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,

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

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

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

where,

$$z = \frac{1}{M} (\mathcal{D}^T \cdot \mathcal{D})^{-1} \cdot \mathcal{D}^T \cdot (n - n^*), \quad \mathcal{D} : \mathbb{R}^N \to \mathbb{R}^R.$$
Thermodynamic conditions

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

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

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

- In non-equilibrium thermodynamics,

\[
dS = d_e S + d_i S,
\]

\[
d_i S = -\frac{1}{T} (\bar{\mu} \cdot dn),
\]

\[
\sigma \equiv \frac{d_i S}{dt} = -\frac{M}{T} \left( \bar{\mu} \cdot \mathcal{D} \cdot \frac{dz}{dt} \right).
\]
• In general,

\[ J = \frac{\partial \dot{w}}{\partial z}, \]

\[ H = \frac{\partial^2}{\partial z \partial z}, \]

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

• Near the system’s equilibrium,

\[ G = G\big|_{z^e} + \left( \frac{\partial G}{\partial z}\big|_{z=z^e} \cdot z' \right) + \left( \frac{1}{2} z'^T \cdot H^e_G \cdot z' \right) + \ldots, \]

\[ \sigma = \sigma\big|_{z^e} + \left( \frac{\partial \sigma}{\partial z}\big|_{z=z^e} \cdot z' \right) + \left( \frac{1}{2} z'^T \cdot H^e_\sigma \cdot z' \right) + \ldots, \]
• Thermodynamics unambiguously tells us $G$ is minimum and $\sigma$ is minimum and zero at equilibrium.

• Thermodynamics does not provide dynamics near equilibrium.

• The eigenvectors of $J^e$ define the dynamics near equilibrium.

• It is easy to show that

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

• The eigenvectors associated with the largest/smallest eigenvalues of $H^e_G$ and $H^e_\sigma$ are aligned with major/minor axes of $G$ and $\sigma$ contours.

• The SIM can be identified from $H_\sigma$ only when $H_G$ is diagonal with equal eigenvalues. This has not been observed in nature.
Model Problem: Zel’dovich mechanism

\[ R_1 \times 10^{-2} \]

\[ \frac{z_2}{mol/g} \]

\[ z_1 \times 10^{-2} \]

\[ [mol/g] \]

\( R_2 \)

\( R_3 \)

\( I_1 \)

\( \text{SIM} \)

\[ A. N. Al-Khateeb et al., J. Chem. Phys. submitted. \]
Thermodynamics and SIM

- At the physical equilibrium point,
  \[ H_{\sigma}^e : (\lambda, \nu) = (8.17 \times 10^{23}, 1.01 \times 10^{20}), \]
  \[
  ([1.78 \times 10^{-3}, -1.00]^T, [-1.00, -1.78 \times 10^{-3}]^T),
  \]
  \[ H_{G}^e : (\lambda, \nu) = (9.44 \times 10^{19}, 1.06 \times 10^{18}), \]
  \[
  ([5.97 \times 10^{-4}, -1.00]^T, [-1.00, -5.97 \times 10^{-4}]^T),
  \]
  \[ J^e : (\lambda, \nu) = (-1.73 \times 10^7, -1.91 \times 10^5), \]
  \[
  ([-0.107, 0.994]^T, [1.00, 1.79 \times 10^{-3}]^T).
  \]

- The difference between the angle at which the SIM approaches \( R_3 \) and the angles at which \( \sigma \) 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

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


- 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 \( z \in \mathbb{R}^2 \).

- Selected species are \( i = \{1, 2\} = \{A, B\} \),
Dynamical system formulation

• The evolution of the system is described by:

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

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

\[
\frac{d}{d\tau} \begin{pmatrix} t \\ Z_1 \\ Z_2 \end{pmatrix} = \begin{pmatrix} Z_2 \\ 10^{-5}Z_2 - Z_1^2 + 10^{-5}Z_1Z_2 (1001 + Z_1 - Z_2) - Z_1^3 \\ -Z_1^2Z_2 + 10^{-5}Z_2^2 (1001 + Z_1 - Z_2) \end{pmatrix} \equiv F(Z).
\]
The system's 1-D SIM

\[ \times 10^{-4} \]

\[ z_2 \]

\[ z_1 \]

\[ R_2 \]

\[ R_1 \]

SIM
Projective space portrait
SIM vs. MEPT

Identical to Lebiedz's Fig. 4.
Idealized Hydrogen-Oxygen

• Kinetic model adopted from Ren et al.\textsuperscript{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.

Time evolution of species

\[ n_i \] [mol]

\[ t \] [s]

- \( \text{H}_2\text{O} \)
- \( \text{H}_2 \)
- \( \text{H} \)
- \( \text{OH} \)
- \( \text{O} \)
System’s equilibria

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

\[
R_1 \equiv (z^e) = (-1.67 \times 10^{-1}, 3.04 \times 10^{-3}, 3.53 \times 10^{-3}) \ mol/g,
\]
\[
R_2 \equiv (z^e) = (6.44 \times 10^{-2}, 1.21 \times 10^{-2}, -7.12 \times 10^{-3}) \ mol/g,
\]
\[
R_3 \equiv (z^e) = (-6.47 \times 10^{-3}, -2.01 \times 10^{-2}, -2.19 \times 10^{-3}) \ mol/g,
\]
\[
R_4 \equiv (z^e) = (1.98 \times 10^{-3}, 5.04 \times 10^{-3}, 9.42 \times 10^{-3}) \ mol/g,
\]
\[
R_5 \equiv (z^e) = (-1.21 \times 10^{-3}, -4.45 \times 10^{-3}, 5.03 \times 10^{-3}) \ mol/g,
\]
\[
R_6 \equiv (z^e) = (2.72 \times 10^{-3}, 3.34 \times 10^{-4}, 4.72 \times 10^{-3}) \ mol/g,
\]
\[
R_7 \equiv (z^e) = (2.03 \times 10^{-3}, 3.10 \times 10^{-4}, 3.07 \times 10^{-3}) \ mol/g.
\]

- 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.