

# Non-Equilibrium Thermodynamics of Reactive Systems

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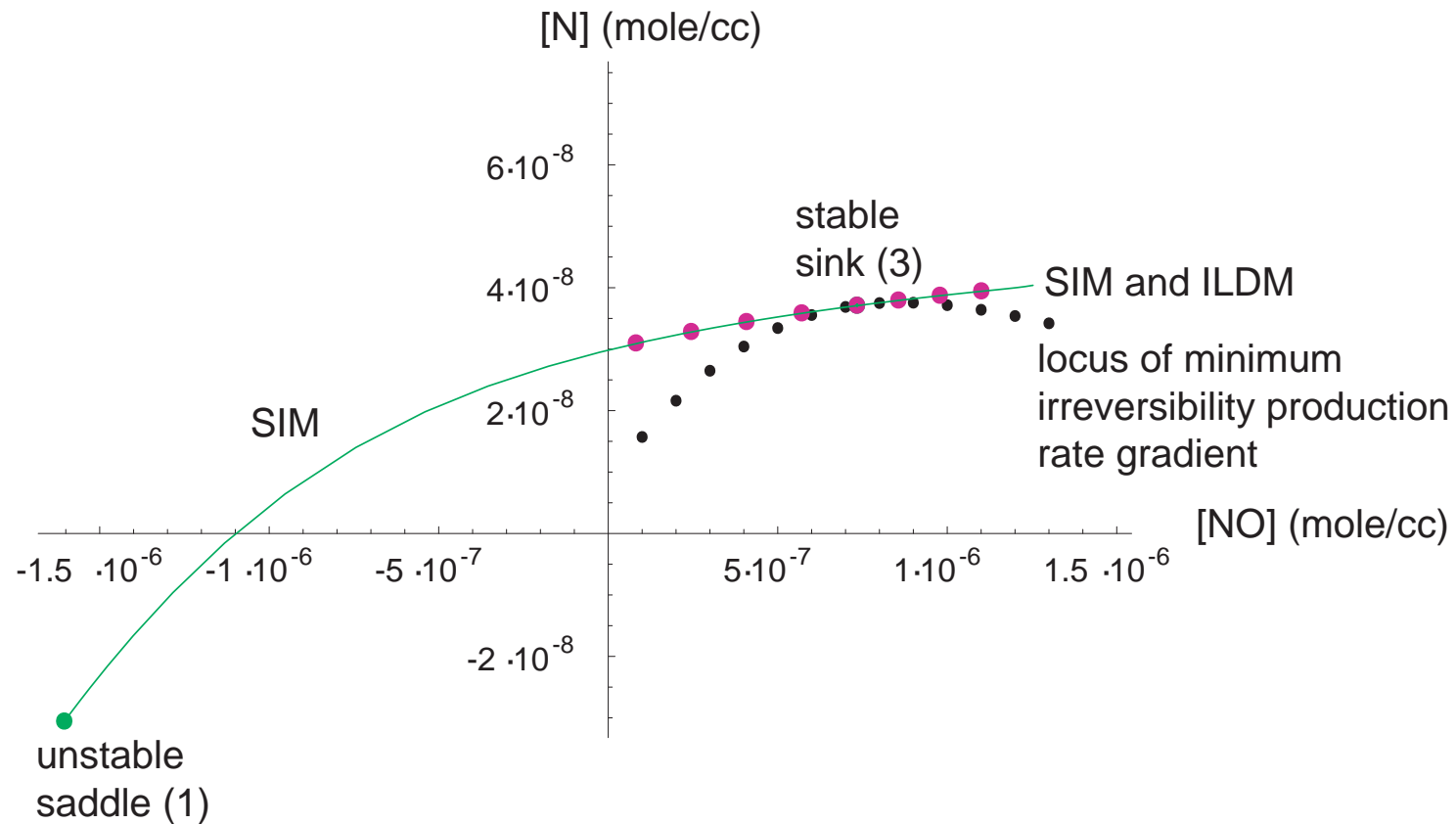
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## *NO* production via Zel'dovich kinetics

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

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.

# 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  $\mu$  is non-unique and singular at equilibrium.

## Potential

If a classical potential  $\phi$  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  $\theta$ . 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  $\phi$  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  $\phi$  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

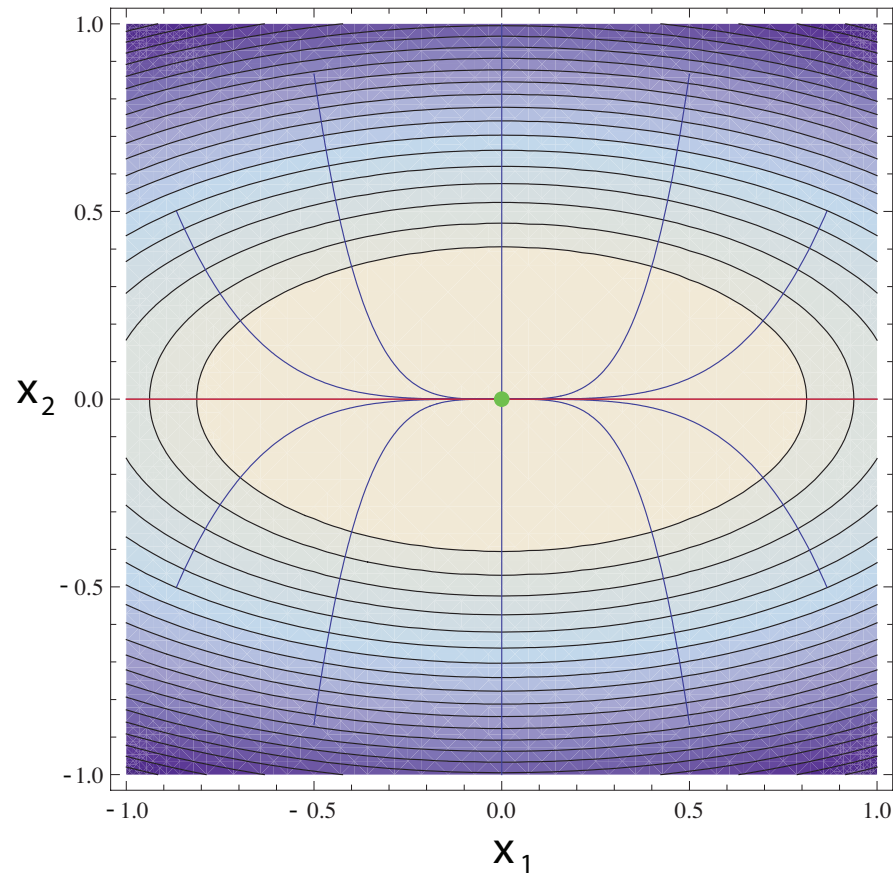
$$\psi = \frac{x_2}{x_1^4} + C_1.$$

It has the property that  $\nabla \times \mathbf{f} = \mathbf{0}$ , so a potential  $\phi$  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  $\phi$ ,  $\psi$ , the SIM, and the equilibrium point. Lines of constant  $\psi$  are orthogonal to lines of constant  $\phi$ .

## 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

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

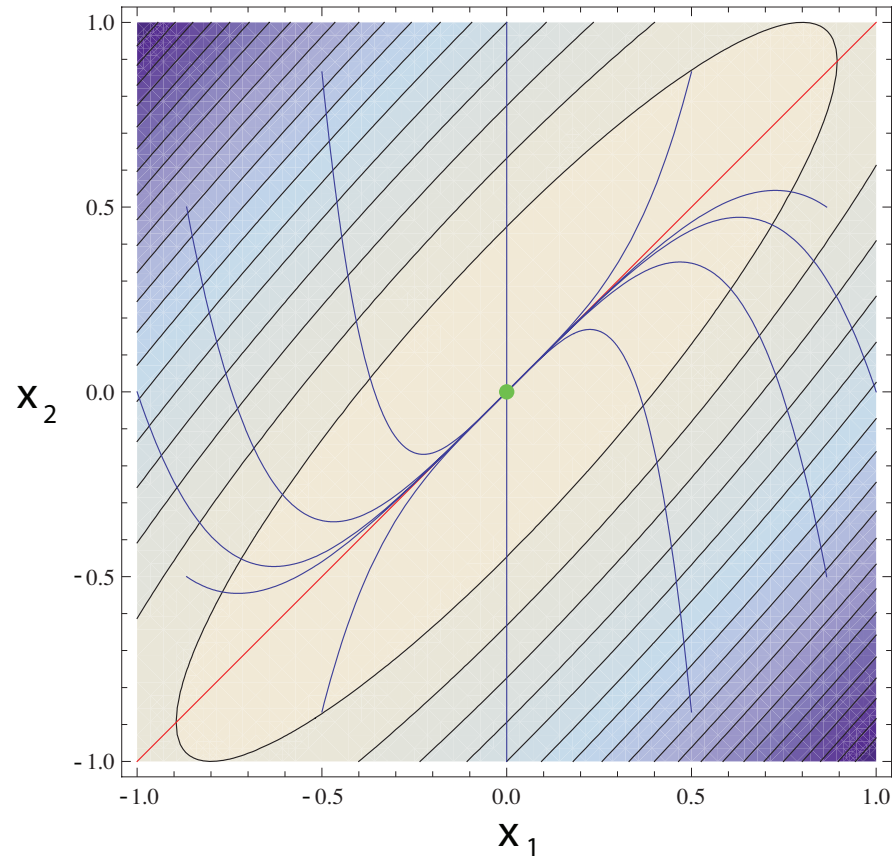
It is noted that  $\nabla \times \mathbf{f} = \mathbf{3}$ , so a classical potential does not exist.

However, a generalized potential  $\phi$  exists and is given by

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

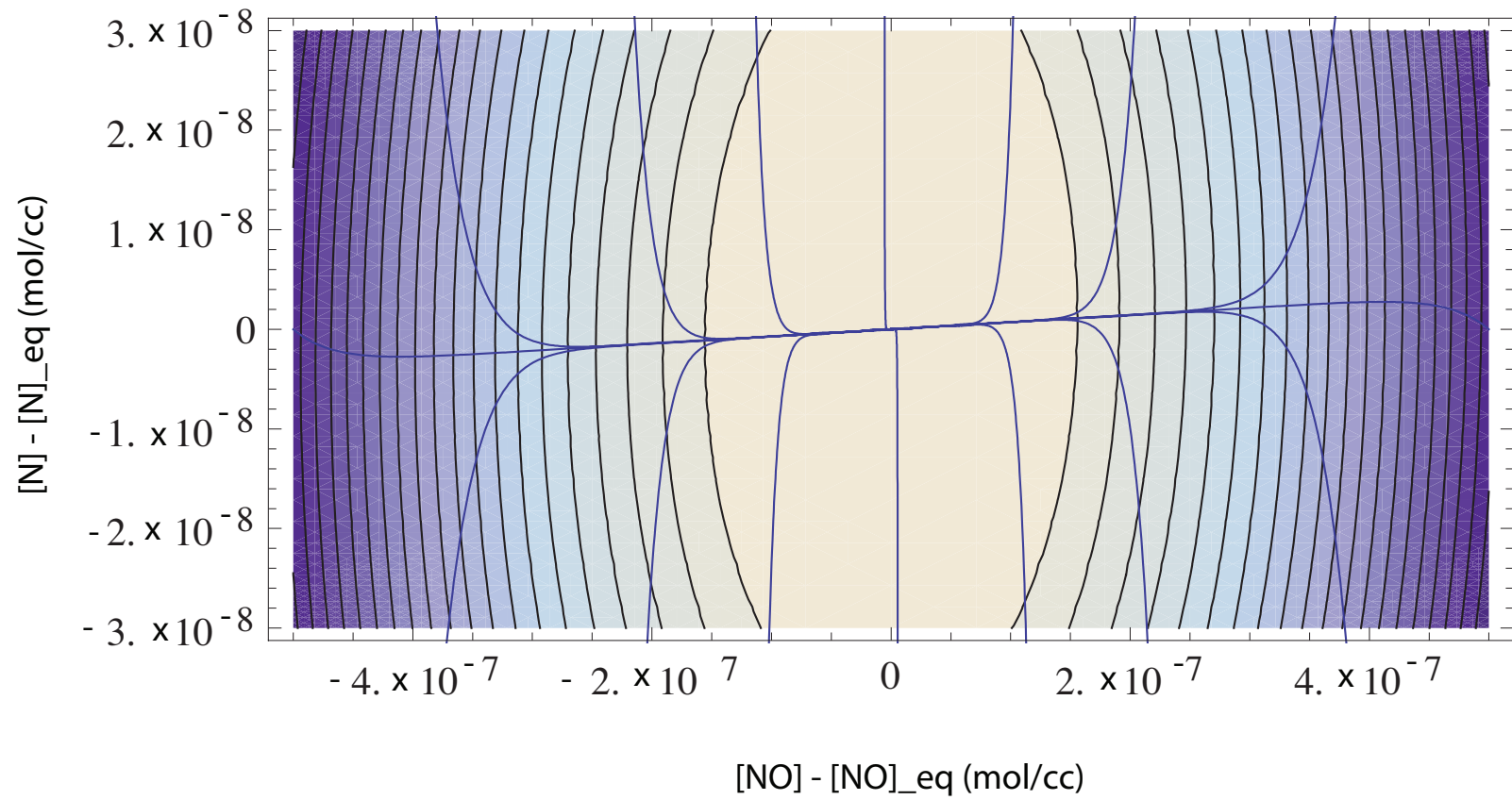
Again,  $C_1$  and  $C_2$  are arbitrary constants that are chosen to be zero.

## Illustrative Example 2 (continued)



The figure shows lines of constant  $\phi$ ,  $\psi$ , the SIM, and the equilibrium point. Lines of constant  $\psi$  are *not* orthogonal to lines of constant  $\phi$  in this space!.

## Zel'dovich Example



The figure shows lines of constant  $\phi$ ,  $\psi$ , 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 . . .