Slow Invariant Manifolds
for Reactive-Diffusive Systems

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7th International Congress on Industrial and Applied Mathematics
Vancouver, British Columbia, Canada
July 21, 2011
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Motivation and Background

- Reactive systems induce a wide range of spatial and temporal scales, and subsequently severe stiffness
- DNS resolves all ranges of continuum physical scales present
- Under-resolved simulations attempt to account for missed physical phenomena with modeling
- Fully resolved simulations are expensive to compute

Manifold methods provide potential savings

Most methods are for spatially homogeneous systems

We employ the slow invariant manifold (SIM) model of Al-Khateeb, et al. (2009, Journal of Chemical Physics)

We adjust for the dynamics of diffusion in the presence of weak spatial heterogeneity

This is valid when diffusion is fast relative to reaction, i.e. thin regions of flames
Assumptions

Model a system of $N$ species reacting in $J$ reactions with diffusion in one spatial dimension

- Ideal mixture
- Calorically perfect
- Ideal gases
- Negligible advection
- Constant specific heat
- Single constant mass diffusivity
- Constant thermal conductivity
Balance Laws

- Evolution of species and energy
  \[
  \rho \frac{\partial Y_i}{\partial t} + \frac{\partial j^m_i}{\partial x} = M_i \dot{\omega}_i(Y_n, T), \quad \text{for } i, n \in [1, N]
  \]
  \[
  \rho \frac{\partial h}{\partial t} + \frac{\partial j^q}{\partial x} = 0
  \]

- Boundary conditions
  \[
  \left. \frac{\partial Y_i}{\partial x} \right|_{x=0} = \left. \frac{\partial Y_i}{\partial x} \right|_{x=\ell} = 0, \quad \text{for } i \in [1, N]
  \]
  \[
  \left. \frac{\partial T}{\partial x} \right|_{x=0} = \left. \frac{\partial T}{\partial x} \right|_{x=\ell} = 0
  \]

- Initial conditions
  \[
  Y_i(x, t = 0) = \tilde{Y}_i(x), \quad \text{for } i \in [1, N]
  \]
  \[
  T(x, t = 0) = \tilde{T}(x)
  \]
Constitutive Equations

- Simple diffusive flux terms

\[ j^m_i = -\rho \mathcal{D} \frac{\partial Y_i}{\partial x}, \quad \text{for } i \in [1, N] \]

\[ j^q = -k \frac{\partial T}{\partial x} + \sum_{i=1}^{N} h_i^f j^m_i \]

- Caloric equation of state

\[ h = \sum_{i=1}^{N} Y_i \left( c_{Pi}(T - T^o) + h_i^f \right) \]

- Ideal gas equation of state

\[ P = \frac{\rho \bar{R} T}{\sum_{i=1}^{N} \frac{M_i}{Y_i}} \]
Molar production rate

\[ \omega_i = \sum_{j=1}^{J} \nu_{ij} r_j, \quad \text{for } i \in [1, N] \]

\[ r_j = k_j \left( \prod_{i=1}^{N} \left( \frac{\rho Y_i}{M_i} \right)^{\nu'_{ij}} - \frac{1}{K_{j}^c} \prod_{i=1}^{N} \left( \frac{\rho Y_i}{M_i} \right)^{\nu''_{ij}} \right), \quad \text{for } j \in [1, J] \]

\[ k_j = a_j T^{\beta_j} \exp \left( \frac{-E_j}{RT} \right), \quad \text{for } j \in [1, J] \]

\[ K_{j}^c = \exp \left( \frac{-\sum_{i=1}^{N} \bar{g}_{i}^{o} \nu_{ij}}{RT} \right), \quad \text{for } j \in [1, J] \]
Generalized Shvab-Zel’dovich

- Certain linear combinations of molar production rate sum to zero,
  \[ \frac{\partial}{\partial t} \left( \sum_{i=1}^{N} \varphi_{li} \frac{Y_i}{M_i} \right) = \mathcal{D} \frac{\partial^2}{\partial x^2} \left( \sum_{i=1}^{N} \varphi_{li} \frac{Y_i}{M_i} \right), \quad \text{for } l \in [1, L] \]

- In adiabatic systems, when the Lewis number is unity
  \[ \frac{\partial}{\partial t} \left( c_P(T - T^o) + \sum_{i=1}^{N} h^f_i Y_i \right) = \mathcal{D} \frac{\partial^2}{\partial x^2} \left( c_P(T - T^o) + \sum_{i=1}^{N} h^f_i Y_i \right) \]

- If initially spatially homogeneous, these PDEs can be integrated
  \[ \sum_{i=1}^{N} \varphi_{li} \frac{Y_i}{M_i} = \sum_{i=1}^{N} \varphi_{li} \tilde{Y}_i, \quad \text{for } l \in [1, L] \]
  \[ c_P(T - T^o) + \sum_{i=1}^{N} h^f_i Y_i = c_P(\tilde{T} - T^o) + \sum_{i=1}^{N} h^f_i \tilde{Y}_i \]
Reduced Variables

- Transform to specific mole concentrations

\[ z_i = \frac{Y_i}{M_i}, \quad \text{for } i \in [1, N - L] \]

- Evolution of remaining \( L \) species and temperature are coupled to these reduced variables by the algebraic constraints

\[
\frac{\partial z_i}{\partial t} = \frac{\dot{\omega}(z_n, T)}{\rho} + D \frac{\partial^2 z_i}{\partial x^2}, \quad \text{for } i, n \in [1, N - L]
\]

\[
T = \begin{cases} 
\tilde{T}, & \text{if isothermal} \\
\bar{h} - \sum_{i=1}^{N} \hat{z}_i(z_n) \bar{h}_i^f + T^o, & \text{if adiabatic} \\
\sum_{i=1}^{N} \hat{z}_i(z_n) \bar{c}_P i & 
\end{cases}
\]
Galerkin Reduction to ODEs

- Assume a spectral decomposition
  \[ z_i(x, t) = \sum_{m=0}^{\infty} z_{i,m}(t) \phi_m(x), \quad \text{for } i \in [1, N - L] \]

- Orthogonal basis functions, \( \phi_m(x) \), are eigenfunctions of diffusion operator that match boundary conditions
  \[ \phi_m(x) = \cos \left( \frac{m\pi x}{\ell} \right), \quad \text{for } m \in [0, \infty) \]

- Finite system of ODEs for amplitude evolution are recovered by taking the inner product with \( \phi_n \), and truncated at \( M \)
  \[ \frac{dz_{i,m}}{dt} = \frac{\langle \phi_m, \dot{\omega}_i (\sum_{m=0}^{\infty} z_{i,n} \phi_n) \rangle}{\langle \phi_m, \phi_m \rangle} - \frac{m^2 \pi^2 D}{\ell^2} z_{i,m}, \quad \text{for } i \in [1, N - L], \text{ and } m \in [0, M] \]

- Diffusion time scale identified, \( \tau_D = \frac{\ell^2}{\pi^2 D} \)
Oxygen Dissociation

\[ O + O + M \iff O_2 + M \]

- \( N = 2 \) species
- \( J = 1 \) reactions
- \( L = 1 \) constraints
- \( N - L = 1 \) reduced variables
  \[ z = z_O \]

- Isochoric,
  \[ \rho = 1.6 \times 10^{-4} \text{ g/cm}^3 \]
- Isothermal, \( T = 5000 \text{ K} \)

Partial differential equation governing evolution

\[
\frac{\partial z}{\partial t} = 249.84130 - 74734.78 \ z^2 - 172406.48 \ z^3 + D \frac{\partial^2 z}{\partial x^2}
\]
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Spatially homogeneous evolution equation

\[
\frac{dz_0}{dt} = 249.84130 - 74734.78 \ z_0^2 - 172406.48 \ z_0^3
\]
- One spatial mode ($M = 1$) evolution equation

\[
\frac{dz_0}{dt} = 249.84130 - 74734.78 \left( z_0^2 + \frac{z_1^2}{2} \right) - 172406.48 \left( z_0^3 + \frac{3z_0z_1^2}{2} \right)
\]

\[
\frac{dz_1}{dt} = -74734.78 \left( 2z_0z_1 \right) - 172406.48 \left( 3z_0^2z_1 + \frac{3z_1^3}{4} \right) - \frac{\pi^2D}{\ell^2}z_1
\]

- Spatially homogeneous evolution when $z_1 = 0$

- Spatially homogeneous equilibria retained

- Eigenvalues about these equilibria are modified

\[
\lambda_1 = \lambda_0 - \frac{\pi^2D}{\ell^2}
\]
• Change in sign of modified eigenvalue, $\lambda_1 = \lambda_0 - \frac{\pi^2D}{\ell^2}$, identifies a critical length where SIM origin changes character

• Bifurcation occurs at $R_2$ equilibrium

\[
\frac{\pi^2D}{\ell^2} = \lambda_0 = 7321.5 \text{ s}^{-1}
\]
\[
\ell = 1.04 \text{ mm}
\]

• Diffusion-corrected SIM origin shifts to bifurcated branches

• Bold branches are saddles; dashed branch is source
Map variables into a space where infinity is on the unit circle

\[ \eta_0 = \frac{\alpha z_0}{\sqrt{1 + \alpha^2 z_0^2} + \alpha^2 z_1^2} \]

\[ \eta_1 = \frac{\alpha z_1}{\sqrt{1 + \alpha^2 z_0^2} + \alpha^2 z_1^2} \]

\[ \ell = 0.334 \, mm \]
Map variables into a space where infinity is on the unit circle

\[
\eta_0 = \frac{\alpha z_0}{\sqrt{1 + \alpha^2 z_0^2 + \alpha^2 z_1^2}}
\]

\[
\eta_1 = \frac{\alpha z_1}{\sqrt{1 + \alpha^2 z_0^2 + \alpha^2 z_1^2}}
\]

\[\ell = 1.05 \, mm\]
Poincaré Sphere

Map variables into a space where infinity is on the unit circle

\[
\eta_0 = \frac{\alpha z_0}{\sqrt{1 + \alpha^2 z_0^2 + \alpha^2 z_1^2}}
\]

\[
\eta_1 = \frac{\alpha z_1}{\sqrt{1 + \alpha^2 z_0^2 + \alpha^2 z_1^2}}
\]

\( \ell = 3.34 \, \text{mm} \)
Zel’dovich Mechanism – Isothermal

\[ N + NO \iff N_2 + O \]
\[ N + O_2 \iff NO + O \]

- \( N = 5 \) species
- \( J = 2 \) reactions
- \( L = 3 \) constraints
- \( N - L = 2 \) reduced variables
  \[ z_1 = z_{NO}, \quad z_2 = z_N \]
- Isochoric, \( \rho = 1.2002 \text{ g/cm}^3 \)
- Isothermal, \( T = 4000 \text{ K} \)
- Bimolecular, isobaric,
  \[ P = 1.6629 \times 10^6 \text{ dyne/cm}^2 = 1.64 \text{ atm} \]

Partial differential equation governing evolution

\[
\frac{\partial z_1}{\partial t} = 250 - 9.97 \times 10^4 z_1 + 1.16 \times 10^7 z_2 - 3.22 \times 10^9 z_1 z_2 + 6.99 \times 10^8 z_2^2 + D \frac{\partial^2 z_1}{\partial x^2}
\]

\[
\frac{\partial z_2}{\partial t} = 250 + 8.47 \times 10^4 z_1 - 1.17 \times 10^7 z_2 - 1.84 \times 10^9 z_1 z_2 - 6.98 \times 10^8 z_2^2 + D \frac{\partial^2 z_2}{\partial x^2}
\]
Zel’’dovich Mechanism – Isothermal

\[ \begin{align*}
N + NO & \quad \iff \quad N_2 + O \\
N + O_2 & \quad \iff \quad NO + O
\end{align*} \]

- \( N = 5 \) species
- \( J = 2 \) reactions
- \( L = 3 \) constraints
- \( N - L = 2 \) reduced variables
  \( z_1 = z_{NO}, \quad z_2 = z_N \)
- Isochoric, \( \rho = 1.2002 \, g/cm^3 \)
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- Bimolecular, isobaric, \( P = 1.6629 \times 10^6 \, dyne/cm^2 = 1.64 \, atm \)

Spatially homogeneous evolution equations – second order polynomials.

\[
\begin{align*}
\frac{dz_{1,0}}{dt} &= 250 - 9.97 \times 10^4 \, z_{1,0} + 1.16 \times 10^7 \, z_{2,0} - 3.22 \times 10^9 \, z_{1,0} z_{2,0} + 6.99 \times 10^8 \, z_{2,0}^2 \\
\frac{dz_{2,0}}{dt} &= 250 + 8.47 \times 10^4 \, z_{1,0} - 1.17 \times 10^7 \, z_{2,0} - 1.84 \times 10^9 \, z_{1,0} z_{2,0} - 6.98 \times 10^8 \, z_{2,0}^2
\end{align*}
\]
- Identify equilibria
- Characterize equilibria by eigenvalues of their Jacobian matrix
- Classify time scales as fast and slow
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Identify equilibria

Characterize equilibria by eigenvalues of their Jacobian matrix

Classify time scales as fast and slow

Identify SIM as a heteroclinic orbit from saddle to sink
First diffusion mode adds modified time scale

Positive eigenvalue identifies critical length scale

Locus of roots near $R_2$

Bifurcation occurs at this length scale

Let us examine a length below this critical length scale, $\ell = 17 \, \mu m$
Two additional fast time scales from diffusion

Spatially inhomogeneous amplitudes decay earlier than either reaction time scale
Zel’dovich Mechanism – Adiabatic

\[ \begin{align*}
N + NO & \iff N_2 + O \\
N + O_2 & \iff NO + O
\end{align*} \]

- $N = 5$ species
- $J = 2$ reactions
- $L = 3$ constraints
- $N - L = 2$ reduced variables
  \[ z_1 = z_{NO}, \quad z_2 = z_N \]
- $T = T(z_1, z_2)$

- Isobaric,
  \[ P = 1.6629 \times 10^6 \text{ dyne/cm}^2 = 1.64 \text{ atm} \]
- Adiabatic,
  \[ h = 9.0376 \times 10^{-10} \text{ erg/g} \]
  chosen to keep chemical equilibrium at same point

Evolution equations highly nonlinear due to temperature-dependance in exponentials
Isothermal Equilibria as a Function of Temperature

- Equilibria of adiabatic system difficult to identify
- Find isothermal equilibria for various temperatures

![Graph showing equilibria as a function of temperature]

- Adiabatic equilibria where enthalpy constraint is met
- Method is not exhaustive
Equilibria and dynamics remain similar to isothermal case

SIM is heteroclinic orbit connecting analogous points
- **Equilibria and dynamics remain similar to isothermal case**
- **SIM is heteroclinic orbit connecting analogous points**
Equilibria and dynamics remain similar to isothermal case

SIM is heteroclinic orbit connecting analogous points
Species and temperature evolution exhibit fast and slow time scales, consistent with equilibrium eigenvalues.

Adiabatic reactive-diffusive systems have yet to be analyzed.
Conclusions

- The SIM isolates the slowest dynamics, making it ideal for a reduction technique.
- A critical length scale has been identified where the diffusion time scale matches a reaction time scale; at this length a bifurcation occurs that affects the slow dynamics of the system.
- For sufficiently short length scales, diffusion time scales are faster than reaction time scales, and the system dynamics are dominated by reaction.
- When lengths are near or above the critical length, diffusion plays a more important role.
- Extension of SIM to spatially homogeneous adiabatic systems is shown to be feasible.
Acknowledgments

Partial support provided by NSF Grant No. CBET-0650843, Notre Dame ACMS Department Fellowship, and SIAM travel grant