Dynamical System Analysis of Ignition in Reactive Systems

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Outline of the Talk

• CSP Basic Concepts
• Applications of CSP diagnostics
• A Toy Model for Ignition
• Illustration of the new Stretching Rate diagnostics
• Applications of Stretching Rate diagnostics in Ignition
Auto-ignition of Hydrocarbon Mixtures

A detailed mathematical model of a batch reactor can produce a number of “natural” outputs and observables such as:

**Time Histories**

- **Propane/Air --- Petersen, et al.**
  - (118 species, 665 reactions)

- **N-Heptane/Air Auto-Ignition - Curran**
  - (561 specs/2600 reacs)

**Ignition Delay Time Sensitivity to Pressure, Equivalence Ratio**

\[ \varphi = 1, \ p_0 = 6.5/13.5/40 \text{ bar (top to bottom)} \quad p_0 = 13.5 \text{ bar, } \varphi = 0.5/1.0/2.0 \text{ (top to bottom)} \]

- Solid thick lines – detailed mechanism; open symbols – comprehensive skeletal mechanisms; filled symbols – states for which CSP inputs have been computed.

**Question:** how can we “extract” more knowledge from the computed datasets?

**Answer:** by approaching the evolution of the kinetics using concepts and tools developed for the analysis of nonlinear dynamical systems.
CSP Basic Concepts
(D.A. Goussis, S.H. Lam)
Computational Singular Perturbation (CSP) Method

\[ \frac{dx}{dt} = g(x) \]

Change of Frame of Reference (Ortho-normal Basis)
\[ I = a_i b^i; \quad b^i \cdot a_j = \delta_j^i \quad i, j = 1, N \]

Example
- \( a_i \) right eigenvector of Jacobian Matrix \( J \) of \( g(x) \)
- \( b^i \) left eigenvector

Existence of a Spectral Gap between mode \( M \) and \( M+1 \)

Fast/Slow Decomposition
\[ I = a_r b^r + a_s b^s \quad r = 1, M \quad s = M + 1, N \]

\[ \frac{dx}{dt} = I g(x) = (a_r b^r + a_s b^s)g(x) = a_r f^r + a_s f^s \]

with mode amplitude defined as \( f^j = b^j g(x) \)

\[ f^r \approx e^{-\lambda_r t} \quad \Rightarrow \quad t \gg O(\tau_r = \lambda_r^{-1}) \quad \Rightarrow \quad f^r \approx 0 \]

\[ \begin{cases} \frac{dx}{dt} = a_r f^r + a_s f^s \\ f^r(x) \equiv b^r \cdot g(x) \approx 0 \end{cases} \]

CSP Projector Matrix \( P = I - a_r b^r = a_s b^s \)

\[ \frac{dx}{dt} \approx a_s f^s = a_s (b^s \cdot g(x)) = a_s (b^s \cdot g(x)) = (I - a_r b^r)g(x) = P g(x) \]

\[ a_r f^r = a_r (b^r \cdot g(x)) = (I - P)g(x) \approx 0 \]

Slow Dynamics (ODE): \( \frac{dx}{dt} \approx P g(x) \)

Equation of state (AE): \( (I - P)g(x) \approx 0 \)

\[ M \text{ (spectral gap) is the dimension of the fast subspace} \]

In general, it is a function of space and time

\[ \tau_{M+1} \sum_{r=1,M} a_r f^r < \epsilon^i \]

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CSP Slow/Fast Importance Indices of the action of a Reaction to the evolution of a Species

Slow (Reduced) Dynamics

\[ \frac{d y^i}{d t} \approx P \ g = \left( \sum_{s=M+1}^{N_s} a^i_s b^s \right) \left( \sum_{k=1,N_r} S_k r^k \right) ; \quad i \in (\text{Slow Species Set}) \]

\[ \{I_{\text{slow}}\}^i_k = \frac{U^i_{kR^k}}{\sum_{j=1,N_r}^{N_r} |U^i_{jR^j}|} ; \quad U^i_k = \sum_{s=M+1,N} a^i_s (b^s \cdot S_k) \]

Fast Subspace (Approximate Slow Invariant Manifold)

\[ (I - P) \ g = \left( \sum_{r=1}^{M} a^i_r b^r \right) \left( \sum_{k=1,N_r} S_k r^k \right) \approx 0 ; \quad i \in (\text{CSP Radicals Set}) \]

\[ \{I_{\text{fast}}\}^i_k = \frac{W^i_{kR^k}}{\sum_{j=1,N_r}^{N_r} |W^i_{jR^j}|} ; \quad W^i_k = \sum_{r=1,M} a^i_r (b^r \cdot S_k) \]
CSP Indices: Participation Index
of the action of a Reaction to the evolution of a Mode

A suitable normalization of the $N_r$ additive terms in:

$$f^r = b^r \cdot \left[ \sum_{k=1}^{2 \times N_r} S_k r^k \right] \approx 0, \quad r = 1, M$$

points out which reactions contribute the most in the occurring cancellations and affect the dynamics of the $r$-th mode.

*Mode Participation Index*: $P^r_k = \frac{b^r \cdot S_k r^k}{\sum_{j=1,2 \times N_r} |b^r \cdot S_j r^j|}$ (no sum on $k$; $k = 1, 2N_r$; $r = 1, M$).

By definition, each $P^r_k$ varies between 0 and 1.

If $|P^r_k|$ is small, the $k$-th reaction contributes very little in the cancellations in $f^r = 0$ and thus can be neglected.

The reactions identified as important with the Mode Participation Index, if perturbed, will cause a significant and direct change in the manifold; the response of the trajectory will be also significant and fast.
CSP Indices: Time Scale Participation Index
of the action of a Reaction to the development of a time scale

What are the reactions responsible for the appearance of a certain time scale in the dynamics of the system?

**Time Scale Participation Index:**

\[
J^n_k = \frac{(b^n \cdot S_n)(G^n \cdot a_k)}{\sum_{j=1,N_p} |(b^k \cdot S_j)(G^j \cdot a_k)|}
\]

where \( G^n = \text{grad}(r^n) \)

The Time Scale Participation expresses the percent contribution of the \( n \)-th reaction in originating the \( k \)-th time scale.

- When the \( n \)-th stoichiometric vector \( S_n \) has no projection on the \( k \)-th direction (\( b^k \cdot S_n = 0 \)), then this reaction contributes nothing to the \( k \)-th time scale \( \tau_k \).
- When the rate of change vector of the \( n \)-th reaction \( G^n \) has no component on the \( k \)-th direction (\( G^n \cdot a_k = 0 \)), then this reaction contributes nothing to the \( k \)-th time scale \( \tau_k \).
- An elementary reaction might appear as significant in more than one time scales.
How to extend the CSP Indices to PDEs

\[ \tilde{h}^i = \rho \left[ \sum_{n=1,N} b_n^i L_c^n + \sum_{n=1,N} b_n^i L_d^n + \sum_{k=1,K} b^i \cdot WS_k \frac{R_k}{\rho} \right] \quad i=1,N \]

- **Convection**
  \[ A_{c,n}^i = \rho b_n^i L_c^n \quad I_c^i = A_{c,n}^i / A^i \]

- **Diffusion**
  \[ A_{d,n}^i = \rho b_n^i L_d^n \quad I_d^i = A_{d,n}^i / A^i \]

- **Chemistry**
  \[ A_{s,k}^i = b^i \cdot WS_k R_k \quad I_{s,k}^i = A_{s,k}^i / A^i \]

\[ A^i = \sum_{n=1,N} |\rho b_n^i L_c^n| + \sum_{n=1,N} |\rho b_n^i L_d^n| + \sum_{k=1,K} |b^i \cdot WS_k R_k| \]

\[ A_{\text{tran}}^i \quad A_{\text{chem}}^i \]
Applications of CSP Diagnostics
Applications of CSP Diagnostics

- Steady Detonations [Valorani, Goussis, ‘96]
- Transient Laminar Flames [Valorani, Goussis, Najm, ‘03]
- Premixed Steady Flames [Goussis, Skevis, ‘04], [Creta, ‘04]
- Ignitions [Lee, 2004], [Creta, ‘04], [Donato, ‘06]
- Biological Systems [Goussis, ‘06]
- Edge Flames in Methane & n-Heptane [Najm, Valorani, ’07,’11]
- Auto-ignition in HCCI Systems [Gupta, Im, Valorani, ‘12]
- ....
An automatic procedure for the simplification of chemical kinetic mechanisms based on CSP
M Valorani, F Creta, DA Goussis, JC Lee, HN Najm
Combustion and flame 146 (1), 29-51
CH4/Air Edge Flame: CSP Time Scales and SIM Dimension

- Fastest time scale: \( \tau_1 \sim \mathcal{O}(1 \text{ ns}) \)
- SIM dimension \( M \):  
  \( \sim 4 \) in the premixed reaction zone  
  \( \sim 40 \) in the diffusion flame behind the edge flame
- Driving time scale (fastest of the slow): \( \tau_{M+1} \)  
  \( \sim \mathcal{O}(10 \text{ ns}) \) in the premixed reaction zone

Analysis of methane–air edge flame structure
HN Najm, M Valorani, DA Goussis, J Prager
Combustion Theory and Modelling 14 (2), 257-294
CH4/Air Edge Flame: HO2 Importance Indices along $\xi=0.075$

- Two minimum plateaus of $M$ coincide with maxima in $w_{HO2}$

- Cold inflow:
  Convection $< 0$; Diffusion $> 0$

- Preheat region/First layer:
  Convection $\leq 0$; Diffusion $\geq 0$
  R170: $CH_3O + O_2 \rightarrow HO_2 + CH_2O$ $> 0$
  R119: $HO_2 + CH_3 \rightarrow OH + CH_3O$ $< 0$

- Main Premixed front/Second layer:
  R168: $HCO + O_2 \rightarrow HO_2 + CO$ $> 0$
  R119: $HO_2 + CH_3 \rightarrow OH + CH_3O$ $< 0$

*WSS/CI Paper*, #07F-18, 2007
Auto-Ignition and Time Scale Analysis

The role of eigenvalues with positive real part
Positive Eigenvalues are characteristic of explosive systems

Ignition in Constant Volume Batch Reactor
\(T_0=750\text{K} \; p_0=1\text{ atm},\) stoichiometric, non-diluted air

Methane/Air GRI 3.0 (53 spcs; 325 rcns)

Propane/Air Petersen et al. (118 spcs; 665 rcns)

n-Heptane/Air Curran et al. (560 spcs; 2538 rcns)

Heptane/Air Edge Flame in Partially-premixed Mixing Layer

\[ \log_{10}(\text{Real part eigenvalue}) \text{ [1/s]} \]
Three Goals

• We look for a simple model of ignition to extract the essence from the complexity of real fuel kinetics

• We want to apply CSP ideas to analyze both the simple and the real fuel kinetics

• We want to study ignition by blending CSP ideas with concepts developed in the geometrical analysis of nonlinear dynamical systems
A Toy Model for Ignition
A Toy Model of Isothermal Chain-Branching Ignition
(Williams, 1985)

Initiation Reaction: \( R \rightarrow C \) \( k_i \)
Propagation Reaction: \( R + C \rightarrow \alpha \ C + P \) \( k_p \)
Termination Reaction: \( C \rightarrow P \) \( k_t \)

\( R \): reactant
\( C \): intermediate species (radical species)
\( P \): product
\( \alpha \): branching factor
\( \alpha = 1 \), linear propagation
\( \alpha > 1 \), branching propagation

Auxiliary parameters
\( \varepsilon = \frac{k_i}{k_p \ r_0} \) nondimensional rate constant of initiation reaction
\( \gamma = \frac{k_t}{k_p \ r_0} \) nondimensional rate constant of termination reaction

Non Dimensional Form
(Creta, et al., 2007)

\[
x_1'(t) = -x_1(t) - x_1(t) x_2(t)
\]
\[
x_2'(t) = \frac{1}{\varepsilon} \left( x_1(t) + (\alpha - 1) x_1(t) x_2(t) - \gamma \ x_2(t) \right)
\]
\( x_1(0) = x_{1,0} \)
\( x_2(0) = 0 \)
Portraits of Toy Model Trajectories
Cartesian and Poincaré Projection Phase Spaces

Two-dimensional Poincaré Projection

\[ x_1 = \frac{u_1}{\sqrt{1 - u_1^2 - u_2^2}} \quad x_2 = \frac{u_1}{\sqrt{1 - u_1^2 - u_2^2}} \]

\[ u_1 = \frac{x_1}{\sqrt{1 + x_1^2 + x_2^2}} \quad u_2 = \frac{x_2}{\sqrt{1 + x_1^2 + x_2^2}} \]

Mapping from

\((x_1, x_2)\)-plane

\Rightarrow

\((u_1, u_2)\)-plane

Red Symbols are Stationary Points at Infinity
Poincarè Projected System at Infinity

Stationary Condition at Infinity

\[
\cos(\theta)\sin(\theta)\left((\alpha - 1)\cos(\theta) + \varepsilon \sin(\theta)\right) = 0
\]

Stationary Points at Infinity

\[
\vartheta_{ss} = \left\{ 0, \frac{\pi}{2}, \pi, \frac{3\pi}{2}, \frac{2}{\alpha - 1} \arctan\left(\varepsilon - \sqrt{1 - 2\alpha + \alpha^2 + \varepsilon^2}\right), \frac{2}{\alpha - 1} \arctan\left(\varepsilon + \sqrt{1 - 2\alpha + \alpha^2 + \varepsilon^2}\right) \right\}
\]

Bifurcation of Stationary Points at Infinity

\[
\begin{align*}
\alpha &< 1 \\
P(\vartheta = 0) &\text{ is stable} \\
P(\vartheta = \frac{3}{2}\pi) &\text{ is unstable}
\end{align*}
\]

\[
\begin{align*}
\alpha &> 1 \\
P(\vartheta = 0) &\text{ is unstable} \\
P(\vartheta = \frac{3}{2}\pi) &\text{ is stable}
\end{align*}
\]

\[
\alpha = 1 \pm 2 \times 10^{-3} \quad \varepsilon = 0.01
\]
Sub and Super Critical Ignition Regimes

\[ x_1'(t) = -x_1(t) - x_1(t)x_2(t) \]
\[ x_2'(t) = \frac{1}{\epsilon} \left[ (x_1(t) + (\alpha-1)x_1(t)x_2(t) - \gamma \cdot x_2(t) \right] \]

**x2 is QSSA**
\[
\frac{x_2'[t]}{\epsilon} = \frac{x_1[t] - \gamma \cdot x_2[t] + (-1 + \alpha) \cdot x_1[t] \cdot x_2[t]}{\epsilon} = 0
\]

**x2 = SIM(x1)**
SIM is an heteroclinic orbit connecting the stable fixed point and one of the unstable stationary point at infinity (theta=\(\pi/2\))
\[
x_2 = \frac{x_1}{x_1 - x_1 \cdot \alpha + \gamma} \quad 0 < x_i < x_i^* = \frac{\gamma}{\alpha-1}
\]

**Ignition Regimes**
\[
x_i^* = \frac{\gamma}{\alpha-1} > x_i(0) \quad \text{sub-critical ignition}
\]
\[
x_i^* = \frac{\gamma}{\alpha-1} < x_i(0) \quad \text{super-critical ignition}
\]
Time Scale Analysis of the Toy Model

Jacobian

\[
\begin{pmatrix}
-1 - x_2 & -x_1 \\
\frac{1 + x_2 (-1 + \alpha)}{\varepsilon} & \frac{x_1 - x_1 \alpha + \gamma}{\varepsilon}
\end{pmatrix}
\]

Eigenvalues of Jac

\[
\begin{pmatrix}
-\frac{x_1 - x_1 \alpha + \gamma + \varepsilon + x_2 \varepsilon}{\varepsilon} + \sqrt{-4 \left(2 x_1 - x_1 \alpha + \gamma + x_2 \gamma\right) \varepsilon + (x_1 - x_1 \alpha + \gamma + \varepsilon + x_2 \varepsilon)^2} \\
-\frac{x_1 - x_1 \alpha + \gamma + \varepsilon + x_2 \varepsilon}{\varepsilon} - \sqrt{-4 \left(2 x_1 - x_1 \alpha + \gamma + x_2 \gamma\right) \varepsilon + (x_1 - x_1 \alpha + \gamma + \varepsilon + x_2 \varepsilon)^2}
\end{pmatrix}
\]

Determinant of Jac

\[
\frac{2 x_1 - x_1 \alpha + \gamma + x_2 \gamma}{\varepsilon}
\]

Trace of Jac

\[
-\frac{x_1 - x_1 \alpha + \gamma + \varepsilon + x_2 \varepsilon}{\varepsilon}
\]
Significant Loci of Ignition in Phase Space

**Ignition Regimes**

\[ x_1^* = \frac{\gamma}{\alpha - 1} > x_1(0) \]  
sub-critical ignition

\[ x_1^* = \frac{\gamma}{\alpha - 1} < x_1(0) \]  
super-critical ignition

Loci of zero imaginary part of eigenvalues (Black Dashed Lines)

Locus of Zero Trace of Jac (Green Solid Line)

SIM Approx by QSSA on x2 (Red Solid Line)
Sub, Critical, and Super Critical Ignition Regimes

\[ x_i^* = \frac{\gamma}{\alpha - 1} > x_i(0) = 1 \quad \text{sub-critical ignition regime} \]

\[ x_i^* = \frac{\gamma}{\alpha - 1} < x_i(0) = 1 \quad \text{super-critical ignition regime} \]
Toy model and complex kinetics feature similar dynamics in term of eigvals !!!

Red lines: supercritical
Blue lines: subcritical

Super-critical ignition regime -> crossing the complex eigvals region (from pos to cmplx to neg eigvals)
Sub-critical ignition regime -> no crossing the complex eigvals region (no pos eigvals)

Equilibrium point always attained following the SIM (neg eigvals)
Eigenvector Dynamics
Supercritical Ignition Regime

Real eigenvectors become co-linear with vector field while entering and leaving the region of complex eigenvalues, where no timescales gap exists

(blue: slow eigenvector; red: fast eigenvector)
Linearized Dynamics from within cmplx region

\[
\begin{aligned}
\frac{d(\delta x)}{d\tau} &= g(\bar{x}) + J(\bar{x})\delta x \\
\delta x(\tau = 0) &= 0
\end{aligned}
\]

\[x(t + \tau) = \bar{x}(t) + \delta x(\tau)\]

\[\alpha = 2 \quad \varepsilon = 0.01 \quad \gamma = 0.5\gamma_{cr}\]

Linearized dynamics is a spiraling motion aiming at infinity/fixed point

Pos/neg real part of complex eigval controls the growth rate of vector field module

Imaginary part control the rotation rate of the vector field direction
CSP Analysis
Characteristic time scale

The real part of the cmplx eigenvalue crossing the zero cannot be a proper measure of the local time scale.

In the cmplx region, only one time scale is active and might be identified by taking the inverse of the MODULUS [!!] of the cmplx eigenvalue.

The determinant is never zero (Jacobian never singular), and its max corresponds to the max of the cmplx eigenvalue modulus.

CSP defines the local characteristic scale on the basis of the heuristic criterion

$$\delta y_{err} \sim \tau_{M+1} \sum_{r=1,M} a_r f^r$$

At $t = 0.32$, the local characteristic scale abruptly switches from the fast to the slow scale, when the CSP fast mode amplitude (red) equals the slow mode amplitude (blue).

The trajectory stays nearly tangent to the fast eigenvector until $t=0.345$, when the SIM is reached.

There the trajectory becomes tangent to the slow eigenvector (blue).
A Few Intermediate Conclusions

1. Toy model and complex kinetics feature similar dynamics in term of eigvals !!!
2. Super-critical ignition regime -> crossing the complex eigvals region (from pos to cmplx to neg eigvals);
3. Sub-critical ignition regime -> no crossing the complex eigvals region (no pos eigvals)
4. Real eigenvectors become co-linear with vector field while entering and leaving the region of complex eigenvalues, where no timescales gap exists
5. Linearized dynamics starting from cmplx region is a spiraling motion aiming at infinity/fixed point
6. SIM Approx by QSSA on x2 is an heteroclinic orbit connecting the stable fixed point and the unstable stationary point at infinity (theta=Pi/2)
7. In the complex region, only one time scale is active and might be identified by taking the inverse of the MODULUS [!!] of the cmplx eigenvalue
8. In the complex region, the max value of the cmplx eigenvalue modulus corresponds to the max value of the determinant
9. The determinant is never zero and thus the Jacobian is never singular, even when the real part of the eigvals crosses the zero
10. The CSP local characteristic time scale abruptly switches from the fast to the slow scale when the CSP fast mode amplitude (red) equals the slow mode amplitude (blue)

Let us now take a different perspective to analyze the same dynamics, on the basis of the Stretching Rate Analysis
Stretching Rate Diagnostics

(M. Valorani and S. Paolucci)
Stretching Rate Analysis

\[ \frac{dz}{dt} = g(z) \quad z(0) = z_0 \]

State vector \( z \): species concentration vector
Vector field: \( g(z) = S \cdot r(z) \) with the species reaction rate vector
   \( S \): stoichiometric coefficients matrix
   \( r \): net reaction rates vector
\( z_0 \): initial concentrations vector

Consider a nearby trajectory:
\[ z_1 = z_0 + \varepsilon \]

Define a scaled vector distance between the two as:
\[ \tilde{v} := \lim_{\varepsilon \to 0} \left( \frac{z_1 - z_0}{\varepsilon} \right) \]

Vector Dynamics
\[ \frac{d\tilde{v}}{dt} = Jac_g(z)\tilde{v}(t) \quad \tilde{v}(0) = 1 \quad Jac_g := \frac{\partial g(z)}{\partial z} \]

Vector Norm Dynamics
\[ \frac{d\|\tilde{v}\|}{dt} = \frac{\tilde{v}^T Jac_g \tilde{v}}{\|\tilde{v}\|^2 \|\tilde{v}\|} \quad \|\tilde{v}\|(0) = 1 \]

Stretching Rate along any \( \tilde{u} \)
\[ \omega_{\tilde{u}} := \tilde{u}^T Jac_g \tilde{u} \quad \tilde{u} := \frac{\tilde{v}(t)}{\|\tilde{v}\|} \]

This stretching rate is NOT related to the flame stretch concept or any stretch rate associated to the kinematic field.
Definition of Tangential Stretching Rate along $g$

$$\omega_\tau := \tilde{\tau}^T J \tilde{\tau}$$

where $\tilde{\tau} := \frac{g}{|g|}$

Stretching Rate along (unit norm) eigen-directions

$$\omega_{a_j} := a_j^T J a_j$$

Easily proved: after CSP expansion of $J = A \Lambda B$, we obtain:

$$\omega_{a_j} = a_j^T J a_j = a_j^T A \Lambda B a_j = a_j^T \sum_{i=1}^{N} a_i \lambda_i (b^i . a_j) =$$

$$= a_j^T \left( \sum_{i=1}^{N} a_i \lambda_i \delta^i_j \right) = (a_j^T . a_j) \lambda_j = \lambda_j |a_j|^2 = \lambda_j$$

The stretching rate along the direction $a_j$ coincides with the eigenvalue $\lambda_j$ corresponding to the eigen-direction $a_j$, e.g., a unit vector along $a_j$ is modified by a factor $\lambda_j$ by the action of the linearized dynamics represented by $J$. 

Stretching Rate Analysis combined with CSP decomposition

Valorani and Paolucci(2012), to appear
TSR can be recast after CSP expansion of $J = A \Lambda B$ and $g = \sum a_i f^i$

$$\omega_\tau := \tilde{\tau}^T J \tilde{\tau} \quad \text{where} \quad \tilde{\tau} = \frac{g}{|g|} = \frac{1}{|g|} \sum_{i=1}^{N} a_i f^i, \quad \text{with} \quad f^i := b^i . g \quad \text{and} \quad g = \sum_{i=1}^{N} a_i f^i$$

$$\omega_\tau = \tilde{\tau}^T J \tilde{\tau} = \frac{1}{|g|^2} \left( g^T A \Lambda B g \right) = \frac{g^T}{|g|^2} \sum_{i=1}^{N} a_i \lambda_i (b^i . g) = \frac{g^T}{|g|^2} \sum_{i=1}^{N} a_i \lambda_i f^i = \frac{1}{|g|^2} \sum_{i=1}^{N} (g^T \cdot a_i) \lambda_i f^i$$

$$g^T \cdot a_i = \left( \sum_{k=1}^{N} a_k f^k \right)^T \cdot a_i = \sum_{k=1}^{N} f^k \left( a_k^T \cdot a_i \right)$$

where $a_k^T \cdot a_i$ is the direction cosine between $a_i$ and $a_k$ (with $|a_k^T \cdot a_i| \leq 1$)
TSR is a weighted sum of the eigenvalues

\[ \omega_T = \frac{1}{|g|^2} \sum_{i=1}^{N} (g^T \cdot a_i) \lambda_i f_i^i = \sum_{i=1}^{N} \left( \frac{1}{|g|^2} \sum_{k=1}^{N} f^k (a_k^T \cdot a_i) \right) \lambda_i f_i^i = \]

\[ = \sum_{i=1}^{N} \left( \frac{f_i}{|g|^2} \sum_{k=1}^{N} f^k (a_k^T \cdot a_i) \right) \lambda_i = \sum_{i=1}^{N} W_i \lambda_i \]

\[ W_i := \frac{f_i g^T \cdot a_i}{|g|} = \frac{f_i}{|g|} \sum_{k=1}^{N} f^k (a_k^T \cdot a_i). \]

Weights depend on:

- mode amplitudes \( f^i \)
- relative orientation of vector field \( g \) wrt eigen-directions \( a_i \)
\[
\omega_\tau = \frac{1}{|g|^2} \sum_{i=1}^{N} (g^T \cdot a_i) \lambda_i f^i = \sum_{i=1}^{N} \left( \frac{1}{|g|^2} \sum_{k=1}^{N} f^k (a_k^T \cdot a_i) \right) \lambda_i f^i = \sum_{i=1}^{N} \left( \frac{f^i}{|g|^2} \sum_{k=1}^{N} f^k (a_k^T \cdot a_i) \right) \lambda_i = \sum_{i=1}^{N} W_i \lambda_i
\]

\[
W_i := \frac{f^i}{|g|} \frac{g^T \cdot a_i}{|g|} = \frac{f^i}{|g|} \sum_{k=1}^{N} f^k (a_k^T \cdot a_i).
\]

where \(a_k^T \cdot a_i\) is the direction cosine between \(a_i\) and \(a_k\) (with \(|a_k^T \cdot a_i| \leq 1\))

\(\omega_\tau\) can, at most, takes the value corresponding at the circumstance (never verified) of all \(a_i\) being co-linear with \(g\), that is:

\[
\frac{g^T \cdot a_i}{|g|} = \sum_{k=1}^{N} f^k (a_k^T \cdot a_i) \leq \frac{f^i}{|g|}
\]

then

\[
\omega_\tau \leq \sum_{i=1}^{N} \left( \frac{f^i}{|g|} \right)^2 \lambda_i
\]

Note that because of the quadratic term, the sign of \(\omega_\tau\) relies on that of the prevailing eigenvalues.
Let us consider three typical situations:

- let us consider the case of \( \{ f^r \approx 0 \}_{r=1,M} \), that is, the state point lies on a \((N-M)\)-dimensional SIM; after ordering the terms in the summation by the descending value of the module of the eigenvalue, we find

\[
\omega_r = \sum_{s=M+1}^{N} \left( \frac{f_s}{|g|} \right)^2 \lambda_s + \sum_{r=1}^{M} \left( \frac{f_r}{|g|} \right)^2 \lambda_r \approx \sum_{s=M+1}^{N} \left( \frac{f_s}{|g|} \right)^2 \lambda_s
\]

In this case, the tangential stretching rate is contributed only by slow scales.

- let us consider the case of \( \{ f^s \approx 0 \}_{s=K,N} \), that is, the state point is along a fast fiber (away from a SIM), for which we obtain

\[
\omega_r = \sum_{s=K}^{N} \left( \frac{f_s}{|g|} \right)^2 \lambda_s + \sum_{r=1}^{K} \left( \frac{f_r}{|g|} \right)^2 \lambda_r \approx \sum_{r=1}^{K} \left( \frac{f_r}{|g|} \right)^2 \lambda_r
\]

In this case, the tangential stretching rate is contributed only by fast scales.

- let us consider the case of \( \{ f^r \approx 0 \}_{r=1,M} \) and \( \{ f^s \approx 0 \}_{s=K,N} \), with \( M < K \).

\[
\omega_r = \sum_{s=K}^{N} \left( \frac{f_s}{|g|} \right)^2 \lambda_s + \sum_{a=M+1}^{K-1} \left( \frac{f_a}{|g|} \right)^2 \lambda_a + \sum_{r=1}^{M} \left( \frac{f_r}{|g|} \right)^2 \lambda_r \approx \sum_{a=M+1}^{K-1} \left( \frac{f_a}{|g|} \right)^2 \lambda_a
\]

In this case, the tangential stretching rate is contributed only by the active scales, e.g., if some \( \lambda_{a+} \) is positive, it is likely that the corresponding \( f^{a+} \) will be the largest of all active mode amplitudes. In this case \( \omega_r \) will be mostly affected by \( \lambda_{a+} \).
TSR Decomposition
Three scales

Let us consider the case of \( \{ f^r \approx 0 \}_{r=1,M} \) and \( \{ f^s \approx 0 \}_{s=K,N} \), with \( M < K \).

\[
\omega_\tau = \sum_{s=K}^{N} \left( \frac{f^s}{|g|} \right)^2 \lambda_s + \sum_{a=M+1}^{K-1} \left( \frac{f^a}{|g|} \right)^2 \lambda_a + \sum_{r=1}^{M} \left( \frac{f^r}{|g|} \right)^2 \lambda_r \approx \sum_{a=M+1}^{K-1} \left( \frac{f^a}{|g|} \right)^2 \lambda_a
\]

\( \omega_{a_i} \equiv \lambda_i \)

\[
\omega_\tau = \sum_{i=1,N} W_i \lambda_i \quad W_i := \frac{f^i}{|g|} g^T \cdot a_i \sim O \left( \frac{f^i}{|g|} \right)^2 \quad f^i := b^i \cdot g
\]

Three scales:
1) \( \omega_\tau \) most energy containing scale
2) \( \lambda_{K-1} \) slowest scale contributing to the making of \( \omega_\tau \)
3) \( \lambda_{M+1} \) fastest scale contributing to the making of \( \omega_\tau \)

Scales contributing to the making of \( \omega_\tau \) are in the range \( \{ \lambda_{K-1}, \lambda_{M+1} \} \)
The tangential stretching rate computed on the basis of the original definition \( \omega_\tau := \tilde{\tau}^T J \tilde{\tau} \) will be largely inaccurate when complex conjugate eigenvalues occur.

It is expected that the driving scale will be a weighted average of the module of the \( N \) (possibly complex) eigenvalues. This implies scaling the weights so to have unit norm.

The suggested formula for \( \omega_\tau \) at any state value \( x \) reads:

\[
\omega_\tau[x] := \sum_{i=1}^{N} \tilde{W}_i[x] \text{Abs}[\lambda_i[x]]
\]

with

\[
W_i := \frac{f^i}{|g|} \frac{g^T \cdot a_i}{|g|}
\]

and

\[
\tilde{W}_i := \frac{W_i}{\sum_{j=1, N_s} |W_j|}
\]

where it is intended that all complex conjugate eigenvectors pairs have been converted into real numbers with the usual transformation.
Lu, et al., introduced a chemical explosive mode (CEM) scale defined as

$$\tau_{chem} = \left| \frac{1}{\lambda_{a+}} \right|$$

where $\lambda_{a+}$ is the fastest eigenvalue with positive real part in the system.

Our analysis indicates that the proper characteristic chemical time scale is

$$\tau_{chem} = \left| \frac{1}{\omega_{\tau}} \right|$$

This scale

(i) is the most relevant one during both the explosive and relaxation regimes,

(ii) is always automatically identified without the need of any ad-hoc assumption

(iii) recovers the CEM scale when:

$$\tau_{chem} = \left| \frac{1}{\omega_{\tau}} \right| = \left| \frac{1}{\sum_{i} W_{i} \lambda_{i}} \right| = \left| \frac{1}{\lambda_{a+}} \right|$$

if $W_{a+} = 1$ and $W_{i \neq a+} = 0$

when all modes but $i = a+$ have zero amplitude and $a_{a+}$ is co-linear with the vector field.
Comparing CSP vs TSR vs CVODE
Auto-ignition (GRI 3.0)

1. The fastest of the modes contributing to TSR coincides with the fastest of the slow CSP modes
2. TSR coincides first with the fastest of the pos eigenvalues (the most energy containing mode) and later with the fastest of the slow CSP modes
3. CVODE’s integration time step envelopes the fastest of the modes contributing to TSR
Participation indices related to tangential stretching rate

CSP PI index between reaction & mode

\[ f^i = b^i \cdot g = \sum_{k=1,Nr} (b^i \cdot S_k)r^k \]

\[ P_k^i = \frac{|(b^i \cdot S_k)r^k|}{\sum_{k'=1,Nr} |(b^i \cdot S_{k'})r^{k'}|} \]

PI index between mode & TSR

\[ \omega_\tau = \sum_{i=1,N} \tilde{W}_i |\lambda_i| \]

\[ P_{i,0\tau} = \frac{|\tilde{W}_i| |\lambda_i|}{\sum_{j=1,N} |\tilde{W}_j| |\lambda_j|} \]

PI index between reaction & TSR

\[ P_{k,0\tau} = P_{i,0\tau} P_k^i \]

Modes with a large \( P_{i,0\tau} \) are the most contributing to the \( \omega_\tau \) scale (energy containing)

Reactions with a large \( P_k^i \) are the most contributing to the i-th mode

Reactions with a large \( P_{k,0\tau} = P_{i,0\tau} P_k^i \) are the most contributing to the \( \omega_\tau \) scale
TSR Break-down
Participation Index

npick = 54;

npick = 90;

mode amplitude
direction cosine

weight

log(eigval)

log(eigval)

log(eigval)

KAUST Seminar, September 2012
TSR analysis of Gri-1.2, Propane, and n-Heptane Autoignition

Autoignition iso-choric batch reactor:
$T_0=1000K$ $p_0=1$ atm, stoichiometric, non-diluted air.

Following Bisetti’s conjecture, we observe that the most energetic scale in 3 fuels takes a max value of about the same magnitude [$\tau \sim 1/(2 \times 10^5) s \sim 50 \times 10^{-6} s = 50$ microsec]
TSR analysis of Gri-1.2, Propane, and n-Heptane Autoignition

Autoignition iso-choric batch reactor:
T0=1000K  p0=1 atm, stoichiometric, non-diluted air.

The most energetic scale in 3 fuels takes a max value of about the same magnitude \( [\tau \approx 1/(2 \times 10^5)] \) s \( \approx 50 \times 10^{-6} \) s = 50 microsec

TSR (red symbols) captures the most energetic scale at all times

The modes mostly contributing to TSR are in green
Comparison CSP-TSR: Propane

PI index between mode & TSR

\[ \omega_\tau = \sum_{i=1,N} \tilde{W}_i |\lambda_i| \]

\[ P_\omega^\tau = \frac{|\tilde{W}_i |\lambda_i|}{\sum_{j=1,N} |\tilde{W}_j |\lambda_j|} \]

The first non exhausted mode indicated by CSP has a very low PI.

Modes with the highest PI are in the “middle” of the active subspace.
Reaction Index: Propane

PI index between reaction & TSR

\[ P_k^{\omega} = P_i^{\omega}; P_k^i \]

The reactions contributing to the slowest positive eigvals do not contribute to TSR.
The reactions contributing to the fastest positive eigvals do contribute to TSR.
There are reactions contributing to TSR which do not contribute to positive eigvals.
### Table 1:
List of important reactions at iter = 30 (omega tau = 5.52714)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2+CH2O &lt;=&gt; HO2+HCO</td>
<td>32 0.040129</td>
</tr>
<tr>
<td>H+O2 &lt;=&gt; O+OH</td>
<td>38 0.020577</td>
</tr>
<tr>
<td>H+CH2O(+M) &lt;=&gt; CH3O(+M)</td>
<td>57 0.0124224</td>
</tr>
<tr>
<td>2OH(+M) &lt;=&gt; HO2(+M)</td>
<td>85 0.111698</td>
</tr>
<tr>
<td>OH+H2O2 &lt;=&gt; HO2+H2O</td>
<td>89 0.0349801</td>
</tr>
<tr>
<td>OH+CH4 &lt;=&gt; CH3+H2O</td>
<td>98 0.058769</td>
</tr>
<tr>
<td>OH+CH2O &lt;=&gt; HCO+H2O</td>
<td>101 0.0168309</td>
</tr>
<tr>
<td>2HO2 &lt;=&gt; O2+H2O2</td>
<td>115 0.0163524</td>
</tr>
<tr>
<td>2HO2 &lt;=&gt; O2+H2O2</td>
<td>116 0.104433</td>
</tr>
<tr>
<td>HO2+CH3 &lt;=&gt; O2+CH4</td>
<td>118 0.0173129</td>
</tr>
<tr>
<td>HO2+CH3 &lt;=&gt; OH+CH3O</td>
<td>119 0.107882</td>
</tr>
<tr>
<td>HO2+CO &lt;=&gt; OOH+CO2</td>
<td>120 0.0808342</td>
</tr>
<tr>
<td>HO2+CH2O &lt;=&gt; HCO+H2O2</td>
<td>121 0.0261494</td>
</tr>
<tr>
<td>CH3+O2 &lt;=&gt; OH+CH2O</td>
<td>156 0.0221534</td>
</tr>
<tr>
<td>CH3+H2O2 &lt;=&gt; HO2+CH4</td>
<td>157 0.0960371</td>
</tr>
<tr>
<td>CH3+CH2O &lt;=&gt; HCO+CH4</td>
<td>161 0.0252745</td>
</tr>
<tr>
<td>HCO+M &lt;=&gt; H+CO+M</td>
<td>167 0.0151391</td>
</tr>
<tr>
<td>HCO+O2 &lt;=&gt; HO2+CO</td>
<td>168 0.0179481</td>
</tr>
<tr>
<td>CH3O+O2 &lt;=&gt; HO2+CH2O</td>
<td>170 0.0173865</td>
</tr>
</tbody>
</table>

### Table 2:
List of important reactions at iter = 50 (omega tau = 212718)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>O+H2 &lt;=&gt; H+OH</td>
<td>3 0.0309192</td>
</tr>
<tr>
<td>O+CH3 &lt;=&gt; H+CH2O</td>
<td>10 0.0251784</td>
</tr>
<tr>
<td>H+O2 &lt;=&gt; O+OH</td>
<td>38 0.201172</td>
</tr>
<tr>
<td>H+CH4 &lt;=&gt; CH3+H2</td>
<td>53 0.0554681</td>
</tr>
<tr>
<td>H+HCO &lt;=&gt; H2+CO</td>
<td>55 0.0171357</td>
</tr>
<tr>
<td>H+CH2O &lt;=&gt; HCO+H2</td>
<td>58 0.0100996</td>
</tr>
<tr>
<td>OH+H2 &lt;=&gt; H+H2O</td>
<td>84 0.0522106</td>
</tr>
<tr>
<td>2OH &lt;=&gt; O+H2O</td>
<td>86 0.0107618</td>
</tr>
<tr>
<td>OH+CH3 &lt;=&gt; CH2(S)+H2O</td>
<td>97 0.0204665</td>
</tr>
<tr>
<td>OH+CH4 &lt;=&gt; CH3+H2O</td>
<td>98 0.0253432</td>
</tr>
<tr>
<td>OH+CO &lt;=&gt; H+CO2</td>
<td>99 0.0148563</td>
</tr>
<tr>
<td>CH2+O2 &lt;=&gt; OH+HCO</td>
<td>135 0.0223359</td>
</tr>
<tr>
<td>CH2(S)+O2 &lt;=&gt; H+OH+CO</td>
<td>144 0.0127997</td>
</tr>
<tr>
<td>HCO+H2O &lt;=&gt; H+CO+H2O</td>
<td>166 0.0338651</td>
</tr>
<tr>
<td>HCO+M &lt;=&gt; H+CO+M</td>
<td>167 0.0208143</td>
</tr>
<tr>
<td>HCO+O2 &lt;=&gt; HO2+CO</td>
<td>168 0.0180102</td>
</tr>
</tbody>
</table>
Conclusions

Tangential Stretching Rate diagnostics seems a promising tool of analysis

It retrieves the same results found by CSP in terms of fast/slow decomposition

It also provides additional information about
(i) the most energetic scale
(ii) the range of active scales, which are not uniquely identified in CSP

It can be used to define
(i) the Damköhler number in a reactive flow
(ii) the proper integration time step during the numerical integration of the stiff problem.

TSR and CSP participation indices can also be used in mechanism simplification procedures.
Questions ...