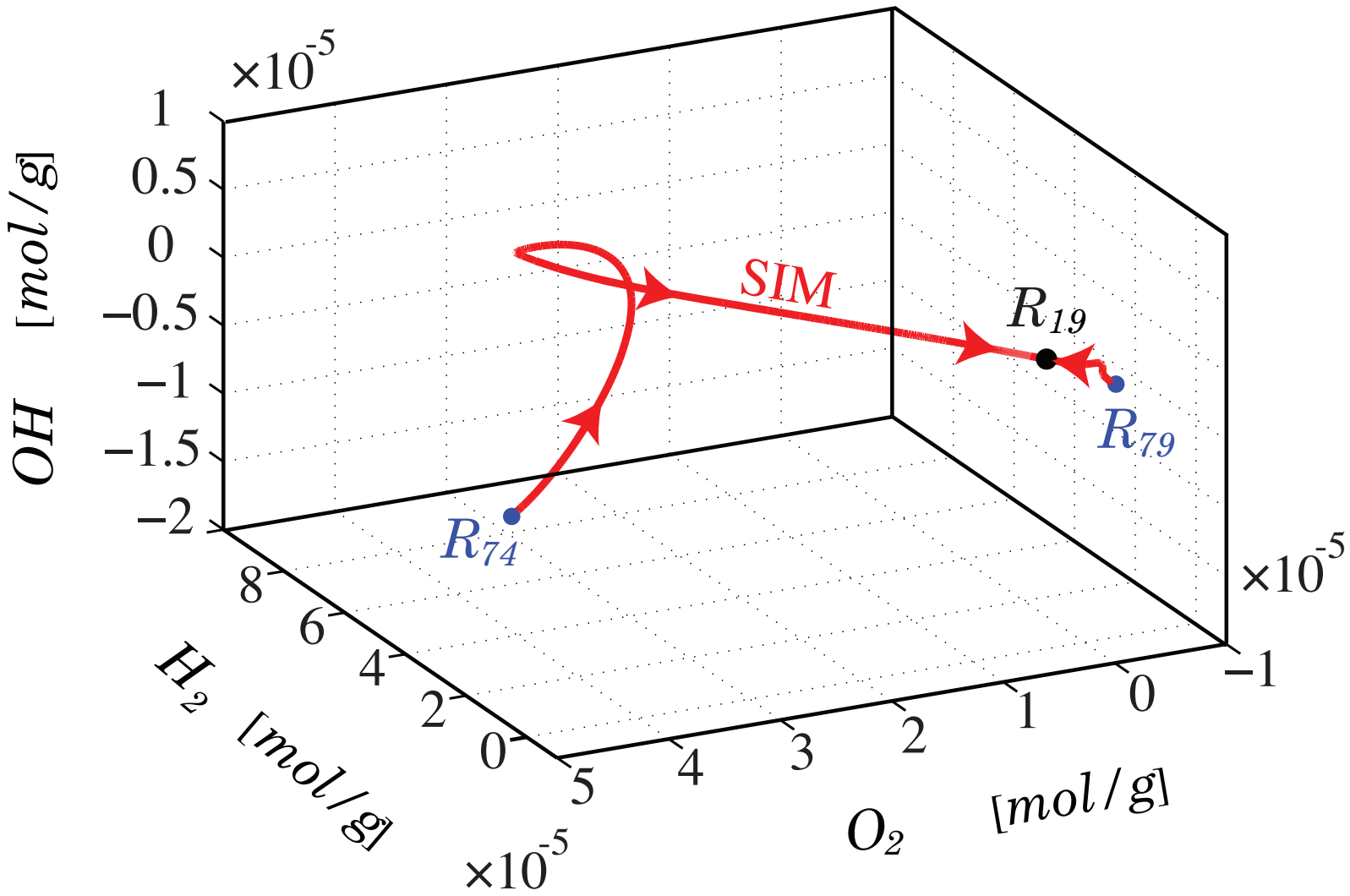


- The major/minor axes are aligned with the Hessian eigenvectors.
- Eigenvectors of equilibrium thermodynamic potentials do not coincide with system's SIM, even at the physical equilibrium point!

Hydrogen-Air System

- The mechanism (Miller *et al.*, 1982) consists of $J = 19$ reversible reactions involving $N = 9$ species, $L = 3$ elements, and $C = 0$, so that $\mathbf{z} \in \mathbb{R}^6$.
- Closed and spatially homogenous system of $2H_2 + (O_2 + 3.76N_2)$ with isothermal and isochoric conditions at $T = 1500\ K$, and $p_0 = 10^7\ dyne/cm^2$.
- The system has 284 finite (90 0-D real) and 42 infinite (18 0-D real) equilibria.
- Only 14 critical points have an eigenvalue spectrum that contains only one unstable direction.
- There is a unique physical equilibrium, R_{19}.

3-D Projection of the system's SIM



Summary

- 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.
- Irreversibility production rate and equilibrium thermodynamic potentials do not provide information on the dynamics towards physical equilibrium.

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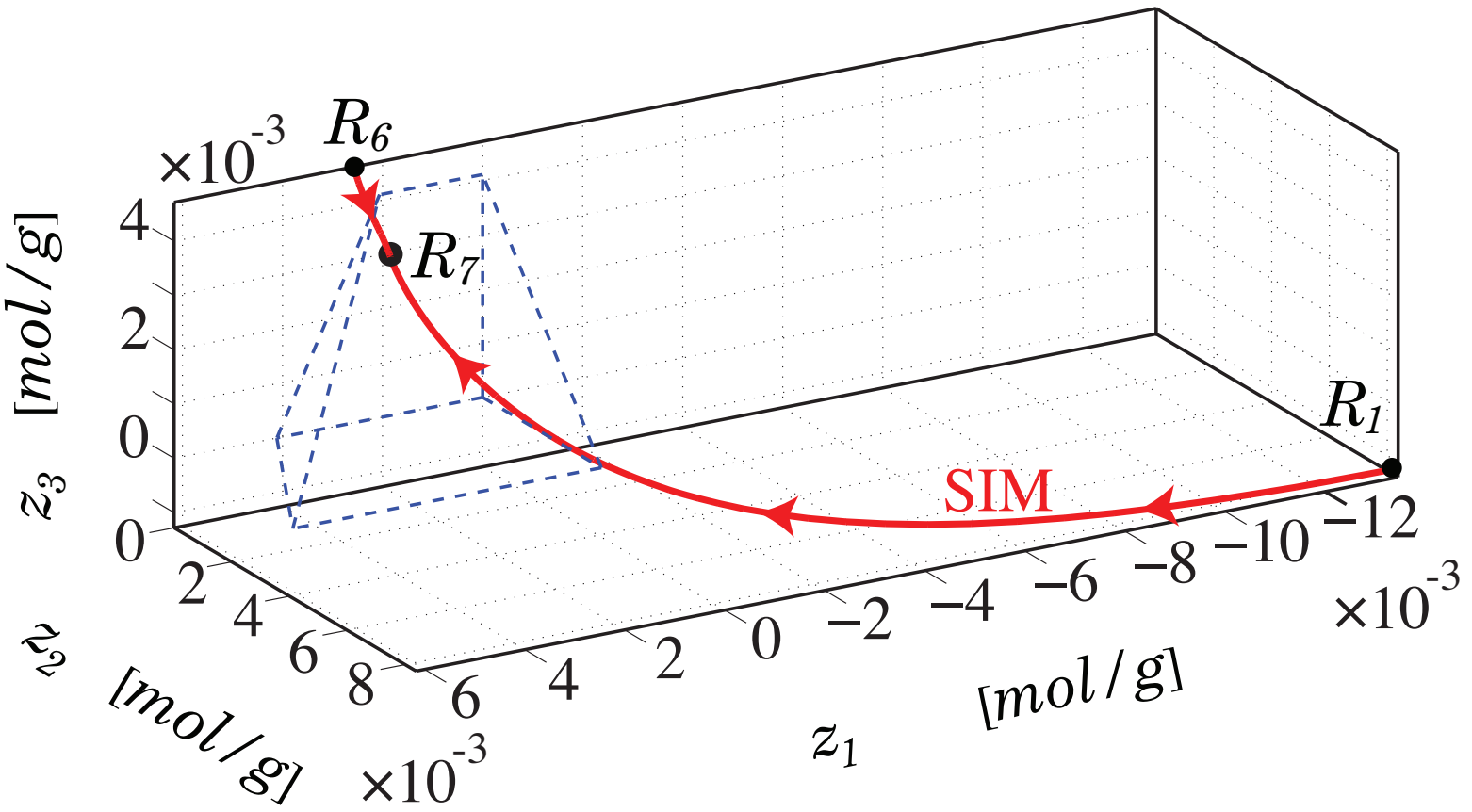
Idealized Hydrogen-Oxygen

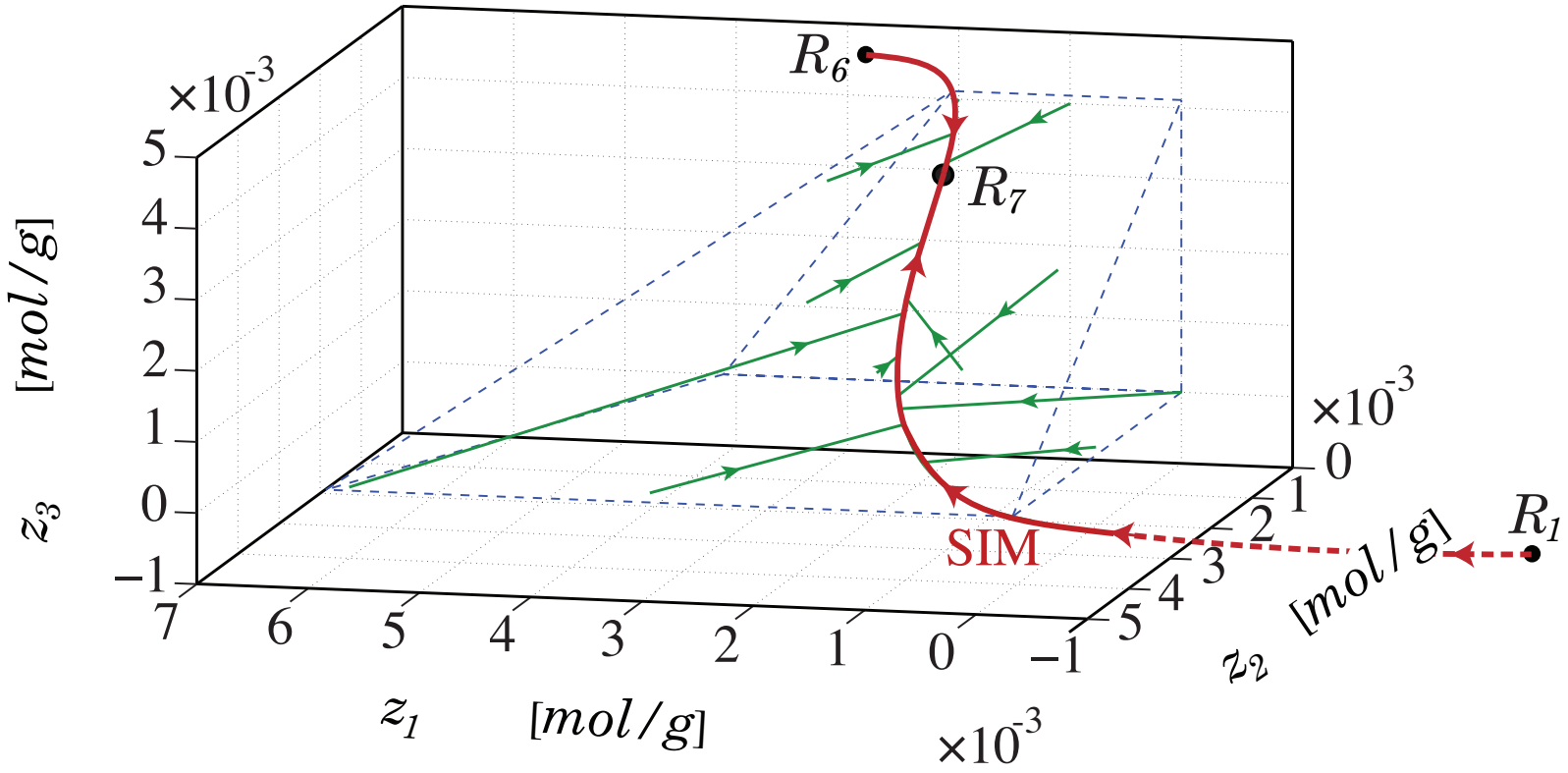
- Kinetic model adopted from Ren *et al.*[a]
- Model consists of $J = 6$ reversible reactions involving $N = 6$ species $\{H_2, O, H_2O, H, OH, N_2\}$ and $L = 3$ elements $\{H, O, N\}$, with $C = 0$, so that $\mathbf{z} \in \mathbb{R}^3$.
- Spatially homogenous with isothermal and isobaric conditions with $T = 3000\ K, p_0 = 1\ atm$.
- 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.

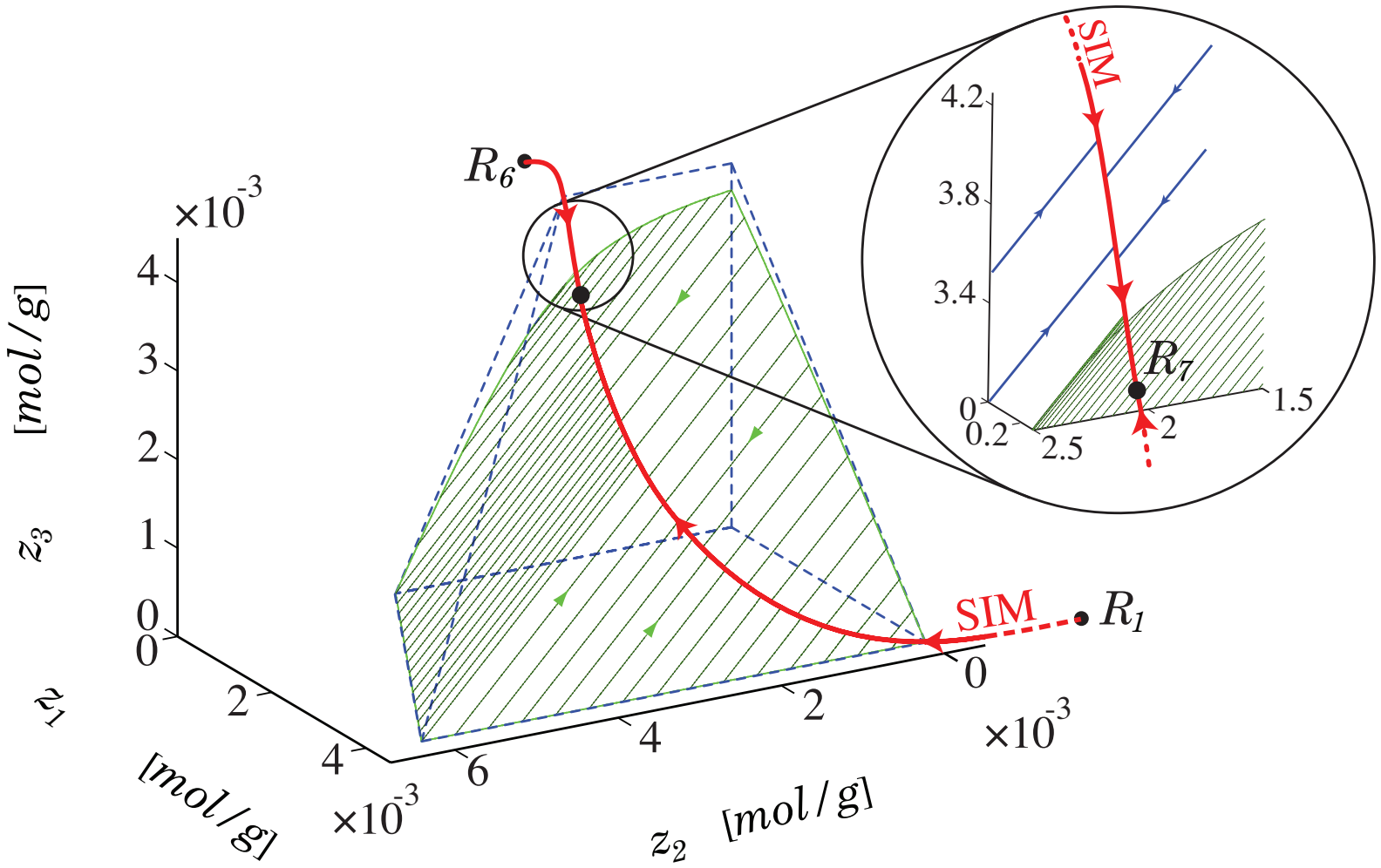
The system's 1-D SIM



The system's 1-D SIM



1-D SIM *vs.* 2-D ICE manifold



Outline

- Introduction
- Slow Invariant Manifold (SIM)
- Method of Construction
- Illustration Using Model Problem
- Application to Hydrogen-Air Reactive System
- Summary

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

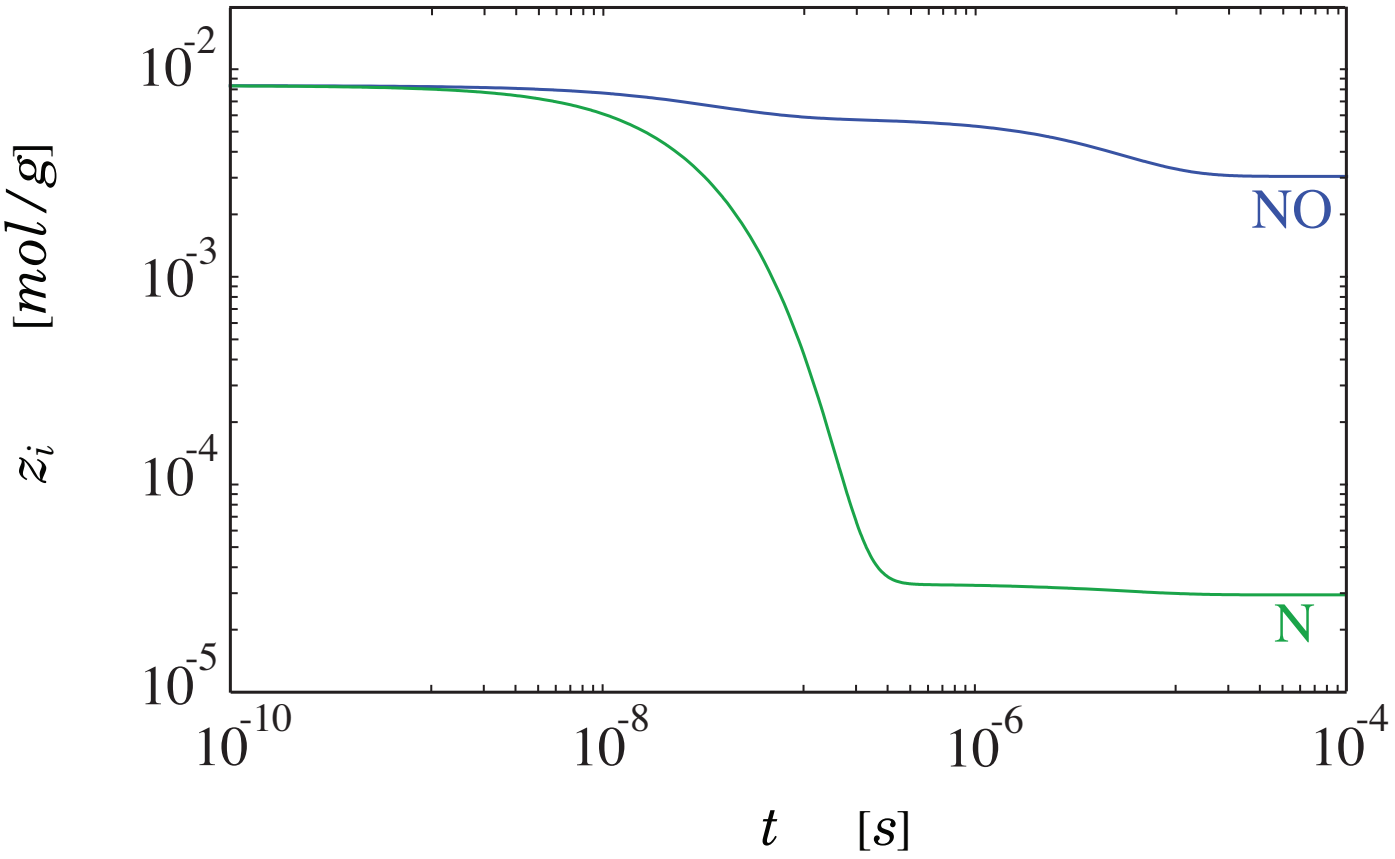
The construction of 1-D Slow Invariant Manifolds (SIMs) for dynamical system arising from modeling unsteady spatially homogenous closed reactive systems.

Partial review of manifold construction in reactive systems

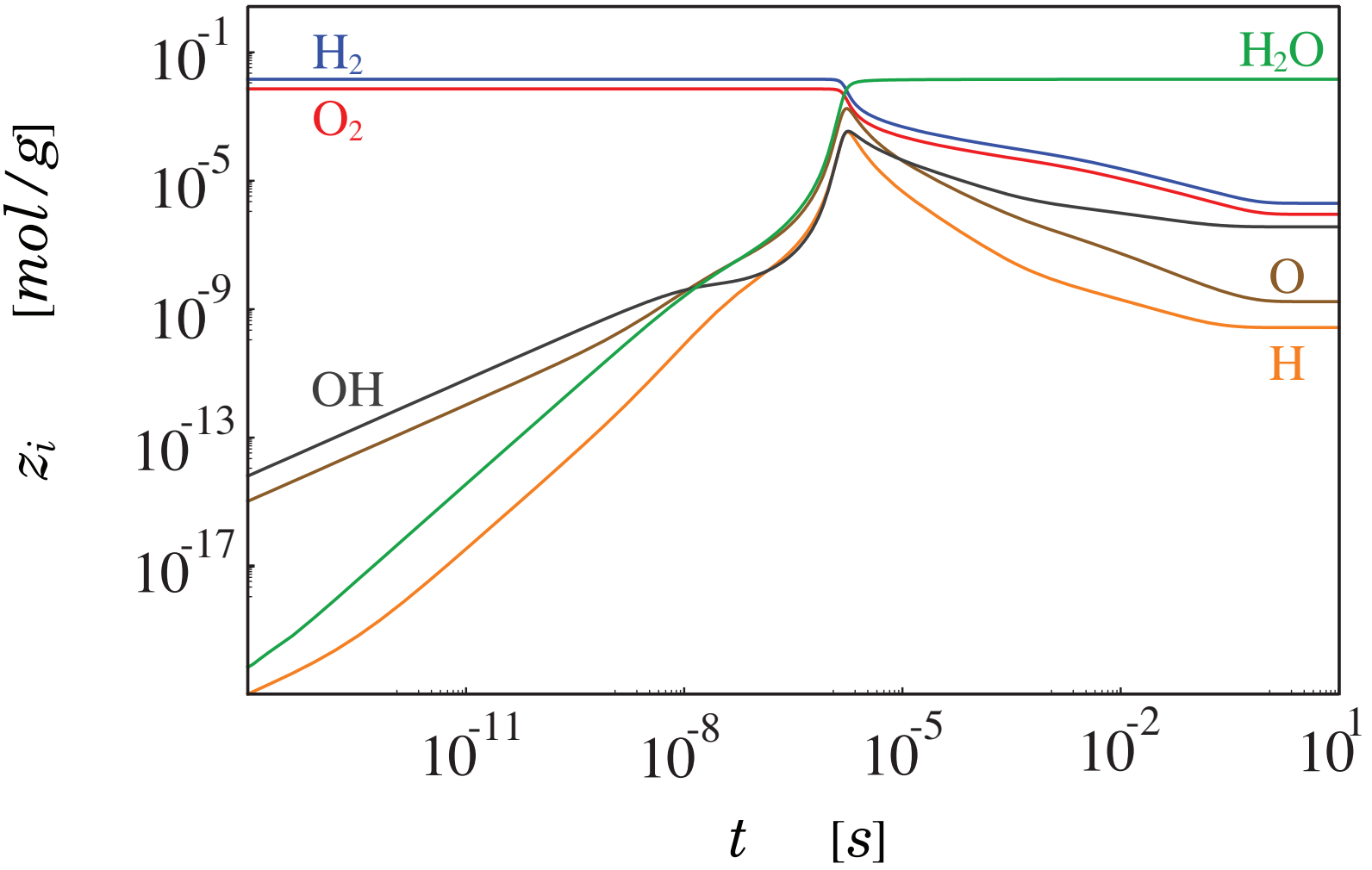
- ILDM, CSP, and ICE-PIC are approximations of the reaction slow invariant manifold.
- MEPT and similar methods are based on minimizing a thermodynamics potential function.
- Iterative methods require "*reasonable*" initial conditions.
- Davis and Skodje, 1999, present a technique to construct the 1-D SIM based on global phase analysis,
- Creta *et al.* and Giona *et al.*, 2006, extend the technique to slightly higher dimensional reactive systems.

- An invariant manifold is defined as an open subset $\mathcal{S} \subset \mathbb{R}^{N-L-C}$ 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.

Reactive system evolution



Reactive system evolution



Finite equilibria

$$\left.\begin{aligned}
\frac{dz_1}{dt} &= 2.51\times10^{2} + 1.16\times10^{7} z_2 + 6.99\times10^{8} z_2^2 \\
&\quad -9.98\times10^{4} z_1 - 3.22\times10^{9} z_2 z_1, \\
\frac{dz_2}{dt} &= 2.51\times10^{2} - 1.17\times10^{7} z_2 - 6.98\times10^{8} z_2^2 \\
&\quad +8.47\times10^{4} z_1 - 1.84\times10^{9} z_2 z_1,
\end{aligned}\right\} \equiv \mathbf{f}(\mathbf{z}).$$

$$\begin{aligned}
R_1 \equiv (z_1^e, z_2^e) &= \left(-1.78\times10^{-5}, -1.67\times10^{-2}\right), \\
(\lambda_1, \lambda_2) &= (4.18\times10^{7}, 2.35\times10^{7}) \quad \textit{source}, \\
R_2 \equiv (z_1^e, z_2^e) &= \left(-4.20\times10^{-3}, -2.66\times10^{-5}\right), \\
(\lambda_1, \lambda_2) &= (-4.64\times10^{6}, 7.11\times10^{5}) \quad \textit{saddle}, \\
R_3 \equiv (z_1^e, z_2^e) &= \left(3.05\times10^{-3}, 2.94\times10^{-5}\right), \\
(\lambda_1, \lambda_2) &= \left(-1.73\times10^{7}, -1.91\times10^{5}\right) \quad \textit{sink}.
\end{aligned}$$

R_3 is the physical equilibrium. Stiffness = $\left|\lambda_1/\lambda_2\right| = 90.5$

Infinite equilibria

- Employ the projective space mapping with $n = 2$ and $k = 1$:

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

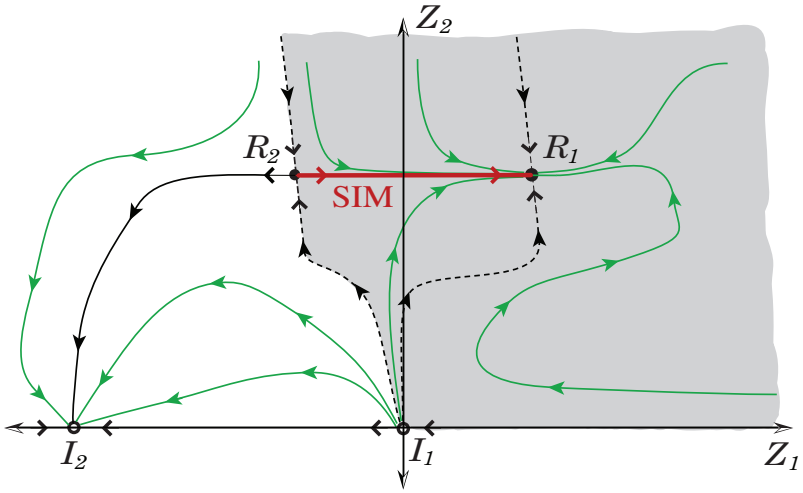
$$\begin{aligned}
I_1 \equiv (Z_1^e, Z_2^e) &= (0,0)\,, \\
(\lambda_1, \lambda_2) &= \left(-1.53 \times 10^{13}, 0\right) \qquad saddle - node, \\
I_2 \equiv (Z_1^e, Z_2^e) &= (0, 1.01)\,, \\
(\lambda_1, \lambda_2) &= \left(2.12 \times 10^{13}, 9.36 \times 10^{12}\right) \qquad source, \\
I_3 \equiv (Z_1^e, Z_2^e) &= (0, 2.60)\,, \\
(\lambda_1, \lambda_2) &= \left(3.04 \times 10^{13}, 2.41 \times 10^{13}\right) \qquad source.
\end{aligned}$$

Simple Reactive System

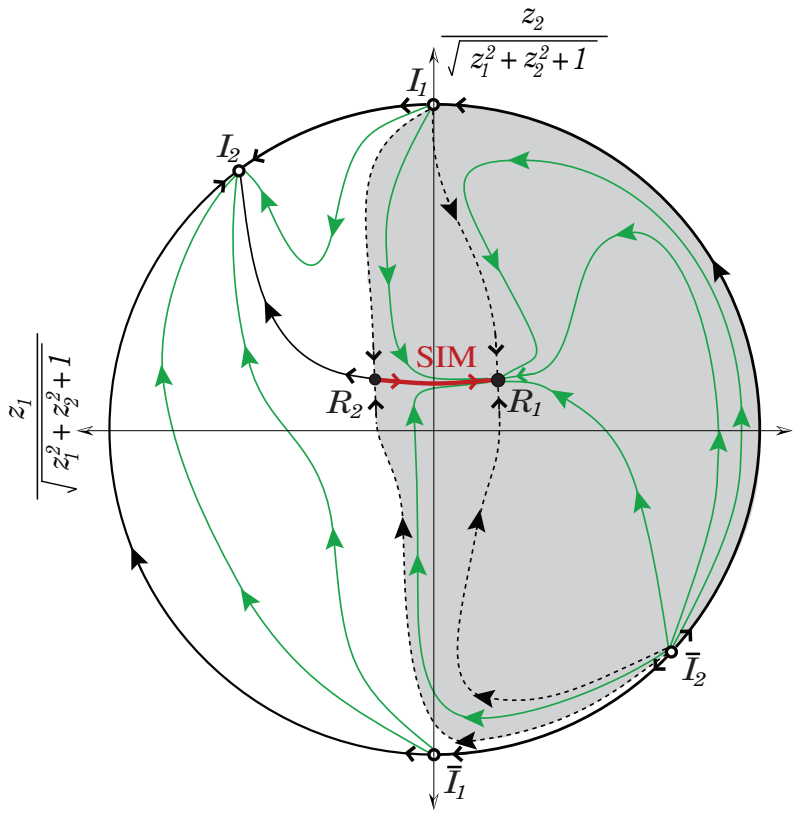
$$\begin{aligned} A + A &\rightleftharpoons B \qquad k^f = 1, k^b = 10^{-5}. \\ B &\rightleftharpoons C \qquad k^f = 10, k^b = 10^{-5}. \end{aligned}$$

- 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 and MEPT