Slow Invariant Manifolds in Chemically 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.

Zel'dovich Mechanism for NO Production

$$N + NO \rightleftharpoons N_2 + O$$

$$N + O_2 \rightleftharpoons NO + O$$

- spatially homogeneous,
- isothermal and isobaric, $T = 6000\ K$, $P = 2.5\ bar$,
- law of mass action with reversible Arrhenius kinetics.

Classical Dynamic Systems Form

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

Algebraic constraints from element conservation absorbed into ODEs.

Dynamical Systems Approach to Construct SIM

Finite equilibria and linear stability:

$$1.\ ([NO],[N]) = (-1.6\times10^{-6}, -3.1\times10^{-8}),$$
$$(\lambda_1,\lambda_2) = (5.4\times10^{6}, -1.2\times10^{7})$$ saddle (unstable)

$$2.\ ([NO],[N]) = (-5.2\times10^{-8}, -2.0\times10^{-6}),$$
$$(\lambda_1,\lambda_2) = (4.4\times10^{7} \pm 8.0\times10^{6} i)$$ spiral source (unstable)

$$3.\ ([NO],[N]) = (7.3\times10^{-7}, 3.7\times10^{-8}),$$
$$(\lambda_1,\lambda_2) = (-2.1\times10^{6}, -3.1\times10^{7})$$ sink (stable, physical)

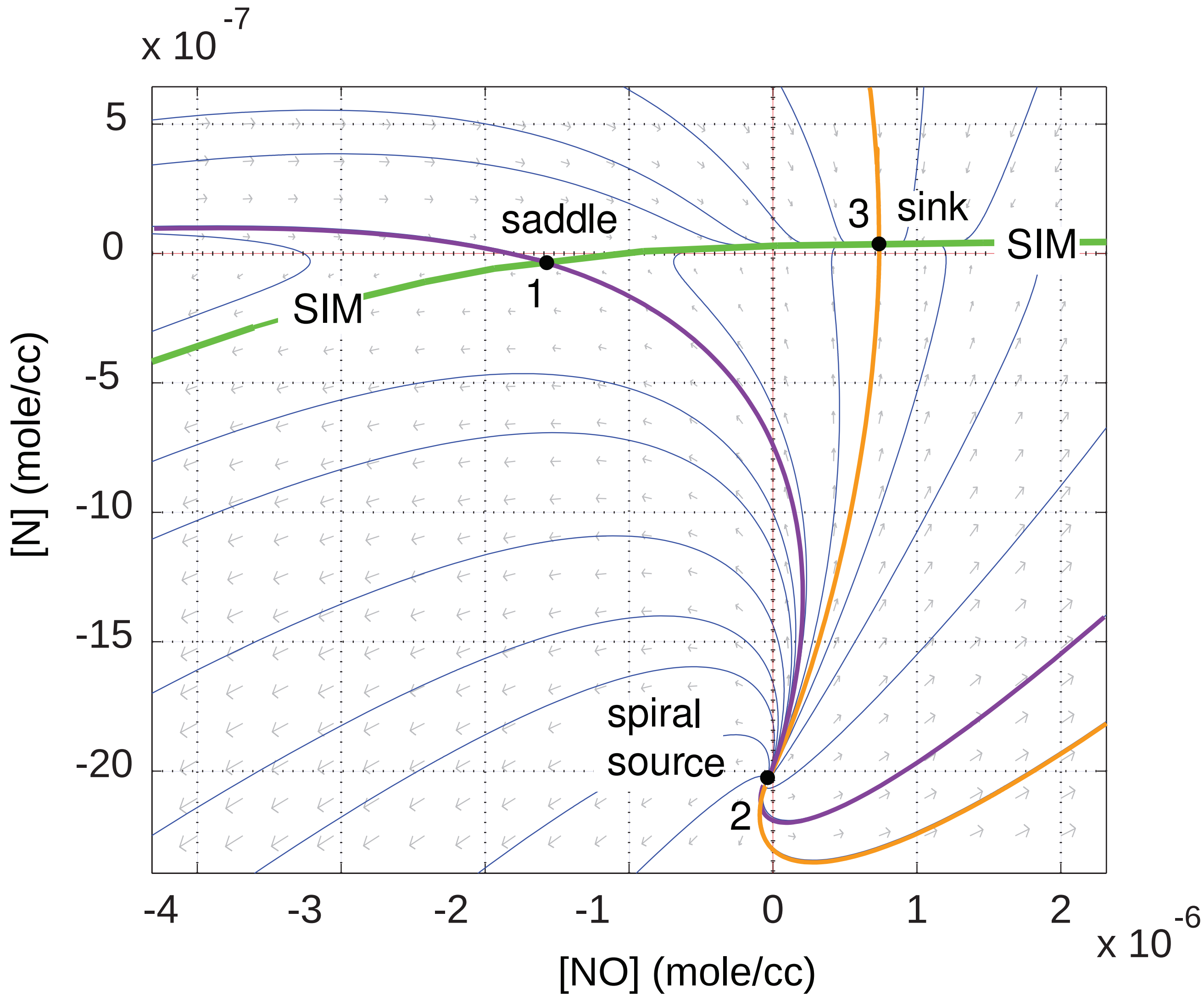
stiffness ratio = $\lambda_2/\lambda_1 = 14.7$

Equilibria at infinity and non-linear stability

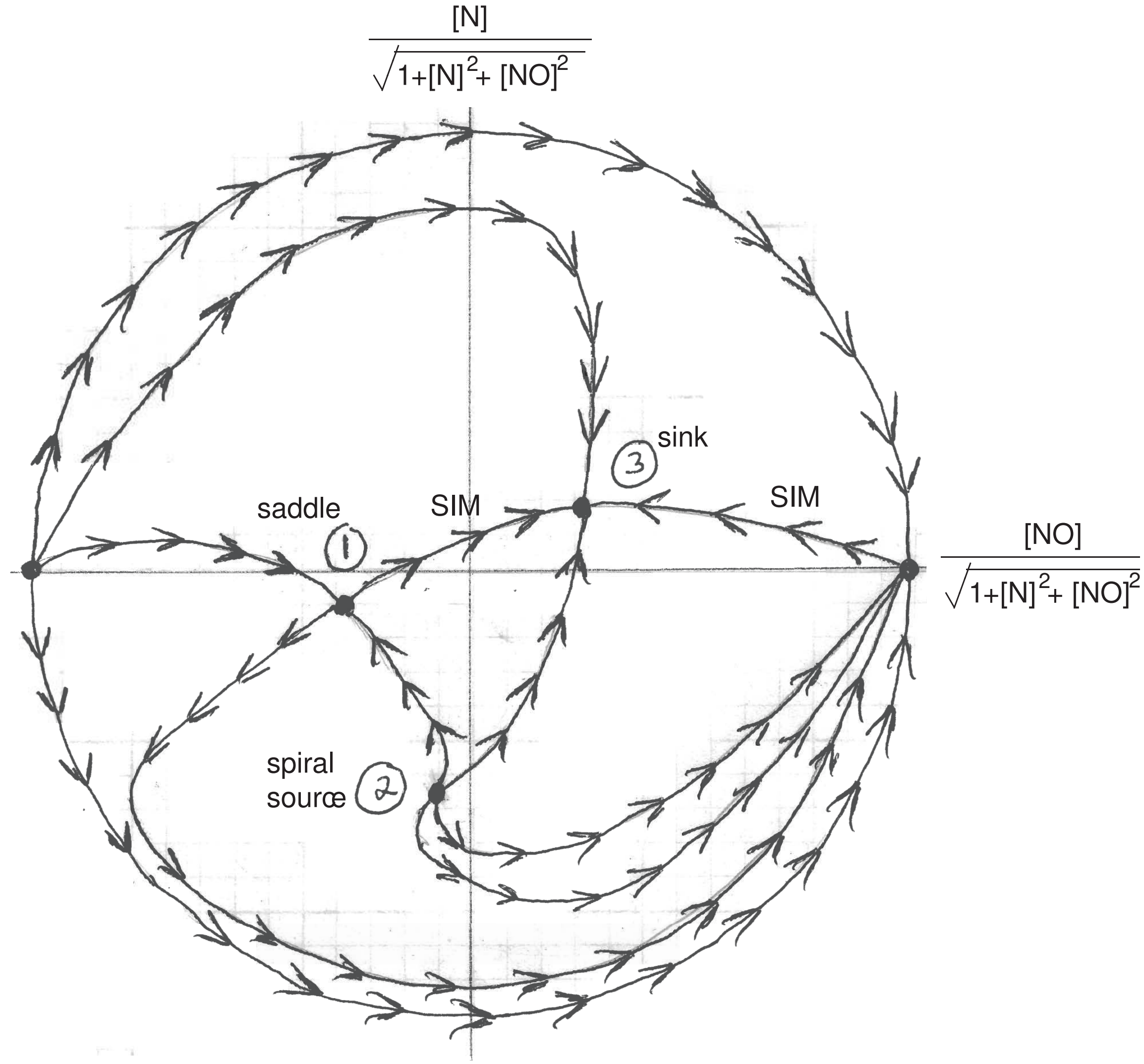
$$1.\ ([NO],[N]) \rightarrow (+\infty, 0)$$ sink/saddle (unstable),

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

Detailed Phase Space Map with All Finite Equilibria



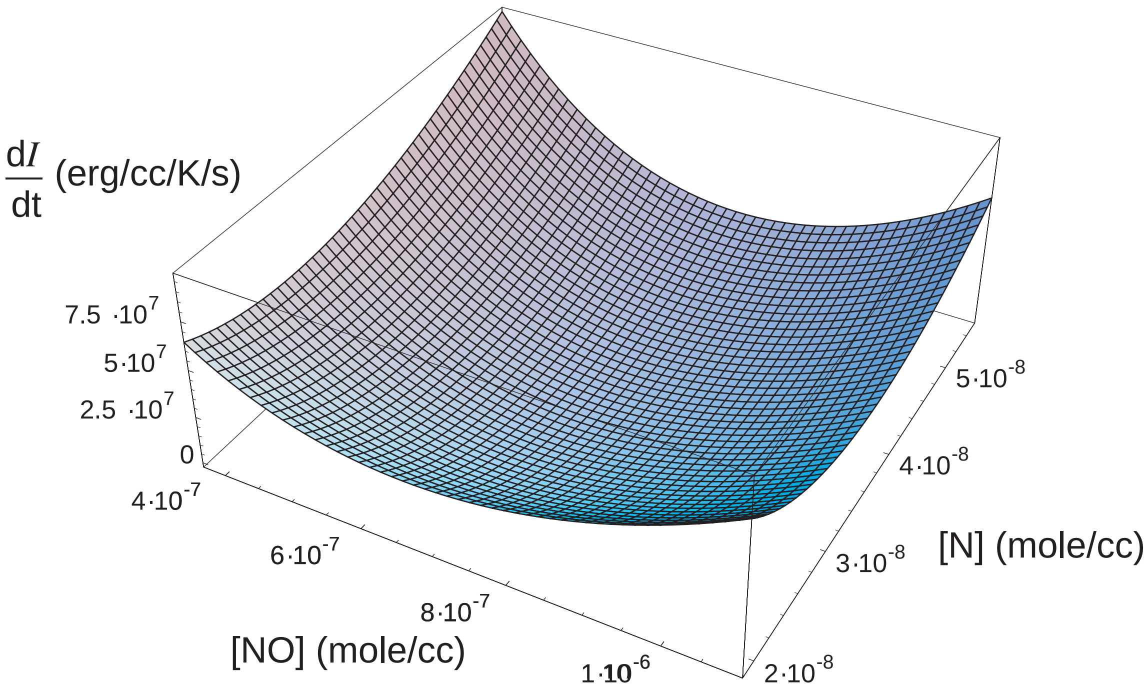
Projected Phase Space from Poincaré's Sphere



Connections of SIM with Thermodynamics

- Classical thermodynamics identifies equilibrium with the minimum of Gibbs free energy.
- Far from equilibrium, the Gibbs free energy potential appears to have no value in elucidating the dynamics.
- Non-equilibrium thermodynamics contends (Prigogine?, , ,) that far-from-equilibrium systems relax to minimize the irreversibility production rate.
- We demonstrate that this is not true for the $[NO] - [N]$ mechanism, and thus is not true in general.
- This is consistent with Müller's 2005 result for heat conduction.

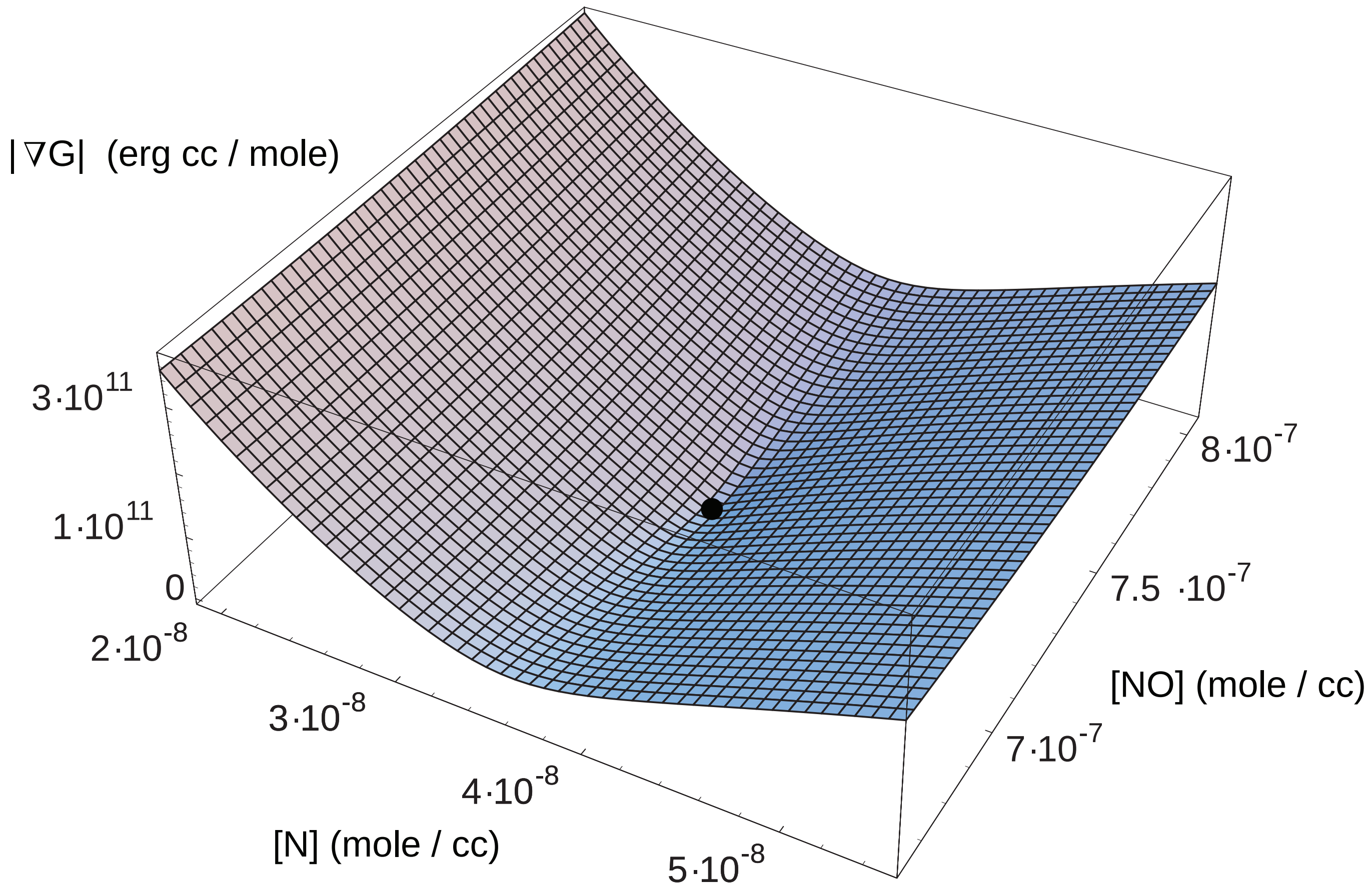
Physical Dissipation: Irreversibility Production Rate



$$\frac{d\mathcal{I}}{dt} = -\frac{1}{T}\hat{\dot{\boldsymbol{\omega}}} \cdot \nabla G \geq 0.$$

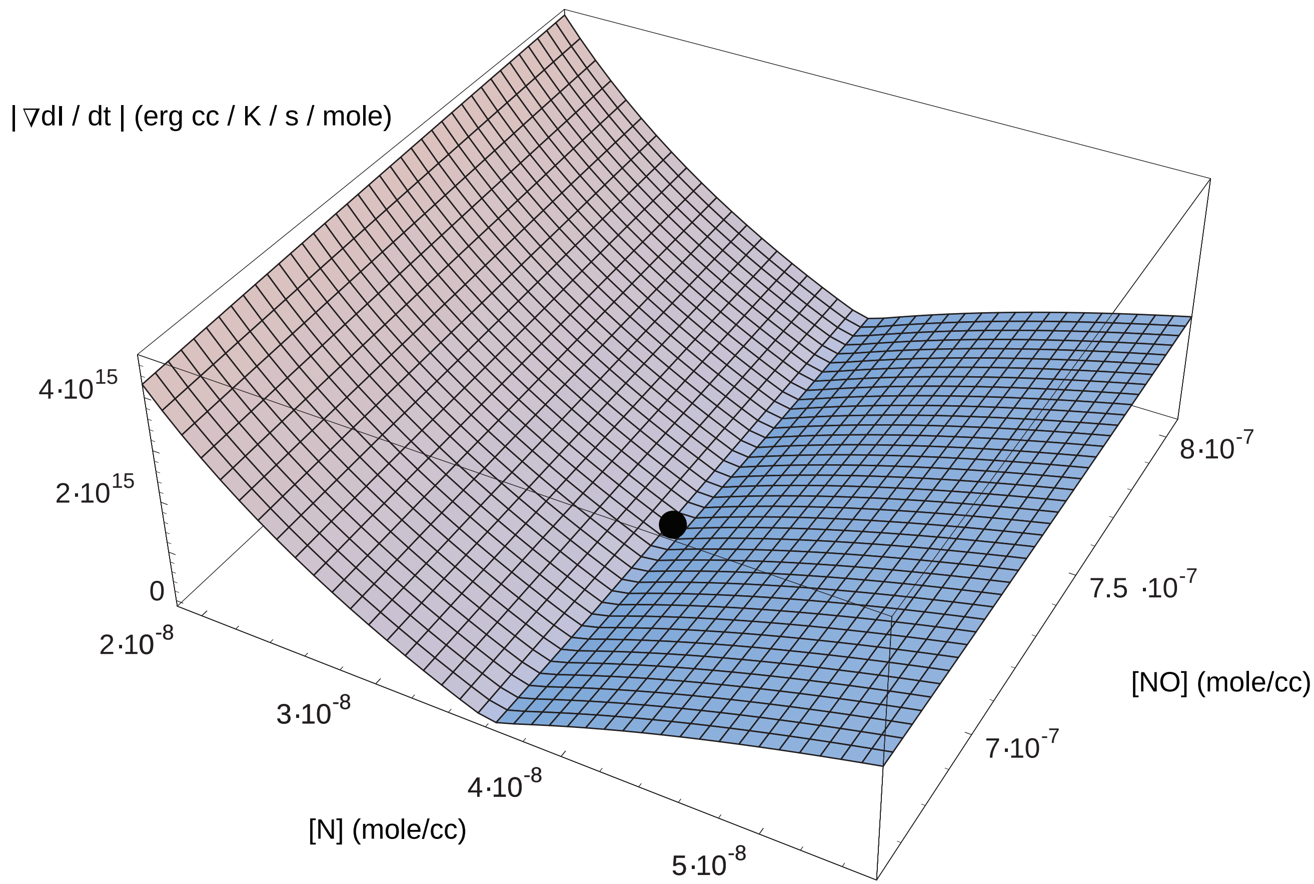
The physical dissipation rate is everywhere positive semi-definite.

Gibbs Free Energy Gradient Magnitude



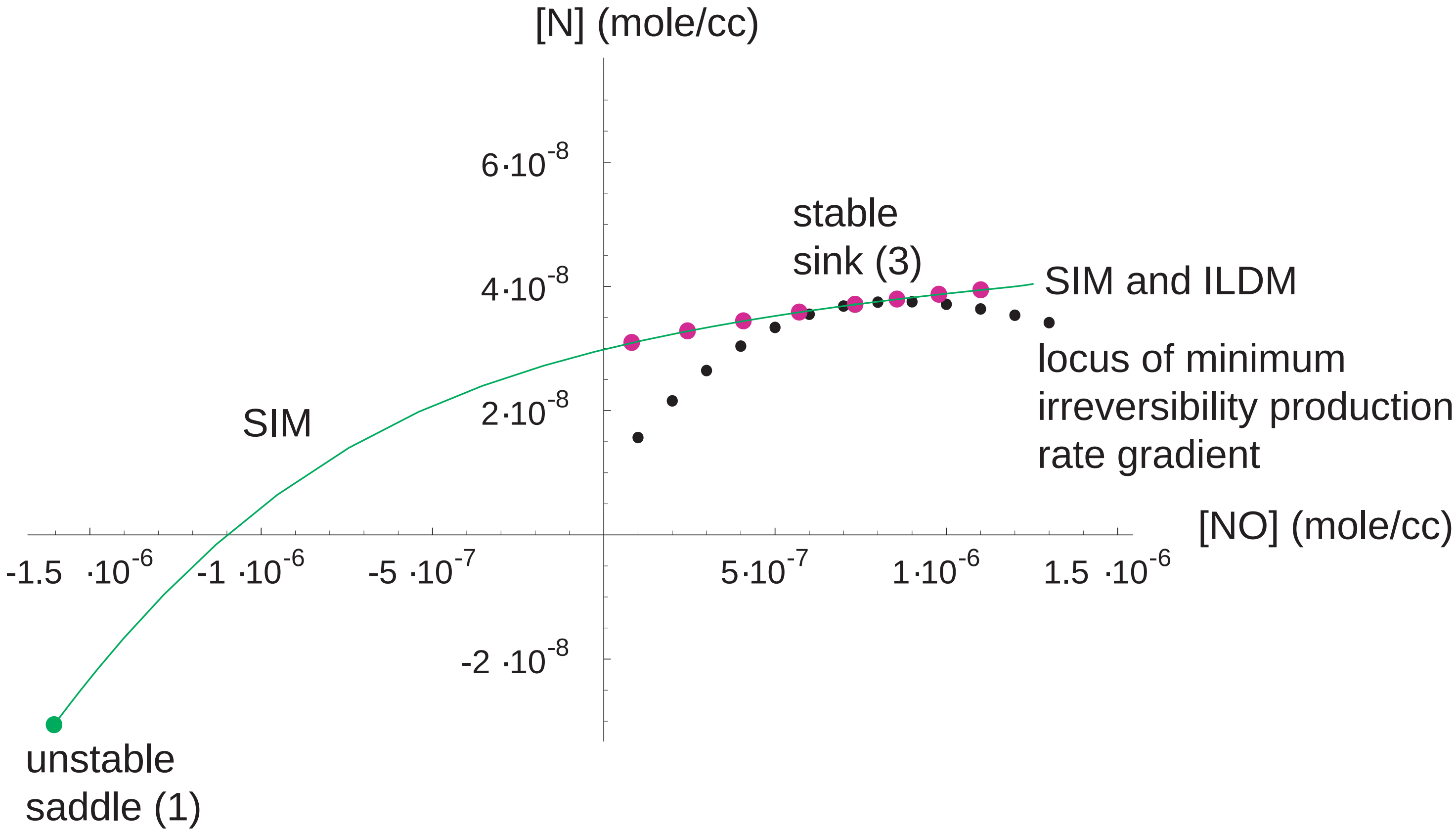
$$\frac{\partial}{\partial \xi_p} \frac{d\mathcal{I}}{dt} = -\frac{1}{T} \sum_{k=1}^{N-L} \left(\frac{\partial \widehat{\dot{\omega}}_k}{\partial \xi_p} \frac{\partial G}{\partial \xi_k} + \widehat{\dot{\omega}}_k \frac{\partial^2 G}{\partial \xi_p \partial \xi_k} \right), \qquad \xi_1 = [NO],\ \xi_2 = [N].$$

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 physical equilbrium.
- While such potentials are valuable near equilibrium, they offer no guidance for non-equilibriium kinetics.