

On the Relation Between Reaction Dynamics and Thermodynamics in Closed Systems

A. N. Al-Khateeb J. M. Powers S. Paolucci J. D. Mengers

Department of Aerospace and Mechanical Engineering

A. J. Sommesse J. A. Diller

Department of Mathematics

UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA

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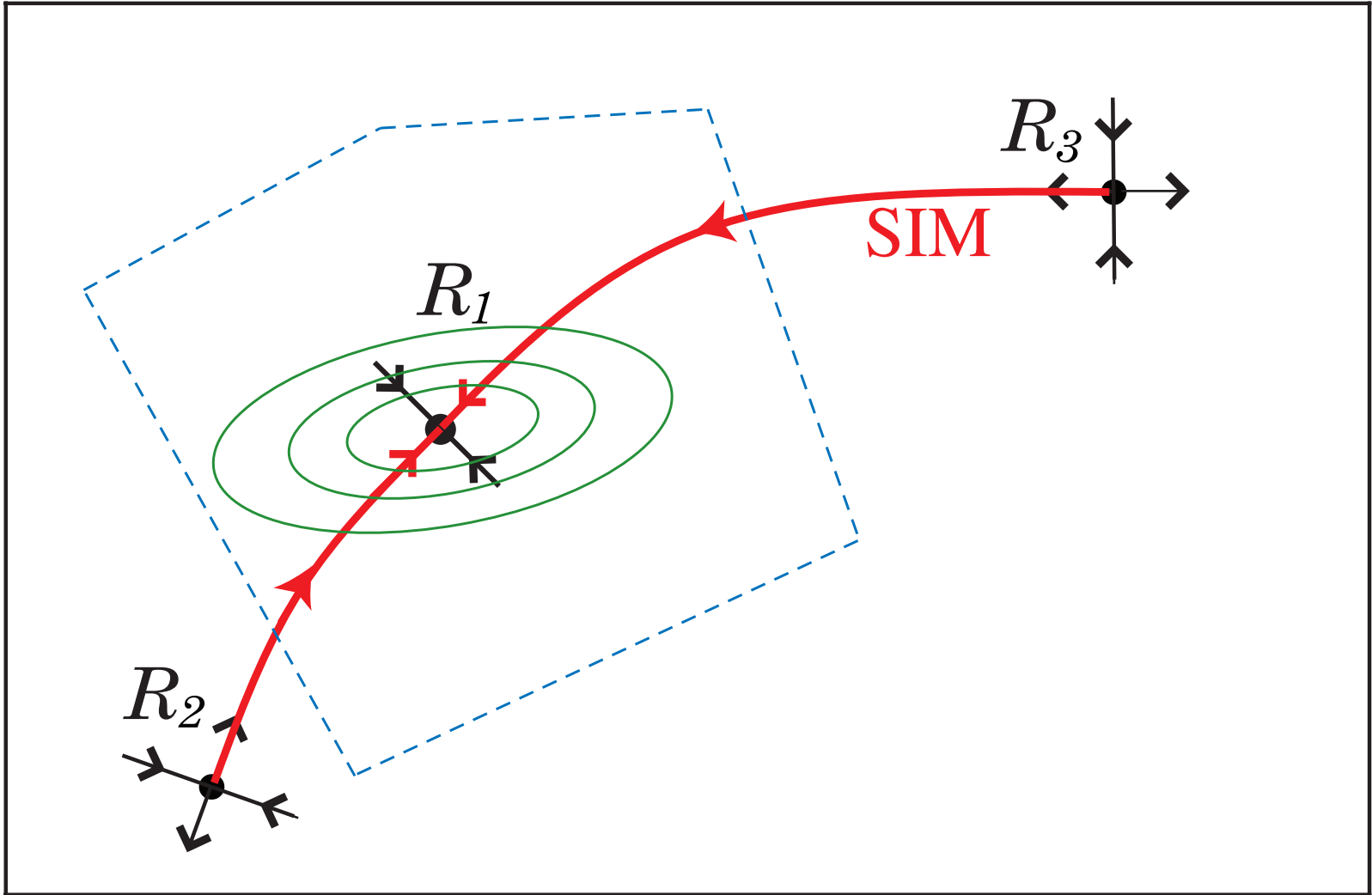
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Introduction

Motivation and Background

- Dimension reduction can reduce the computational cost of modeling reactive systems.
- Several methods (e.g. RCCE, MIM, ICE-PIC, MEPT) employ assumptions from thermodynamics to aid construction of reactive systems' attractive manifolds.
- The alternate SIM construction based on the projective space method relies on the direct use of the reaction dynamics.



Analysis

- For a mixture of mass M confined in a closed volume V containing N species composed of L elements that undergo J reversible isothermal reactions,

$$\frac{d\mathbf{n}}{dt} = V (\boldsymbol{\nu} \cdot \mathbf{r}), \quad \mathbf{n} \in \mathbb{R}^N, \quad \mathbf{r} \in \mathbb{R}^J.$$

- The evolution of this system in the reduced space is described by

$$\frac{d\mathbf{z}}{dt} = \dot{\mathbf{w}}, \quad \{\mathbf{z}, \dot{\mathbf{w}}\} \in \mathbb{R}^R, \quad \mathbb{R}^R \subset \mathbb{R}^N,$$

where,

$$\mathbf{z} = \frac{1}{M} (\mathfrak{D}^T \cdot \mathfrak{D})^{-1} \cdot \mathfrak{D}^T \cdot (\mathbf{n} - \mathbf{n}^*), \quad \mathfrak{D} : \mathbb{R}^N \rightarrow \mathbb{R}^R.$$

Thermodynamic conditions

- Adopting Dalton's law for this reactive mixture, which is at temperature T and pressure p ,

$$S = \mathbf{n} \cdot \bar{\mathbf{s}} = \mathbf{n} \cdot \left(\bar{\mathbf{s}}^o - \bar{\mathcal{R}} \ln \left(\frac{p}{p^o} \right) \right), \quad \bar{\mathbf{s}} \in \mathbb{R}^N,$$

$$G = \mathbf{n} \cdot \bar{\boldsymbol{\mu}} = \mathbf{n} \cdot \left(\bar{\boldsymbol{\mu}}^o + \bar{\mathcal{R}}T \ln \left(\frac{p}{p^o} \right) \right), \quad \bar{\boldsymbol{\mu}} \in \mathbb{R}^N.$$

- In non-equilibrium thermodynamics,

$$dS = d_e S + d_i S,$$

$$d_i S = -\frac{1}{T} (\bar{\boldsymbol{\mu}} \cdot d\mathbf{n}),$$

$$\sigma \equiv \frac{d_i S}{dt} = -\frac{M}{T} \left(\bar{\boldsymbol{\mu}} \cdot \mathfrak{D} \cdot \frac{d\mathbf{z}}{dt} \right).$$

- In general,

$$\mathbf{J} = \frac{\partial \dot{\mathbf{w}}}{\partial \mathbf{z}},$$

$$\mathbf{H} = \frac{\partial^2}{\partial \mathbf{z} \partial \mathbf{z}},$$

$$\sigma = -\frac{1}{T} \left(\frac{\partial G}{\partial \mathbf{z}} \cdot \dot{\mathbf{w}} \right).$$

- Near the system's equilibrium,

$$G = G|_{\mathbf{z}^e} + \underbrace{\left(\frac{\partial G}{\partial \mathbf{z}} \Big|_{\mathbf{z}=\mathbf{z}^e} \cdot \mathbf{z}' \right)}_{=0} + \left(\frac{1}{2} \mathbf{z}'^T \cdot \mathbf{H}_G^e \cdot \mathbf{z}' \right) + \dots,$$

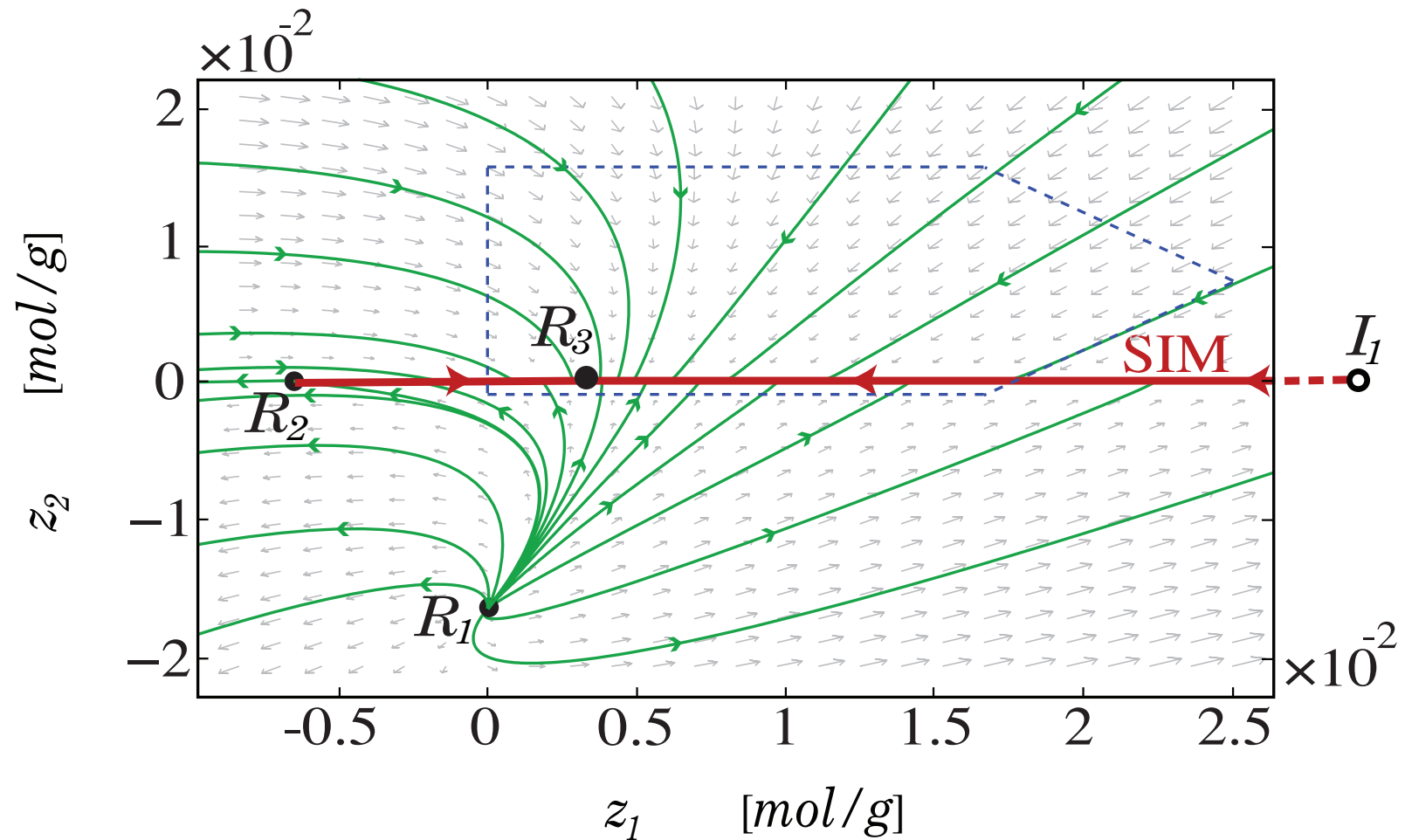
$$\sigma = \underbrace{\sigma|_{\mathbf{z}^e} + \left(\frac{\partial \sigma}{\partial \mathbf{z}} \Big|_{\mathbf{z}=\mathbf{z}^e} \cdot \mathbf{z}' \right)}_{=0} + \left(\frac{1}{2} \mathbf{z}'^T \cdot \mathbf{H}_\sigma^e \cdot \mathbf{z}' \right) + \dots,$$

- Thermodynamics unambiguously tells us G is minimum and σ is minimum and zero at equilibrium.
- Thermodynamics does not provide dynamics near equilibrium.
- The eigenvectors of \mathbf{J}^e define the dynamics near equilibrium.
- It is easy to show that

$$\mathbf{H}_\sigma^e = -\frac{1}{T} \left(\mathbf{H}_G^e \cdot \mathbf{J}^e + (\mathbf{H}_G^e \cdot \mathbf{J}^e)^T \right).$$

- The eigenvectors associated with the largest/smallest eigenvalues of \mathbf{H}_G^e and \mathbf{H}_σ^e are aligned with major/minor axes of G and σ contours.
- The SIM can be identified from \mathbf{H}_σ **only** when \mathbf{H}_G is diagonal with equal eigenvalues. This has not been observed in nature.

Model Problem: Zel'dovich mechanism^a



^aA. N. Al-Khateeb *et al.*, *J. Chem. Phys.* submitted.

Thermodynamics and SIM

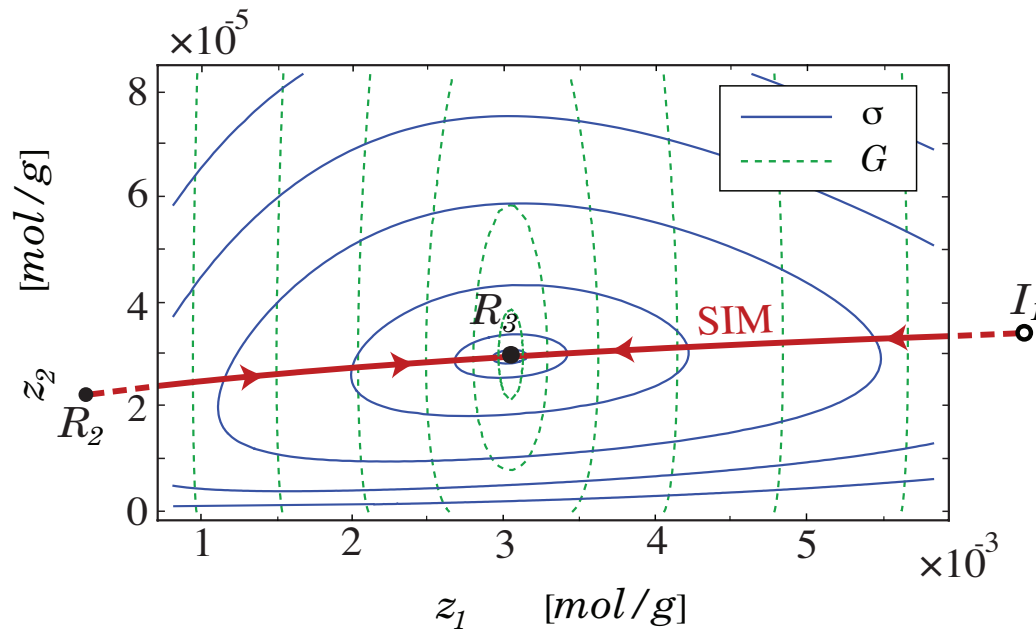
- At the physical equilibrium point,

$$\mathbf{H}_\sigma^e : (\boldsymbol{\lambda}, \mathbf{v}) = (8.17 \times 10^{23}, 1.01 \times 10^{20}), \\ ([1.78 \times 10^{-3}, -1.00]^T, [-1.00, -1.78 \times 10^{-3}]^T),$$

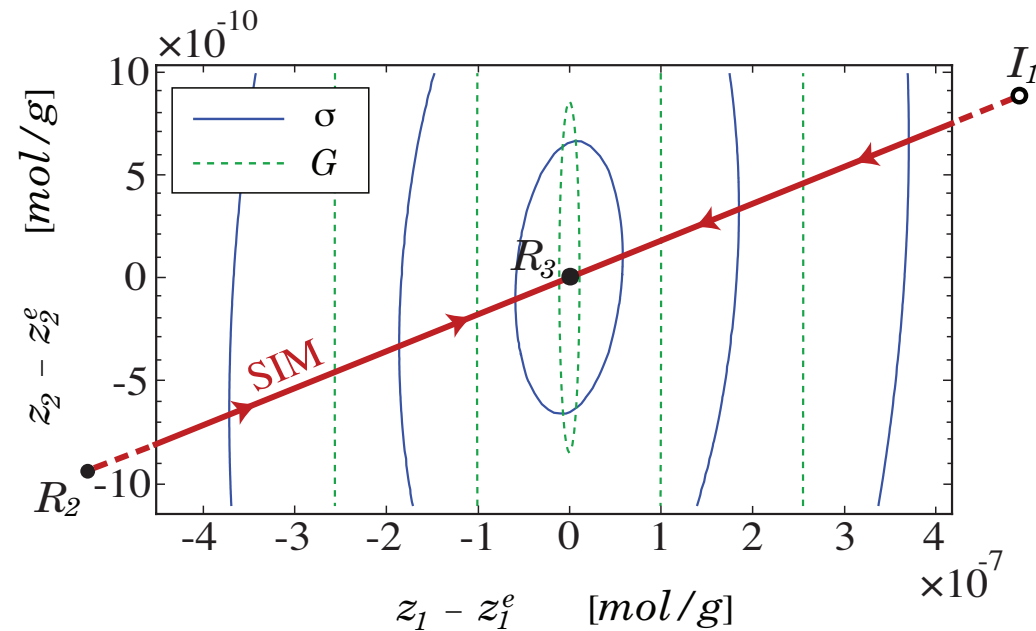
$$\mathbf{H}_G^e : (\boldsymbol{\lambda}, \mathbf{v}) = (9.44 \times 10^{19}, 1.06 \times 10^{18}), \\ ([5.97 \times 10^{-4}, -1.00]^T, [-1.00, -5.97 \times 10^{-4}]^T),$$

$$\mathbf{J}^e : (\boldsymbol{\lambda}, \mathbf{v}) = (-1.73 \times 10^7, -1.91 \times 10^5), \\ ([-0.107, 0.994]^T, [1.00, 1.79 \times 10^{-3}]^T).$$

- The difference between the angle at which the SIM approaches R_3 and the angles at which σ approaches R_3 increases as T increases.

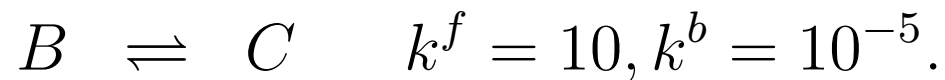


- Equilibrium thermodynamic functions do not coincide with the system's actual SIM.



- The gradients of these thermodynamic scalar functions do not drive the system's dynamics.

Simple Reactive System



- System of Lebiedz, 2004, *J. Chem. Phys.* **120** (15), pp. 6890-6897.
- 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 $\mathbf{z} \in \mathbb{R}^2$.
- Selected species are $i = \{1, 2\} = \{A, B\}$,

Dynamical system formulation

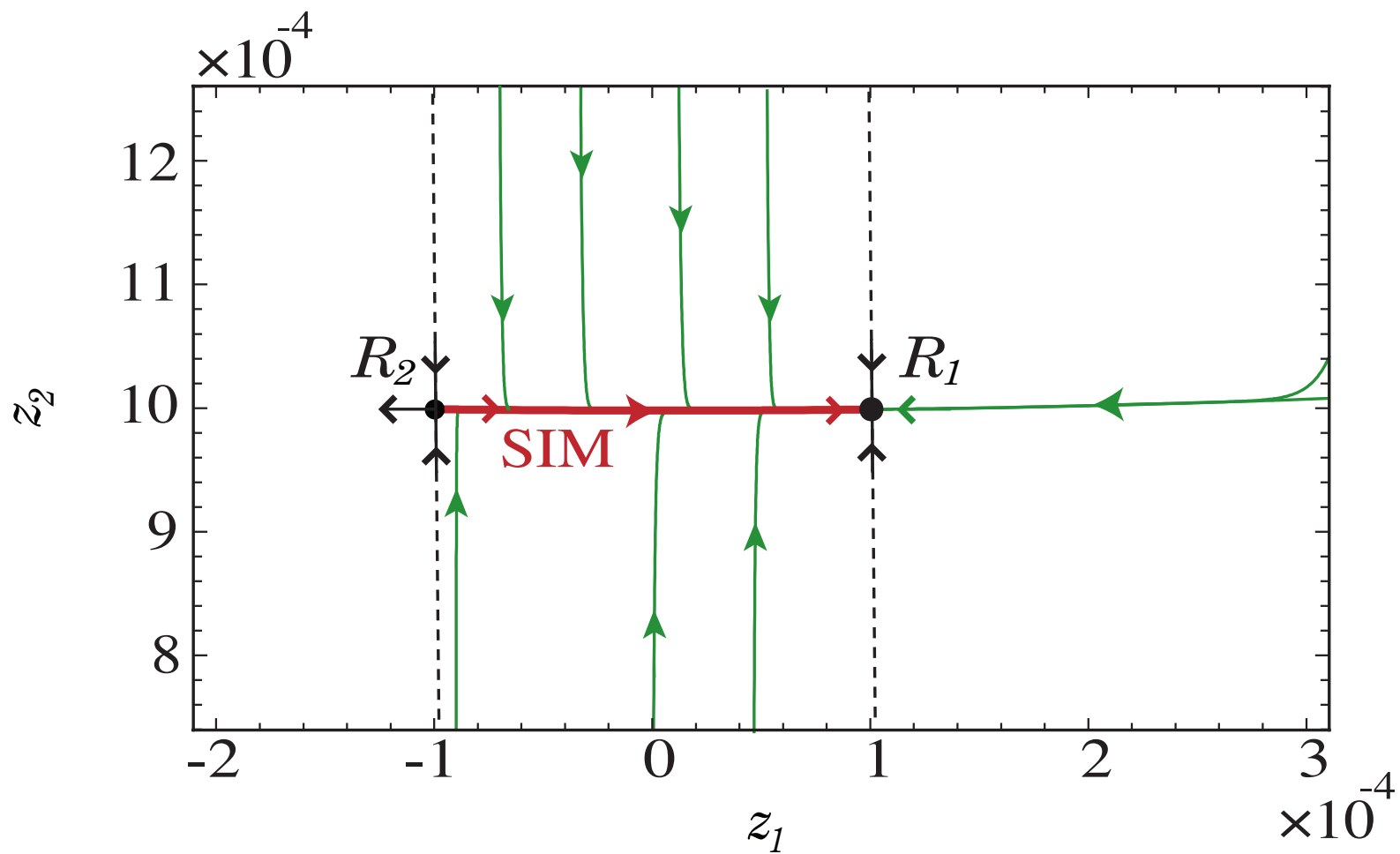
- The evolution of the system is described by:

$$\frac{d}{dt} \begin{pmatrix} z_1 \\ z_2 \end{pmatrix} = \begin{pmatrix} 10^{-5} z_2 - z_1^2 \\ z_1^2 + (1 - 1001 z_2 - z_1) \times 10^{-5} \end{pmatrix} \equiv \mathbf{f}(\mathbf{z}).$$

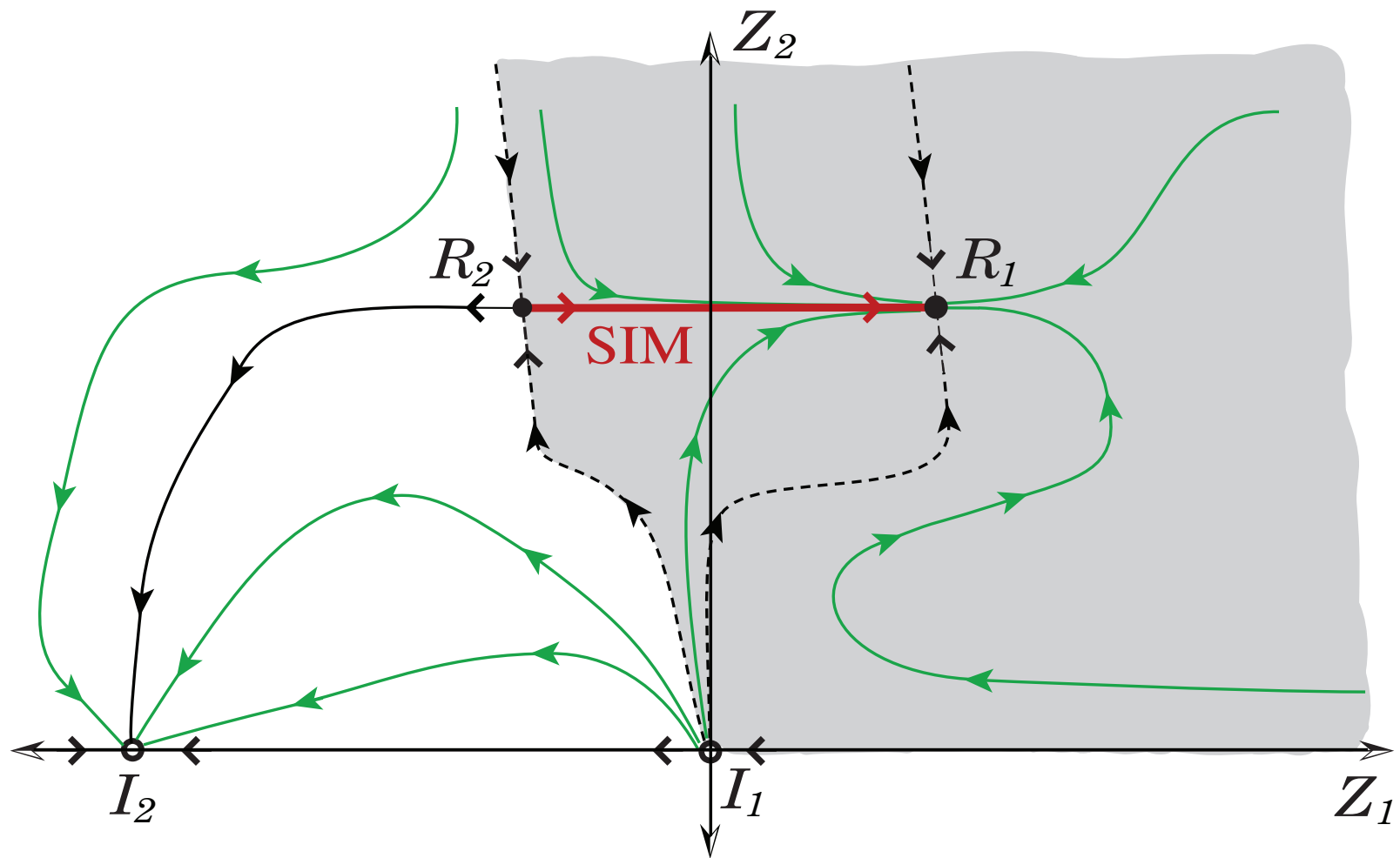
- Employ the projective space mapping with $d = 2$ and $k = 2$:

$$\begin{aligned} \frac{d}{d\tau} \begin{pmatrix} t \\ Z_1 \\ Z_2 \end{pmatrix} &= \begin{pmatrix} Z_2 \\ 10^{-5} Z_2 - Z_1^2 + 10^{-5} Z_1 Z_2 (1001 + Z_1 - Z_2) - Z_1^3 \\ -Z_1^2 Z_2 + 10^{-5} Z_2^2 (1001 + Z_1 - Z_2) \end{pmatrix} \\ &\equiv \mathbf{F}(\mathbf{Z}). \end{aligned}$$

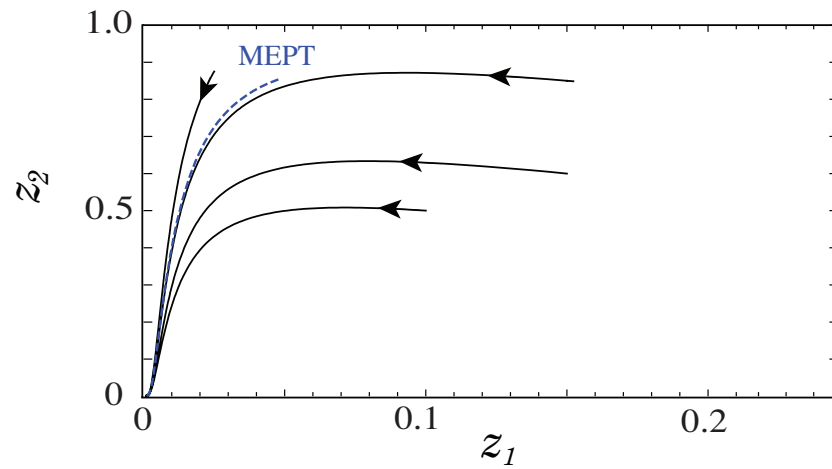
The system's 1-D SIM



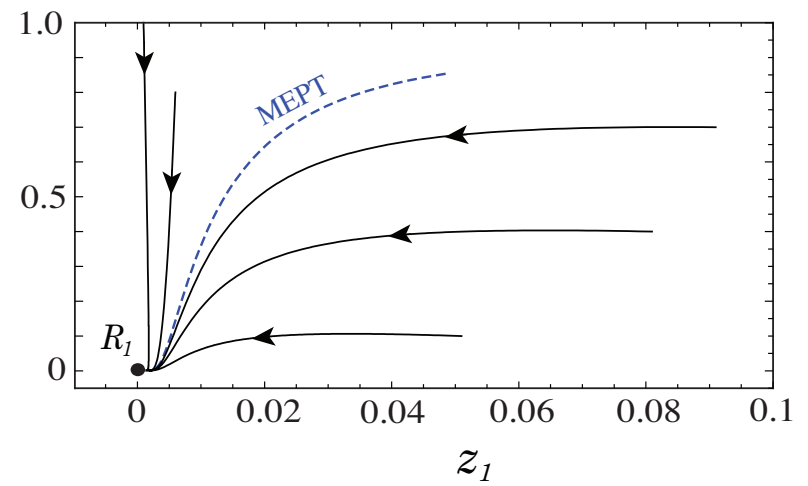
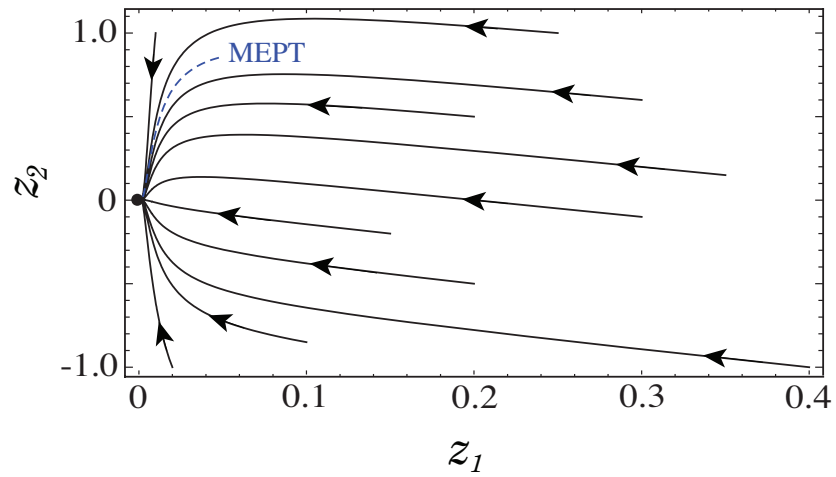
Projective space portrait



SIM vs. MEPT



Identical to Lebedz's Fig. 4.

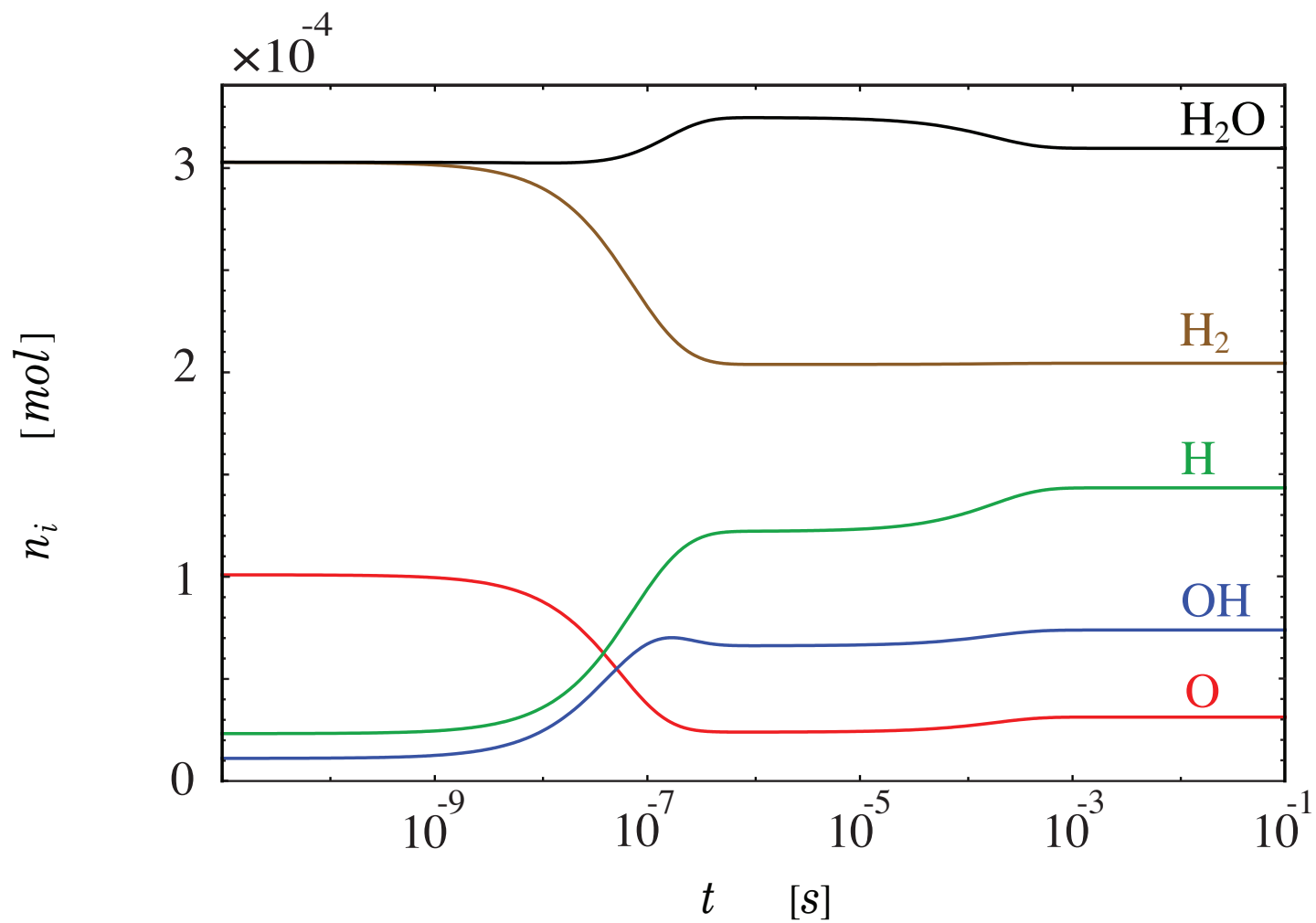


Idealized Hydrogen-Oxygen

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

^bZ. Ren, S. Pope, A. Vladimirov, J. Guckenheimer, 2006, *J. Chem. Phys.* **124**, 114111.

Time evolution of species



System's equilibria

- The set of finite equilibria contains 7 real and 8 complex 0- D equilibria. The real ones are:

$$R_1 \equiv (\mathbf{z}^e) = (-1.67 \times 10^{-1}, 3.04 \times 10^{-3}, 3.53 \times 10^{-3}) \text{ mol/g},$$

$$R_2 \equiv (\mathbf{z}^e) = (6.44 \times 10^{-2}, 1.21 \times 10^{-2}, -7.12 \times 10^{-3}) \text{ mol/g},$$

$$R_3 \equiv (\mathbf{z}^e) = (-6.47 \times 10^{-3}, -2.01 \times 10^{-2}, -2.19 \times 10^{-3}) \text{ mol/g},$$

$$R_4 \equiv (\mathbf{z}^e) = (1.98 \times 10^{-3}, 5.04 \times 10^{-3}, 9.42 \times 10^{-3}) \text{ mol/g},$$

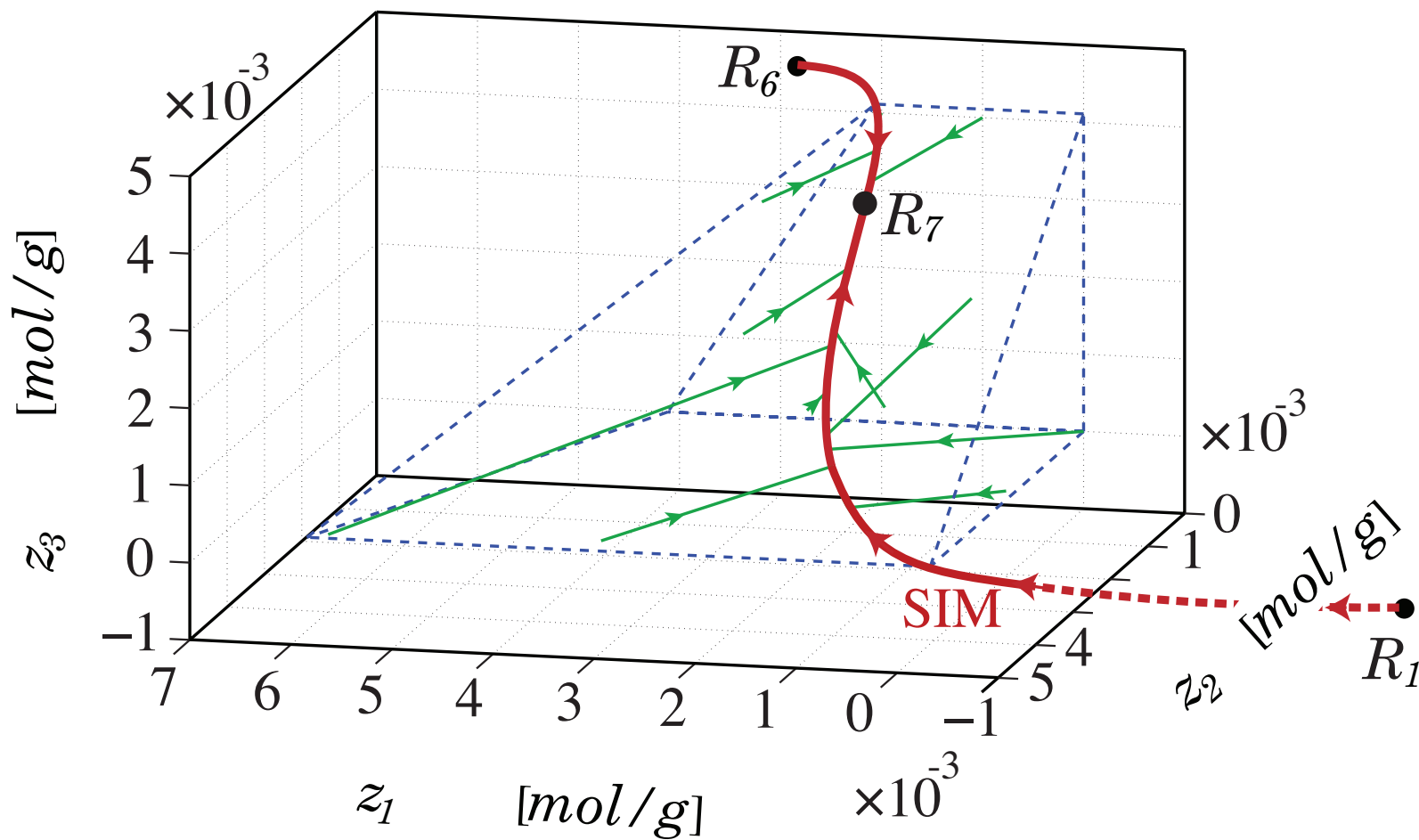
$$R_5 \equiv (\mathbf{z}^e) = (-1.21 \times 10^{-3}, -4.45 \times 10^{-3}, 5.03 \times 10^{-3}) \text{ mol/g},$$

$$R_6 \equiv (\mathbf{z}^e) = (2.72 \times 10^{-3}, 3.34 \times 10^{-4}, 4.72 \times 10^{-3}) \text{ mol/g},$$

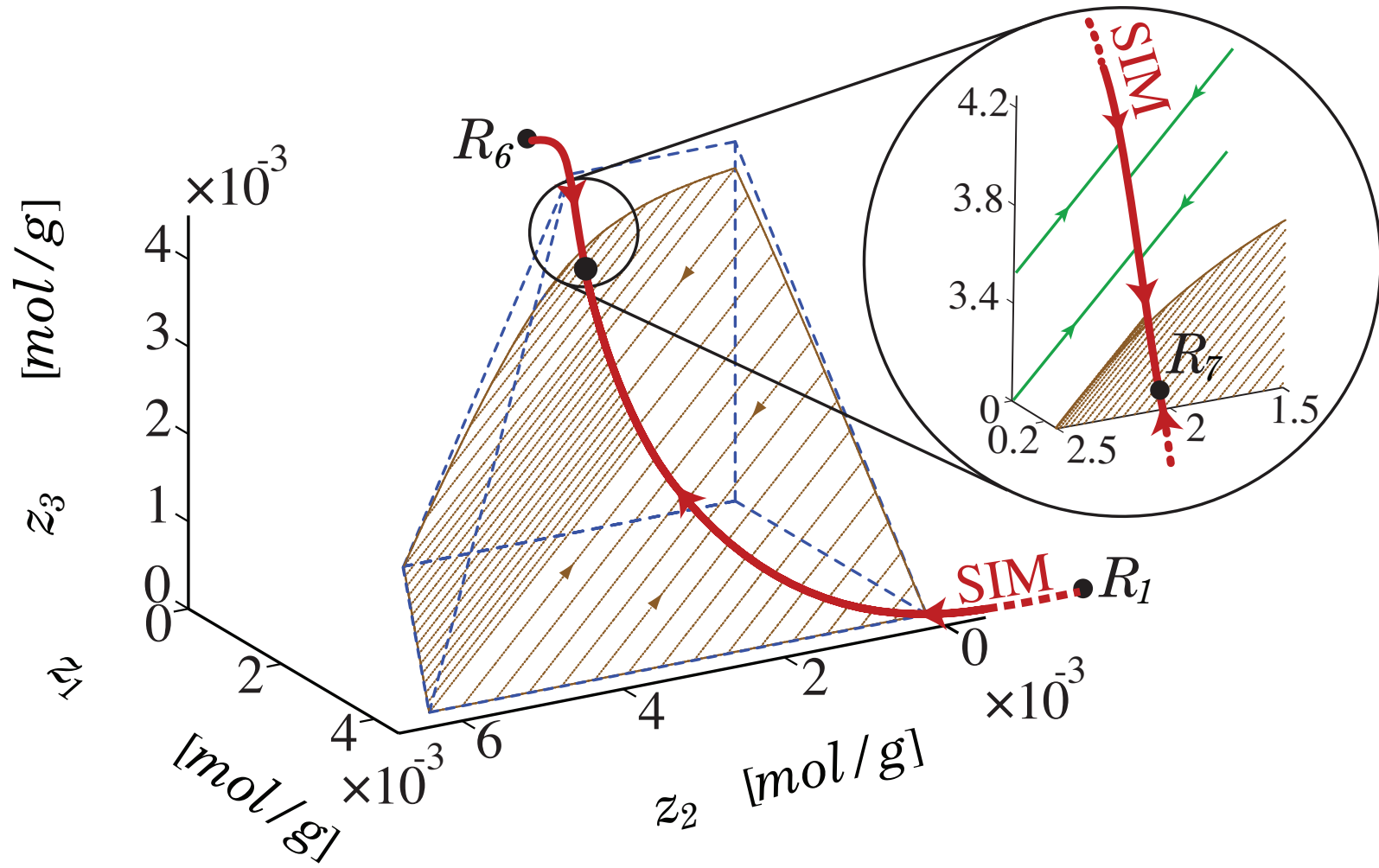
$$R_7 \equiv (\mathbf{z}^e) = (2.03 \times 10^{-3}, 3.10 \times 10^{-4}, 3.07 \times 10^{-3}) \text{ mol/g}.$$

- The set of infinite equilibria contains one 1- D and one 2- D equilibria.

The system's 1-D SIM



1-D SIM vs. 2-D ICE-PIC



Summary and Conclusions

- Equilibrium thermodynamic potentials do not in general determine reactive systems' dynamics.
- **Even near the physical equilibrium state**, a reactive system's SIM cannot be identified by consideration of the topology of a classical thermodynamic function.
- Many modern approaches to estimate SIMs over-rely on thermodynamic potentials, both near and far from equilibrium; consequently, slow dynamics throughout physical phase space are not accurately captured.