

The Thermodynamics of Slow Invariant Manifolds for Reactive Systems

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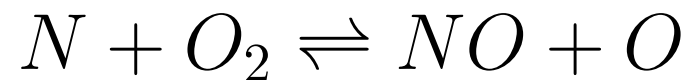
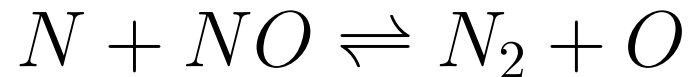
Motivation

- Manifold methods offer a rational strategy for reducing stiff systems arising from detailed chemical kinetics for spatially homogeneous systems (ODEs), or operator split (PDEs) reactive flows.
- Calculation of the actual **Slow Invariant Manifold** (SIM) can be algorithmically easier and computationally more efficient than using approximate methods (ILDM, CSP) that furthermore cannot be used reliably for arbitrary initial conditions.
- Global phase maps developed in the construction of SIMs also identify information essential to proper use of manifold methods.
- We will try to understand the connections between SIMs and thermodynamics with the ultimate goal of exploiting the relationship.

Tactics

- Examine the relationship between the global dynamics and dynamics on the SIM with thermodynamics using a simple physical mechanism of reaction kinetics (Zel'dovich NO production) as well as other pedagogical models.
- Employ realistic constitutive models.
- Rigorously determine the mathematical properties of linear and nonlinear models.

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.

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

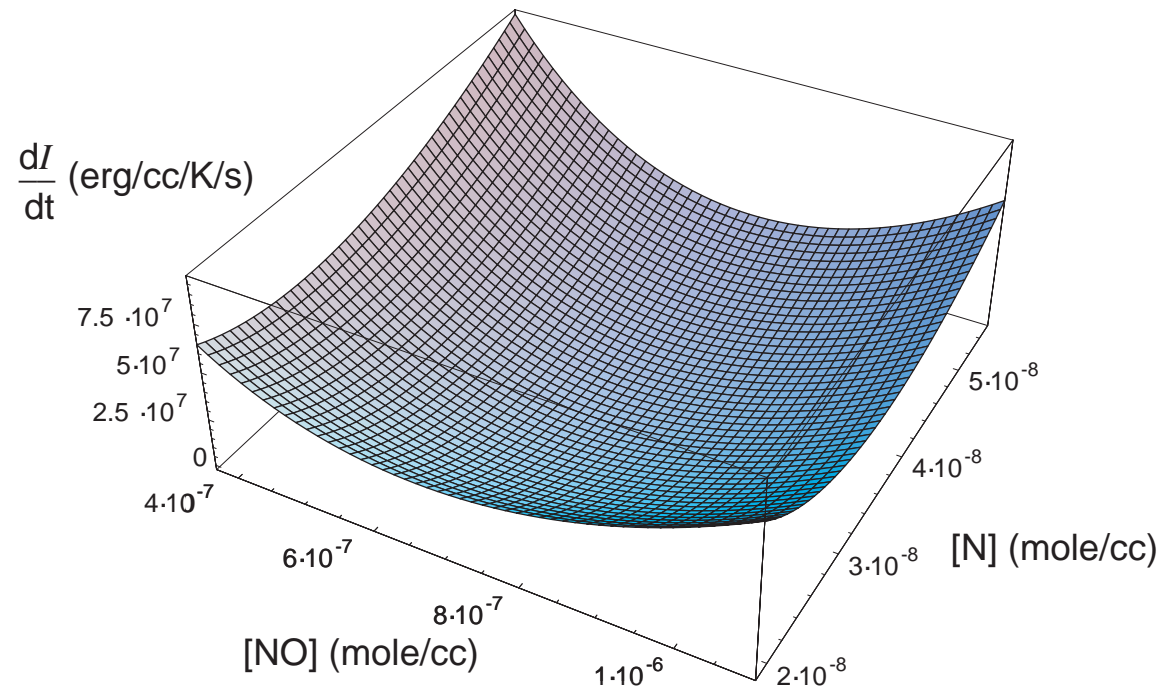
$$1. ([NO], [N]) \rightarrow (+\infty, 0) \quad \text{sink/saddle (unstable),}$$

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

Connections of SIM with Thermodynamics

- Classical thermodynamics identifies equilibrium with the maximum of entropy.
- Far from equilibrium, entropy has no value in elucidating the dynamics.
- Present non-equilibrium thermodynamics contends that far-from-equilibrium systems relax to minimize the irreversibility production rate.
- We demonstrate that this is not true for our standard chemical kinetics.

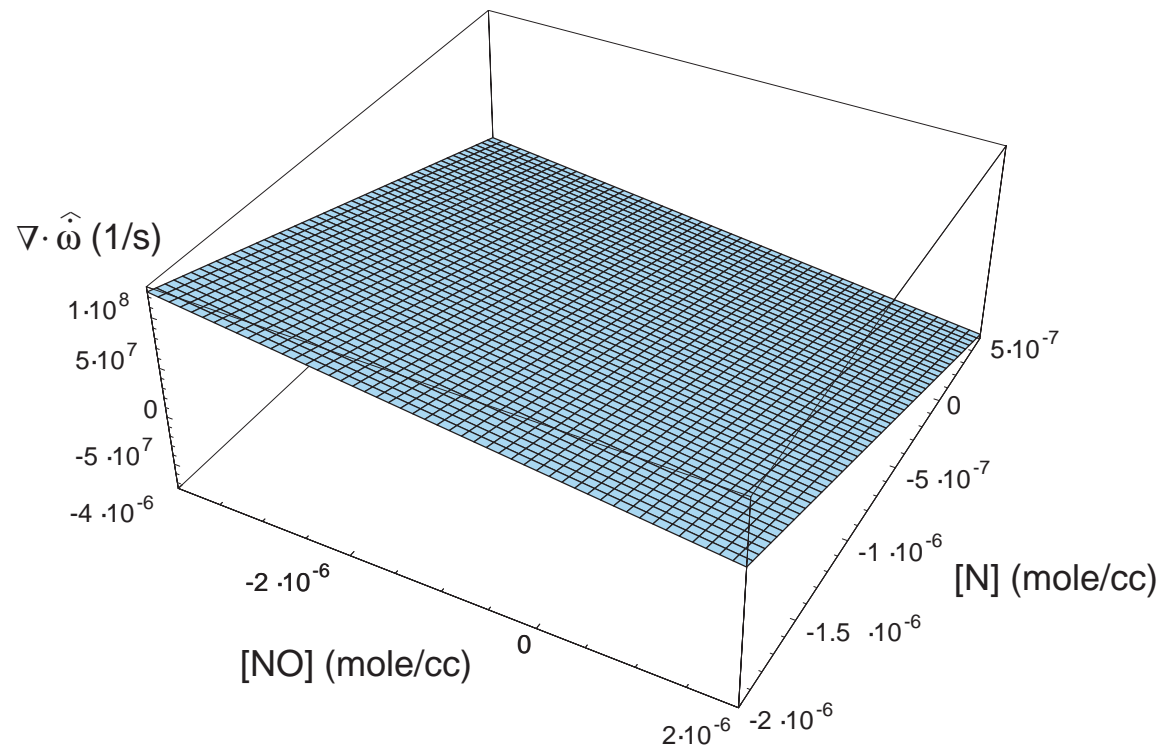
Physical Dissipation: Irreversibility Production Rate



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

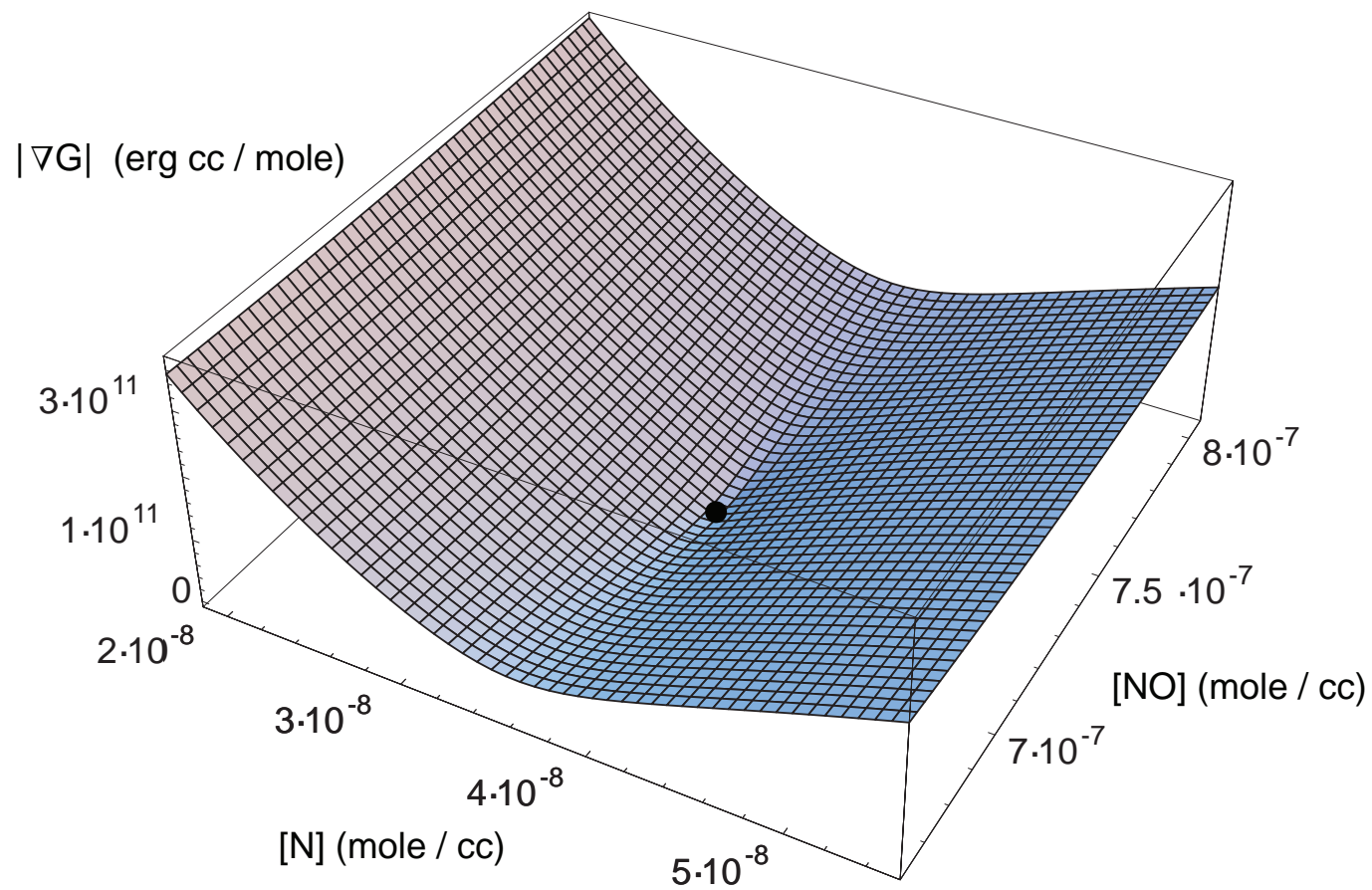
The physical dissipation rate is everywhere positive semi-definite.

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

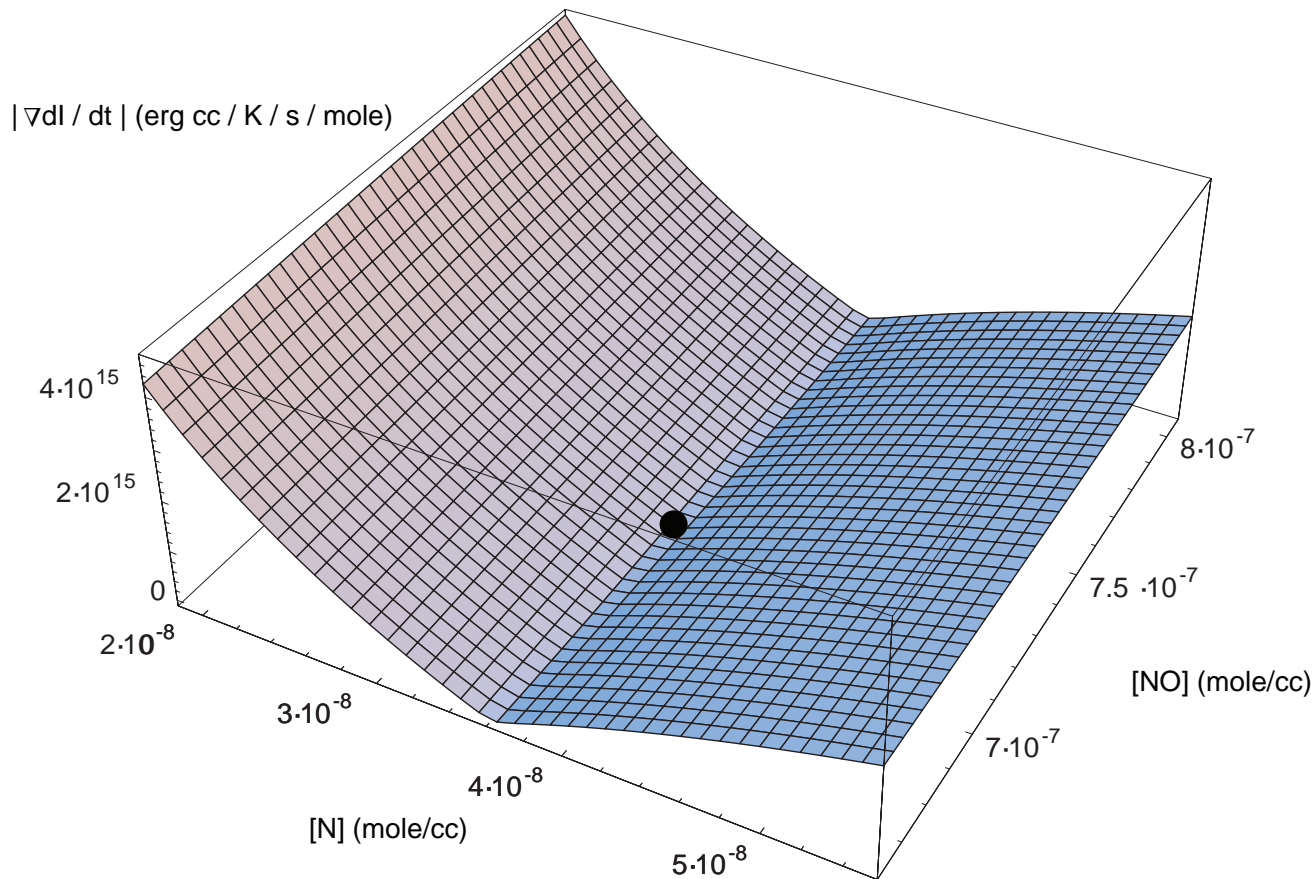


$\nabla \cdot \hat{\omega}$, the tendency of a volume in phase space to contract or expand, can be **positive or negative**. Here, its field is described by a plane, and it takes on a value of zero on a line.

Gibbs Free Energy Gradient Magnitude

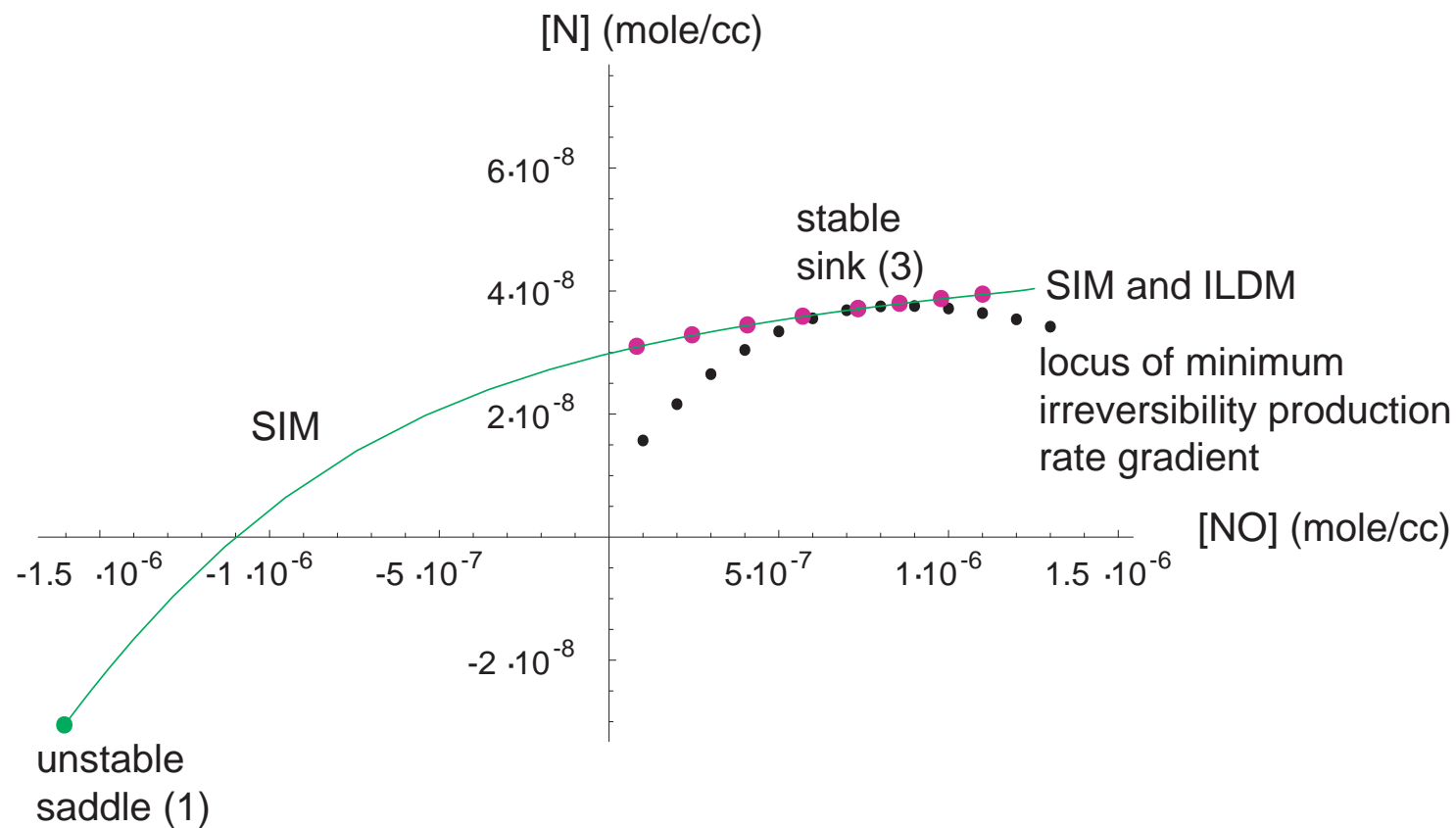


Irreversibility Production Rate Gradient Magnitude



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

SIM vs. Irreversibility Minimization vs. ILDM



Similar to variational method of Lebiedz, 2004.

Model Problem

We seek to identify the generalized stream function $\psi(\mathbf{x})$ and potential $\phi(\mathbf{x})$ which can be associated with the dynamic system

$$\frac{d\mathbf{x}}{dt} = \mathbf{f}(\mathbf{x}),$$

where $\mathbf{x} = (x_1, x_2)^T$, $\mathbf{f} = (f_1, f_2)^T$. We assume the origin has been transformed to the frame in which

$$\mathbf{f}(\mathbf{0}) = \mathbf{0}.$$

Stream Function

To find $\psi(\mathbf{x})$, recast the equations as the differential one-form

$$f_1 dx_2 - f_2 dx_1 = 0.$$

If $\nabla \cdot \mathbf{f} = 0$, the equation is exact and can be integrated directly. However, we are concerned with the more general case in which $\nabla \cdot \mathbf{f} \neq 0$. For our case, it is always possible to find $\mu(\mathbf{x})$ such that

$$d\psi = \mu(f_1 dx_2 - f_2 dx_1) = 0.$$

It can be shown that $\mu(\mathbf{x})$ must satisfy the hyperbolic equation

$$\mathbf{f}^T \cdot \nabla \mu = -\mu \nabla \cdot \mathbf{f}.$$

Fluid mechanics analog: $\mathbf{f} \rightarrow \mathbf{u}$, $\mu \rightarrow \rho$, $\psi \rightarrow$ the compressible stream function, and $\phi \rightarrow$ the velocity potential, if it exists.

Note μ is non-unique and singular at equilibrium.

Potential

If a classical potential ϕ exists, its gradient must yield \mathbf{f} , so

$$\nabla\phi = \mathbf{f}.$$

In order for a potential to exist, the vector \mathbf{f} must be irrotational:

$$\nabla \times \mathbf{f} = \mathbf{0}.$$

This is not the case in general!

While a potential may not exist in a certain space, there may exist a transformation to another space in which a generalized potential does exist.

Analysis Near Equilibrium

In the neighborhood of the origin $\mathbf{x} = \mathbf{0}$, the system is in equilibrium: $\mathbf{f} = \mathbf{0}$. Thus, near the origin

$$\mathbf{f} = \mathbf{J} \cdot \mathbf{x} + \dots ,$$

where \mathbf{J} is a *constant* matrix which is the Jacobian of \mathbf{f} evaluated at the origin. We are concerned with forms of \mathbf{f} which arise from mass action kinetics. Note that \mathbf{J} itself need not be symmetric, and in general is not. Onsager reciprocity still requires a symmetry, but it is manifested in the expression for entropy evolution near equilibrium, and not directly in \mathbf{J} .

Analysis Near Equilibrium (continued)

We consider Jacobians that have eigenvalues $\Lambda = \text{diag}(\lambda_1, \lambda_2)$ which are real and negative, and \mathbf{P} is the matrix whose columns correspond to the eigenvectors of \mathbf{J} . Neglecting higher order terms, it can be shown that

$$(\mathbf{J} \cdot \mathbf{x})^T \cdot \nabla \mu = -\mu \text{Tr}(\mathbf{J}),$$

or with $\mathbf{x} = \mathbf{P} \cdot \mathbf{y}$, and subsequently $y_i = z_i^{-\lambda_i}$ and ($z_1 = r \cos \theta, z_2 = r \sin \theta$) we obtain

$$\mu = g(\theta) r^{\lambda_1 + \lambda_2},$$

where $g(\theta)$ is an arbitrary function of θ . Now at the equilibrium point, obtained as $r \rightarrow 0$, one finds, for $\lambda_1, \lambda_2 < 0$, that $\mu \rightarrow \infty$.

Analysis Near Equilibrium (continued)

In addition, for the potential ϕ to exist,

$$\nabla \times \mathbf{f} = \nabla \times \mathbf{J} \cdot \mathbf{x} = \mathbf{0}.$$

This demands the symmetry of \mathbf{J} , a condition that will not be satisfied in general!

However, for arbitrary \mathbf{J} and with $\mathbf{x} = \mathbf{P} \cdot \mathbf{y}$, it can be easily shown that a generalized potential exists and is given by

$$\phi = \frac{1}{2} (\lambda_1 y_1^2 + \lambda_2 y_2^2) + C,$$

where C is an arbitrary constant. Since $\lambda_1, \lambda_2 < 0$, it is easily seen that ϕ has a maximum at the equilibrium point $\mathbf{y} = \mathbf{0}$.

Illustrative Example 1

Consider the simple example

$$\frac{dx_1}{dt} = -x_1, \quad \frac{dx_2}{dt} = -4x_2.$$

This problem has a stable equilibrium at $\mathbf{x} = \mathbf{0}$ and has eigenvalues $\lambda_1 = -1$ and $\lambda_2 = -4$. It is already in diagonal form, so no transformation will be necessary. It has similar properties to chemically reacting systems near a physical equilibrium point, when cast in appropriate coordinates. We also note that it has the exact solution

$$x_1 = x_{10}e^{-t}, \quad x_2 = x_{20}e^{-4t}.$$

Illustrative Example 1 (continued)

This induces the differential one-form

$$x_1 dx_2 - 4 x_2 dx_1 = 0.$$

Since $\nabla \cdot \mathbf{f} = -5$, this is not exact, but can be rendered exact by the integrating factor (i.e. the generalized density) which is $\mu = x_1^{-5}$.

Note that this approaches positive infinity at the equilibrium point.

Subsequently we obtain the stream function

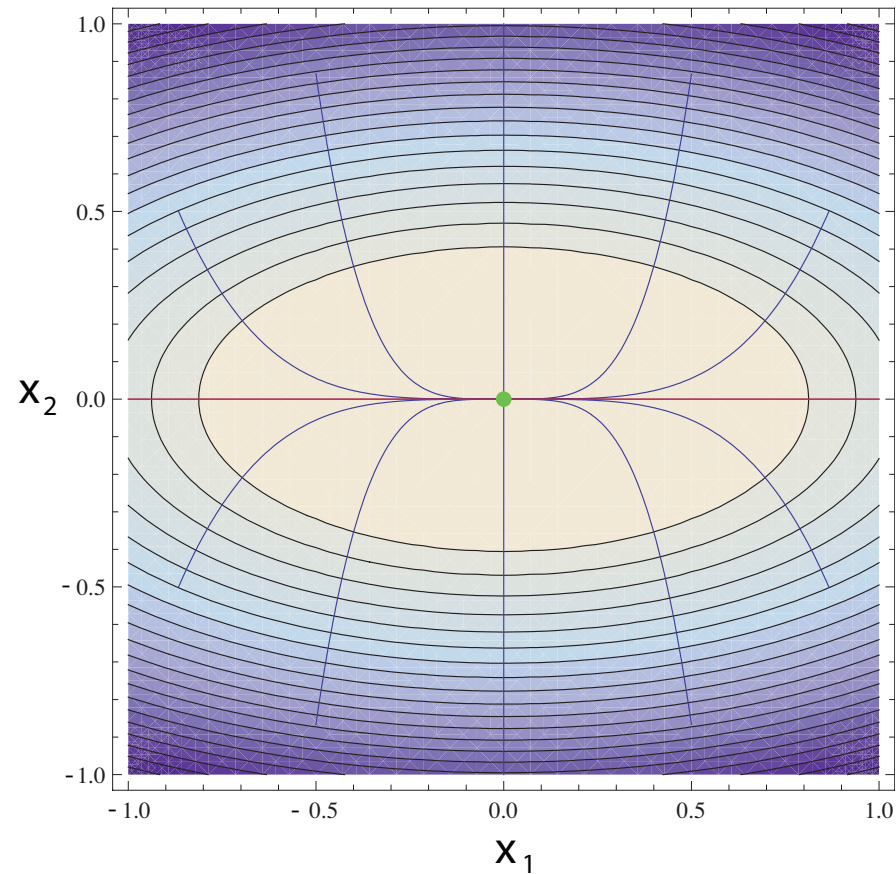
$$\psi = \frac{x_2}{x_1^4} + C_1.$$

It has the property that $\nabla \times \mathbf{f} = \mathbf{0}$, so a potential ϕ exists and is

$$\phi = -\frac{1}{2} (x_1^2 + 4 x_2^2) + C_2.$$

C_1 and C_2 are arbitrary constants that are chosen to be zero.

Illustrative Example 1 (continued)



The figure shows lines of constant ϕ , ψ , the SIM, and the equilibrium point. Lines of constant ψ are orthogonal to lines of constant ϕ .

Illustrative Example 2

Consider the slightly more complicated example

$$\frac{dx_1}{dt} = -x_1, \quad \frac{dx_2}{dt} = 3x_1 - 4x_2.$$

This problem has the same stable equilibrium at $\mathbf{x} = \mathbf{0}$ and eigenvalues $\lambda_1 = -1$ and $\lambda_2 = -4$. This system also has similar properties to chemically reacting systems near the equilibrium point.

It has the exact solution

$$x_1 = x_{10}e^{-t}, \quad x_2 = (x_{20} - x_{10})e^{-4t} + x_{10}e^{-t}.$$

Illustrative Example 2 (continued)

This induces the differential one-form

$$x_1 dx_2 - 4 x_2 dx_1 = 0.$$

Since $\nabla \cdot \mathbf{f} = -5$, this is not exact, but can be rendered exact by the integrating factor (i.e. the generalized density) $\mu = x_1^{-5}$.

Subsequently we obtain the stream function

$$\psi = \frac{x_2 - x_1}{x_1^4} + C_1.$$

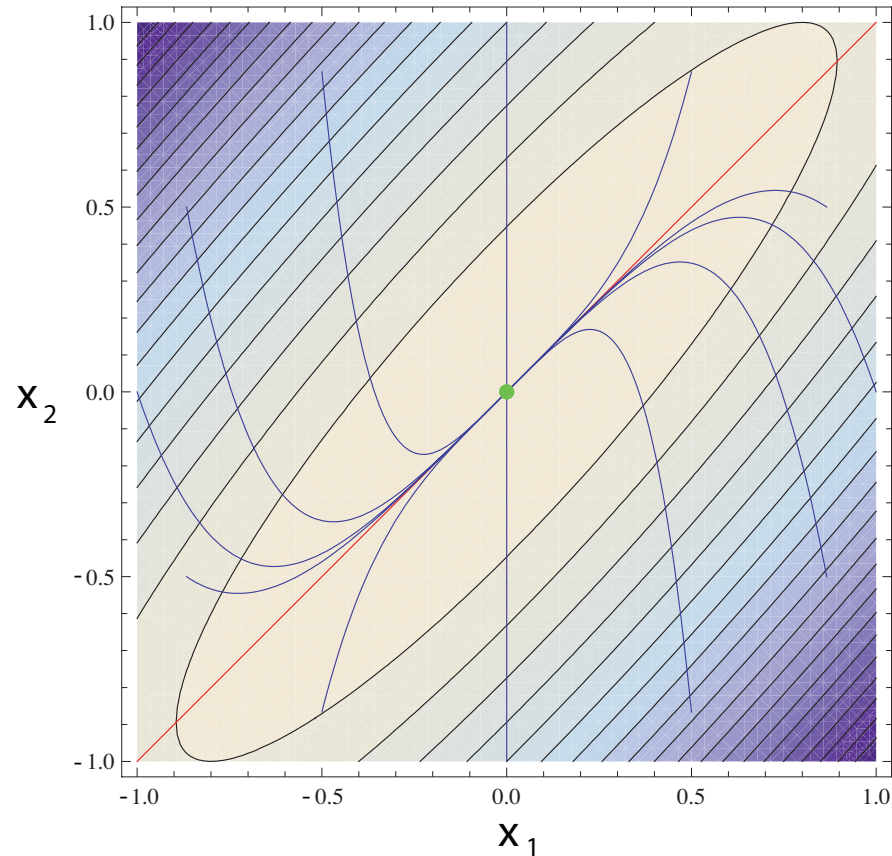
It is noted that $\nabla \times \mathbf{f} = \mathbf{3}$, so a classical potential does not exist.

However, a generalized potential ϕ exists and is given by

$$\phi = -\frac{1}{2} [x_1^2 + 4(x_2 - x_1)^2] + C_2.$$

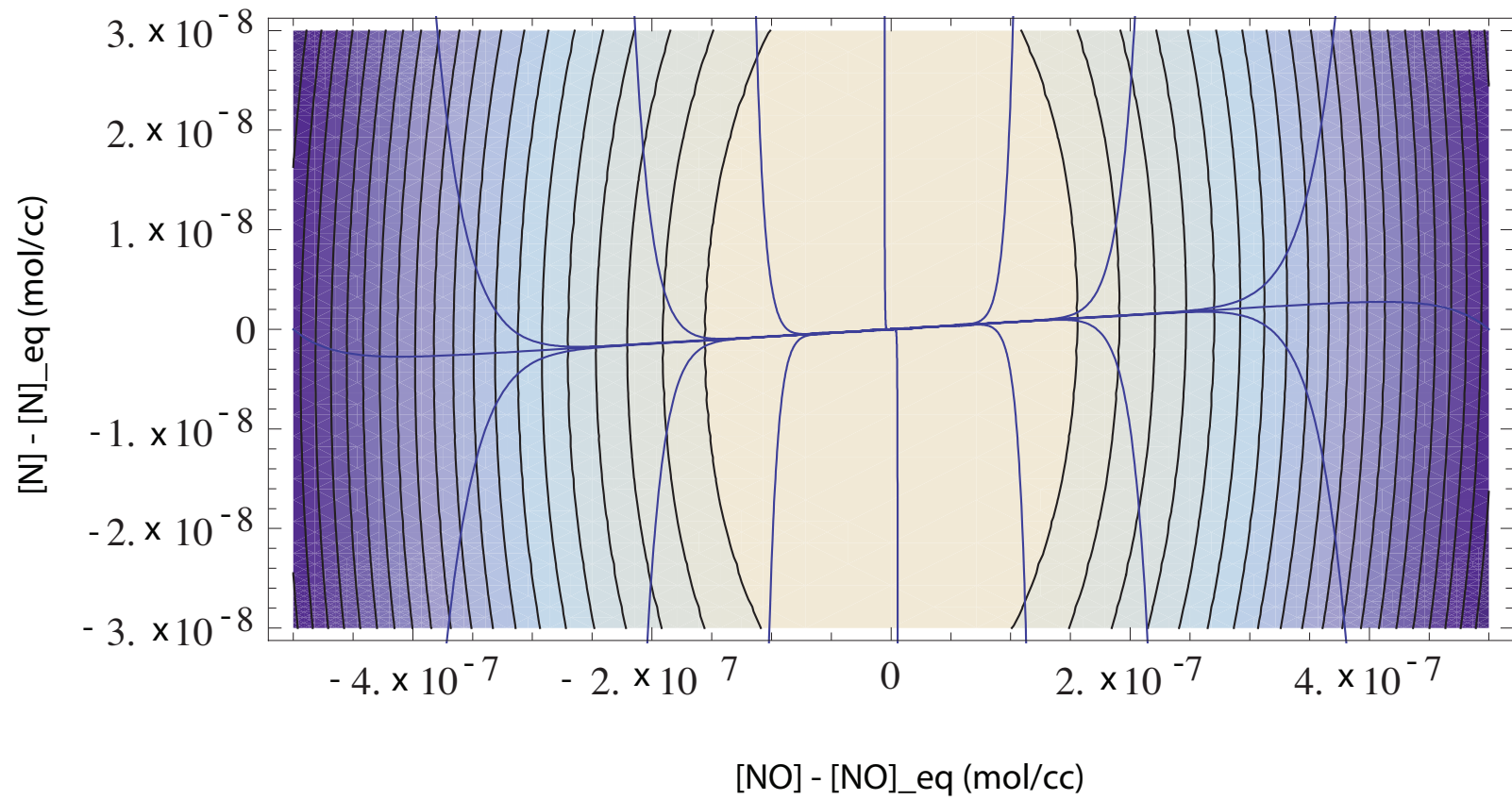
Again, C_1 and C_2 are arbitrary constants that are chosen to be zero.

Illustrative Example 2 (continued)



The figure shows lines of constant ϕ , ψ , the SIM, and the equilibrium point. Lines of constant ψ are *not* orthogonal to lines of constant ϕ in this space!.

Zel'dovich Example



The figure shows lines of constant ϕ , ψ , etc. for the *linearized* Zel'dovich problem.

Conclusions

- In general, a classical potential does not exist in reaction coordinate space; however, a generalized potential can always be found in the linear regime.
- The magnitude of the gradient of the potential **in the transformed space** is minimized on the SIM **in the linear regime**.
- 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 nonlinear (non-equilibrium!) kinetics.
- Work on the nonlinear (non-equilibrium!) regime is ongoing . . .