Geometrical Investigation of Low-Dimensional Manifolds in Reaction-Diffusion Systems

Michael J. Davis, Chemistry Division,
Argonne National Laboratory

Study of R-D Equations

- Adapt and build framework for studying phase space structure
- *Driven by numerical experiments and the dynamics of model systems with analytical solutions*
  - Linear and nonlinear cases

Bottom Line

- Systems are dissipative
- Relax to equilibrium distribution
  - 0-D manifold in ∞-D space
- When there is a sufficient separation of time scales there are low-dimensional manifolds on the way to equilibrium
- Find ways to observe/generate manifolds
  - Project onto physical space

Comments

- Examples chosen are meant to fit within combustion research framework
- Most interested in chemical behavior
- In the combustion community test cases typically have one spatial dimension
  - Standard test examples are one-dimensional flames with complex chemistry
  - Possibly many species
    - *H_2/O_2 has 10-12, including temperature*
    - *Methane models have ~40, depending on model*
- *Spatial distributions are generally simple*

Ozone Combustion

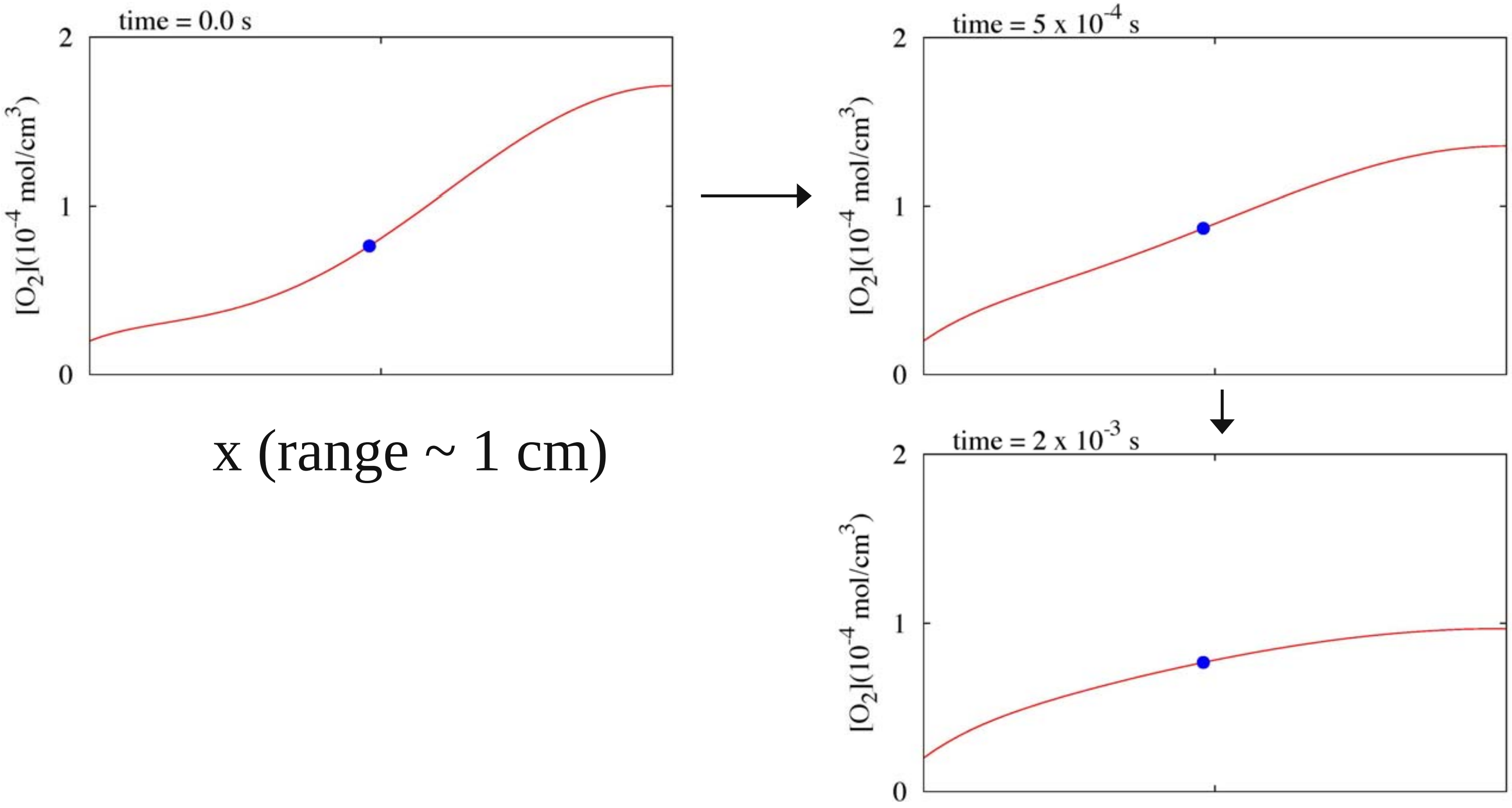
- Example from:
  - S. B. Margolis, J. Comp. Phys. **27**, 410 (1978).
  - S. Singh, J. M. Powers, S. Paolucci, J. Chem. Phys. **117**, 1482 (2002).
- 14 reactions, 3 species (O, O_2, O_3)
  - Simplified further in current study: isothermal and reaction-diffusion system only:

$$\frac{\partial [O_2]}{\partial t} = -\mathrm{k}_3[\mathrm{O}_2][\mathrm{O}_3] + \ldots + \mathrm{D}\frac{\partial^2 [O_2]}{\partial x^2}$$

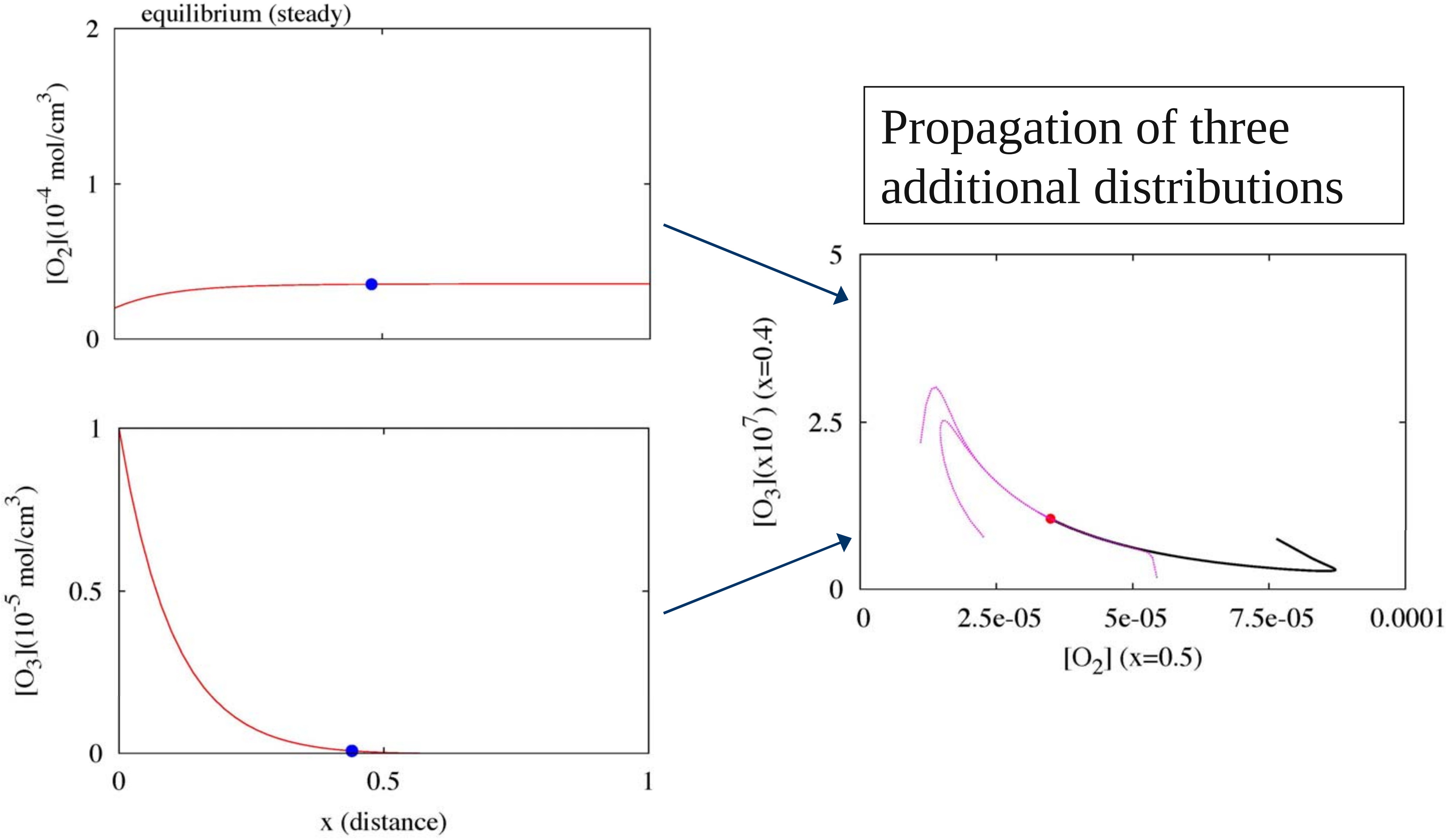
  - Scaled length. Mixed boundary conditions
  - Method-of-lines: 100 points for each species
    - *Solve 300 ODEs*

Time development of species distribution

- Solving the reaction-diffusion equations defines the species spatial distributions as a function of time:



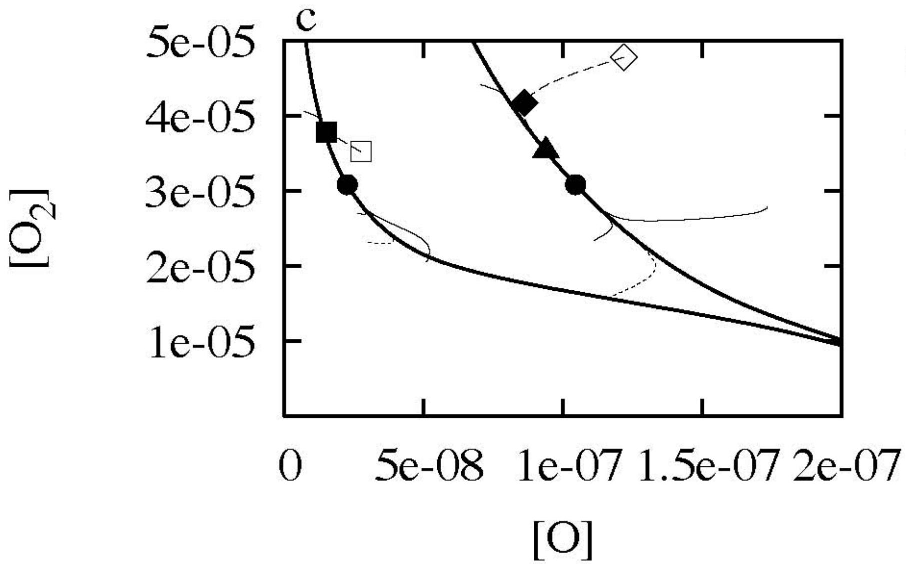
Geometric Representation



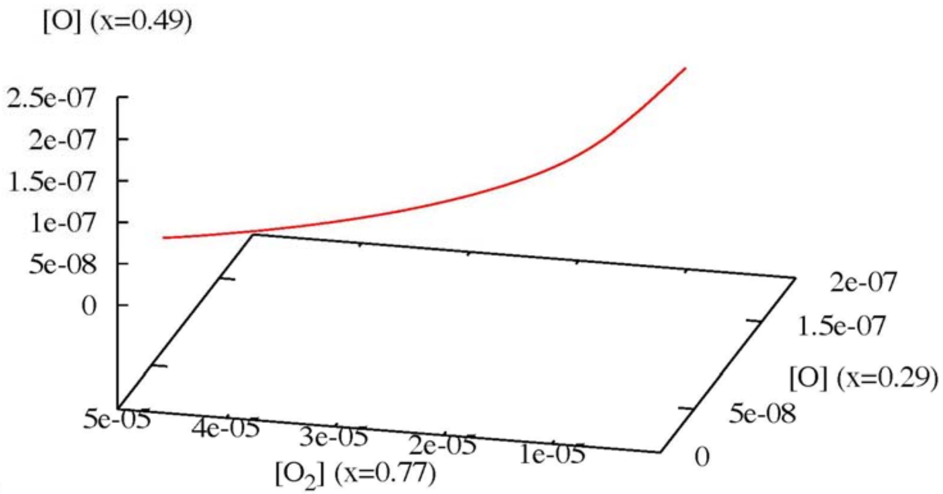
Propagation of three additional distributions

More Projections of 1-D Manifold

Two 2-D projections



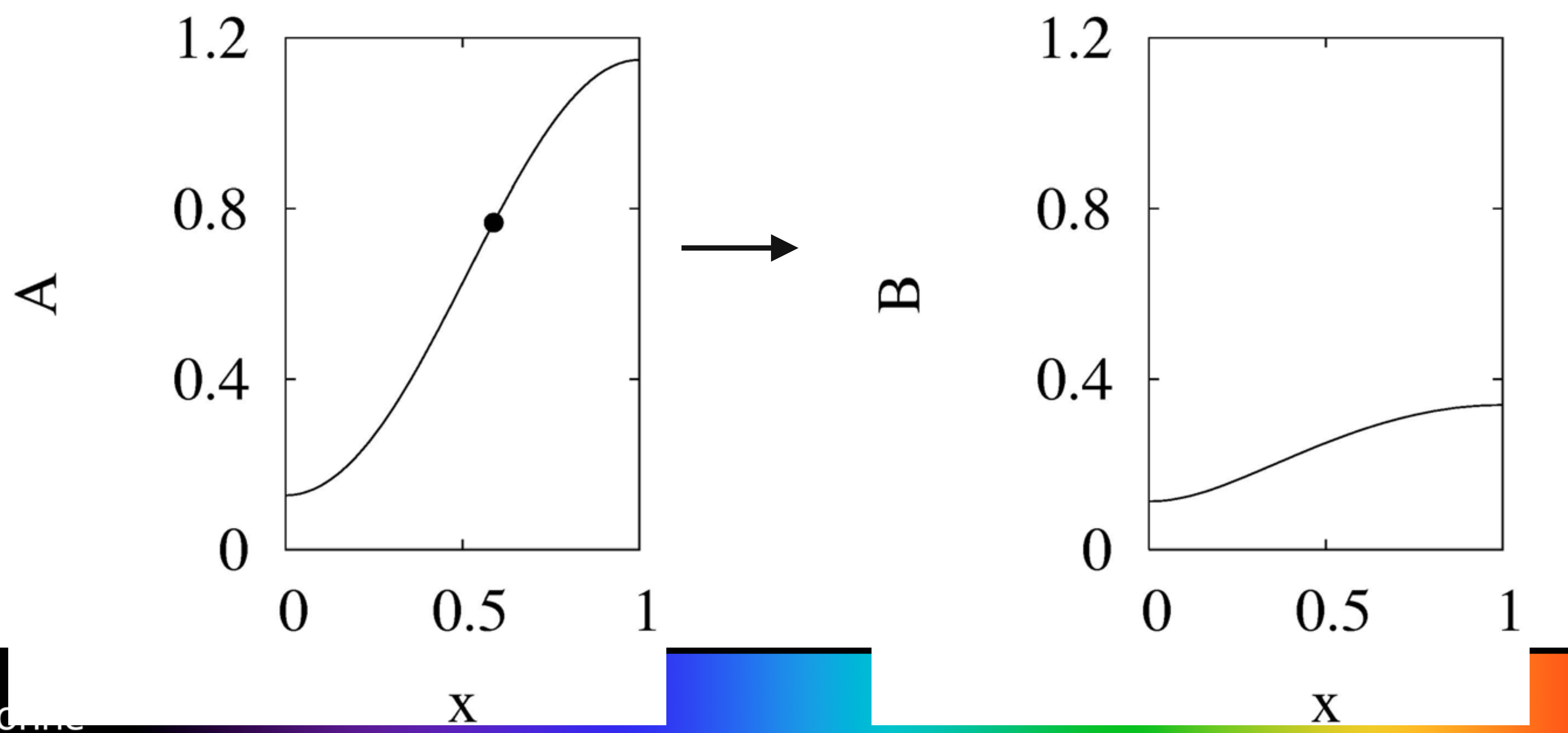
3-D projection



Left: $[O_2]$ (x=.49), [O] (x=.49)
Right: $[O_2]$ (x=.77), [O] (x=.29)

Implications of 1-D Manifold

- Time development of *all* species spatial distributions follow from a single point along any of their spatial distributions



Investigate Low-Dimensional Manifolds for Reaction-Diffusion Equations

- Studied many simple systems, including:
  - Nonlinear model
  - Ozone combustion
- Two papers:
  - "Low-Dimensional Manifolds in Reaction-Diffusion Equations 1: Fundamental Aspects", J. Phys. Chem. A **110**, 5235 (2006)
  - "Low-Dimensional Manifolds in Reaction-Diffusion Equations 2: Numerical Analysis and Method Development", J. Phys. Chem. A **110**, 5257 (2006)

Nonlinear test system with an exact solution

- System:

$$\frac{\partial y_1}{\partial t} = -y_1 + D_1 \frac{\partial^2 y_1}{\partial x^2}$$

$$\frac{\partial y_2}{\partial t} = -\gamma y_2 + a y_1^2 + D_2 \frac{\partial^2 y_2}{\partial x^2}$$

- Boundary Conditions:

$$y_1(x=0) = y_{10},\ \ y_2(x=0) = y_{20},\ \ \frac{\partial y_1}{\partial x}(x=1) = \frac{\partial y_2}{\partial x}(x=1) = 0$$

- Study $\gamma >> 1, D_1$
- Pure chemical kinetics ($D_1 = D_2 = 0$, $a = \gamma - 2$) has an exact manifold ("chemical manifold"):

$$y_2 = y_1^2$$

Solution Nonlinear Reaction-Diffusion

$$y_1(x,0) = y_1^{\text{eq}}(x) + \sum_m b_{1m}(0) \sin\left[\left(m + \frac{1}{2}\right)\pi x\right] \quad (3.3a)$$

and

$$y_2(x,0) = y_2^{\text{eq}}(x) + \sum_m b_{2m}(0) \sin\left[\left(m + \frac{1}{2}\right)\pi x\right] \quad (3.3b)$$

$$r_{kn}^m = 2 \int \sin\left[\left(m + \frac{1}{2}\right)\pi x\right] \sin\left[\left(k + \frac{1}{2}\right)\pi x\right] \sin\left[\left(n + \frac{1}{2}\right)\pi x\right] \mathrm{d}x \quad (4.3a)$$

$$s_j^m = 2 \int y_1^{\text{eq}} \sin\left[\left(m + \frac{1}{2}\right)\pi x\right] \sin\left[\left(j + \frac{1}{2}\pi x\right)\right] \mathrm{d}x \quad (4.3b)$$

Solution Nonlinear Reaction-Diffusion 2

$$y_1(x,t) = y_1^{\text{eq}} + \sum_{m=0} b_{1m} \sin\left[\left(m+\frac{1}{2}\right)\pi x\right] e^{-[1+(m+1/2)^2\pi^2 D_1]t} \tag{E.1a}$$

$$y_2 = y_2^{\text{eq}} + \sum_m \sin\left[\left(m+\frac{1}{2}\right)\pi x\right]\left[b_{2m} - \sum_k \sum_n \frac{a b_{1k} b_{1n} r_{kn}^m}{(\gamma-2) + \left(m+\frac{1}{2}\right)^2 \pi^2 D_2 - \left[\left(k+\frac{1}{2}\right)^2 + \left(n+\frac{1}{2}\right)^2\right]\pi^2 D_1} - \sum_j \frac{2 b_{1j} a s_j^m}{(\gamma-1) + \left(m+\frac{1}{2}\right)^2 \pi^2 D_2 - \left(j+\frac{1}{2}\right)^2 \pi^2 D_1}\right] e^{-[\gamma+(m+1/2)^2\pi^2 D_2]t} +$$

$$\sum_m \sin\left[\left(m+\frac{1}{2}\right)\pi x\right] \times \left[\sum_k \sum_n \frac{a b_{1k} b_{1n} r_{kn}^m \, e^{-\{2+[(k+1/2)^2+(n+1/2)^2]\pi^2 D1\}t}}{(\gamma-2) + \left(m+\frac{1}{2}\right)^2 \pi^2 D_2 - \left[\left(k+\frac{1}{2}\right)^2 + \left(n+\frac{1}{2}\right)^2\right]\pi^2 D_1} + \sum_j \frac{2 b_{1j} a s_j^m \, e^{-[1+(j+1/2)^2\pi^2 D_1]t}}{(\gamma-1) + \left(m+\frac{1}{2}\right)^2 \pi^2 D_2 - \left(j+\frac{1}{2}\right)^2 \pi^2 D_1}\right] \tag{E.1b}$$

Manifold Equation

- Relaxation
- Define manifold in physical space
  - Eliminate time

$$e^{-[1+\frac{\pi^2 D_1}{4}]} = \frac{y_{1\beta}}{\sin(\frac{\pi x_\beta}{2})}$$

$$y_{1\beta} \equiv y_1(x = x_\beta) - y_1^{eq}(x = x_\beta)$$

Dimension reduction for nonlinear model

- So, at longest time, the following hold (1-D manifold):

$$y_{1\sigma} = \frac{\sin\left(\frac{\pi x_\sigma}{2}\right)}{\sin\left(\frac{\pi x_\beta}{2}\right)} y_{1\beta}$$

$$y_{2\phi} = f(x_\phi)\frac{y_{1\beta}^2}{[\sin\left(\frac{\pi x_\beta}{2}\right)]^2} + g(x_\phi)\frac{y_{1\beta}}{\sin\left(\frac{\pi x_\beta}{2}\right)}$$

y_1 and y_2 at different spatial points are functions of y_1 at one spatial point (x_β). Good for all species at all spatial points.

Develop numerical methods for dimension reduction

- Dimension reduction represents orders of magnitude reduction at long time
- Develop a geometric approach
- Adapt two methods
  - Maas-Pope ILDM algorithm
    - *Approximate, but can be implemented for manifolds of any dimension*
  - Predictor-Corrector (Davis and Skodje)
    - *Accurate, but only developed for one-dimensional manifolds.*
    - *Easily implemented*

ILDMs

- Test ILDM for nonlinear model
  - Analytic results
- Develop numerical procedure
- Test on ozone example
  - For 1-D manifolds, compare to predictor-corrector

ILDM Calculation for Model

$$\mathbf{J} = \begin{pmatrix} J^{11} & J^{12} \\ J^{21} & J^{22} \end{pmatrix} \quad \text{(A.4)}$$

$$J^{11}_{km} = 0 \quad \text{except} \quad J^{11}_{kk} = -\left[1 + \left(k + \frac{1}{2}\right)^2 \pi^2 D_1\right] \quad \text{(A.5a)}$$

$$J^{21}_{km} = 2aS^k_m + 2a \sum_n r^k_{mn} b_{1n} \quad \text{(A.5b)}$$

$$J^{12}_{km} = 0 \quad \text{(A.5c)}$$

$$J^{22}_{km} = 0 \quad \text{except} \quad J^{22}_{kk} = -\left[\gamma + \left(k + \frac{1}{2}\right)^2 \pi^2 D_2\right] \quad \text{(A.5d)}$$

There are two sets of eigenvalues

$$\lambda^1_k = -\left[1 + \left(k + \frac{1}{2}\right)^2 \pi^2 D_1\right] \quad \text{(A.6a)}$$

$$\lambda^2_k = -\left[\gamma + \left(k + \frac{1}{2}\right)^2 \pi^2 D_2\right] \quad \text{(A.6b)}$$

For one-dimensional manifolds of type 1 (ref 1) the lowest eigenvalue is $\lambda_0{}^1$. The right eigenvectors are written as

$$\mathbf{R} = \begin{pmatrix} R^{11} & R^{12} \\ R^{21} & R^{22} \end{pmatrix} \quad \text{(A.7)}$$

It is straightforward to find the eigenvectors. For the algorithm outlined in section III, the following eigenvector is needed for one-dimensional manifolds of type 1

$$R^{11}_{m0} = 0 \quad \text{except} \quad R^{11}_{00} = 1 \quad \text{(A.8a)}$$

$$R^{21}_{m0} = \frac{2aS^0_m + 2a \sum_n r^0_{mn} b_{1n}}{(\gamma - 1) + \left(m + \frac{1}{2}\right)^2 \pi^2 D_2 - \frac{\pi^2 D_1}{4}} \quad \text{(A.8b)}$$

Error Analysis for nonlinear model

- ILDM can be found analytically. Error in quadratic term.

$$y_{2\phi} = f(x_\phi)\frac{y_{1\beta}^2}{[\sin(\frac{\pi x_\beta}{2})]^2} + g(x_\phi)\frac{y_{1\beta}}{\sin(\frac{\pi x_\beta}{2})}$$

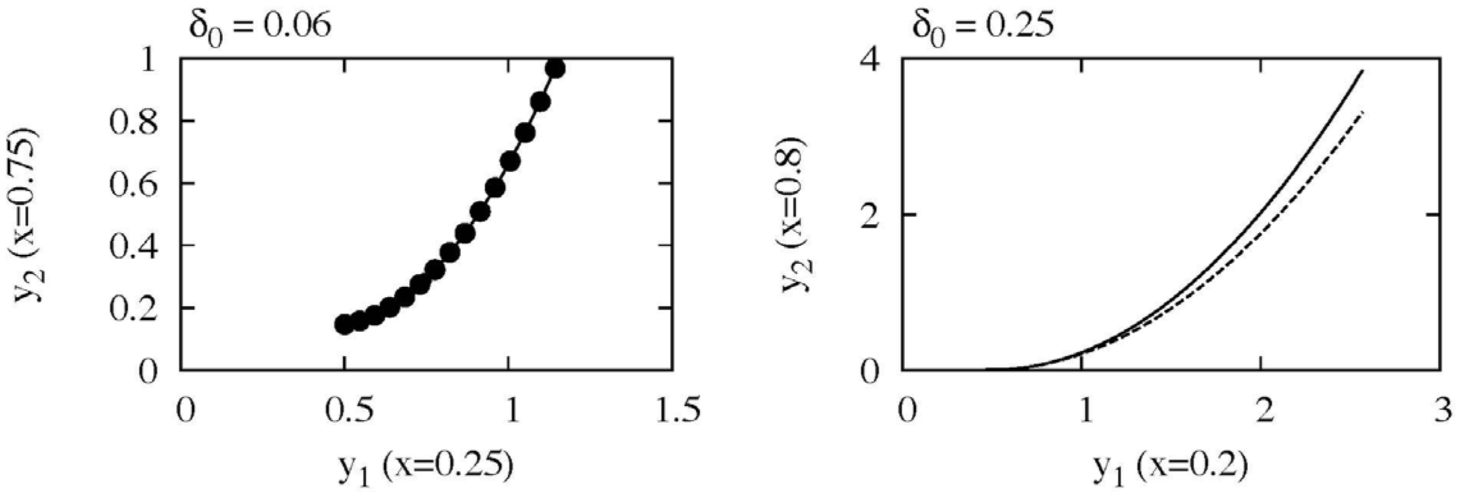
$$f(x) = \sum_m T_m \sin[(m+\frac{1}{2})\pi x]$$

$$\frac{T_m - T_m^{MP}}{T_m} = \frac{2(\delta_m)^2}{(1-\delta_m)} \qquad \delta_m \equiv \frac{\lambda_0^{(1)}}{\lambda_m^{(2)}}$$

$$\lambda_0^{(1)} = -1 - \frac{\pi^2 D_1}{4} \qquad \lambda_m^{(2)} = -\gamma - \pi^2 (m+\frac{1}{2})^2 D_2$$

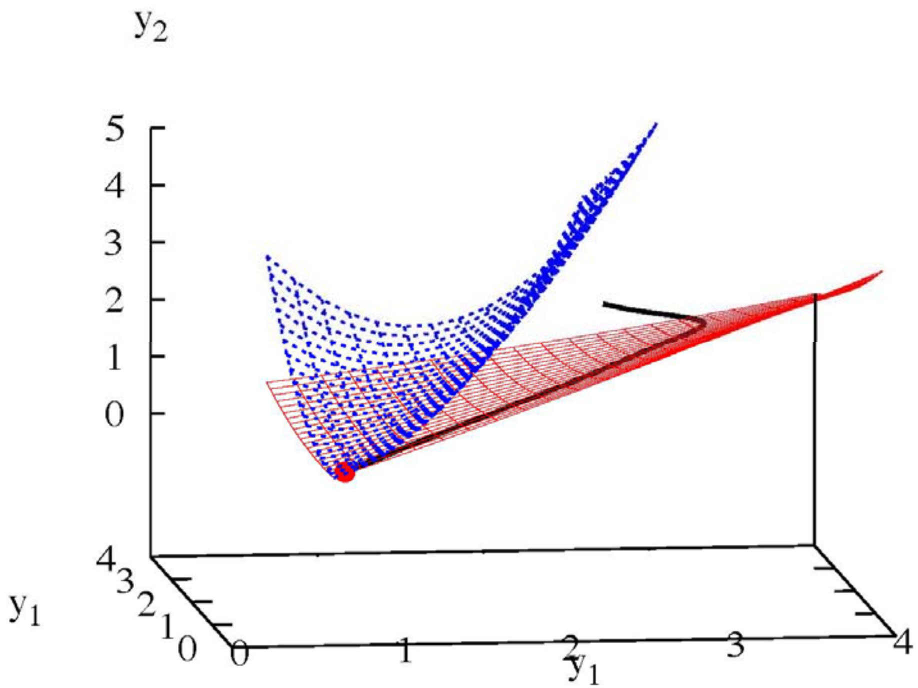
Error Analysis for nonlinear model (2)

- Relative error depends on interplay between reaction stiffness (γ) and diffusion (the D's)
- Sum of terms, so may be difficult to pin down
- Generally the errors are greatest when δ_0 is largest



Error Analysis for nonlinear model (3)

- Error analysis more complicated for 2-D manifolds
- 2-D generally accurate, but not always:



Need more accurate method for 2-D manifolds

Numerical Generation of ILDMs: Start near equilibrium

Dynamics near equilibrium:

$$[O](x,t) = [O]_{eq}(x) + y_1(x,t)$$

$$[O_2](x,t) = [O_2]_{eq}(x) + y_2(x,t)$$

$$[O_3](x,t) = [O_3]_{eq}(x) + y_3(x,t)$$

For:

$$\frac{\partial [O_2]}{\partial t} = -k_3[O_2][O_3] + \ldots + D\frac{\partial^2 [O_2]}{\partial x^2}$$

The following results:

$$\frac{\partial y_2}{\partial t} = -k_3([O_2]_{eq} y_3 + [O_3]_{eq} y_2) + D\frac{\partial^2 y_2}{\partial x^2}$$

Near equilibrium (cont)

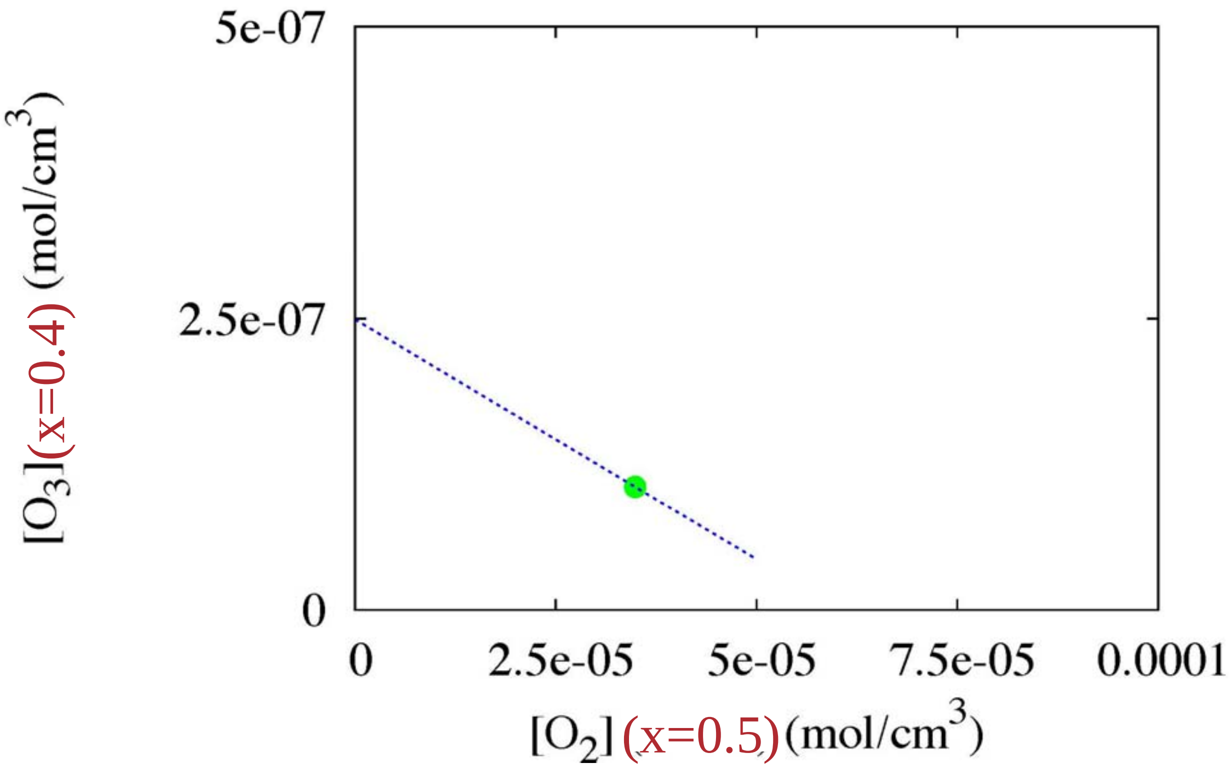
- The linear system which includes terms like this:

$$\frac{\partial y_2}{\partial t} = -k_3([O_2]_{eq} y_3 + [O_3]_{eq} y_2) + D\frac{\partial^2 y_2}{\partial x^2}$$

  can be solved as an eigenvalue/eigenvector problem on a grid or with a basis set
  - Information often available in computer codes
- One-dimensional manifold extends this away from equilibrium and into nonlinear region.

Dynamics near Equilibrium: Contrast Chemical-Kinetic case with R-D

- Projection of equilibrium distribution for R-D Equations
- Projection of linear, 1-D manifold near equilibrium distribution of Reaction-Diffusion Equations



ILDM: Manifold for Chemical Kinetics vs. 1-D Manifold for Reaction-Diffusion

- ILDM (Maas-Pope) for Reaction-Diffusion

$$\frac{\partial y_i}{\partial t} = G = f_i(\{y_j\}) + D_i \frac{\partial^2 y_i}{\partial x^2}$$

$$\tilde{v}_f, \tilde{v}_s : \text{eigenvectors. of } \mathbf{J},\ J_{ij} = \frac{\partial f_i}{\partial y_j} + D_i \frac{\partial^2 (\delta y_i)}{\partial x^2}$$

- ILDM: Least steepest descent lies along G

1486 J. Chem. Phys., Vol. 117, No. 4, 22 July 2002 Singh, Powers, and Paolucci

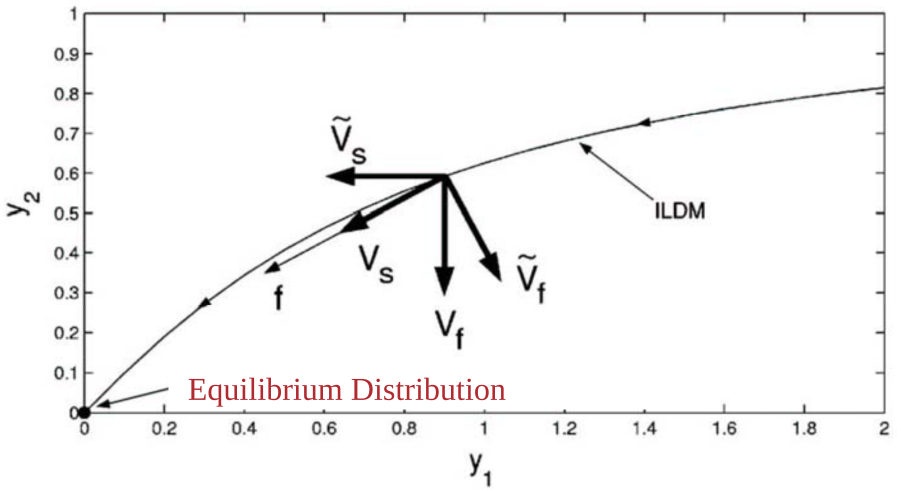


FIG. 1. Graphical representation of the ILDM for a two-dimensional dynamical system, depicting that the ILDM is a set of points in the phase space where the vector $\mathbf{V}_s$ has the same orientation as the vector **f**.

New algorithm for ILDMs

- Extra care needed because:
  - True spectrum is infinite and all calculations are truncated versions
    - *Only a few eigenvectors sufficiently converged*
    - *Even truncated versions are large*
- New algorithm is faster and more stable
  - Only "slow" space used to find manifold
    - *Reduces need for unconverged eigenvectors*
  - "Analytic" eigenvector derivatives used in search
    - *Reduces number of matrix diagonalizations*
  - Generated 1-D and 2-D manifolds

Description of algorithm for 1-D ILDMs

Dynamical system:

$$\frac{dy_k}{dt} = G_k(\{y_j\}),\ j = 1 \rightarrow n$$

Define Jacobian:

$$J_{km} = \frac{\partial G_k}{\partial y_m}$$

Diagonalization of Jacobian:

$$\mathbf{L}^T \mathbf{JR} = \Lambda$$

Elements of the right eigenvectors:

$$R_{km}$$

Description of algorithm for 1-D ILDMs: 2

Eigenvector of interest:

$$R_{k1}$$

Maas Pope conditions:

$$\frac{R_{k1}}{R_{m1}} = \frac{G_k}{G_m}, \ k = 1 \rightarrow n, \ k \neq m$$

Search for zeros:

$$S_k = 0, \ k = 1 \rightarrow n, \ k \neq m$$

$$S_k \equiv R_{m1} G_k(x) - R_{k1} G_m(x), \ k = 1 \rightarrow n, \ k \neq m$$

Description of algorithm for 1-D ILDMs: 3

Search requires:

$$J^{S}_{kj} = \frac{\partial S_k}{\partial y_j} = R_{m1}\frac{\partial G_k}{\partial y_j} + G_k\frac{\partial R_{m1}}{\partial y_j} + R_{k1}\frac{\partial G_m}{\partial y_j} + G_m\frac{\partial R_{k1}}{\partial y_j}$$

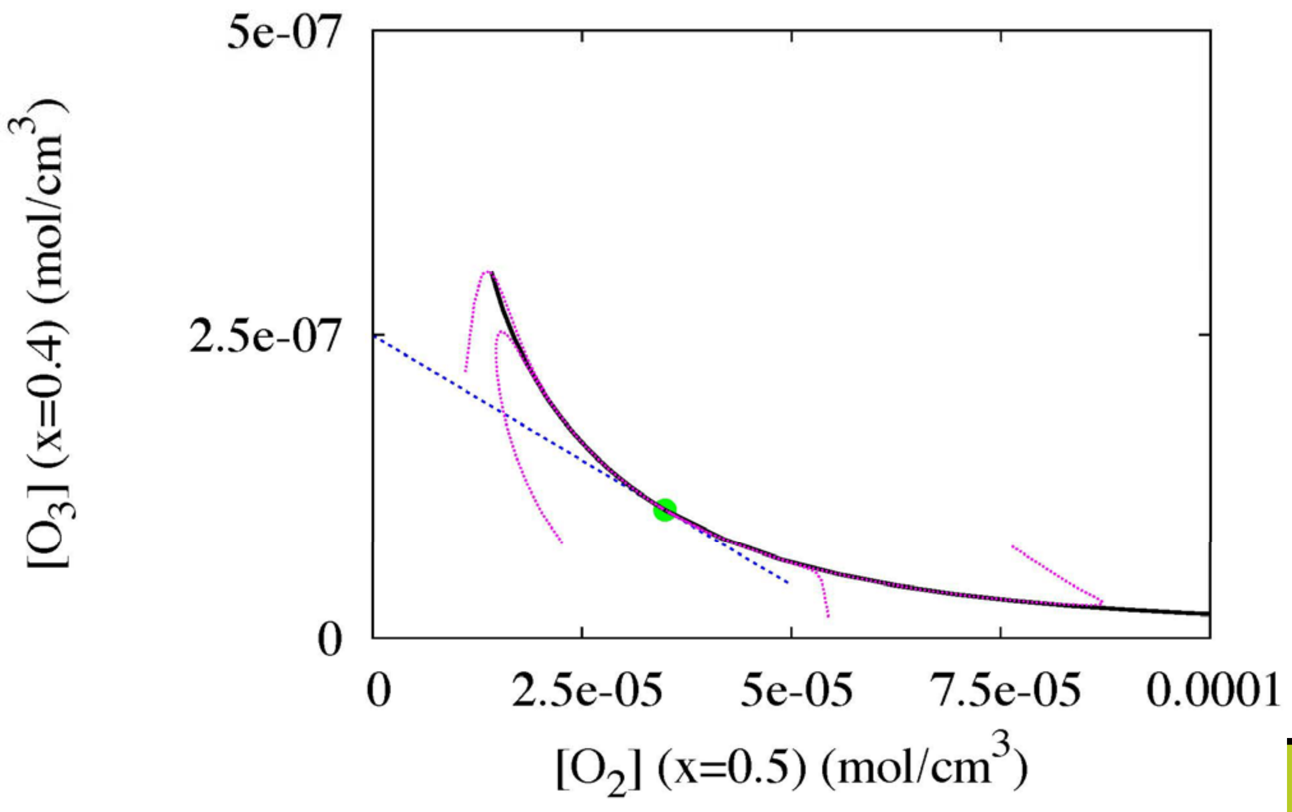
A single diagonalization and linear algebra used for derivatives like these:

$$\frac{\partial R_{m1}}{\partial y_j}, \frac{\partial R_{k1}}{\partial y_j}$$

“Analytical” eigenvector derivatives

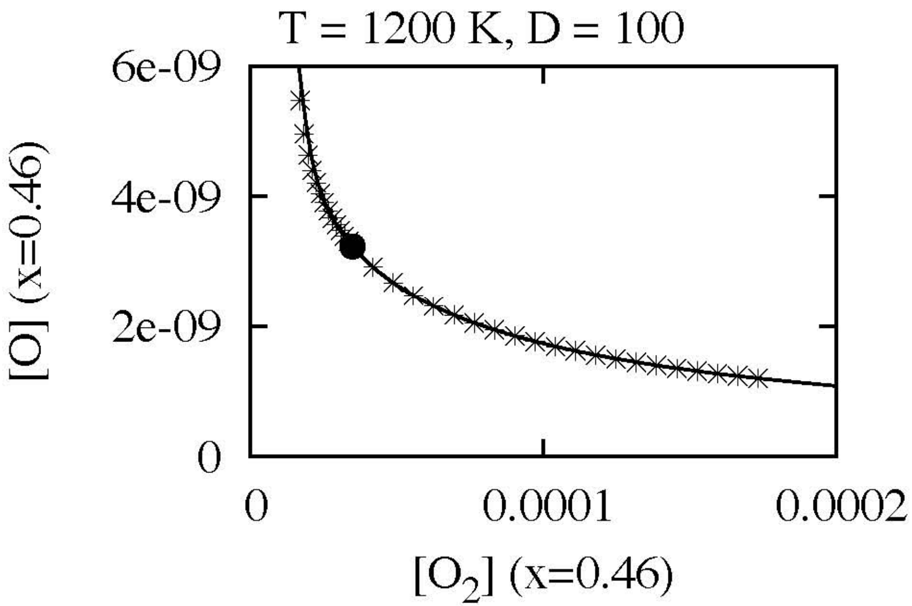
1-D Manifold

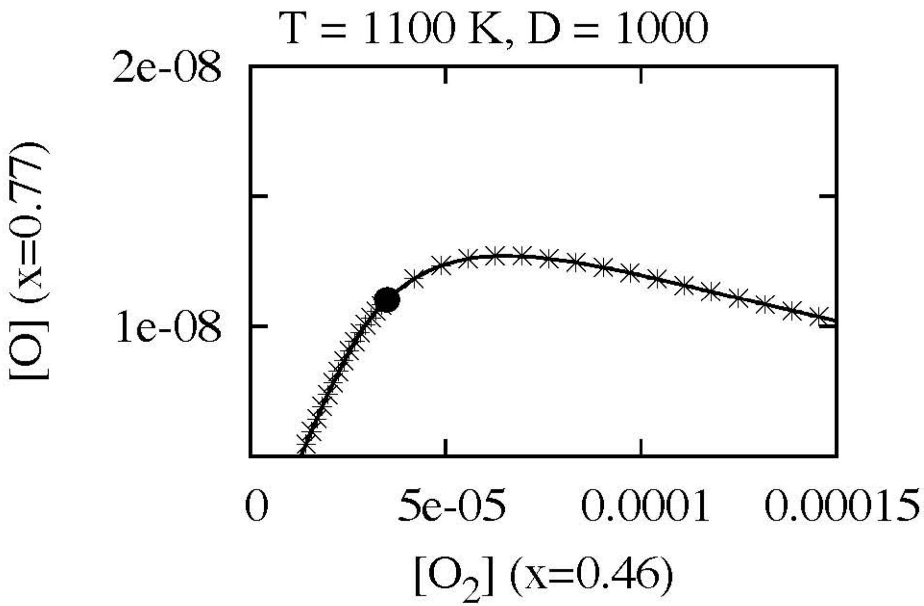
- Manifold is nonlinear
  - Compare to exact dynamics
- Dimension reduction: 1 ODE instead of 150-300



Compare Predictor-Corrector and ILDM

- Good agreement between predictor-corrector and ILDM

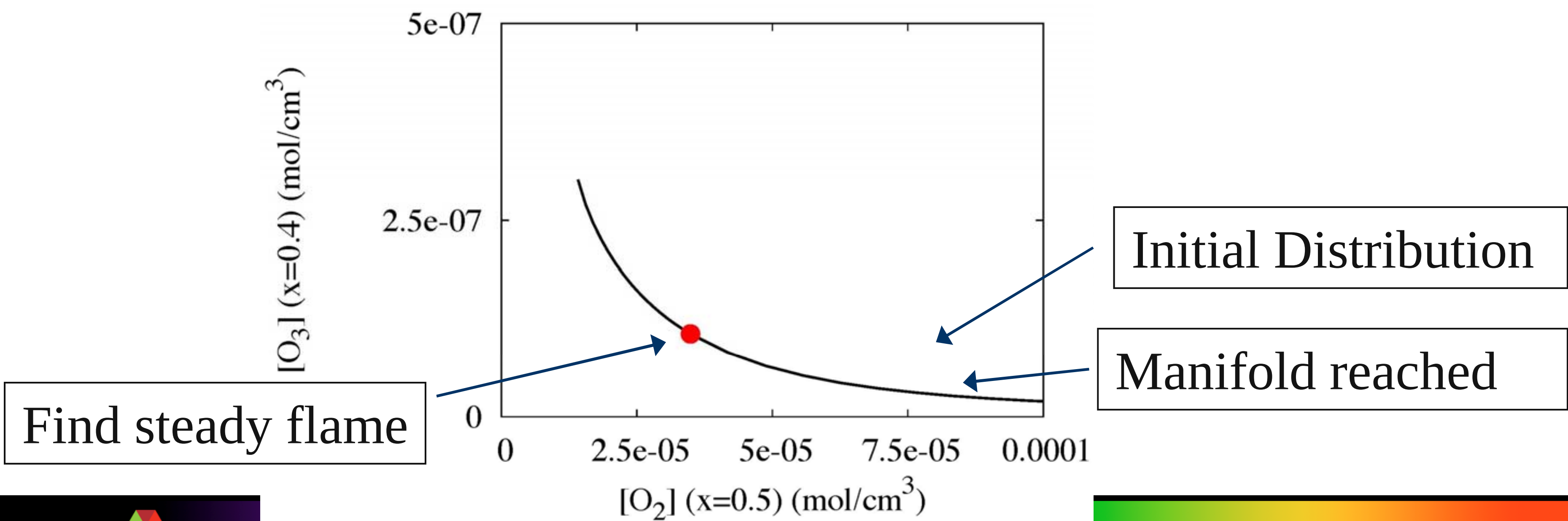




* : ILDM   Lines: Predictor-corrector

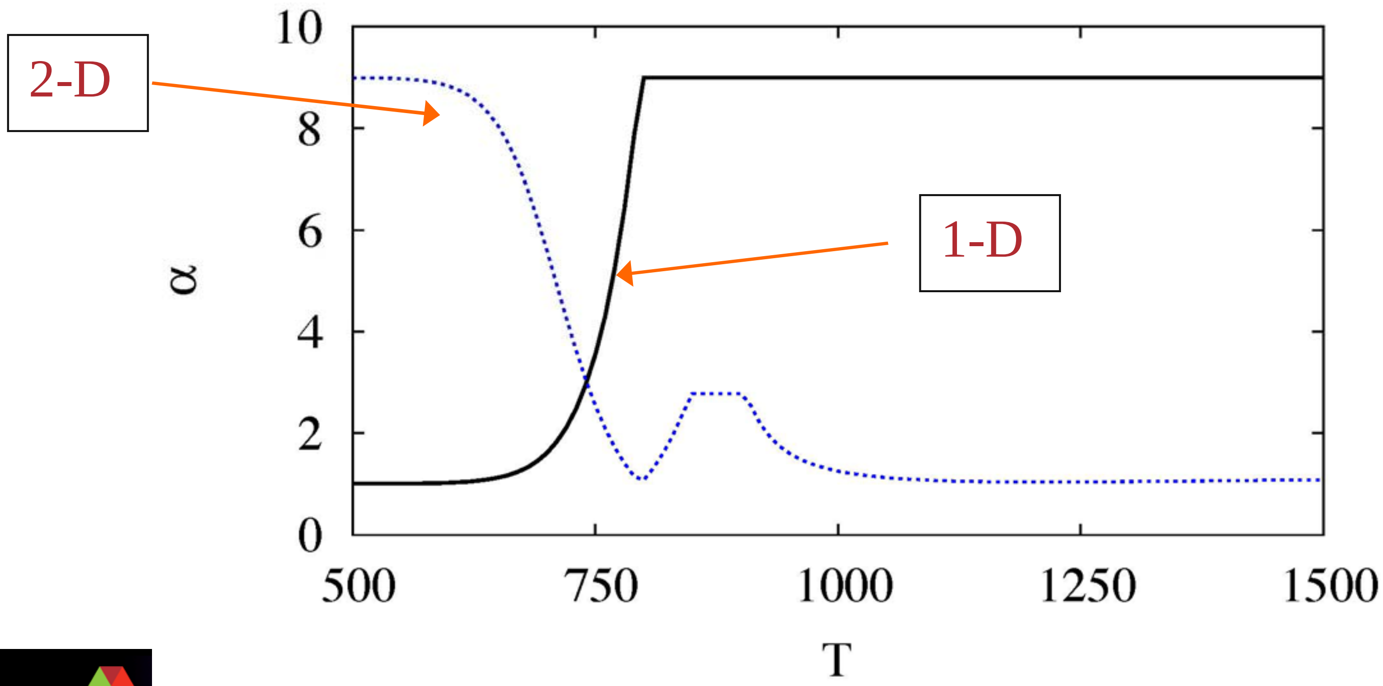
Moving Toward Equilibrium

- Find manifold and steady conditions
  - Use manifold idea as an aid to find steady flames, etc
    - *Alternative approach to full integration, which is used when shooting and Newton methods fail*
- Short time propagation to manifold, then follow manifold.
  - Newton method near steady for maximum accuracy



Attraction to manifold near equilibrium for ozone combustion

- Defines best manifold near equilibrium
  - Ratio of adjacent eigenvalues (labeled "α")
  - Two-dimensional manifolds at lower T and 1-D manifolds at higher T
- Function of temperature for ozone combustion:



Summary

- Low-dimensional manifolds in systems with reaction and diffusion
  - Reduces effort from hundreds of ODEs to a few
  - Different than species reduction
- Modification of ILDM algorithm for high dimensional systems with truncated spectra
  - Large computational savings
- Need better algorithm for 2-D manifolds
- Attractive manifolds over significant regions of parameter space
  - Attractiveness limited