

Strategies for Computing Slow Invariant Manifolds in Reactive Systems

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Motivation

- Manifold methods offer a rational strategy for reducing stiff systems of detailed chemical kinetics.
- Manifold methods are suited for spatially homogeneous systems (ODEs), or operator split (PDEs) reactive flows.
- Approximate methods (ILDM, CSP) cannot be used reliably for arbitrary initial conditions.
- Calculation of the actual **Slow Invariant Manifold** (SIM) can be algorithmically easier and computationally more efficient.
- Global phase maps identify information essential to proper use of manifold methods.
- We will illustrate strategies to obtain the SIM.

Tactics

- Examine different methods for constructing SIMs using a simple physical mechanism of reaction kinetics (Zel'dovich NO production).
- Employ realistic constitutive models.
- Rigorously determine the mathematical properties.
- Explore physical and non-physical regions of phase space, which is essential to construct the SIM as well as understand global dynamics.

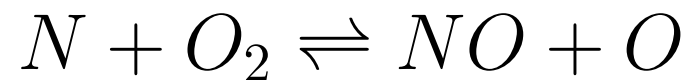
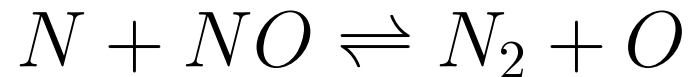
Literature Review

- Maas, Pope, *Comb. Flame*, 1992,
- Roussel, Fraser, *J. Phys. Chem.*, 1993,
- Davis, Skodje, *J. Chem. Phys.*, 1999,
- Singh, Powers, Paolucci, *J. Chem. Phys.*, 2002,
- Lebiecz, *J. Chem. Phys.*, 2004.
- Ren, Pope, Vladimirov, Guckenheimer, *J. Chem. Phys.*, 2006.

Computational Methods

- dynamical systems (shooting, e.g. Davis-Skodje)
- ILDM/CSP (Maas-Pope/Lam-Goussis)
- iterative methods (Roussel-Fraser/Davis-Skodje/Gorban-Karlin)
- ICE-PIC (Pope-Guckenheimer)
- variational method based on minimum entropy production rate (Lebiedz)

Zel'dovich Mechanism for NO Production



- spatially homogeneous,
- isothermal and isobaric, $T = 6000\text{ K}$, $P = 2.5\text{ bar}$,
- law of mass action with reversible Arrhenius kinetics,
- kinetic data from Baulch, *et al.*, 2005,
- thermodynamic data from Sonntag, *et al.*, 2003.

Zel'dovich Mechanism: ODEs

$$\frac{d[NO]}{dt} = r_2 - r_1 = \dot{\omega}_{[NO]}, \quad [NO](t = 0) = [NO]_o,$$

$$\frac{d[N]}{dt} = -r_1 - r_2 = \dot{\omega}_{[N]}, \quad [N](t = 0) = [N]_o,$$

$$\frac{d[N_2]}{dt} = r_1 = \dot{\omega}_{[N_2]}, \quad [N_2](t = 0) = [N_2]_o,$$

$$\frac{d[O]}{dt} = r_1 + r_2 = \dot{\omega}_{[O]}, \quad [O](t = 0) = [O]_o,$$

$$\frac{d[O_2]}{dt} = -r_2 = \dot{\omega}_{[O_2]}, \quad [O_2](t = 0) = [O_2]_o,$$

$$r_1 = k_1[N][NO] \left(1 - \frac{1}{K_{eq1}} \frac{[N_2][O]}{[N][NO]} \right), \quad K_{eq1} = \exp \left(\frac{-\Delta G_1^o}{\mathfrak{R}T} \right)$$

$$r_2 = k_2[N][O_2] \left(1 - \frac{1}{K_{eq2}} \frac{[NO][O]}{[N][O_2]} \right), \quad K_{eq2} = \exp \left(\frac{-\Delta G_2^o}{\mathfrak{R}T} \right).$$

Zel'dovich Mechanism: DAEs

$$\frac{d[NO]}{dt} = \dot{\omega}_{[NO]},$$

$$\frac{d[N]}{dt} = \dot{\omega}_{[N]},$$

$$[NO] + [O] + 2[O_2] = [NO]_o + [O]_o + 2[O_2]_o \equiv C_1,$$

$$[NO] + [N] + 2[N_2] = [NO]_o + [N]_o + 2[N_2]_o \equiv C_2,$$

$$[NO] + [N] + [N_2] + [O_2] + [O] = [NO]_o + [N]_o + [N_2]_o \\ + [O_2]_o + [O]_o \equiv C_3.$$

Constraints for element and molecule conservation.

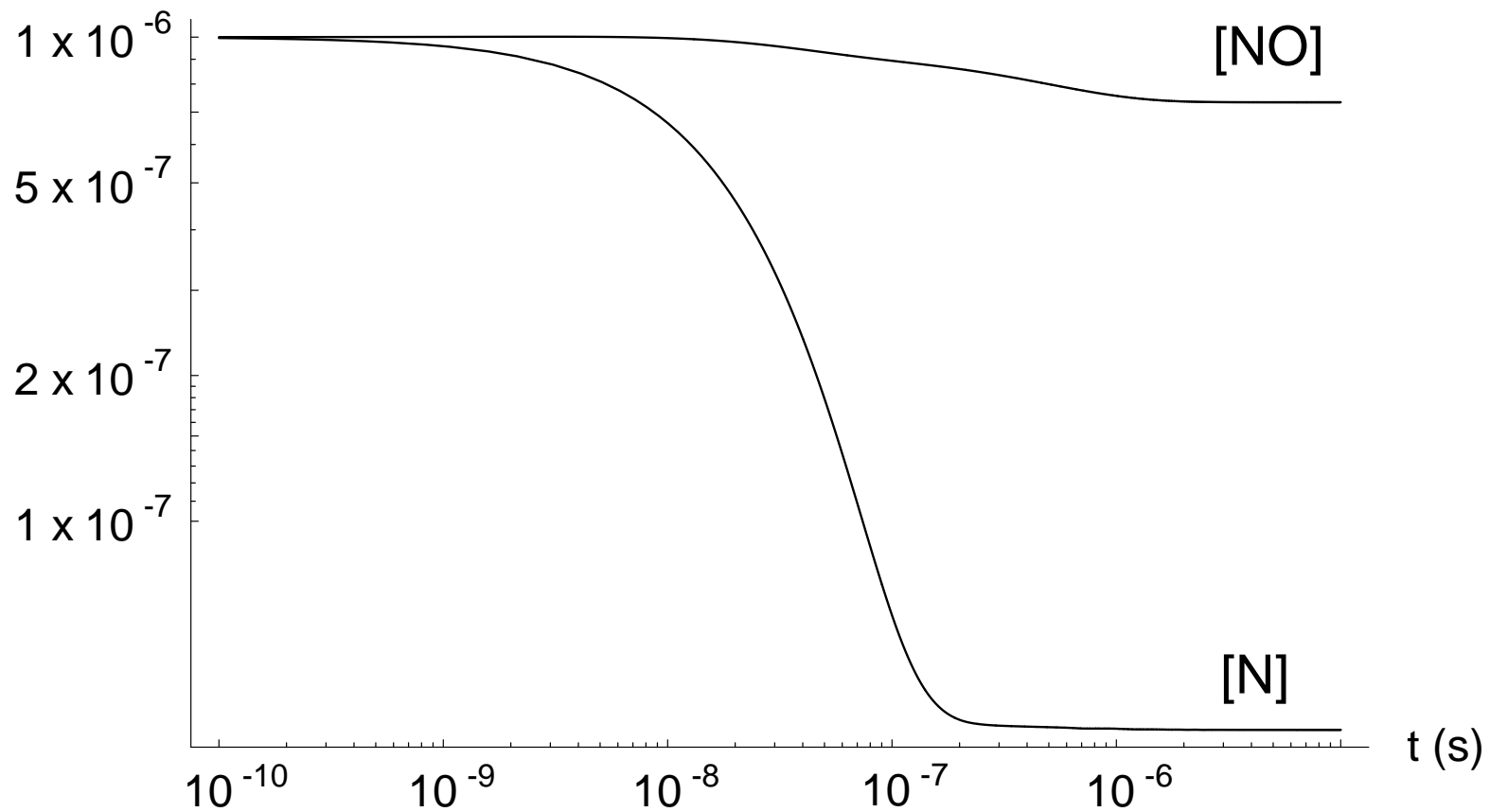
Classical Dynamic Systems Form

$$\begin{aligned}\frac{d[NO]}{dt} &= \hat{\omega}_{[NO]} = 0.72 - 9.4 \times 10^5 [NO] + 2.2 \times 10^7 [N] \\ &\quad - 3.2 \times 10^{13} [N][NO] + 1.1 \times 10^{13} [N]^2, \\ \frac{d[N]}{dt} &= \hat{\omega}_{[N]} = 0.72 + 5.8 \times 10^5 [NO] - 2.3 \times 10^7 [N] \\ &\quad - 1.0 \times 10^{13} [N][NO] - 1.1 \times 10^{13} [N]^2.\end{aligned}$$

Constants evaluated for $T = 6000 \text{ K}$, $P = 2.5 \text{ bar}$, $C_1 = C_2 = 4 \times 10^{-6} \text{ mole/cc}$, $\Delta G_1^o = -2.3 \times 10^{12} \text{ erg/mole}$, $\Delta G_2^o = -2.0 \times 10^{12} \text{ erg/mole}$. Algebraic constraints absorbed into ODEs.

Species Evolution in Time

concentration (mole/cc)



Dynamical Systems Approach to Construct SIM

Finite equilibria and linear stability:

$$1. ([NO], [N]) = (-1.6 \times 10^{-6}, -3.1 \times 10^{-8}),$$

$$(\lambda_1, \lambda_2) = (5.4 \times 10^6, -1.2 \times 10^7) \quad \text{saddle (unstable)}$$

$$2. ([NO], [N]) = (-5.2 \times 10^{-8}, -2.0 \times 10^{-6}),$$

$$(\lambda_1, \lambda_2) = (4.4 \times 10^7 \pm 8.0 \times 10^6 i) \quad \text{spiral source (unstable)}$$

$$3. ([NO], [N]) = (7.3 \times 10^{-7}, 3.7 \times 10^{-8}),$$

$$(\lambda_1, \lambda_2) = (-2.1 \times 10^6, -3.1 \times 10^7) \quad \text{sink (stable, physical)}$$

$$\text{stiffness ratio} = \lambda_2 / \lambda_1 = 14.7$$

Equilibria at infinity and non-linear stability

$$1. ([NO], [N]) \rightarrow (+\infty, 0) \quad \text{sink/saddle (unstable),}$$

$$2. ([NO], [N]) \rightarrow (-\infty, 0) \quad \text{source (unstable).}$$

Continuum Time Scales vs. Collision Time Scales

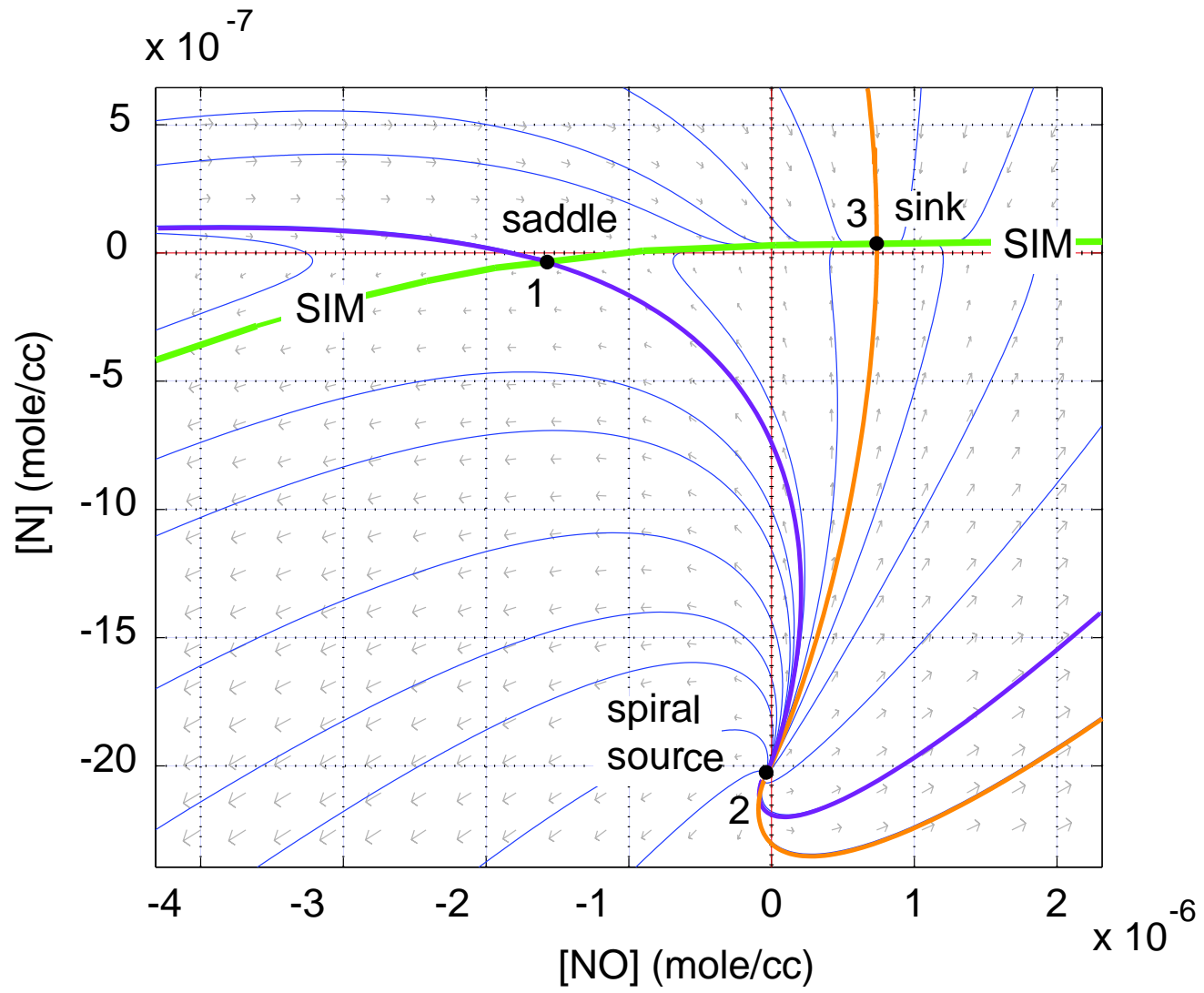
- Continuum theory is an averaged collision theory.
- The finest time scale of our continuum model is

$$\tau_{continuum} = \left| \frac{1}{\lambda_2} \right| \sim 10^{-8} \text{ s.}$$

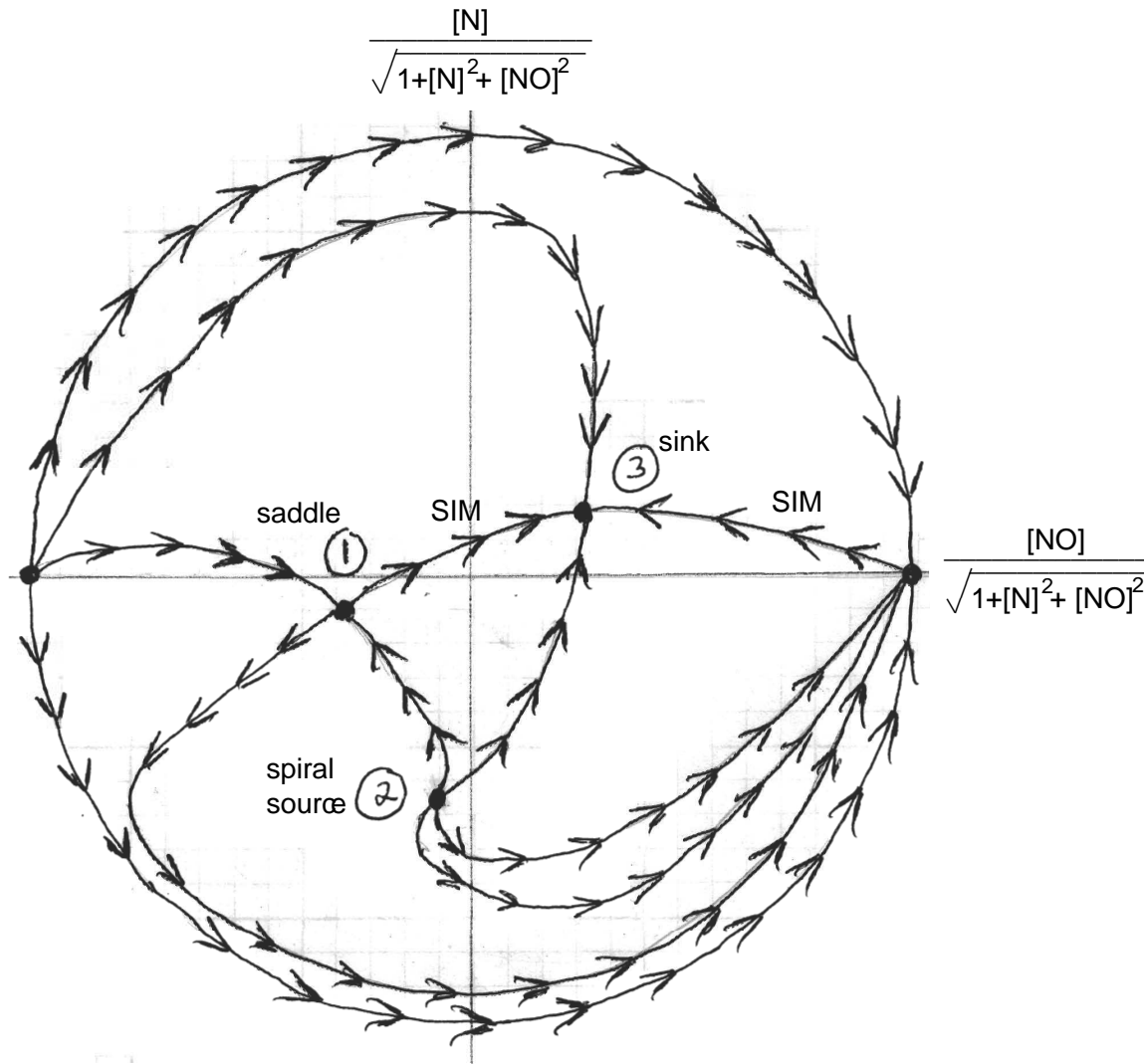
- The collision time from kinetic theory is

$$\tau_{collision} \sim \underbrace{\frac{m}{d^2 \rho}}_{\ell_{mfp}} \underbrace{\sqrt{\frac{\rho}{p}}}_{1/v} \sim 10^{-9} \text{ s.}$$

Detailed Phase Space Map with All Finite Equilibria



Projected Phase Space from Poincaré's Sphere



Behavior Near Equilibrium at Infinity

- Consider the behavior of the SIM as $[NO] \rightarrow \infty$
- Calculations suggest $\hat{\omega}_{[N]} \rightarrow 0$ as $[NO] \rightarrow \infty$.
- $\hat{\omega}_{[N]} = 0$ implies that

$$\lim_{[NO] \rightarrow \infty} [N] = 5.8 \times 10^{-8} \text{ mole/cc.}$$

- Identical to that realized in full calculations.

Roussel-Fraser Iterative Scheme to Calculate SIM

$$\frac{d[NO]}{dt} = \dot{\omega}_{[NO]}, \quad \frac{d[N]}{dt} = \dot{\omega}_{[N]}$$

becomes

$$\frac{d[NO]}{d[N]} = \frac{\dot{\omega}_{[NO]}}{\dot{\omega}_{[N]}}$$

or

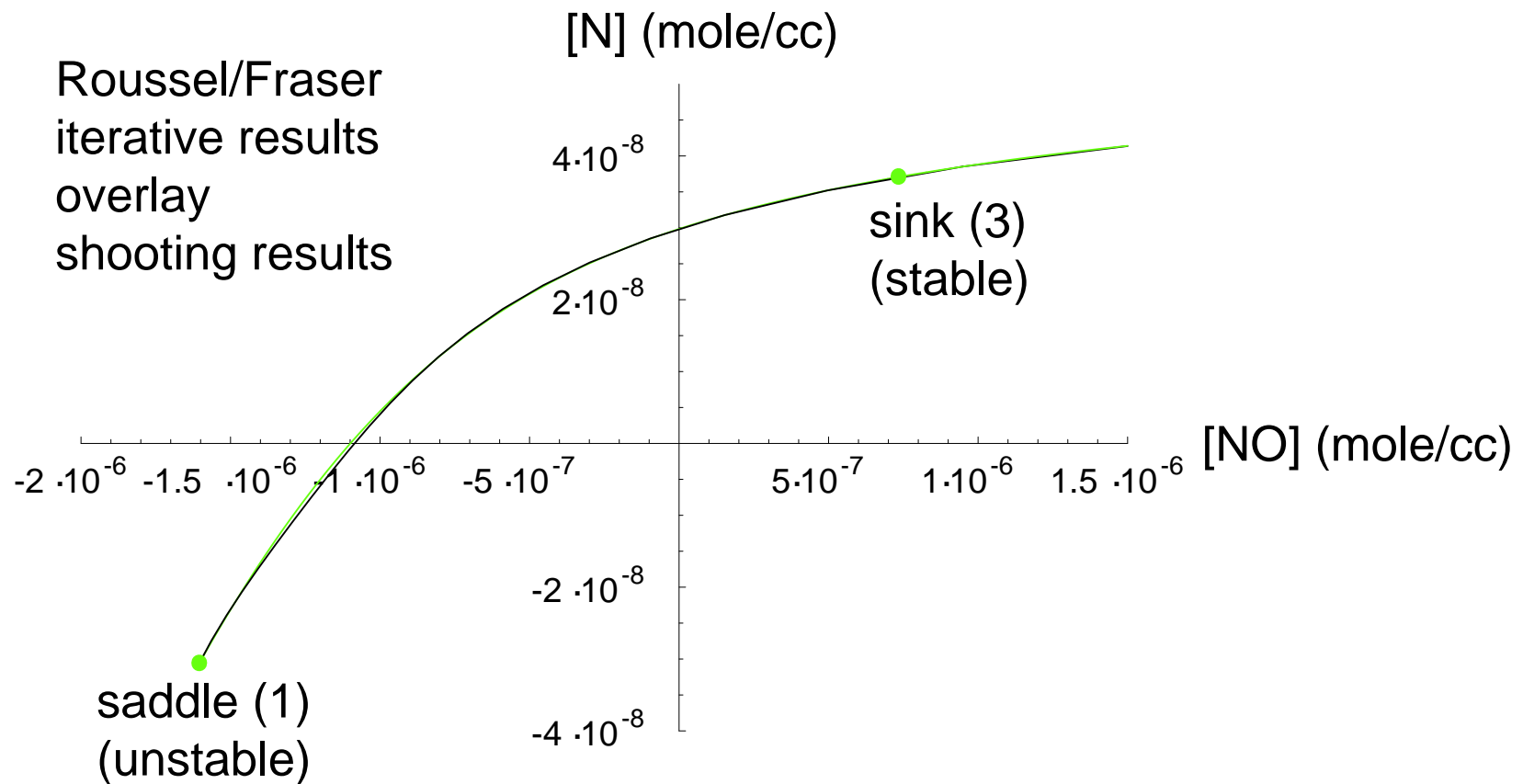
$$\dot{\omega}_{[NO]} - \dot{\omega}_{[N]} \frac{d[NO]}{d[N]} = 0.$$

Guess an initial $[NO]([N])$ distribution and iterate on

$$\dot{\omega}_{[NO]}([NO]_{n+1}, [N]) - \dot{\omega}_{[N]}([NO]_n, [N]) \left. \frac{d[NO]}{d[N]} \right|_n = 0.$$

to find $[NO]_n$. Convergence achieved in four/five iterations.

SIM from Roussel-Fraser Iteration

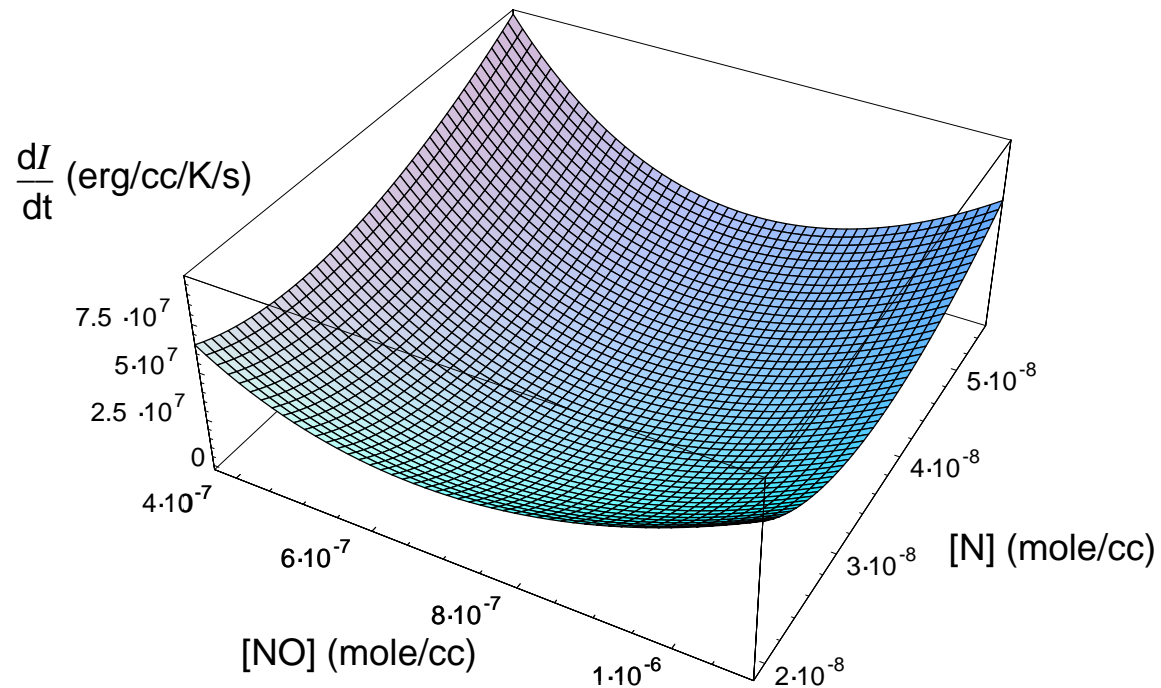


The variant Davis-Skodje iterative method yields similar results.

Connections of SIM with Thermodynamics

- Classical thermodynamics identifies equilibrium with the minimum of Gibbs free energy.
- Far from equilibrium, the Gibbs free energy potential has no value in elucidating the dynamics.
- Non-equilibrium thermodynamics contends far-from-equilibrium systems relax to minimize the irreversibility production rate.
- We demonstrate that this is not true for our standard chemical kinetics.

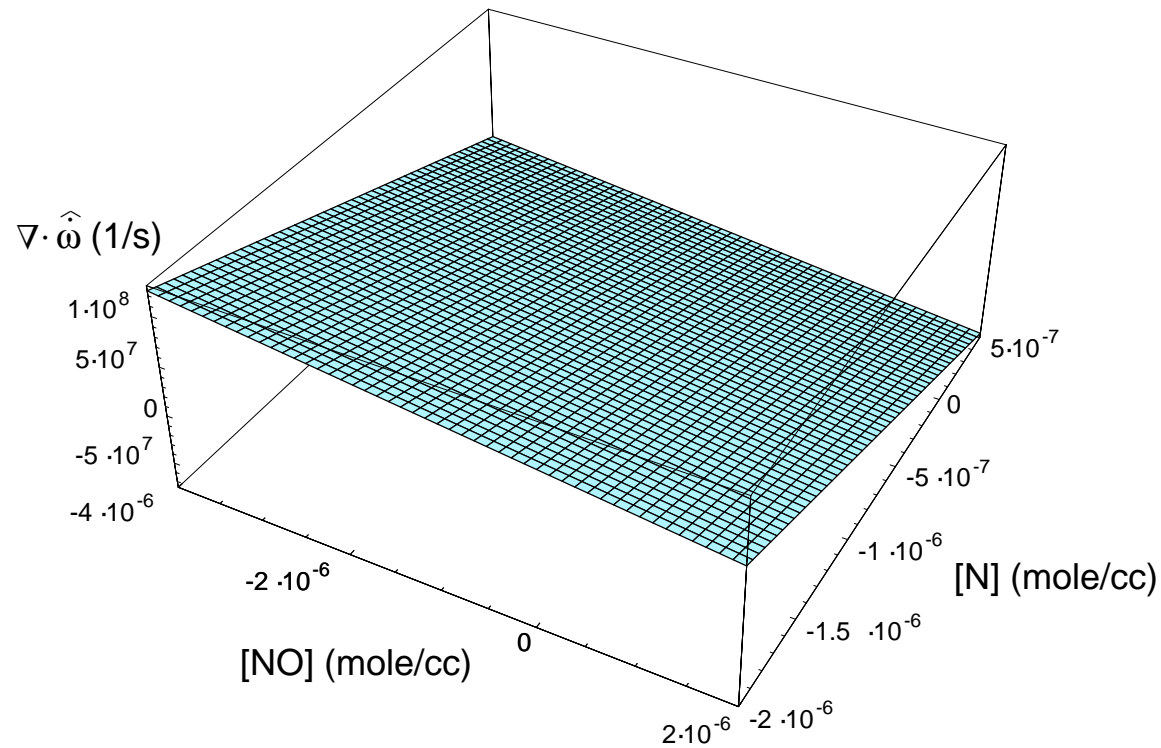
Physical Dissipation: Irreversibility Production Rate



$$\frac{dI}{dt} = -\frac{1}{T} \hat{\omega} \cdot \nabla G \geq 0.$$

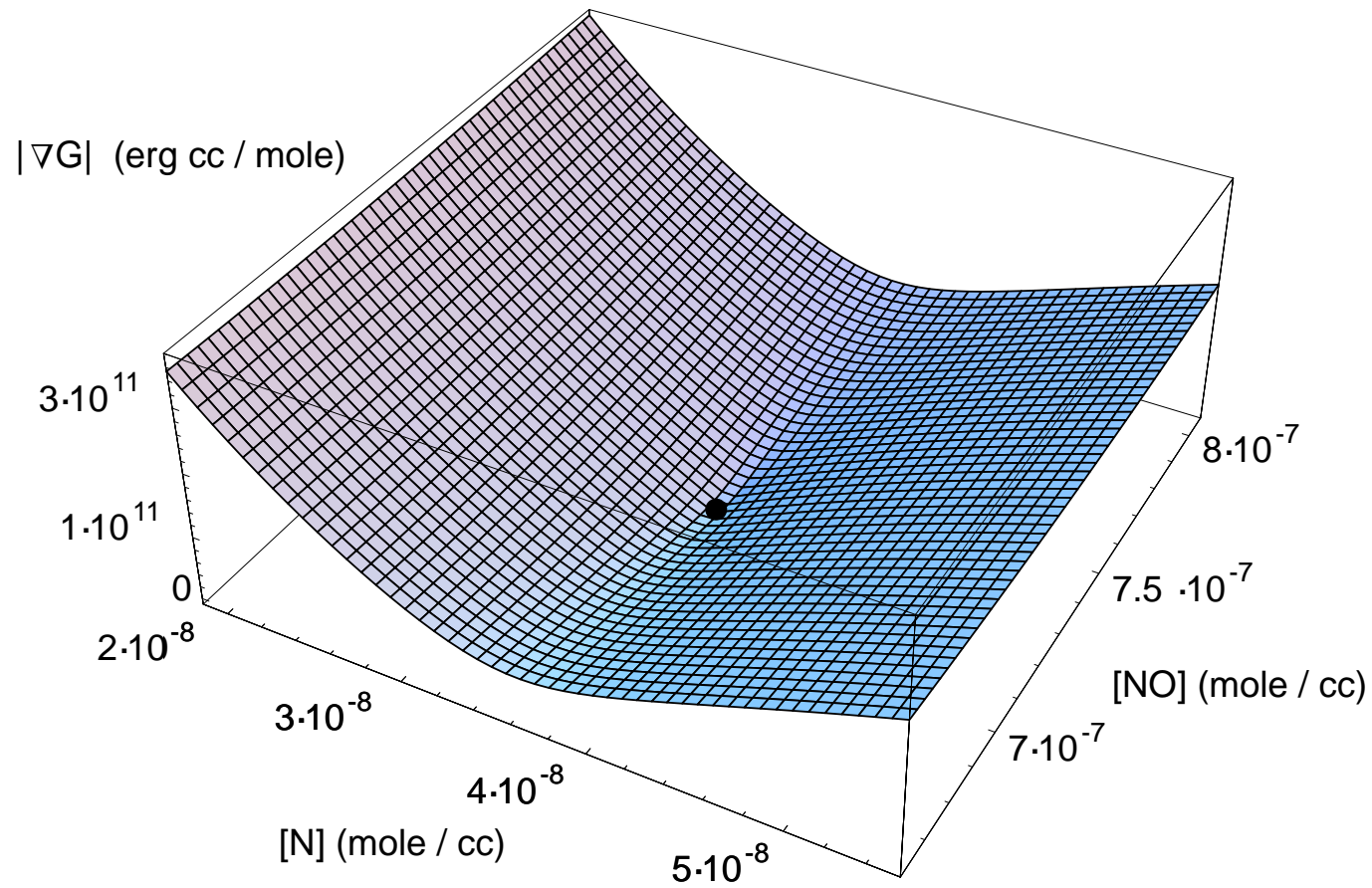
The physical dissipation rate is everywhere positive semi-definite.

Mathematical “Dissipation”: $\nabla \cdot \hat{\omega}$



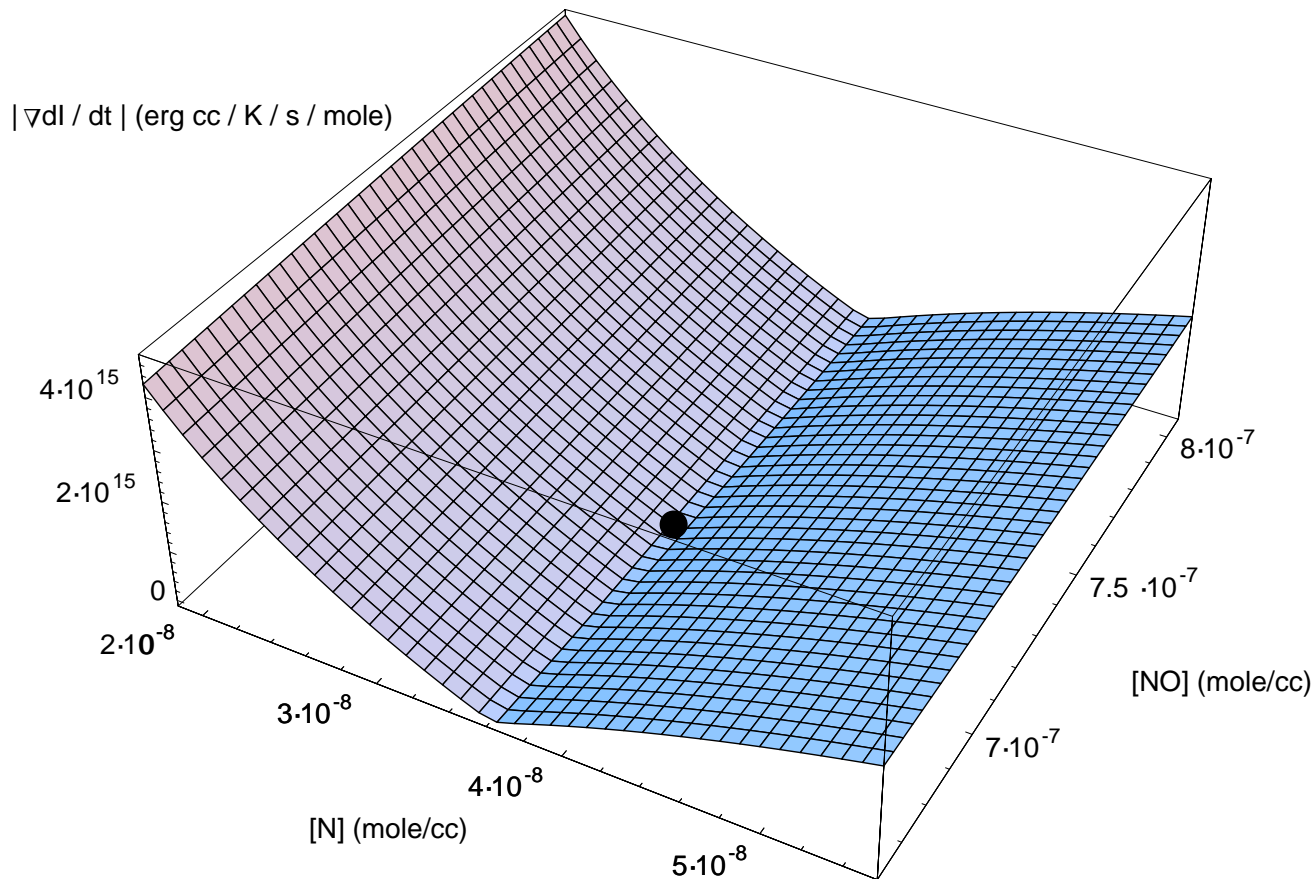
$\nabla \cdot \hat{\omega}$, the tendency of a volume in phase space to contract or expand, can be **positive or negative**. Here, its field is described by a plane, and it takes on a value of zero on a line.

Gibbs Free Energy Gradient Magnitude



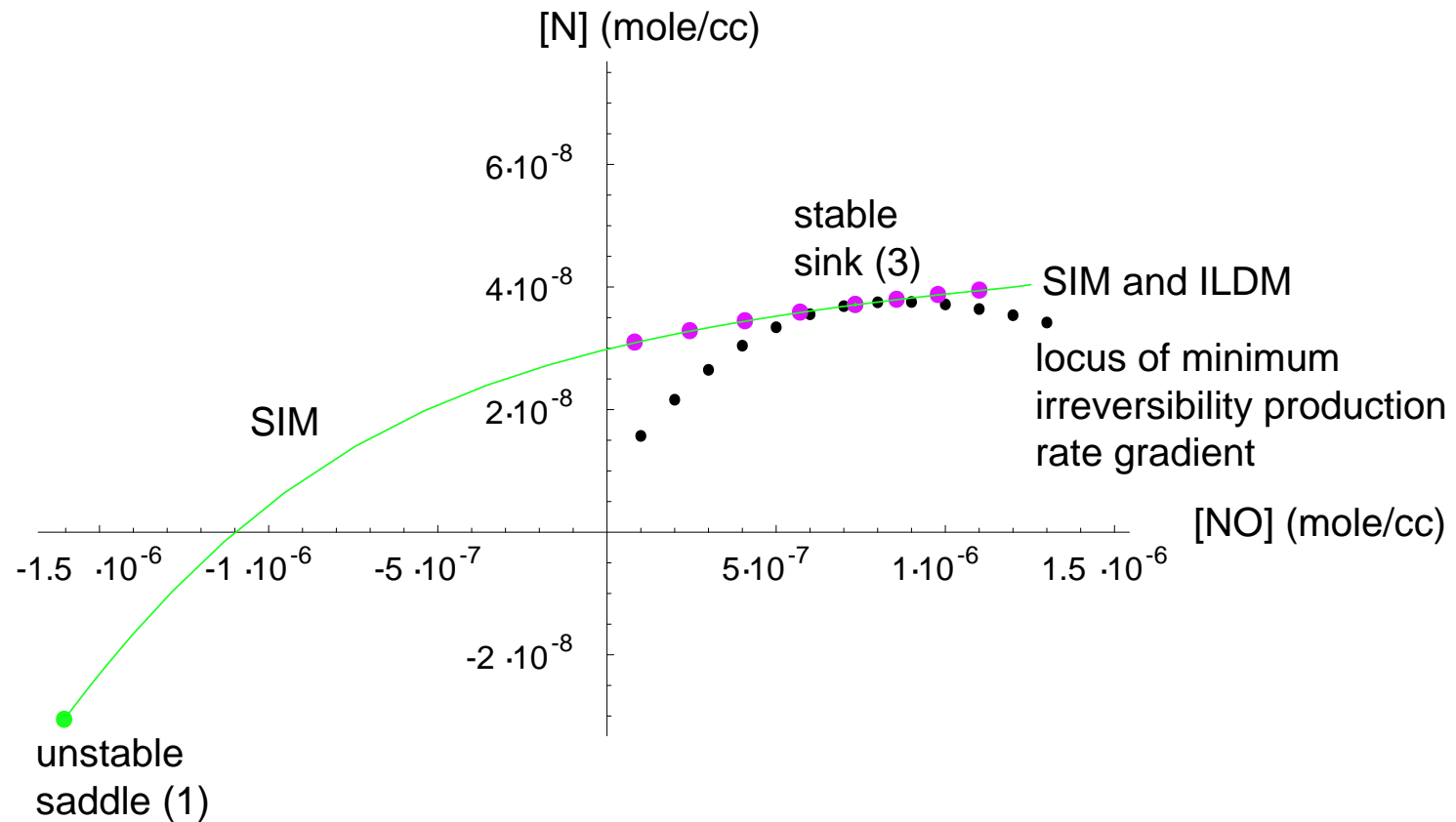
$$\frac{\partial}{\partial \xi_p} \frac{dI}{dt} = -\frac{1}{T} \sum_{k=1}^{N-L} \left(\frac{\partial \hat{\omega}_k}{\partial \xi_p} \frac{\partial G}{\partial \xi_k} + \hat{\omega}_k \frac{\partial^2 G}{\partial \xi_p \partial \xi_k} \right), \quad \xi_1 = [NO], \xi_2 = [N].$$

Irreversibility Production Rate Gradient Magnitude



$|\nabla d\mathcal{I}/dt|$ “valley” coincident with $|\nabla G|$.

SIM vs. Irreversibility Minimization vs. ILDM



Lebiedz, 2004, uses this in a variational method.

Conclusions

- Global phase maps are useful in constructing the SIM.
- Global phase maps give guidance in how to project onto the SIM.
- Global phase maps shows when manifold-based reductions should not be used.
- The SIM does not coincide with either the local minima of irreversibility production rates or Gibbs free energy, except near a physical equilibrium.
- While such potentials are valuable **near equilibrium**, they offer no guidance for non-equilibrium kinetics.