On the Relation Between Reaction Dynamics and Thermodynamics in Closed Systems

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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,

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

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

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

where,

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

Thermodynamic conditions

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

$$S = \mathbf{n} \cdot \overline{s} = \mathbf{n} \cdot \left(\overline{s}^{o} - \overline{\Re} \ln \left(\frac{p}{p^{o}} \right) \right), \quad \overline{s} \in \mathbb{R}^{N},$$
$$G = \mathbf{n} \cdot \overline{\mu} = \mathbf{n} \cdot \left(\overline{\mu}^{o} + \overline{\Re} T \ln \left(\frac{p}{p^{o}} \right) \right), \quad \overline{\mu} \in \mathbb{R}^{N}.$$

• In non-equilibrium thermodynamics,

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

$$d_i S = -\frac{1}{T} \left(\overline{\mu} \cdot d\mathbf{n} \right),$$

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

• In general,

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

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

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

• Near the system's equilibrium,

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

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

- 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 H_{σ} only when H_{G} is diagonal with equal eigenvalues. This has not been observed in nature.



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

Thermodynamics and SIM

• At the physical equilibrium point,

$$\begin{split} \mathbf{H}_{\sigma}^{e} &: \quad (\boldsymbol{\lambda}, \boldsymbol{v}) = (8.17 \times 10^{23}, 1.01 \times 10^{20}), \\ & ([1.78 \times 10^{-3}, -1.00]^{T}, [-1.00, -1.78 \times 10^{-3}]^{T}), \\ \mathbf{H}_{G}^{e} &: \quad (\boldsymbol{\lambda}, \boldsymbol{v}) = (9.44 \times 10^{19}, 1.06 \times 10^{18}), \\ & ([5.97 \times 10^{-4}, -1.00]^{T}, [-1.00, -5.97 \times 10^{-4}]^{T}), \\ \mathbf{J}^{e} &: \quad (\boldsymbol{\lambda}, \boldsymbol{v}) = (-1.73 \times 10^{7}, -1.91 \times 10^{5}), \\ & ([-0.107, 0.994]^{T}, [1.00, 1.79 \times 10^{-3}]^{T}). \end{split}$$

• 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.



Simple Reactive System

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

- 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:

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

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

$$\frac{d}{d\tau} \begin{pmatrix} t \\ Z_1 \\ Z_2 \end{pmatrix} = \begin{pmatrix} 10^{-5}Z_2 - Z_1^2 + 10^{-5}Z_1Z_2 (1001 + Z_1 - Z_2) - Z_1^3 \\ -Z_1^2Z_2 + 10^{-5}Z_2^2 (1001 + Z_1 - Z_2) \end{pmatrix}$$
$$\equiv \mathbf{F}(\mathbf{Z}).$$







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, $z \in \mathbb{R}^3$.
- Spatially homogenous with isothermal and isobaric conditions with $T = 3000 \ K, p = 1 \ atm$.
- 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. Vladimirsky, J. Guckenheimer, 2006, *J. Chem. Phys.* **124**, 114111.



System's equilibria

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

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

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

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

$$R_{4} \equiv (\mathbf{z}^{e}) = (1.98 \times 10^{-3}, 5.04 \times 10^{-3}, 9.42 \times 10^{-3}) \ mol/g,$$

$$R_{5} \equiv (\mathbf{z}^{e}) = (-1.21 \times 10^{-3}, -4.45 \times 10^{-3}, 5.03 \times 10^{-3}) \ mol/g,$$

$$R_{6} \equiv (\mathbf{z}^{e}) = (2.72 \times 10^{-3}, 3.34 \times 10^{-4}, 4.72 \times 10^{-3}) \ mol/g,$$

$$R_{7} \equiv (\mathbf{z}^{e}) = (2.03 \times 10^{-3}, 3.10 \times 10^{-4}, 3.07 \times 10^{-3}) \ mol/g.$$

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





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.