Slow Attractive Canonical Invariant Manifolds for Hydrogen-Air Kinetics

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Taxonomy

We seek *Slow Attractive Canonical Invariant Manifolds* (SACIMs) for realistic spatially homogeneous gas phase kinetic systems.

- *Invariant Manifolds* (IMs) are sets of points which are invariant under the action of an underlying dynamic system.
- Any trajectory of a dynamic system is an IM.
- IMs may be locally or globally fast or slow, attracting or repelling.
- Slow or fast does not imply attracting or repelling and *vice versa*.
- We will evaluate the fast/slow and attracting/repelling nature of *Canonical Invariant Manifolds* (CIMs) constructed by connecting equilibria to determine *heteroclinic orbits* (Davis-Skodje, *J. Chem. Phys.*, 1999).

Taxonomy, cont.

- It is relatively easy to construct CIMs by numerical integration.
- Many CIMs exist, but we are only interested in those that connect to physical equilibrium.
- It is desirable to identify those CIMs to which
    - dynamics are restricted to those which are *slow*, and
    - neighboring trajectories are rapidly *attracted*.

  We call such CIMs *Slow Attracting Canonical Invariant Manifolds* (SACIMs).
- A global SACIM may represent the *optimal reduction* potentially enabling dramatic accuracy and efficiency in multiscale problems.
- Manifolds identified by Davis-Skodje construction are guaranteed to be CIMs; they are not guaranteed to be SACIMs, even locally!
- See Powers, Paolucci, Mengers, Al-Khateeb, *J. Math. Chem.*, 2015 for a full exposition of our results here.

Theoretical framework for spatially homogeneous combustion within a closed volume

$$\frac{d\mathbf{z}}{dt} = \mathbf{f}(\mathbf{z}), \qquad \mathbf{z}(0) = \mathbf{z}_o, \qquad \mathbf{z}, \mathbf{z}_o, \mathbf{f} \in \mathbb{R}^N.$$

- $\mathbf{z}$ represents a set of N specific mole numbers, assuming all linear constraints have been removed.
- $\mathbf{f}(\mathbf{z})$ embodies the law of mass action and other thermochemistry.
- $\mathbf{f}(\mathbf{z}) = \mathbf{0}$ defines *multiple equilibria* within $\mathbb{R}^N$.
- $\mathbf{f}(\mathbf{z})$ is such that a *unique stable equilibrium* exists for physically realizable values of $\mathbf{z}$; the eigenvalues of the Jacobian

$$\mathbf{J} = \frac{\partial \mathbf{f}}{\partial \mathbf{z}},$$

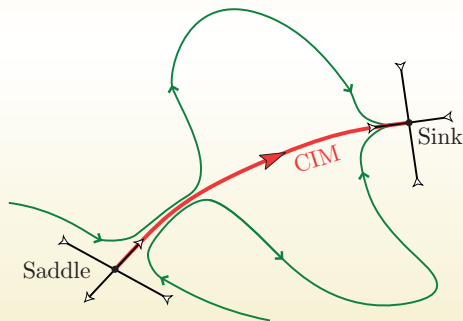are guaranteed real and negative at such an equilibrium (Powers & Paolucci, *Am. J. Phys.*, 2008).

SACIM construction strategy: heteroclinic orbit connection

- Davis and Skodje suggested a CIM construction strategy.
- It employs numerical integration from a saddle to the sink.
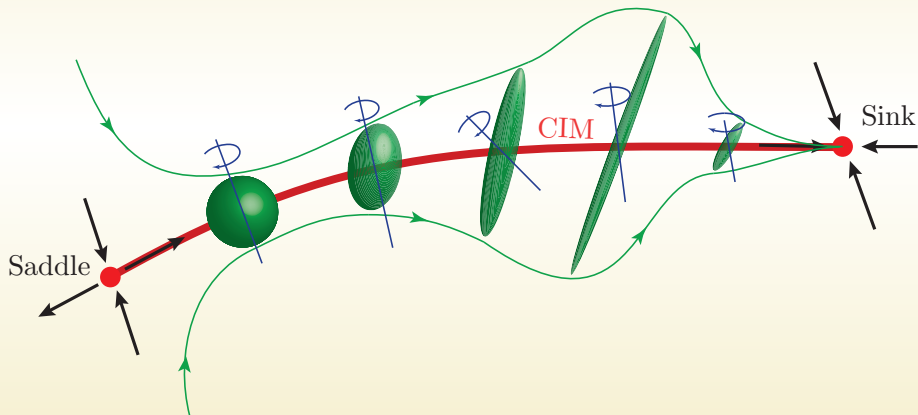- This guarantees a CIM.
- It *may* be a SACIM.
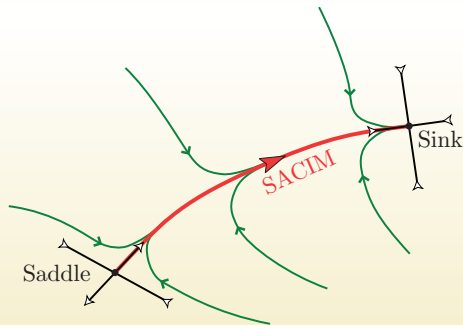
- It *may not* be a SACIM.
- The CIM will be attracting in the neighborhood of each equilibrium.
- The CIM need not be attractive away from either equilibrium.

The local differential volume 1) translates, 2) stretches, and 3) rotates. Its magnitude can decrease as it travels, but elements can still be repelled from the CIM. All trajectories are ultimately attracted to the sink.

Local decomposition of motion

$$\frac{d\mathbf{z}}{dt} = \mathbf{f}(\mathbf{z}), \qquad \mathbf{z}(0) = \mathbf{z}_o, \qquad \mathbf{z}_o \in \text{CIM},$$

$$\frac{d}{dt}(\mathbf{z} - \mathbf{z}_o) = \underbrace{\mathbf{f}(\mathbf{z}_o)}_{\text{translation}} + \underbrace{\mathbf{J}_s|_{\mathbf{z}_o} \cdot (\mathbf{z} - \mathbf{z}_o)}_{\text{stretch}} + \underbrace{\mathbf{J}_a|_{\mathbf{z}_o} \cdot (\mathbf{z} - \mathbf{z}_o)}_{\text{rotation}} + \dots.$$

Here, we have

$$\mathbf{J} = \frac{\partial \mathbf{f}}{\partial \mathbf{z}} = \mathbf{J}_s + \mathbf{J}_a,$$

$$\mathbf{J}_s = \frac{\mathbf{J} + \mathbf{J}^T}{2}, \quad \mathbf{J}_a = \frac{\mathbf{J} - \mathbf{J}^T}{2}.$$

The symmetry of $\mathbf{J}_s$ allows definition of a real orthonormal basis.

In 3d, the rotation vector $\boldsymbol{\omega}$ of the anti-symmetric $\mathbf{J}_a$ defines the axis of rotation; can be extended for higher dimensions. Geometric interpretation for 4d or greater is *unclear*; we confine to 3d or lesser.

Stretching rates

- See Adrover, et al. *J. Comp. Phys.*, 2007.
- The local relative volumetric stretching rate is

$$\frac{1}{v}\frac{dv}{dt} \equiv \overline{\dot{\ln v}} = \operatorname{tr}\mathbf{J} = \operatorname{tr}\mathbf{J}_s.$$

- The stretching rate σ associated with *any* unit vector $\boldsymbol{\alpha}$ is

$$\sigma = \boldsymbol{\alpha}^T \cdot \mathbf{J} \cdot \boldsymbol{\alpha} = \boldsymbol{\alpha}^T \cdot \mathbf{J}_s \cdot \boldsymbol{\alpha}.$$

- The above result is general; $\boldsymbol{\alpha}$ need not be an eigenvector of $\mathbf{J}$ or $\mathbf{J}_s$, and σ need not be an eigenvalue of $\mathbf{J}$ or $\mathbf{J}_s$.
- If they were eigenvalue/eigenvector pairs of $\mathbf{J}_s$, they would represent the principal axes of stretch and the associated principal values.

Stretching rates, cont.

Consider now the motion along a given CIM:

- The unit tangent vector, $\boldsymbol{\alpha}_t$, need not be a principal axis of stretch.
- The tangential stretching rate, $\sigma_t = \boldsymbol{\alpha}_t^T \cdot \mathbf{J}_s \cdot \boldsymbol{\alpha}_t$, can be positive or negative.
- The normal stretching rates, $\sigma_{n,i} = \boldsymbol{\alpha}_{n,i}^T \cdot \mathbf{J}_s \cdot \boldsymbol{\alpha}_{n,i}$, can be positive or negative.
- The sum of stretching rates equals the relative volumetric stretching rate:

$$\overline{\ln v} = \operatorname{tr} \mathbf{J} = \operatorname{tr} \mathbf{J}_s = \sigma_t + \sigma_{n,1} + \cdots + \sigma_{n,N-1}.$$

Necessary conditions for a SACIM

- For a *slow* CIM, attraction *to* the CIM must be faster than motion *on* the CIM (a type of *normal hyperbolicity*):

$$\kappa \equiv \frac{\min_i |\sigma_{n,i}|}{|\sigma_t|} > 1.$$

- for an *attractive* CIM, either
  - *all* normal stretching rates, $\sigma_{n,i}$, must be negative,

  $$\sigma_{n,i} < 0, \quad i = 1, \ldots, N-1,$$

  - or, if *some* of the normal stretching rates are positive, then
    - the relative volumetric stretching rate must be negative,

    $$\overline{\ln v} < 0, \qquad \underline{\text{and}}$$

    - the component of the rotation velocity in the normal plane must be much greater than the largest normal stretching rate,

    $$\mu \equiv \frac{\omega}{\max_i \sigma_{n,i}} = \frac{||\mathbf{Q}_n^T \cdot \mathbf{J}_a \cdot \mathbf{Q}_n||}{\max_i \sigma_{n,i}} = \frac{||\mathbf{J}_{na}||}{\max_i \sigma_{n,i}} > 1.$$

Procedure for local SACIM identification

- Identify all equilibria $\mathbf{f}(\mathbf{z}) = \mathbf{0}$.
- Determine the Jacobian, $\mathbf{J} = \partial \mathbf{f} / \partial \mathbf{z}$.
- Evaluate $\mathbf{J}$ near each equilibrium to determine its source, sink, saddle, etc. character.
- Numerically integrate from candidate saddles into the unique physical sink to determine a CIM, $\mathbf{z}_{CIM}$: a candidate SACIM.
- Numerically determine the unit tangent, $\boldsymbol{\alpha}_t$, along the CIM:

$$\boldsymbol{\alpha}_t = \frac{\mathbf{f}(\mathbf{z}_{CIM})}{||\mathbf{f}(\mathbf{z}_{CIM})||}.$$

- Determine the tangential stretching rate, σ_t, via

$$\sigma_t = \boldsymbol{\alpha}_t^T \cdot \mathbf{J}_s \cdot \boldsymbol{\alpha}_t = \boldsymbol{\alpha}_t^T \cdot \mathbf{J} \cdot \boldsymbol{\alpha}_t.$$

Procedure for local SACIM identifcation, cont.

- Use a Gram-Schmidt procedure to identify $N - 1$ unit normal vectors, thus forming the orthonormal basis

$$\{\boldsymbol{\alpha}_t, \boldsymbol{\alpha}_{n,1}, \ldots, \boldsymbol{\alpha}_{n,N-1}\}.$$

Note that $\boldsymbol{\alpha}_{n,i}$ are not eigen-directions of $\mathbf{J}$, so the procedure works for non-normal systems, though questions remain for highly non-normal, near singular systems.

- Form the $N \times (N - 1)$ orthogonal matrix $\mathbf{Q}_n$ composed of the unit normal vectors

$$\mathbf{Q}_n = \begin{pmatrix} \vdots & \vdots & \vdots & \vdots \\ \boldsymbol{\alpha}_{n,1} & \boldsymbol{\alpha}_{n,2} & \vdots & \boldsymbol{\alpha}_{n,N-1} \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix}.$$

Procedure for local SACIM identification, conc.

- Form the reduced $(N-1) \times (N-1)$ Jacobian $\mathbf{J}_{ns}$ for the motion in the hyperplane normal to the CIM:

$$\mathbf{J}_{ns} = \mathbf{Q}_n^T \cdot \mathbf{J}_s \cdot \mathbf{Q}_n.$$
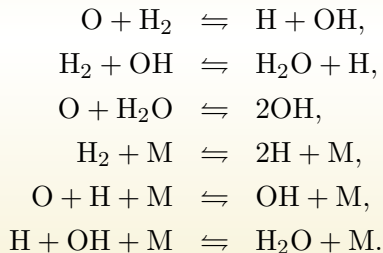
- Find the eigenvalues and eigenvectors of $\mathbf{J}_{ns}$. The eigenvalues give the extreme values of normal stretching rates $\sigma_{n,i}$, $i = 1, \ldots, N-1$. The normalized eigenvectors of $\mathbf{J}_{ns}$ give the directions associated with the extreme values of normal stretching, $\boldsymbol{\alpha}_{n,i}$.

- We have thus

$$\sigma_{n,i} = \boldsymbol{\alpha}_{n,i}^T \cdot \mathbf{J} \cdot \boldsymbol{\alpha}_{n,i} = \boldsymbol{\alpha}_{n,i}^T \cdot \mathbf{J}_s \cdot \boldsymbol{\alpha}_{n,i}, \qquad i = 1, \ldots, N-1.$$

- Identify $\mathbf{J}_{na}$ and then ω.

Example: simplified H_2-air kinetics

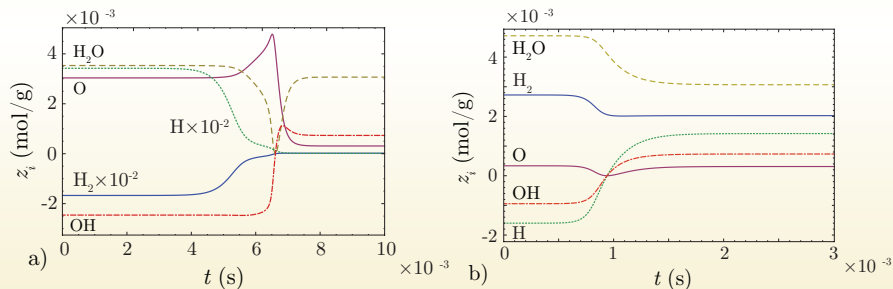- From Ren, Pope, et al., *J. Chem. Phys.*, 2006,
- 6 reactions:

$$
\begin{aligned}
O + H_2 &\rightleftharpoons H + OH, \\
H_2 + OH &\rightleftharpoons H_2O + H, \\
O + H_2O &\rightleftharpoons 2OH, \\
H_2 + M &\rightleftharpoons 2H + M, \\
O + H + M &\rightleftharpoons OH + M, \\
H + OH + M &\rightleftharpoons H_2O + M.
\end{aligned}
$$

- 6 species: H_2, O, H_2O, H, OH, N_2.
- 3 elements: H, O, N
- $T = 3000$ K, $P = 1$ atm.
- Constraints give reduction to 3 ODEs for z_{H_2}, z_O, and z_{H_2O}.
- $d\mathbf{z}/dt = \mathbf{f}(\mathbf{z})$.
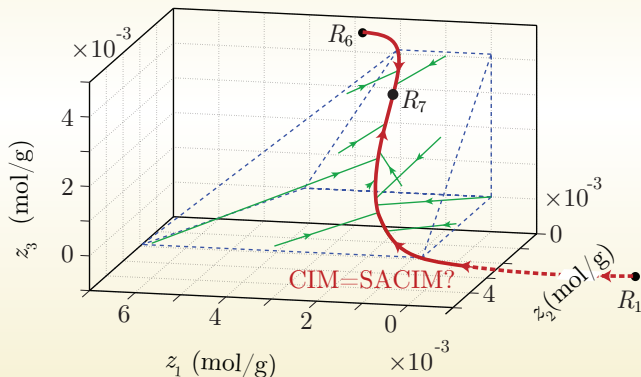
- We identified a CIM for this system (*J. Chem. Phys.*, 2009).
- Is this CIM a SACIM?

a) / b)

Trajectories originating near both unphysical saddles approach the same unique physical equilibrium.
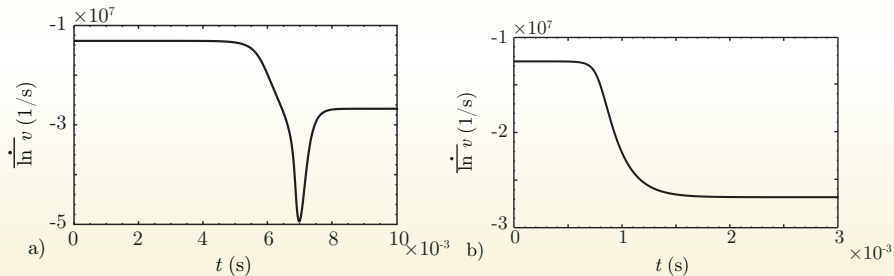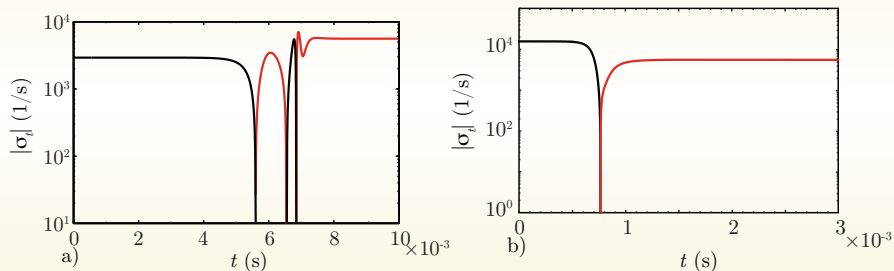
Volumes are shrinking everywhere on the CIMs during the approach to physical equilibrium.
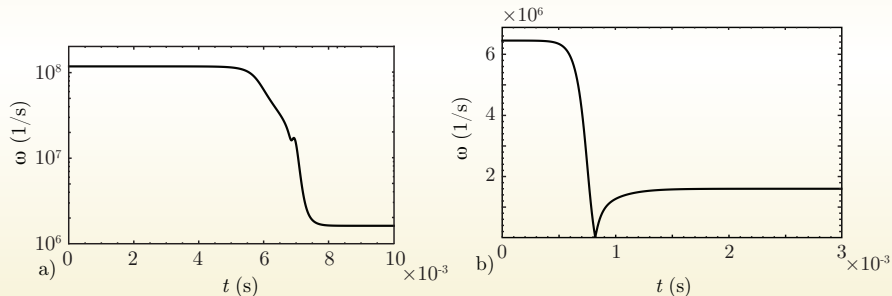
Volumes are rotating everywhere on the CIMs during the approach to physical equilibrium.

Tangential stretching rates along the CIMs

- **Red**: negative tangential stretching along the CIM
- Black: positive tangential stretching along the CIM
- In general, there is positive stretching near the saddle, and negative stretching near the physical sink.
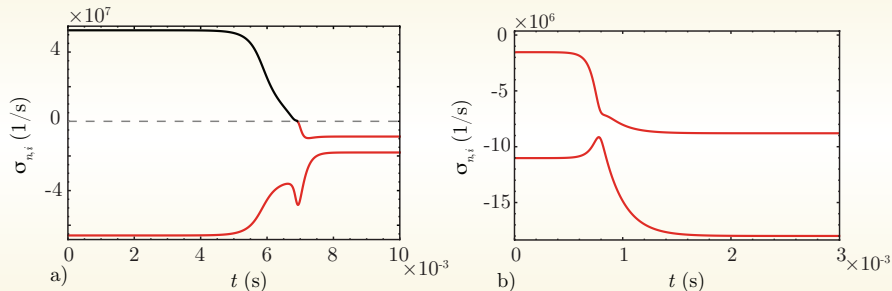
- Red: negative normal stretching along the CIM
- Black: positive normal stretching along the CIM
- There is one component of positive normal stretching near one saddle, otherwise the normal stretching is negative.
- The possibility of a non-attractive CIM exists where there is positive normal stretching.

Ratio of rotation to normal stretching along the CIMs
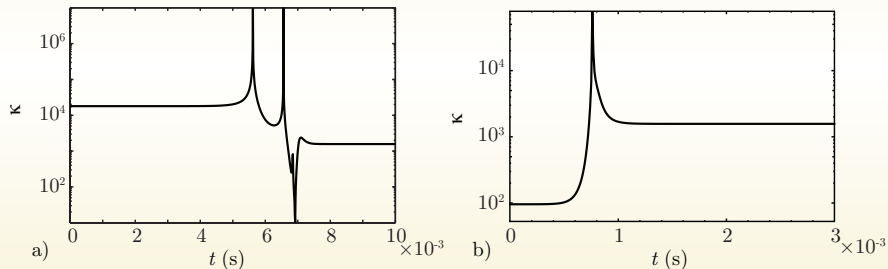

a) and b) plots of μ versus t (s)
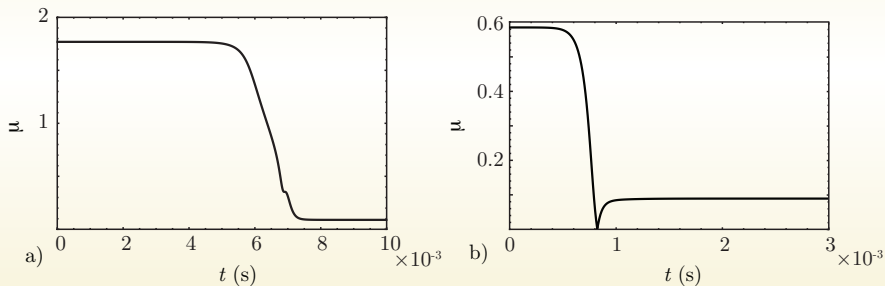
For the portion of the CIM with positive normal stretching, local rotation is able to compensate, thus rendering the CIM everywhere attracting. These CIMs are thus ACIMs.
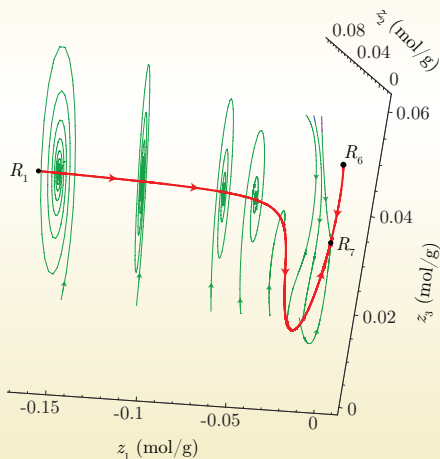
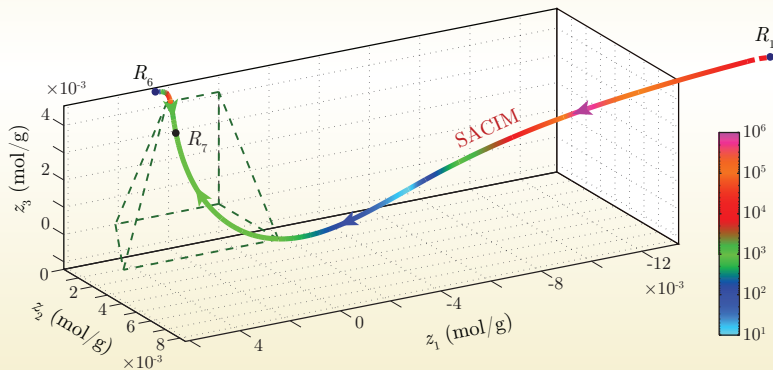Trajectories near the CIM rotate in a plane onto the CIMs.

These ACIMs are SACIMs

The ratio κ of minimum normal stretching to tangential stretching is large, guaranteeing rapid attraction the ACIM, rendering it to be a SACIM.

The SACIM is colored by its degree of attractiveness, κ.

Comment

As shown in our 2013 workshop paper and in our 2015 *J. Math. Chem.* paper, for general systems, one may be able to identify a CIM, but there is no guarantee of a SACIM. Local rotation, associated with the *non-normality* (see Trefethen and Embree, 2005) of the system may be such that trajectories far from equilibrium are *repelled* from the CIM. There are no physics-based proofs of slowness or attractiveness away from equilibrium.

Conclusions

- A SACIM represents a "gold standard" for a reduced kinetics model for a spatially homogeneous reactive system.
- SACIMs can be identified in physically-based gas phase kinetics systems.
- SACIM identification yields a wealth of quantitative information about time scales of various system dynamics.
- SACIM diagnosis is arduous for small systems, unclear for systems of higher dimension than three, and presently impractical for engineering combustion applications.