Mechanism reduction methods based on time scale separation

3rd part

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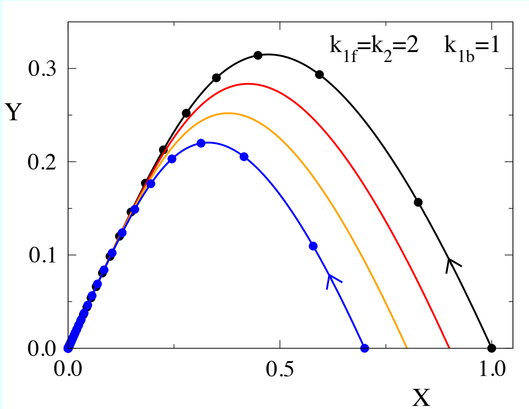
Outline

1. Mathematical background
2. Time scales
3. Traditional reduction tools and their limitations
4. New algorithmic tools
5. Various methodologies
6. Applications
7. Quasi steady-state and partial equilibrium approx.

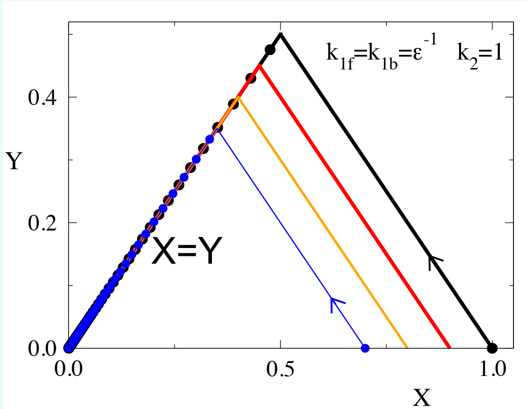
Some common features

$\varepsilon = 10^{-6}$

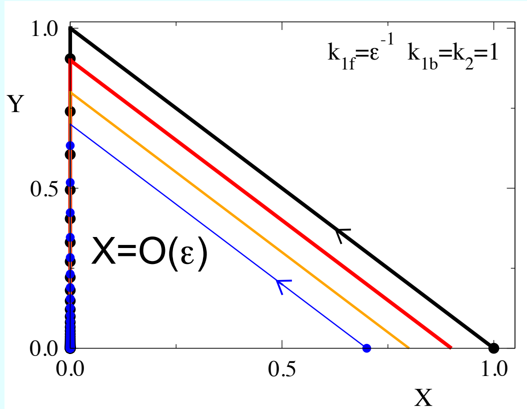
$\tau_1/\tau_2 = 0.25 \qquad \lambda_1 = -4$



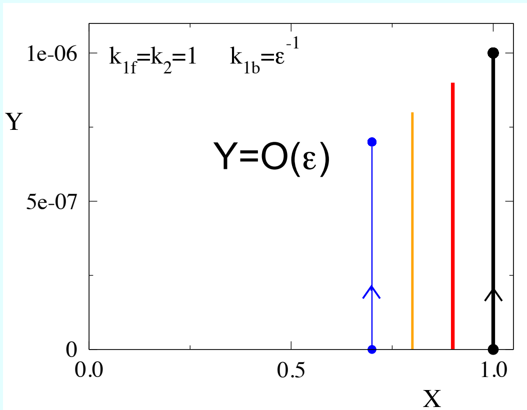
$\tau_1/\tau_2 = \varepsilon/4 \qquad \lambda_1 = -2/\varepsilon$



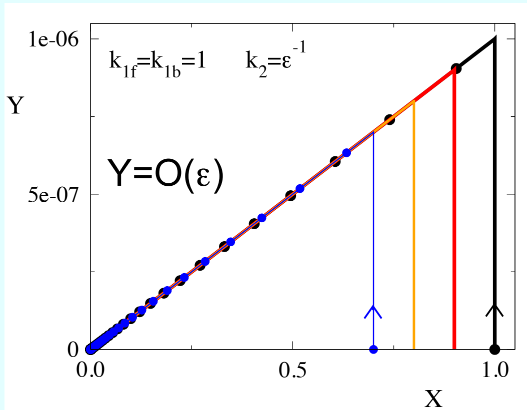
$\tau_1/\tau_2 = \varepsilon \qquad \lambda_1 = -1/\varepsilon$



$\tau_1/\tau_2 = \varepsilon^2 \qquad \lambda_1 = -1/\varepsilon$



$\tau_1/\tau_2 = \varepsilon \qquad \lambda_1 = -1/\varepsilon$



1. Time scale gaps
2. Dissipative time scales
3. Fast/slow behavior
4. Structures in phase space

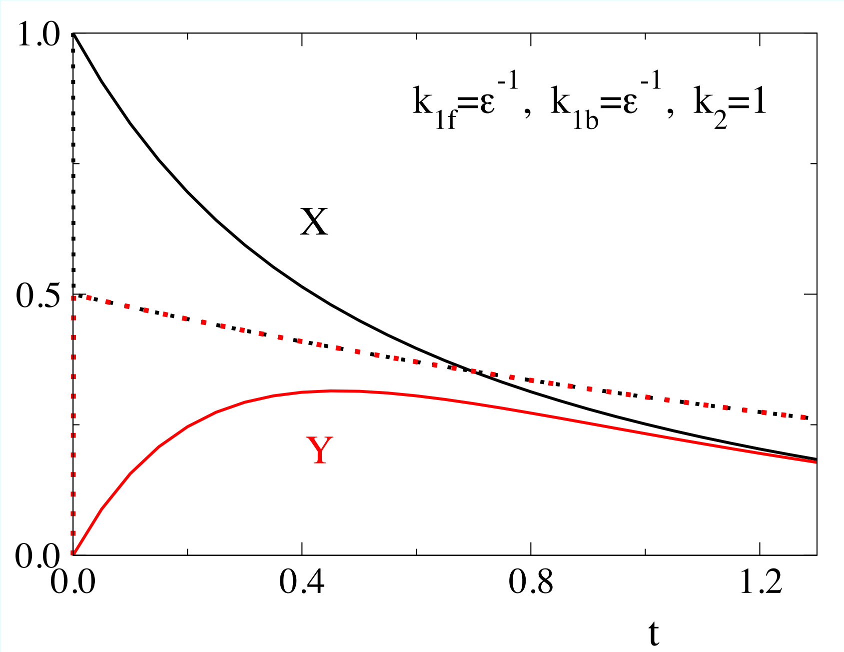
Partial Equilibrium Approximation (1st reaction)

$$x \underset{k_{1b}}{\overset{k_{1f}}{\leftrightarrow}} y \qquad y \xrightarrow{k_2} \text{products}$$

$$\frac{d}{dt}\begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} -1 \\ +1 \end{bmatrix}\left(\frac{X - Y}{\varepsilon}\right) + \begin{bmatrix} 0 \\ -1 \end{bmatrix} Y \qquad \varepsilon = 10^{-6}$$

$$X - Y = O(\varepsilon)$$

$$X - Y = O(\varepsilon) \Rightarrow \frac{dX}{dt} - \frac{dY}{dt} = O(\varepsilon)$$



$$\frac{X - Y}{\varepsilon} = \frac{Y}{2} + O(\varepsilon)$$

$$\frac{dX}{dt} = -\frac{X}{2} + O(\varepsilon) \qquad \frac{dY}{dt} = -\frac{Y}{2} + O(\varepsilon)$$

Quasi Steady-State approximation (X)

$$x \underset{k_{1b}}{\overset{k_{1f}}{\leftrightarrow}} y \qquad y \xrightarrow{k_2} \text{products}$$

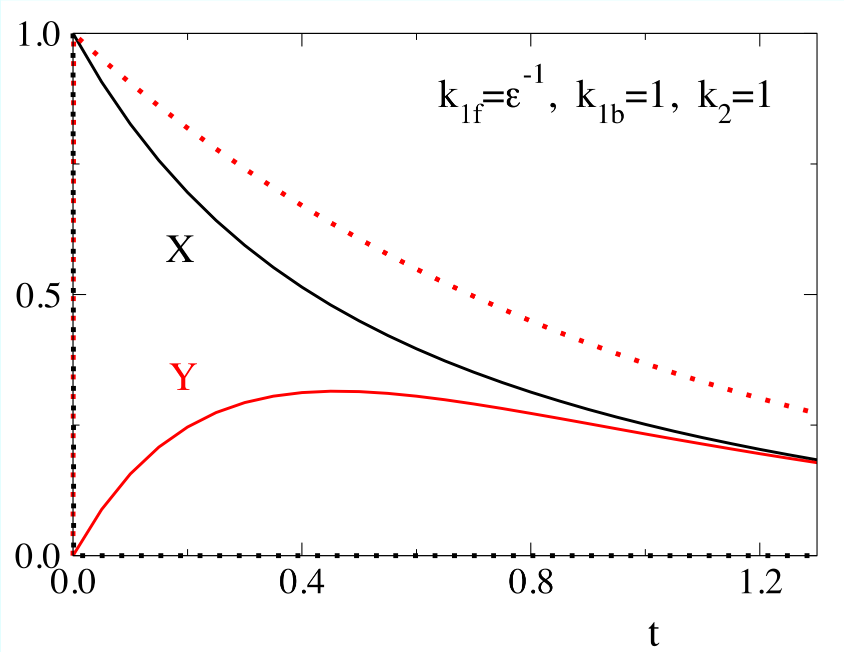
$$\frac{d}{dt}\begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} -1 \\ +1 \end{bmatrix}\left(\frac{X}{\varepsilon} - Y\right) + \begin{bmatrix} 0 \\ -1 \end{bmatrix} Y \qquad \varepsilon = 10^{-6}$$

$$X = O(\varepsilon)$$

$$X = \varepsilon Z \Rightarrow \frac{dZ}{dt} = -\left(\frac{Z-Y}{\varepsilon}\right) \quad \frac{dY}{dt} = (Z-Y) - Y$$

$$Z - Y = O(\varepsilon)$$

$$\frac{X}{\varepsilon} - Y = O(\varepsilon) \qquad \frac{dY}{dt} = -Y + O(\varepsilon)$$



Quasi Steady-State approximation (Y 1st)

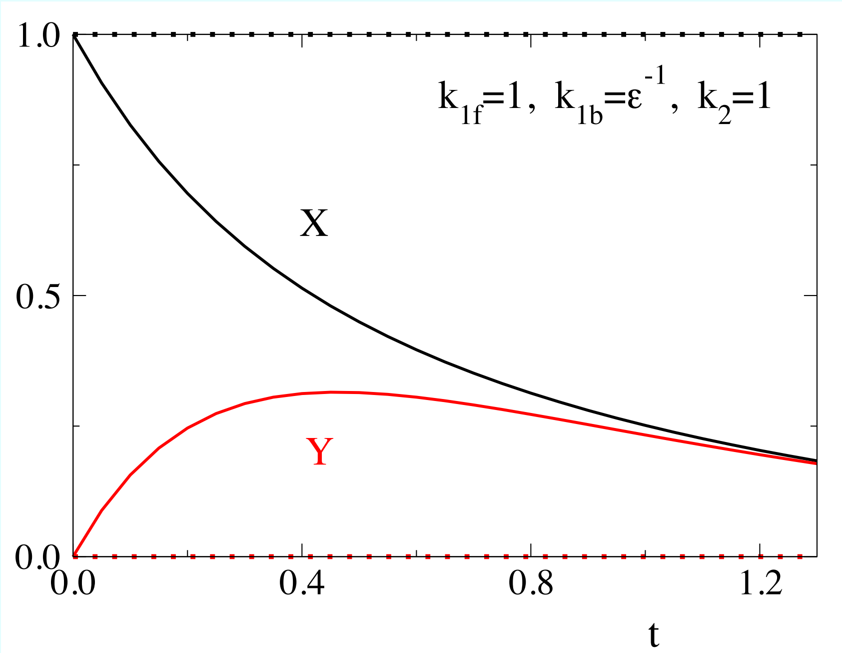
$$x \underset{k_{1b}}{\overset{k_{1f}}{\leftrightarrow}} y \qquad y \xrightarrow{k_2} \text{products}$$

$$\frac{d}{dt}\begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} -1 \\ +1 \end{bmatrix}\left(X - \frac{Y}{\varepsilon}\right) + \begin{bmatrix} 0 \\ -1 \end{bmatrix} Y \qquad \varepsilon = 10^{-6}$$

$$Y = O(\varepsilon)$$

$$Y = \varepsilon Z \quad \Rightarrow \quad \frac{dX}{dt} = -(X - Z) \qquad \frac{dZ}{dt} = \left(\frac{X - Z - \varepsilon Z}{\varepsilon}\right)$$

$$X - Z - \varepsilon Z = O(\varepsilon)$$



$$X - \frac{Y}{\varepsilon} = O(\varepsilon) \qquad \frac{dX}{dt} = -Y + O(\varepsilon)$$

Quasi Steady-State approximation (Y 2nd)

$$x \underset{k_{1b}}{\overset{k_{1f}}{\leftrightarrow}} y \qquad y \xrightarrow{k_2} \text{products}$$

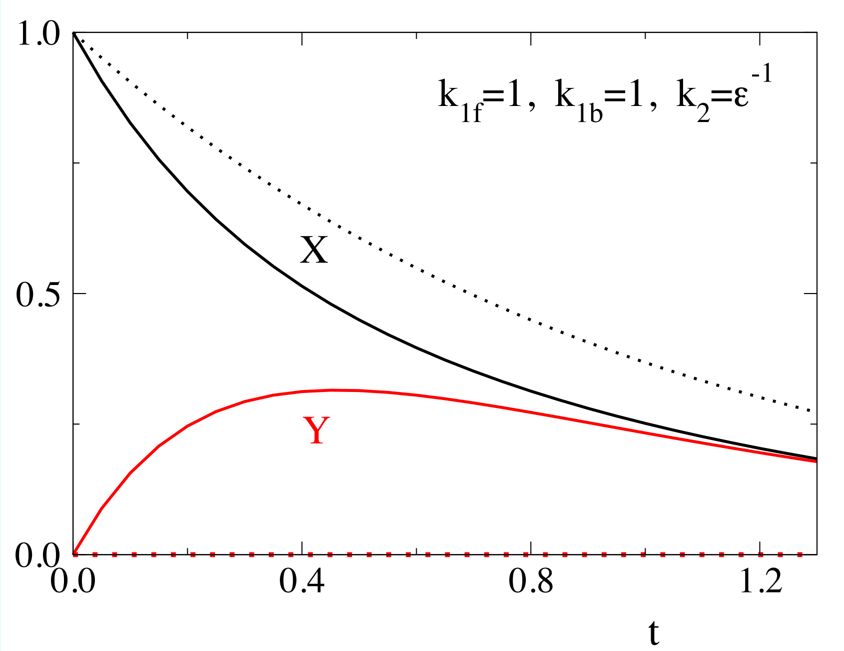
$$\frac{d}{dt}\begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} -1 \\ +1 \end{bmatrix}(X - Y) + \begin{bmatrix} 0 \\ -1 \end{bmatrix}\frac{Y}{\varepsilon} \qquad \varepsilon = 10^{-6}$$

$$Y = O(\varepsilon)$$

$$Y = \varepsilon Z \Rightarrow \frac{dX}{dt} = -(X - \varepsilon Z) \qquad \frac{dZ}{dt} = \left(\frac{X - \varepsilon Z - Z}{\varepsilon}\right)$$

$$X - Z - \varepsilon Z = O(\varepsilon)$$

$$X - \frac{Y}{\varepsilon} = O(\varepsilon) \qquad \frac{dX}{dt} = -Y + O(\varepsilon)$$



QSSA/PEA literature

Bodenstein, Lind, Z. Phys. Chem. 57:168, 1906
Bodenstein, Z. Phys. Chem. 85:327, 1913
Michaelis and Menten, Biochem. Z. 49:333, 1913
Underhill and Chapman, J. Chem. Soc. Trans., 103:496, 1913
Briggs and Haldane, Biochem. J., 19:338, 1925

Acrivos, Benson, Bowen, Deakin, Frank-Kamenetskii, Fraser, Ignetik,

Goddard, Goldbeter, Klonowski, Maini, Oppenheim, Oran, Rein, Roussel,

Schnell, Segel, Slemrod, Tomlin, Turanyi, Tzafriri, Walcher

In combustion: Peters, Williams, Oran, Trevino, Turanyi/Tomlin

The nature of the QSSA/PEA

$$\frac{d\mathbf{y}}{dt} = \mathbf{S}_1 R^1 + \mathbf{S}_2 R^2 + \ldots + \mathbf{S}_K R^K = [\mathbf{S}_1 \,..\, \mathbf{S}_M] \begin{bmatrix} R^1 \\ : \\ R^M \end{bmatrix} + [\mathbf{S}_{M+1} \,..\, \mathbf{S}_K] \begin{bmatrix} R^{M+1} \\ : \\ R^K \end{bmatrix}$$

$$= \underbrace{\mathbf{S}_r \mathbf{R}^r}_{\text{M fast reactions}} + \mathbf{S}_s \mathbf{R}^s$$

$$\mathbf{y} = \begin{bmatrix} \mathbf{y}^r \\ \mathbf{y}^s \end{bmatrix}$$ ← M fast species

$$\frac{d}{dt}\begin{bmatrix} \mathbf{y}^r \\ \mathbf{y}^s \end{bmatrix} = \begin{bmatrix} \mathbf{S}_r^r \\ \mathbf{S}_r^s \end{bmatrix} \mathbf{R}^r + \begin{bmatrix} \mathbf{S}_s^r \\ \mathbf{S}_s^s \end{bmatrix} \mathbf{R}^s$$

QSSA PEA

Accuracy O(ε) $\varepsilon = \dfrac{\tau_M}{\tau_{M+1}}$

The nature of the QSSA/PEA

$$\frac{d\mathbf{y}}{dt} = \mathbf{S}_1 R^1 + \mathbf{S}_2 R^2 + \ldots + \mathbf{S}_K R^K = \mathbf{S}_r \mathbf{R}^r + \mathbf{S}_s \mathbf{R}^s$$

$$\frac{d}{dt}\begin{bmatrix}\mathbf{y}^r \\ \mathbf{y}^s\end{bmatrix} = \begin{bmatrix}\mathbf{S}_r^r \\ \mathbf{S}_r^s\end{bmatrix}\mathbf{R}^r + \begin{bmatrix}\mathbf{S}_s^r \\ \mathbf{S}_s^s\end{bmatrix}\mathbf{R}^s \rightarrow \mathbf{R}^r = (\mathbf{S}_r^r)^{-1}\left(\frac{d\mathbf{y}^r}{dt} - \mathbf{S}_s^r \mathbf{R}^s\right)$$

$= 0$ — QSSA

$\neq 0$ — PEA

QSSA:

$$\mathbf{R}^r = -(\mathbf{S}_r^r)^{-1}\mathbf{S}_s^r \mathbf{R}^s$$

$$\frac{d\mathbf{y}^s}{dt} = (\mathbf{S}_s^s - \mathbf{S}_r^s(\mathbf{S}_r^r)^{-1}\mathbf{S}_s^r)\,\mathbf{R}^s$$

$$\mathbf{S}_r^r \mathbf{R}^r + \mathbf{S}_s^r \mathbf{R}^s = 0$$

$$\frac{d\mathbf{y}^r}{dt} \neq 0$$

The nature of the QSSA/PEA

$$\frac{d\mathbf{y}}{dt} = \mathbf{S}_1 R^1 + \mathbf{S}_2 R^2 + \ldots + \mathbf{S}_K R^K = \mathbf{S}_r \mathbf{R}^r + \mathbf{S}_s \mathbf{R}^s$$

$$\frac{d}{dt}\begin{bmatrix}\mathbf{y}^r \\ \mathbf{y}^s\end{bmatrix} = \begin{bmatrix}\mathbf{S}_r^r \\ \mathbf{S}_r^s\end{bmatrix}\mathbf{R}^r + \begin{bmatrix}\mathbf{S}_s^r \\ \mathbf{S}_s^s\end{bmatrix}\mathbf{R}^s \rightarrow \mathbf{R}^r = (\mathbf{S}_r^r)^{-1}\left(\frac{d\mathbf{y}^r}{dt} - \mathbf{S}_s^r\mathbf{R}^s\right)$$

$= 0$ — QSSA

$\neq 0$ — PEA

PEA:

$$\mathbf{R}^r = \mathbf{0}^r$$

$$\Downarrow$$

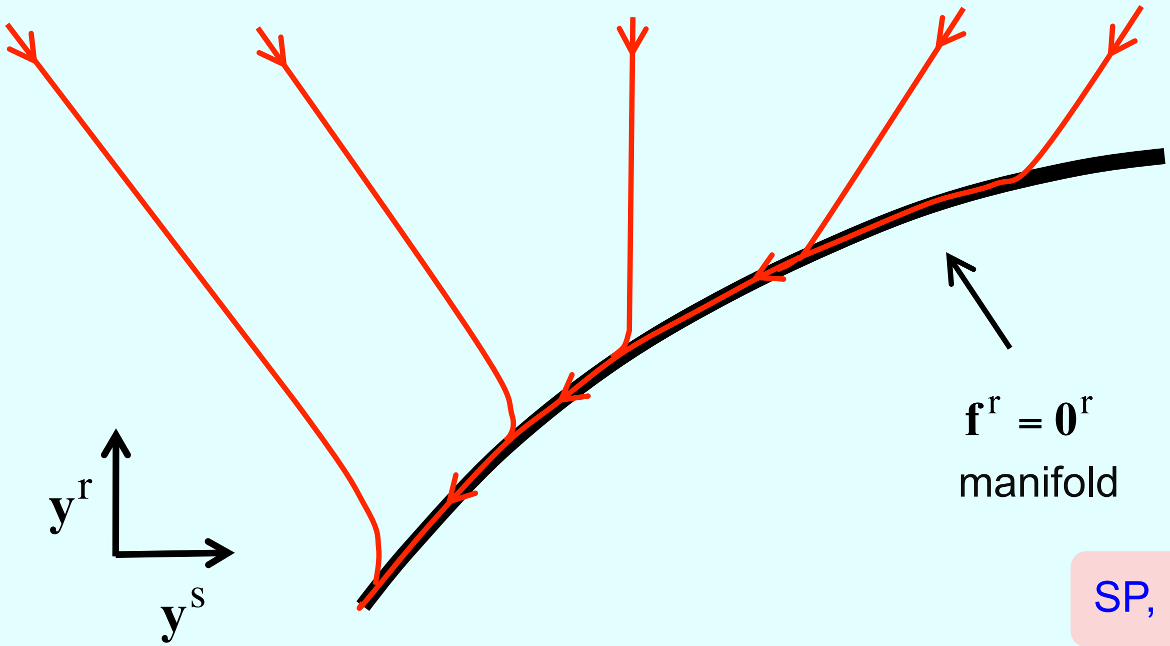
$$\frac{d\mathbf{y}^r}{dt} = -\left(\frac{\partial \mathbf{R}^r}{\partial \mathbf{y}^r}\right)^{-1}\left(\frac{\partial \mathbf{R}^r}{\partial \mathbf{y}^s}\right)\frac{d\mathbf{y}^s}{dt}$$

$\Rightarrow$

$$\mathbf{R}^{r,f} - \mathbf{R}^{r,b} = \mathbf{0}^r$$

$$\frac{d}{dt}\begin{bmatrix}\mathbf{y}^r \\ \mathbf{y}^s\end{bmatrix} = \begin{bmatrix}\mathbf{X}_s^r \\ \mathbf{X}_s^s\end{bmatrix}\mathbf{R}^s$$

The fast/slow basis vectors of QSSA/PEA



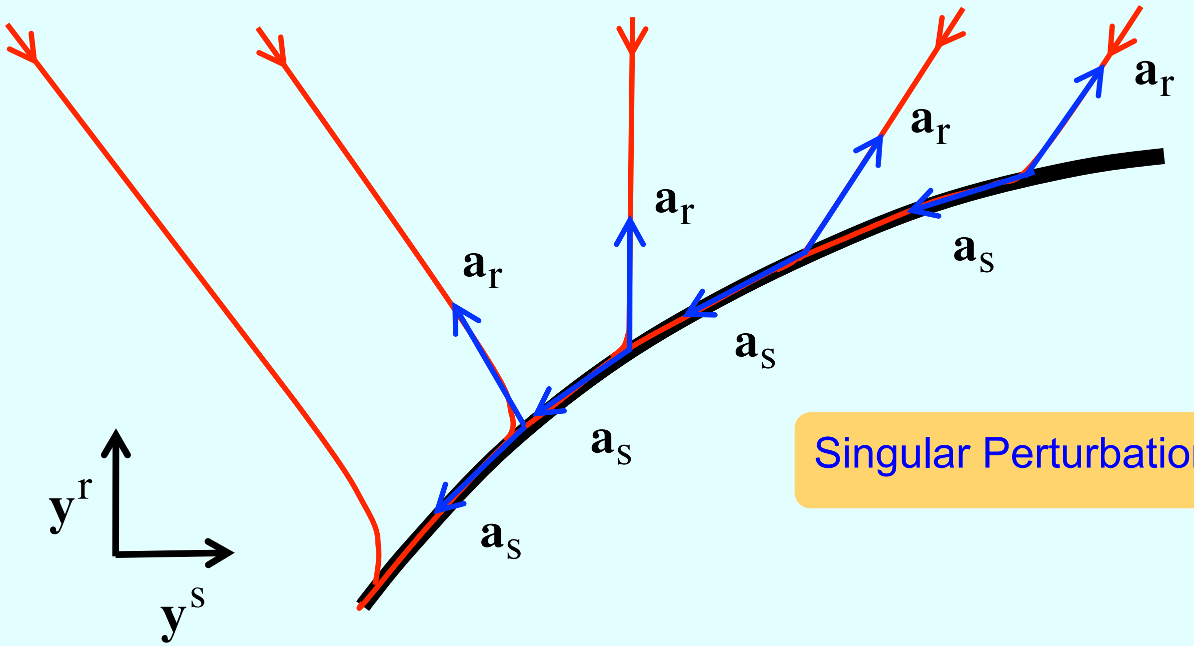
$$\frac{d\mathbf{y}}{dt} = \mathbf{S}_r \mathbf{R}^r + \mathbf{S}_s \mathbf{R}^s$$

SP, PEA, QSSA: different $\mathbf{a}_r$ $\mathbf{a}_s$

Singular Perturbations
PEA
QSSA

$$\Rightarrow \quad \frac{d\mathbf{y}}{dt} = \mathbf{a}_r \mathbf{f}^r + \mathbf{a}_s \mathbf{f}^s \quad \Rightarrow \quad \begin{aligned} \mathbf{f}^r &= \mathbf{0}^r \\ \frac{d\mathbf{y}}{dt} &= \mathbf{a}_s \mathbf{f}^s \end{aligned}$$

The fast/slow basis vectors of CSP



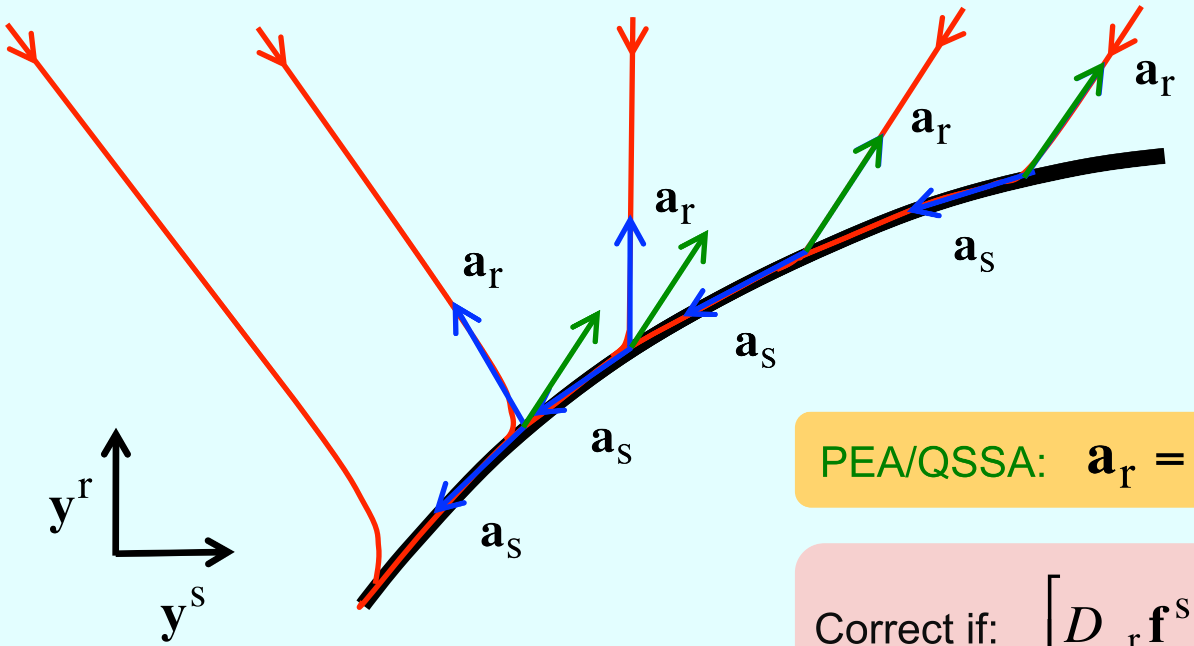
$$\frac{d\mathbf{y}}{dt} = \mathbf{S}_r \mathbf{R}^r + \mathbf{S}_s \mathbf{R}^s$$

Singular Perturbations: can adjust both $\mathbf{a}_r$ $\mathbf{a}_s$

Singular Perturbations
PEA
QSSA

$$\Rightarrow \quad \frac{d\mathbf{y}}{dt} = \mathbf{a}_r \mathbf{f}^r + \mathbf{a}_s \mathbf{f}^s \quad \Rightarrow \quad \begin{aligned} &\mathbf{f}^r = \mathbf{0}^r \\ &\frac{d\mathbf{y}}{dt} = \mathbf{a}_s \mathbf{f}^s \end{aligned}$$

The fast vectors of QSSA/PEA



$$\frac{d\mathbf{y}}{dt} = \mathbf{S}_r R^r + \mathbf{S}_s R^s$$

$$\frac{d}{dt}\begin{bmatrix}\mathbf{y}^r \\ \mathbf{y}^s\end{bmatrix} = \begin{bmatrix}\mathbf{g}^r \\ \mathbf{g}^s\end{bmatrix}$$

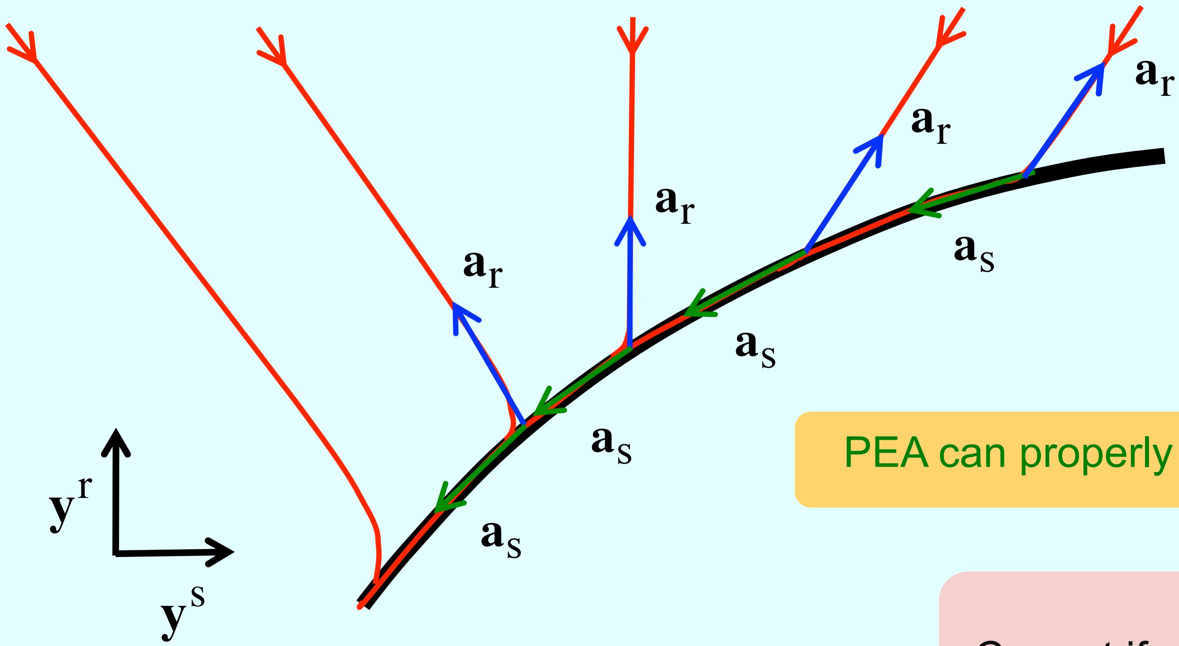
PEA/QSSA: $\mathbf{a}_r = \mathbf{S}_r$

Correct if: $\left[D_{\mathbf{y}^r}\mathbf{f}^s\right]\left[D_{\mathbf{y}^r}\mathbf{g}^r\right]^{-1} = O(\varepsilon)$

Singular Perturbations
PEA
QSSA

$$\Rightarrow \quad \frac{d\mathbf{y}}{dt} = \mathbf{a}_r\mathbf{f}^r + \mathbf{a}_s\mathbf{f}^s \quad \Rightarrow \quad \mathbf{f}^r = \mathbf{0}^r, \quad \frac{d\mathbf{y}}{dt} = \mathbf{a}_s\mathbf{f}^s$$

The slow vectors of PEA



$$\frac{d\mathbf{y}}{dt} = \mathbf{S}_r \mathbf{R}^r + \mathbf{S}_s \mathbf{R}^s$$

$$\frac{d}{dt}\begin{bmatrix} \mathbf{y}^r \\ \mathbf{y}^s \end{bmatrix} = \begin{bmatrix} \mathbf{g}^r \\ \mathbf{g}^s \end{bmatrix}$$

PEA can properly adjust $\mathbf{a}_s$

Correct if: $\left[D_{\mathbf{y}^r}\mathbf{g}^r\right]^{-1}\left[D_{\mathbf{a}_s}\mathbf{g}^r\right] = O(\varepsilon)$

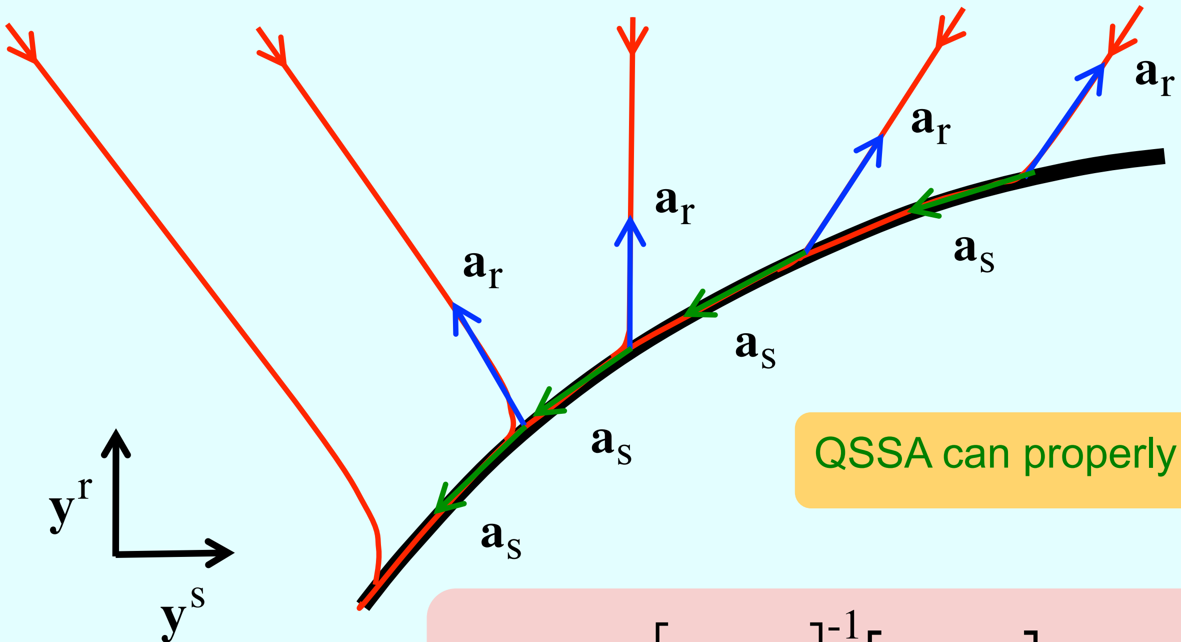
Singular Perturbations

PEA

QSSA

$$\Rightarrow \quad \frac{d\mathbf{y}}{dt} = \mathbf{a}_r\mathbf{f}^r + \mathbf{a}_s\mathbf{f}^s \quad \Rightarrow \quad \mathbf{f}^r = \mathbf{0}^r, \quad \frac{d\mathbf{y}}{dt} = \mathbf{a}_s\mathbf{f}^s$$

The slow vectors of QSSA



$$\frac{d\mathbf{y}}{dt} = \mathbf{S}_r \mathbf{R}^r + \mathbf{S}_s \mathbf{R}^s$$

$$\frac{d}{dt}\begin{bmatrix} \mathbf{y}^r \\ \mathbf{y}^s \end{bmatrix} = \begin{bmatrix} \mathbf{g}^r \\ \mathbf{g}^s \end{bmatrix}$$

QSSA can properly adjust $\mathbf{a}_s$

correct if: $\left[D_{\mathbf{y}^r}\mathbf{g}^r\right]^{-1}\left[D_{\mathbf{a}_s}\mathbf{g}^r\right] = O(\varepsilon)$ $\quad \left[D_{\mathbf{y}^r}\mathbf{R}^r\right]^{-1}\left[D_{\mathbf{y}^s}\mathbf{R}^r\right] = O(\varepsilon)$

Singular Perturbations
PEA
QSSA

$$\Rightarrow \quad \frac{d\mathbf{y}}{dt} = \mathbf{a}_r\mathbf{f}^r + \mathbf{a}_s\mathbf{f}^s \quad \Rightarrow \quad \mathbf{f}^r = \mathbf{0}^r, \quad \frac{d\mathbf{y}}{dt} = \mathbf{a}_s\mathbf{f}^s$$

Criteria for the validity of the QSSA/PEA

$$\frac{\mathrm{d}}{\mathrm{dt}}\begin{bmatrix}\mathbf{y}^r\\ \mathbf{y}^s\end{bmatrix} = \mathbf{S}_r\,\mathbf{R}^r + \mathbf{S}_s\,\mathbf{R}^s = \begin{bmatrix}\mathbf{S}_r^r\\ \mathbf{S}_r^s\end{bmatrix}\mathbf{R}^r + \begin{bmatrix}\mathbf{S}_s^r\\ \mathbf{S}_s^s\end{bmatrix}\mathbf{R}^s = \begin{bmatrix}\mathbf{g}^r\\ \mathbf{g}^s\end{bmatrix}$$

$$\frac{\mathrm{d}\mathbf{y}}{\mathrm{dt}} = \mathbf{a}_\mathrm{r}\mathbf{f}^\mathrm{r} + \mathbf{a}_\mathrm{s}\mathbf{f}^\mathrm{s}$$

$$\left[D_{\mathbf{y}^\mathrm{r}}\mathbf{f}^\mathrm{s}\right]\left[D_{\mathbf{y}^\mathrm{r}}\mathbf{g}^\mathrm{r}\right]^{-1} = O(\varepsilon)$$ ← Stability of PEA and QSSA

$$\left[D_{\mathbf{y}^\mathrm{r}}\mathbf{g}^\mathrm{r}\right]^{-1}\left[D_{\mathbf{a}_\mathrm{s}}\mathbf{g}^\mathrm{r}\right] = O(\varepsilon)$$ ← Accuracy of PEA

$$\left[D_{\mathbf{y}^\mathrm{r}}\mathbf{R}^\mathrm{r}\right]^{-1}\left[D_{\mathbf{y}^\mathrm{s}}\mathbf{R}^\mathrm{r}\right] = O(\varepsilon)$$ ← Accuracy of QSSA

Goussis CTM 2012, C&F 2015

Meaning of the criteria for the validity of the QSSA/PEA

$$\frac{d}{dt}\begin{bmatrix}\mathbf{y}^r\\ \mathbf{y}^s\end{bmatrix} = \mathbf{S}_r\,\mathbf{R}^r + \mathbf{S}_s\,\mathbf{R}^s = \begin{bmatrix}\mathbf{S}_r^r\\ \mathbf{S}_r^s\end{bmatrix}\mathbf{R}^r + \begin{bmatrix}\mathbf{S}_s^r\\ \mathbf{S}_s^s\end{bmatrix}\mathbf{R}^s = \begin{bmatrix}\mathbf{g}^r\\ \mathbf{g}^s\end{bmatrix}$$

$$\frac{d\mathbf{y}}{dt} = \mathbf{a}_r\mathbf{f}^r + \mathbf{a}_s\mathbf{f}^s$$

$$\left[D_{\mathbf{y}^r}\mathbf{f}^s\right]\left[D_{\mathbf{y}^r}\mathbf{g}^r\right]^{-1} = O(\varepsilon)$$

← Stability of PEA and QSSA

$$\mathbf{f}^s = \left(\mathbf{S}_s^s - \mathbf{S}_r^s\left(\mathbf{S}_r^r\right)^{-1}\mathbf{S}_s^r\right)\mathbf{R}^s$$

$$\mathbf{g}^r = \mathbf{S}_r^r\,\mathbf{R}^r + \mathbf{S}_s^r\,\mathbf{R}^s$$

The sensitivity of $\mathbf{R}^r$ along $\mathbf{y}^r$ is $O(\varepsilon^{-1})$ larger than that of $\mathbf{R}^s$

Only the M reactions in $\mathbf{S}_r\mathbf{R}^r$ contribute to the fast dynamics of $\mathbf{y}^r$

Meaning of the criteria for the validity of the QSSA/PEA

$$\frac{d}{dt}\begin{bmatrix}\mathbf{y}^r\\ \mathbf{y}^s\end{bmatrix} = \mathbf{S}_r\,\mathbf{R}^r + \mathbf{S}_s\,\mathbf{R}^s = \begin{bmatrix}\mathbf{S}_r^r\\ \mathbf{S}_r^s\end{bmatrix}\mathbf{R}^r + \begin{bmatrix}\mathbf{S}_s^r\\ \mathbf{S}_s^s\end{bmatrix}\mathbf{R}^s = \begin{bmatrix}\mathbf{g}^r\\ \mathbf{g}^s\end{bmatrix} \qquad \frac{d\mathbf{y}}{dt} = \mathbf{a}_r\mathbf{f}^r + \mathbf{a}_s\mathbf{f}^s$$

$$\left[D_{\mathbf{y}^r}\mathbf{g}^r\right]^{-1}\left[D_{\mathbf{a}_s}\mathbf{g}^r\right] = O(\varepsilon) \longleftarrow \text{Accuracy of PEA}$$

The sensitivity of $\mathbf{g}^r$ along $\mathbf{y}^r$ is $O(\varepsilon^{-1})$ larger than that of $\mathbf{g}^r$ along $\mathbf{a}_s$

$\mathbf{R}^r$ is $O(\varepsilon^{-1})$ more sensitive to perturbations of $\mathbf{y}^r$ than $\mathbf{R}^s$ is sensitive to perturbations of $\mathbf{y}^r$ and $\mathbf{y}^s$ along the manifold

Meaning of the criteria for the validity of the QSSA/PEA

$$\frac{\mathrm{d}}{\mathrm{dt}}\begin{bmatrix}\mathbf{y}^r\\ \mathbf{y}^s\end{bmatrix} = \mathbf{S}_r\,\mathbf{R}^r + \mathbf{S}_s\,\mathbf{R}^s = \begin{bmatrix}\mathbf{S}_r^r\\ \mathbf{S}_r^s\end{bmatrix}\mathbf{R}^r + \begin{bmatrix}\mathbf{S}_s^r\\ \mathbf{S}_s^s\end{bmatrix}\mathbf{R}^s = \begin{bmatrix}\mathbf{g}^r\\ \mathbf{g}^s\end{bmatrix}$$

$$\frac{\mathrm{d}\mathbf{y}}{\mathrm{dt}} = \mathbf{a}_\mathrm{r}\mathbf{f}^\mathrm{r} + \mathbf{a}_\mathrm{s}\mathbf{f}^\mathrm{s}$$

$$\left[D_{\mathbf{y}^\mathrm{r}}\mathbf{g}^\mathrm{r}\right]^{-1}\left[D_{\mathbf{a}_\mathrm{s}}\mathbf{g}^\mathrm{r}\right] = O(\varepsilon)$$

$$\left[D_{\mathbf{y}^\mathrm{r}}\mathbf{R}^\mathrm{r}\right]^{-1}\left[D_{\mathbf{y}^\mathrm{s}}\mathbf{R}^\mathrm{r}\right] = O(\varepsilon)$$

Accuracy of QSSA

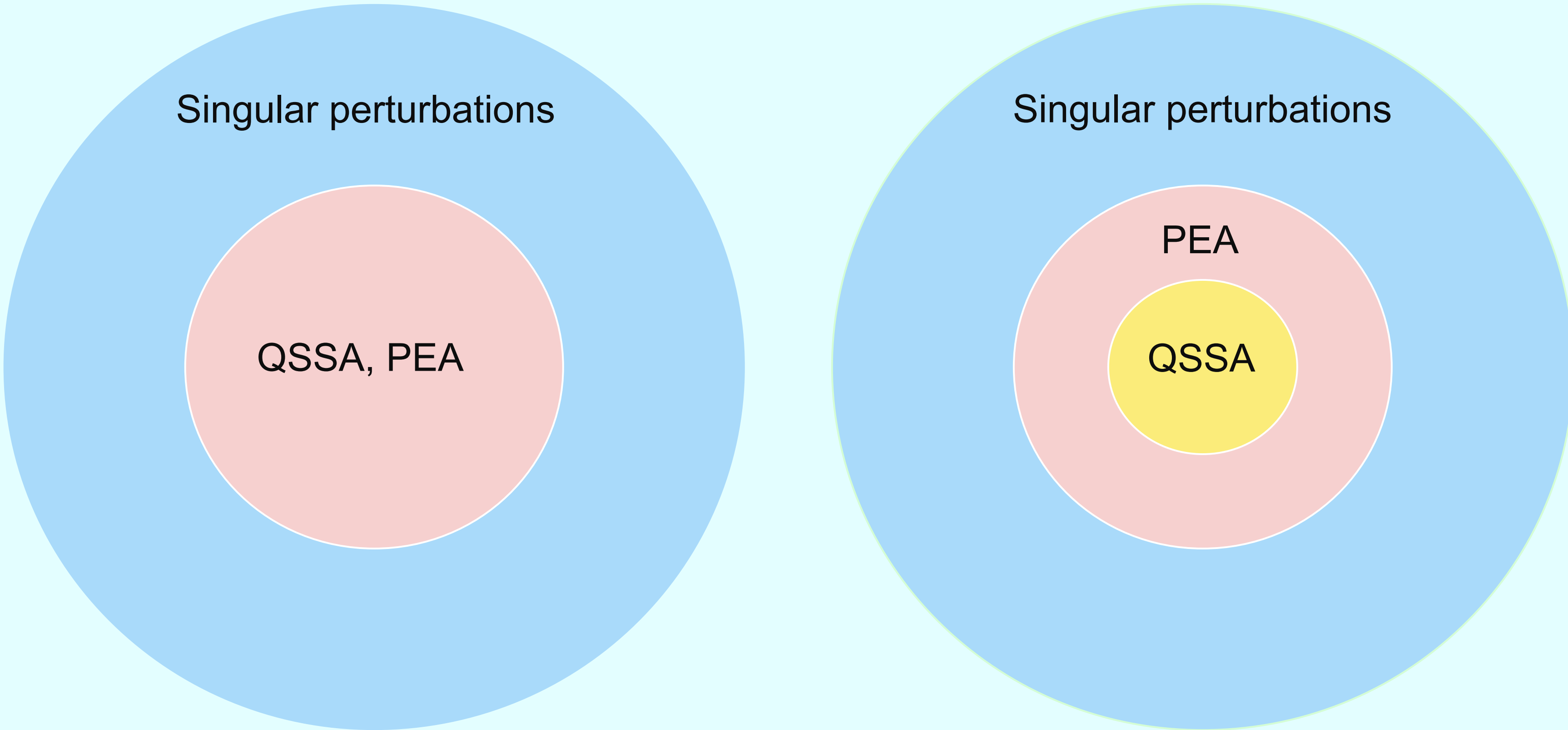
$\mathbf{R}^r$ is $O(\varepsilon^{-1})$ more sensitive to perturbations of $\mathbf{y}^r$ than $\mathbf{R}^s$ is sensitive to perturbations of $\mathbf{y}^r$ and $\mathbf{y}^s$

$\mathbf{R}^r$ is $O(\varepsilon^{-1})$ more sensitive to perturbations of $\mathbf{y}^r$ than $\mathbf{R}^r$ is sensitive to perturbations of $\mathbf{y}^s$

QSSA/PEA: stability and accuracy

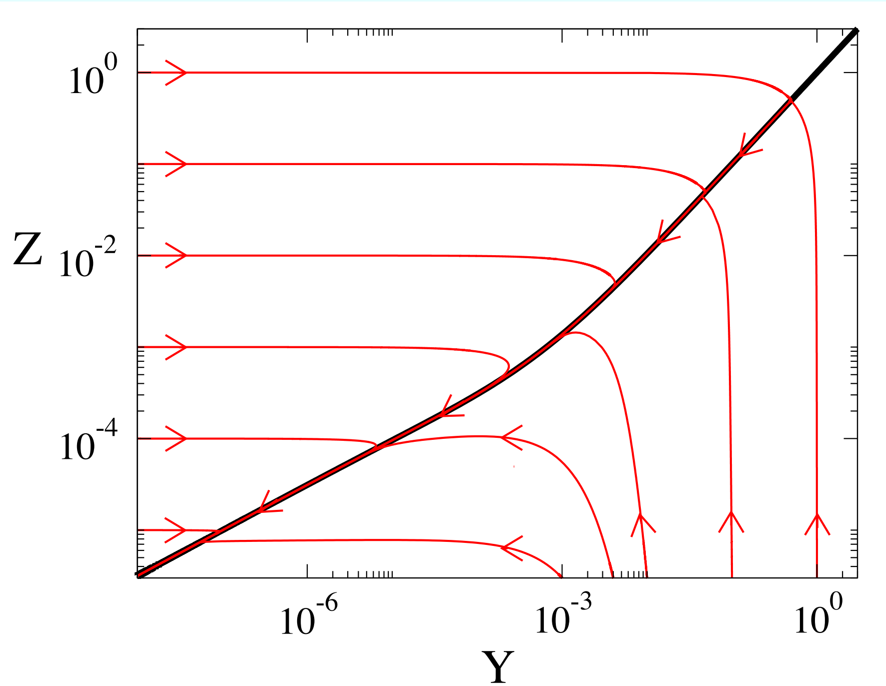
Stability

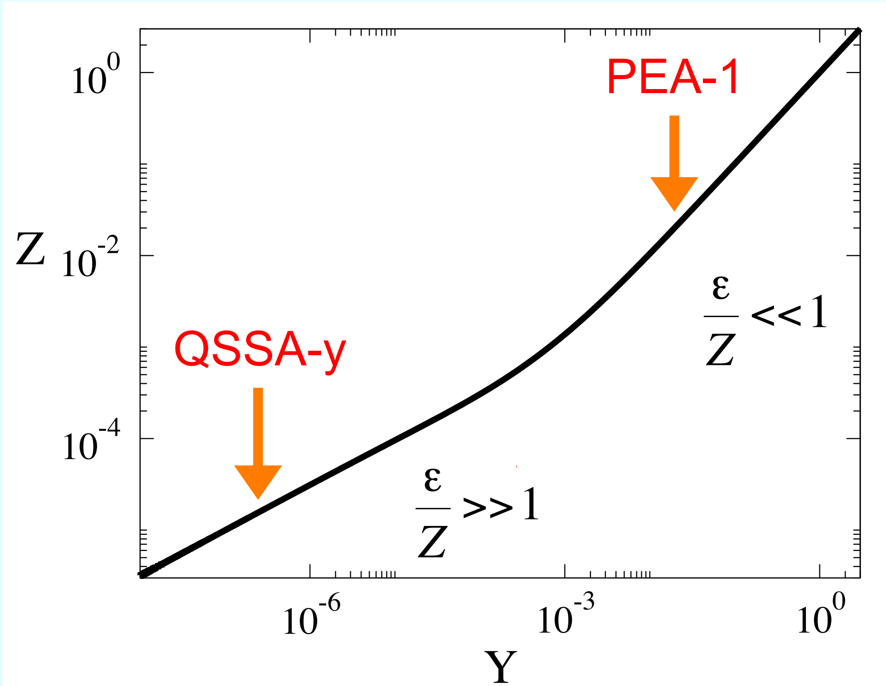
Accuracy



Simple example

$$\frac{d}{dt}\begin{bmatrix} Y \\ Z \end{bmatrix} = \begin{bmatrix} +1 \\ -1 \end{bmatrix}\frac{1}{\varepsilon}Z^2 + \begin{bmatrix} -1 \\ +1 \end{bmatrix}\frac{1}{\varepsilon}YZ + \begin{bmatrix} -1 \\ 0 \end{bmatrix}Y$$





Simple example

$$\frac{d}{dt}\begin{bmatrix} Y \\ Z \end{bmatrix} = \begin{bmatrix} +1 \\ -1 \end{bmatrix} \frac{1}{\varepsilon} Z^2 + \begin{bmatrix} -1 \\ +1 \end{bmatrix} \frac{1}{\varepsilon} YZ + \begin{bmatrix} -1 \\ 0 \end{bmatrix} Y$$

$$\frac{\varepsilon}{Z} << 1$$

1st fast reaction
Y fast variable

$$\left[D_{\mathbf{y}^r} \mathbf{f}^s\right]\left[D_{\mathbf{y}^r} \mathbf{g}^r\right]^{-1} = \frac{\varepsilon}{Z+\varepsilon}$$ Stability of PEA and QSSA — OK

$$\left[D_{\mathbf{y}^r} \mathbf{g}^r\right]^{-1}\left[D_{\mathbf{a}_s} \mathbf{g}^r\right] = \frac{\varepsilon}{Z+\varepsilon}$$ Accuracy of PEA — OK

$$\left[D_{\mathbf{y}^r} \mathbf{R}^r\right]^{-1}\left[D_{\mathbf{y}^s} \mathbf{R}^r\right] = 1$$ Accuracy of QSSA — not OK

Simple example

$$\frac{d}{dt}\begin{bmatrix} Y \\ Z \end{bmatrix} = \begin{bmatrix} +1 \\ -1 \end{bmatrix} \frac{1}{\varepsilon} Z^2 + \begin{bmatrix} -1 \\ +1 \end{bmatrix} \frac{1}{\varepsilon} YZ + \begin{bmatrix} -1 \\ 0 \end{bmatrix} Y$$

$$\frac{\varepsilon}{Z} >> 1$$

2^{nd} fast reaction
Y fast variable

$$\left[D_{\mathbf{y}^r}\mathbf{f}^s\right]\left[D_{\mathbf{y}^r}\mathbf{g}^r\right]^{-1} = \frac{Z}{\varepsilon + Z}$$

Stability of PEA and QSSA OK

$$\left[D_{\mathbf{y}^r}\mathbf{g}^r\right]^{-1}\left[D_{\mathbf{a}_s}\mathbf{g}^r\right] = \frac{Z}{\varepsilon + Z}$$

Accuracy of PEA OK

$$\left[D_{\mathbf{y}^r}\mathbf{R}^r\right]^{-1}\left[D_{\mathbf{y}^s}\mathbf{R}^r\right] = 0$$

Accuracy of QSSA OK

Fast species and reactions

Fast species

The M species whose axis is most aligned with the M fast directions

Fast reactions

The M reaction rates that exhibit the largest slope in the fast subspace

Goussis CTM 2012, C&F 2015

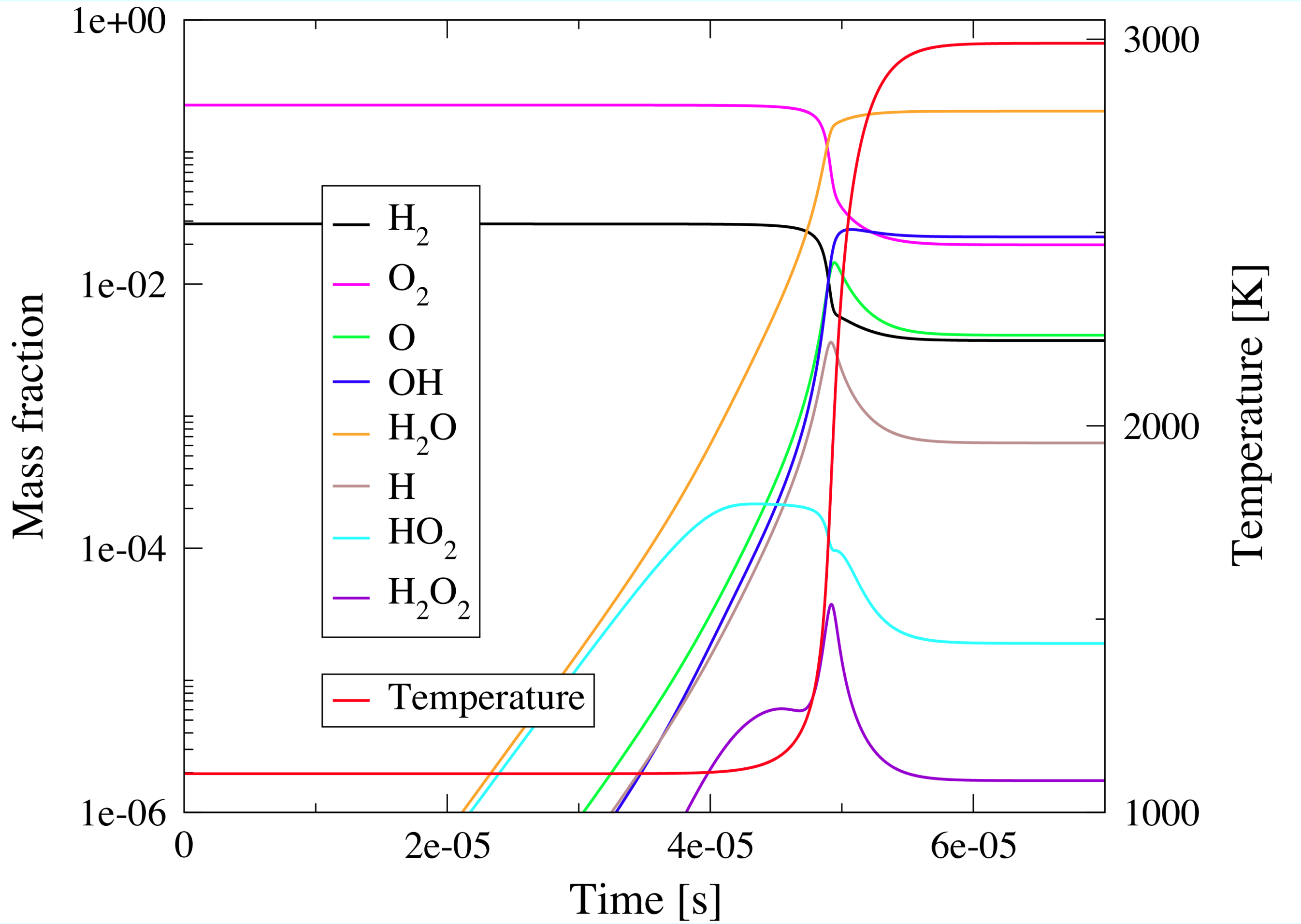
H_2-air ignition

1. $H+O_2$ <=> $OH+O$
2. H_2+O <=> $OH+H$
3. H_2+OH <=> H_2O+H
4. H_2O+O <=> $2\ OH$
5. $2\ H+M$ <=> H_2+M
6. $H+OH+M$ <=> H_2O+M
7. $2\ O+M$ <=> O_2+M
8. $H+O+M$ <=> $OH+M$
9. $O+OH+M$ <=> HO_2+M
10. $H+O_2\ (+M)$ <=> HO_2
11. HO_2+H <=> $2\ OH$
12. HO_2+H <=> H_2+O_2
13. HO_2+H <=> H_2O+O
14. HO_2+O <=> $OH+O_2$
15. HO_2+OH <=> H_2O+O_2
16. $2\ OH(+M)$ <=> $H_2O_2\ (+M)$
17. $2\ HO_2$ <=> $H_2O_2+O_2$
18. H_2O_2+H <=> HO_2+H_2
19. H_2O_2+H <=> H_2O+OH
20. H_2O_2+OH <=> H_2O+HO_2
21. H_2O_2+O <=> HO_2+OH

Adiabatic ignition of stoichiometric mixture at constant volume; T_o=1100K, p_o=2bar

Boivin et. al, Proc. Combust. Inst., 33:517-523, 2011

H_2-air ignition: profiles



Adiabatic ignition of stoichiometric mixture at constant volume; T_o=1100K, p_o=2bar

H_2-air ignition: 3-steps QSSA reduced mechanism

Species: 8

Conservation laws: 2 (O, H)

QSSA: 3 (O, OH, H_2O_2)

Steps: 8 - 3 - 2 = 3

Fast reactions

2. H_2+O <=> OH+H

3. H_2+OH <=> H_2O+H

16. 2 OH(+M) <=> H_2O_2 (+M)

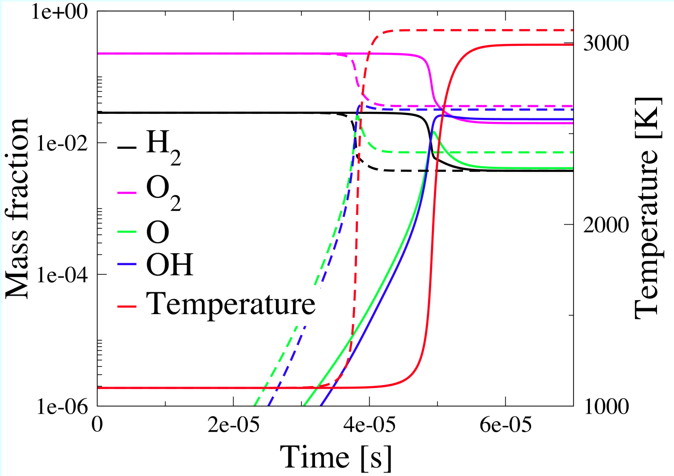
I. 3 H_2 + O_2 <=> 2 H_2O + 2 H

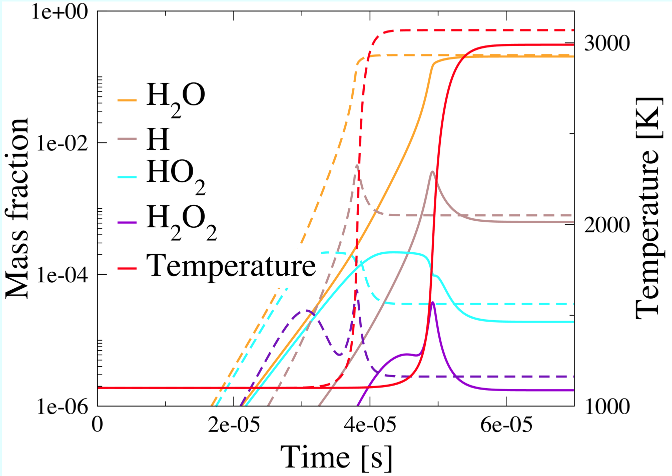
II. H + H + M <=> H_2 + M

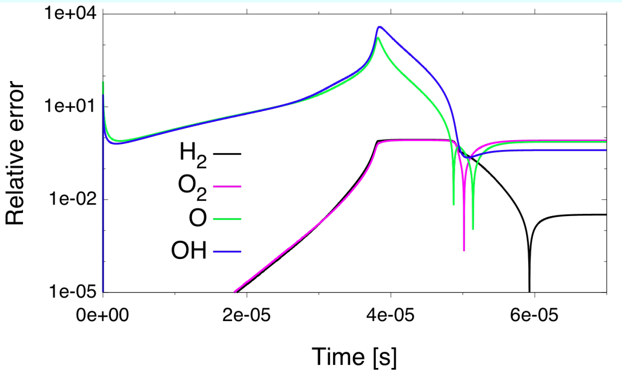
III. H_2 + O_2 <=> HO_2 + H

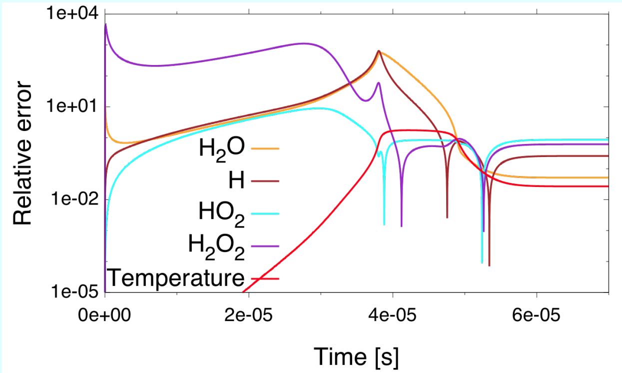
Boivin et. al, Proc. Combust. Inst., 33:517-523, 2011

H_2-air ignition: 3-steps QSSA reduced mechanism

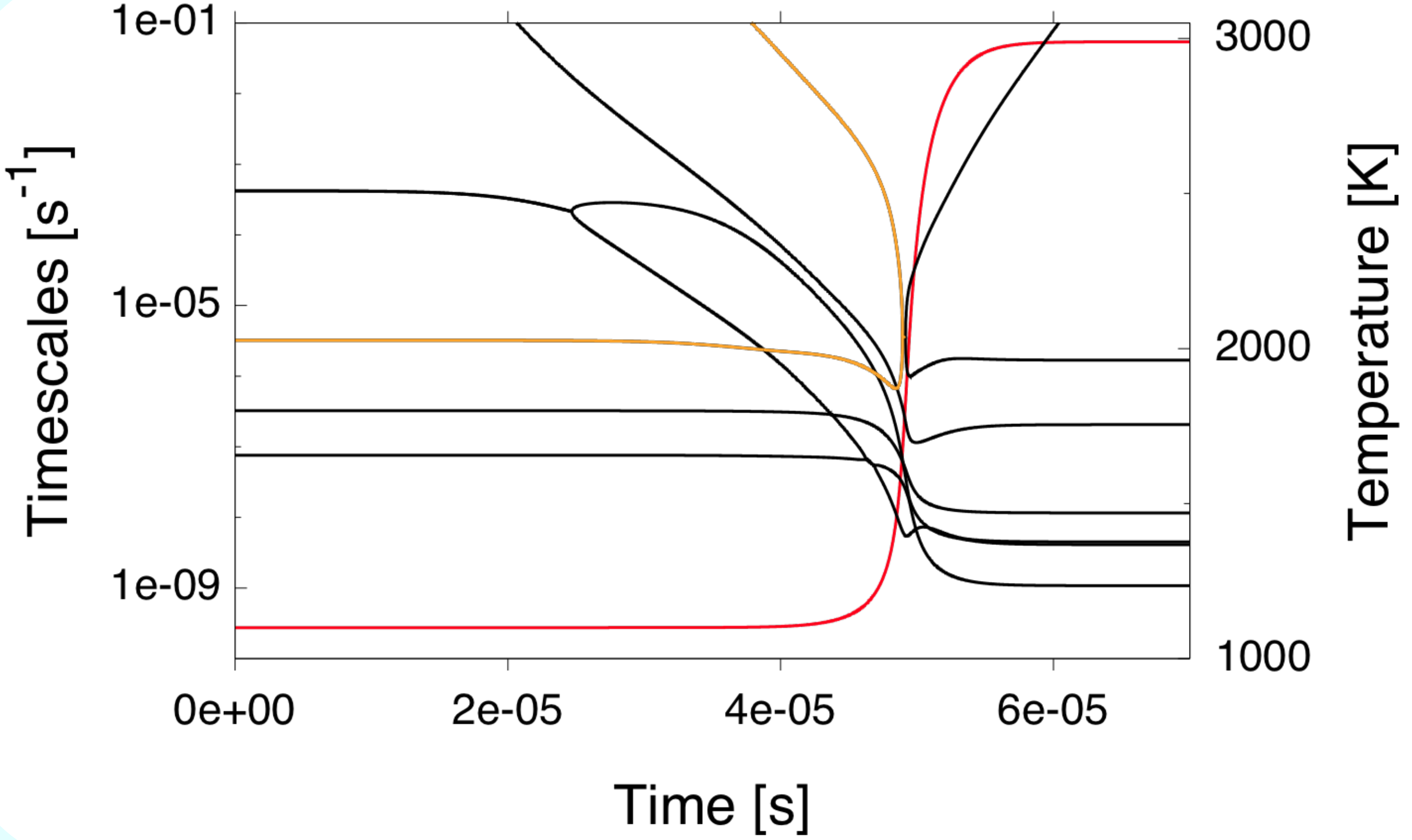






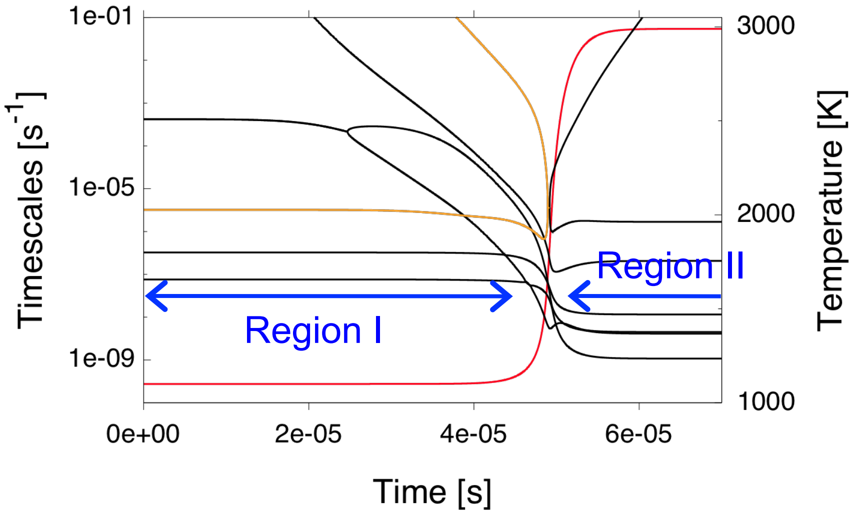


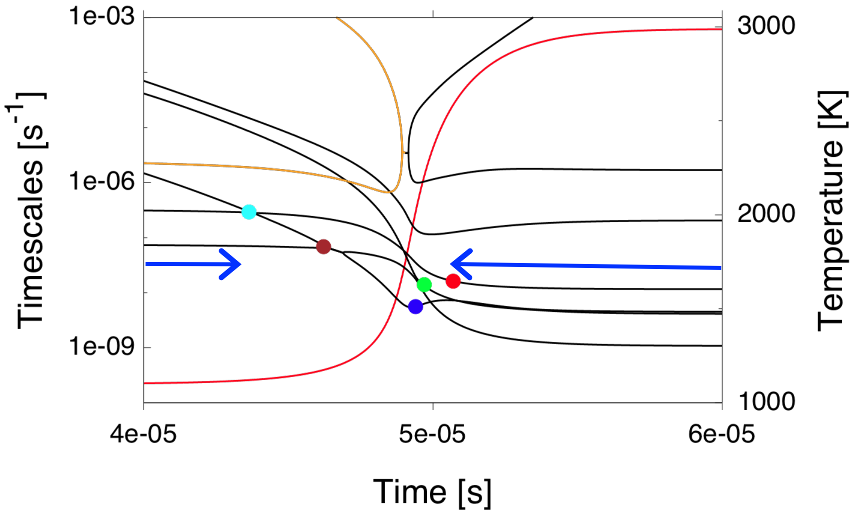
H_2-air ignition: timescales



Explosive/Dissipative Temperature

H_2-air ignition: timescales

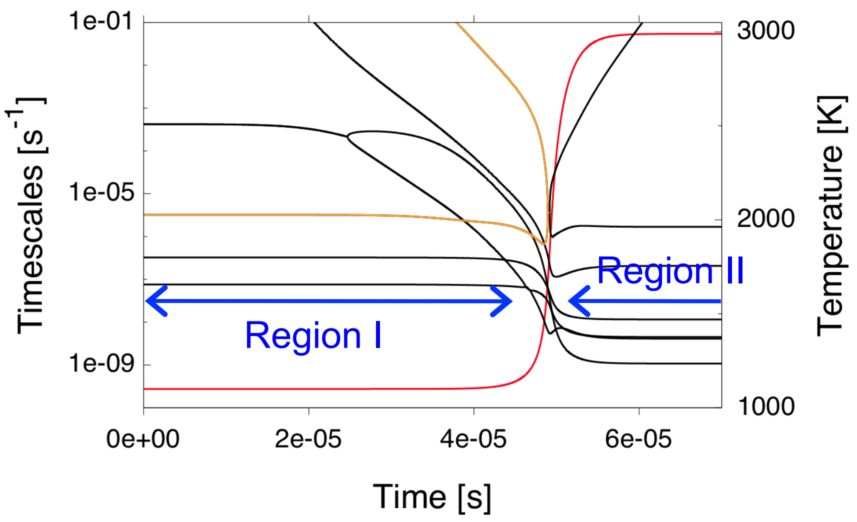


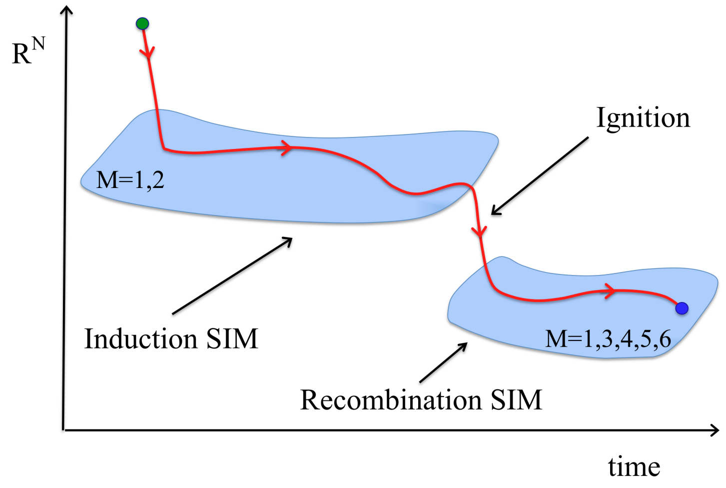


Explosive/Dissipative

Temperature

H_2-air ignition: manifolds



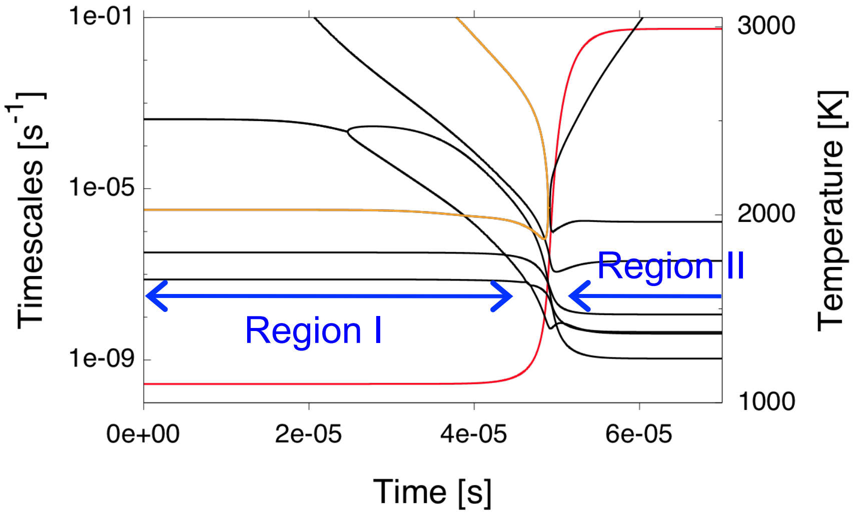


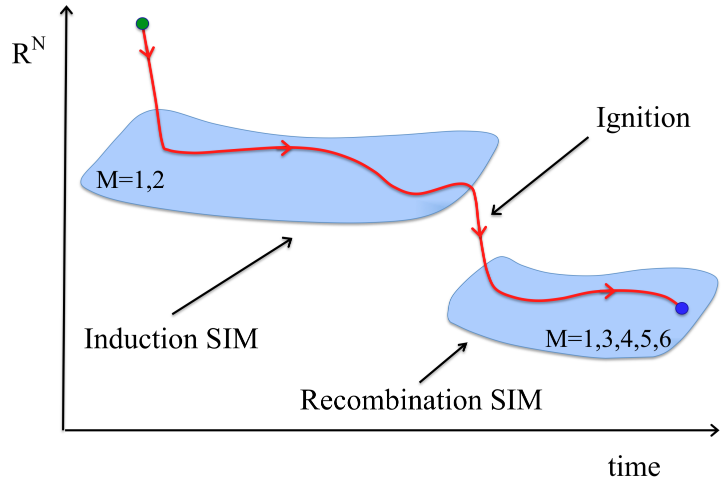
Induction SIM: up to 2 approximations (QSSA, PEA, etc)

Recombination SIM: up to 6 approximations (QSSA, PEA, etc)

Kourdis, PhD Thesis, NTUA 2012

H_2-air ignition: manifolds





Region I (M=1, 2)

Fast species: O, OH

Fast reactions: $H_2 + O \Leftrightarrow OH + H$

$H_2 + OH \Leftrightarrow H_2O + H$

Region II (M=4)

Fast species: H_2O_2, HO_2, O, H

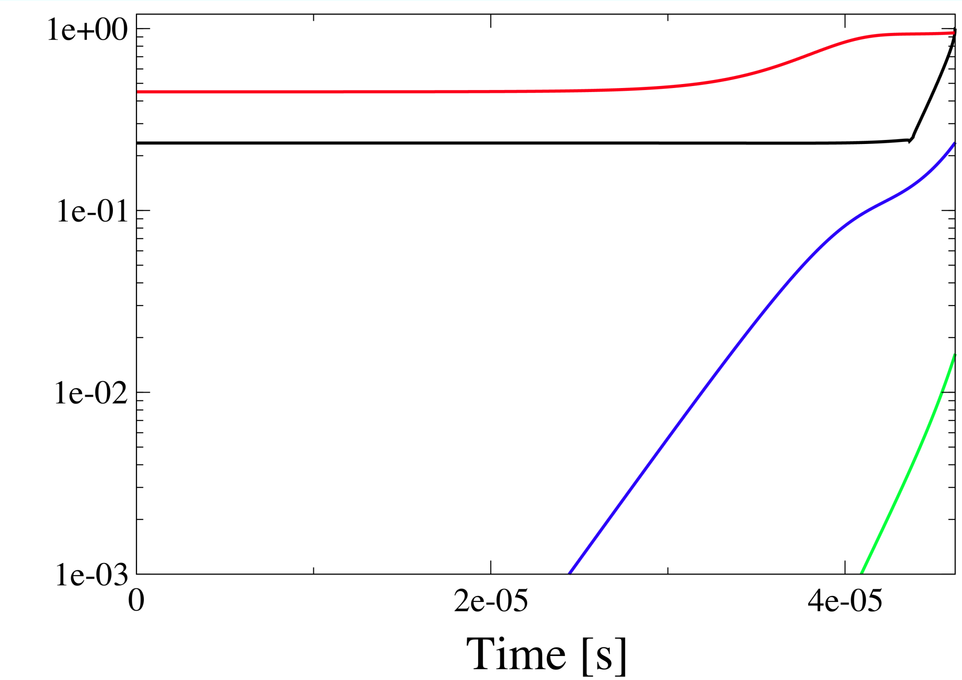
Fast reactions: $2OH\ (+M) \Leftrightarrow H_2O_2\ (+M)$

$O + OH\ (+M) \Leftrightarrow HO_2\ (+M)$

$H_2O + O_2 \Leftrightarrow 2\ OH$

$H_2 + OH \Leftrightarrow H_2O + H$

Region I (M=1): QSSA/PEA



$$\varepsilon = \frac{\tau_{1,\ \text{slowest of fast}}}{\tau_{2,\ \text{fastest of slow}}}$$

$$\left[D_{\mathbf{y}^r}\mathbf{f}^s\right]\left[D_{\mathbf{y}^r}\mathbf{g}^r\right]^{-1} = O(\varepsilon)$$ Stability QSSA/PEA

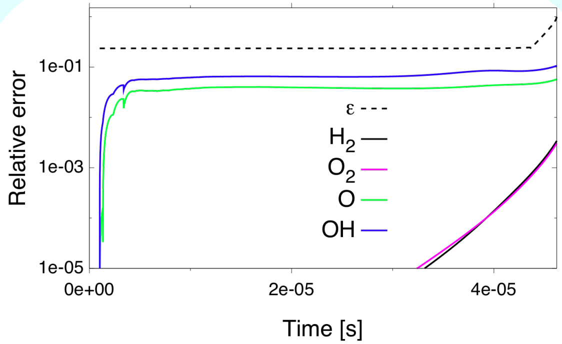
$$\left[D_{\mathbf{y}^r}\mathbf{g}^r\right]^{-1}\left[D_{\mathbf{a}_S}\mathbf{g}^r\right] = O(\varepsilon)$$ Accuracy PEA

$$\left[D_{\mathbf{y}^r}\mathbf{R}^r\right]^{-1}\left[D_{\mathbf{y}^S}\mathbf{R}^r\right] = O(\varepsilon)$$ PEA ->QSSA

QSSA/PEA stability OK
PEA accuracy OK (?)
PEA->QSSA OK

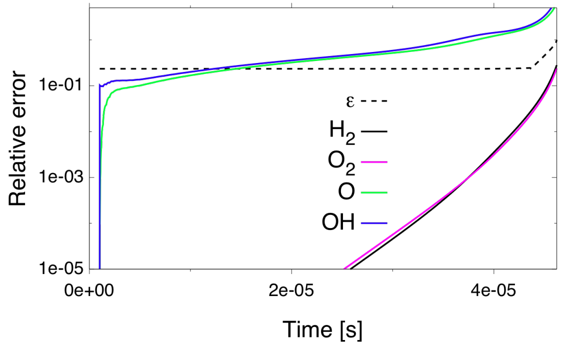
Region I (M=1), QSSA/PEA: accuracy

CSP



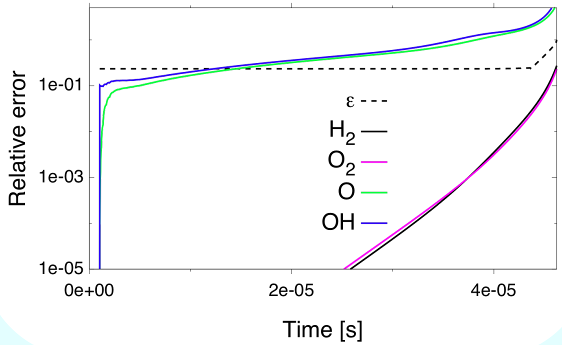
Asymptotics OK

PEA

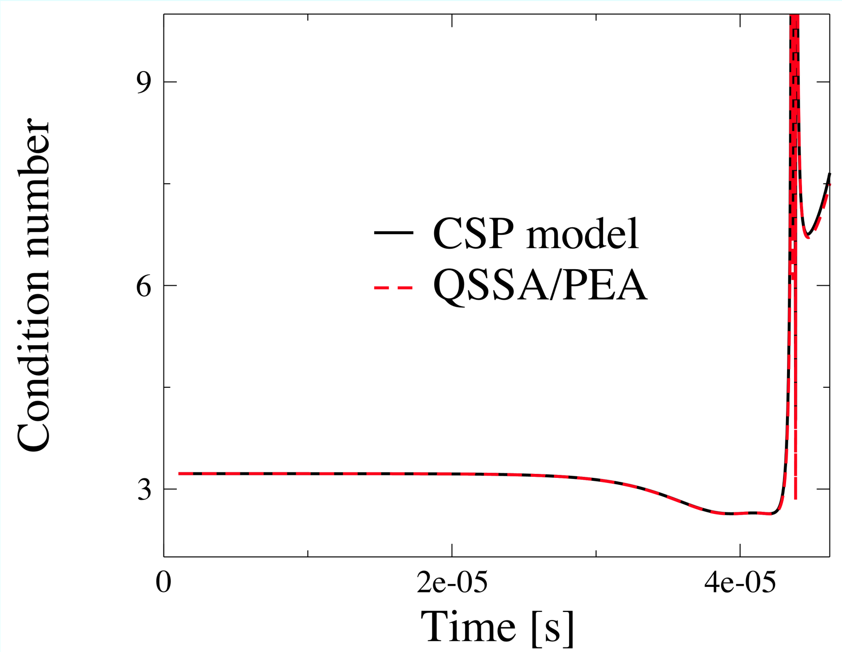


PEA accuracy OK (?)
PEA->QSSA OK

QSSA

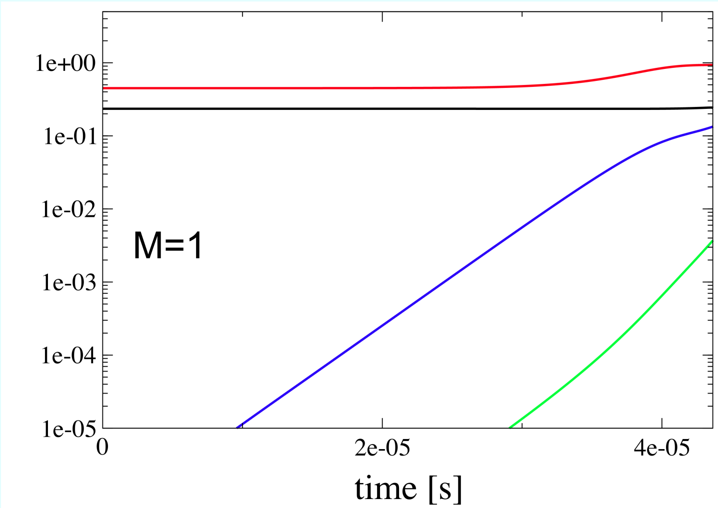


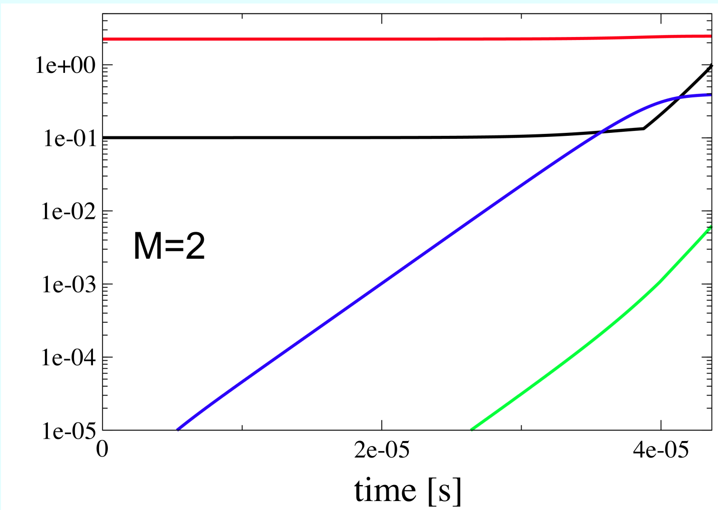
Region I (M=1), QSSA/PEA: stability



QSSA/PEA stability ok
PEA accuracy ok (?)
PEA->QSSA ok

Region I (M=1 and 2): QSSA/PEA





$$\varepsilon = \frac{\tau_{1\text{ or }2,\text{ slowest of fast}}}{\tau_{2\text{ or }3,\text{ fastest of slow}}}$$

$$\left[D_{\mathbf{y}^r}\mathbf{f}^s\right]\left[D_{\mathbf{y}^r}\mathbf{g}^r\right]^{-1} = O(\varepsilon)$$ Stability QSSA/PEA

$$\left[D_{\mathbf{y}^r}\mathbf{g}^r\right]^{-1}\left[D_{\mathbf{a}_s}\mathbf{g}^r\right] = O(\varepsilon)$$ Accuracy PEA

$$\left[D_{\mathbf{y}^r}\mathbf{R}^r\right]^{-1}\left[D_{\mathbf{y}^s}\mathbf{R}^r\right] = O(\varepsilon)$$ PEA ->QSSA

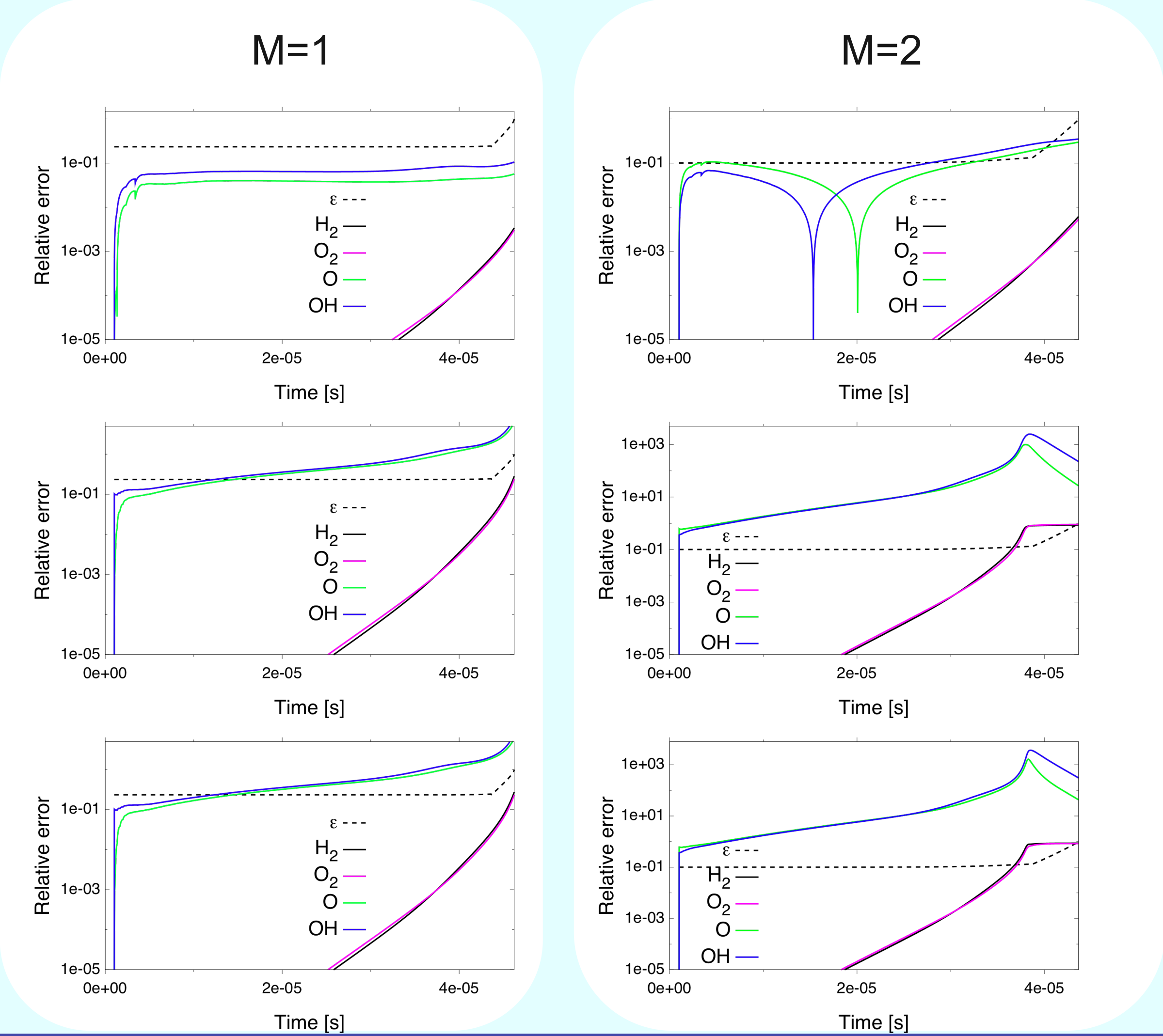
QSSA/PEA stability	M=1: ok	M=2: ok
PEA accuracy	M=1: ok	M=2: not so
PEA->QSSA	M=1: ok	M=2: ok

Region I (M=1 and 2), QSSA/PEA: accuracy

CSP

PEA

QSSA



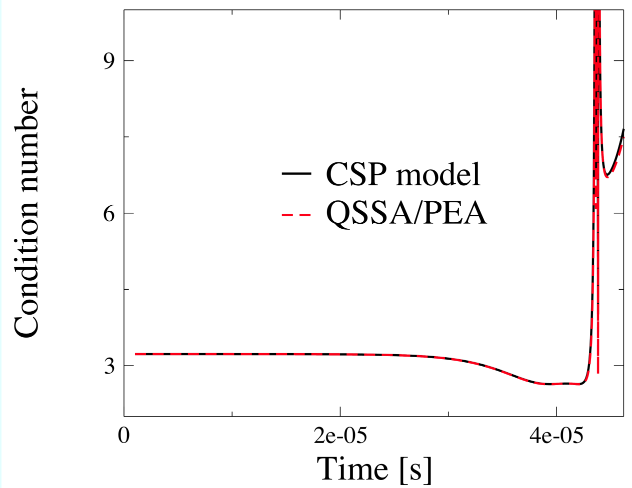
Asymptotics ok

M=1
PEA accuracy ok (?)
PEA->QSSA ok

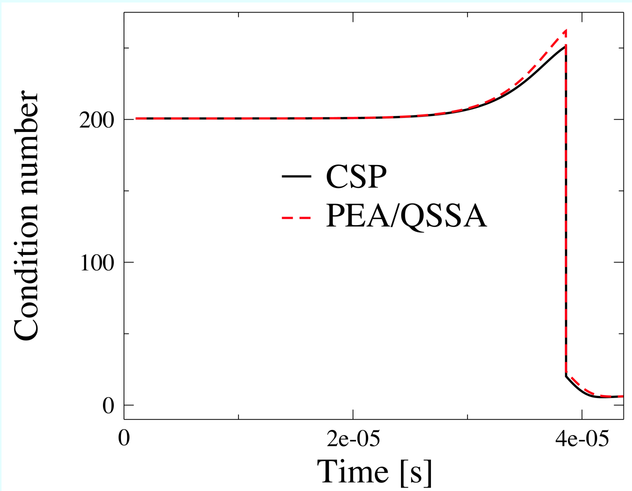
M=2
PEA accuracy not ok
PEA->QSSA ok

Region I (M=2), QSSA/PEA: stability

M=1



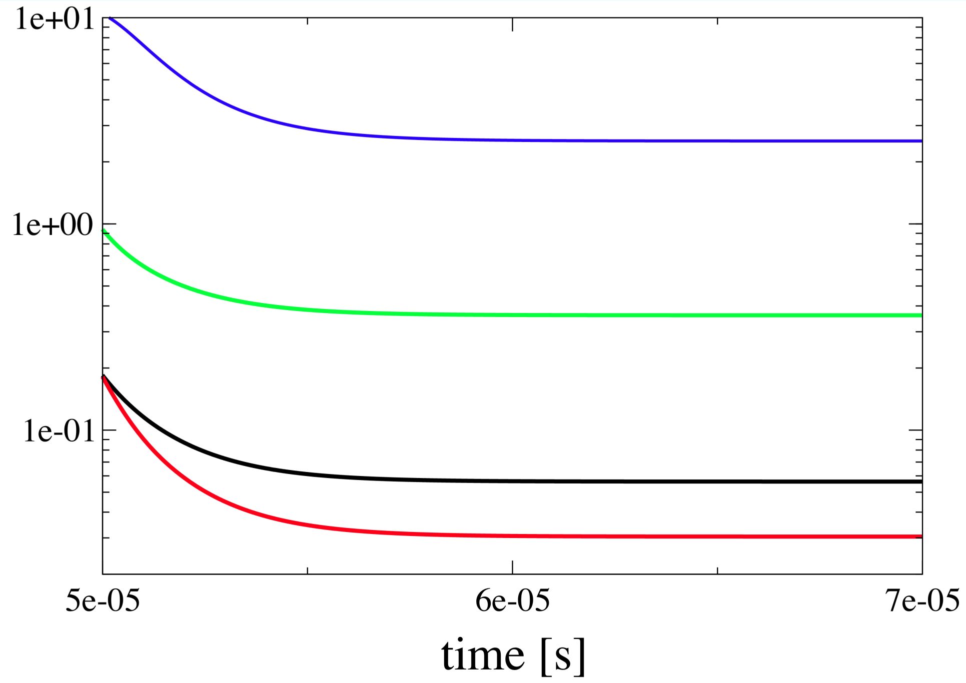
M=2



M=1
QSSA/PEA stability ok
PEA accuracy ok (?)
PEA->QSSA ok

M=2
QSSA/PEA stability ok
PEA accuracy not ok
PEA->QSSA ok

Region II (M=4): QSSA/PEA



$$\varepsilon = \frac{\tau_{4,\ \text{slowest of fast}}}{\tau_{5,\ \text{fastest of slow}}}$$

$$\left[D_{\mathbf{y}^r}\mathbf{f}^s\right]\left[D_{\mathbf{y}^r}\mathbf{g}^r\right]^{-1} = O(\varepsilon)$$ Stability QSSA/PEA

$$\left[D_{\mathbf{y}^r}\mathbf{g}^r\right]^{-1}\left[D_{\mathbf{a}_S}\mathbf{g}^r\right] = O(\varepsilon)$$ Accuracy PEA

$$\left[D_{\mathbf{y}^r}\mathbf{R}^r\right]^{-1}\left[D_{\mathbf{y}^S}\mathbf{R}^r\right] = O(\varepsilon)$$ PEA ->QSSA

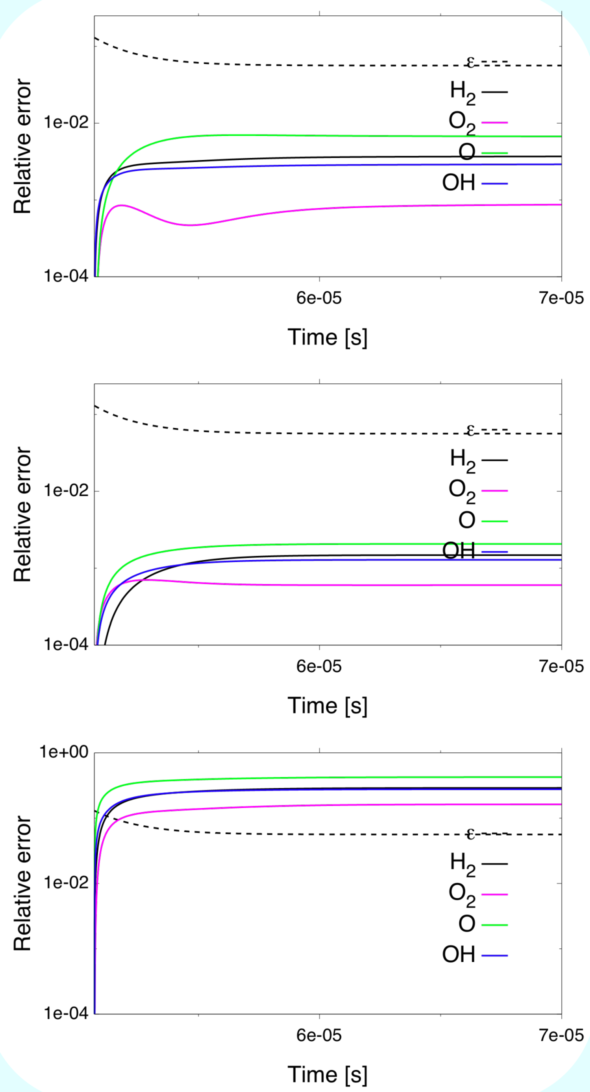
QSSA/PEA stability	not ok
PEA accuracy	ok
PEA->QSSA	not ok

Region II (M=4), QSSA/PEA: accuracy

CSP

PEA

QSSA

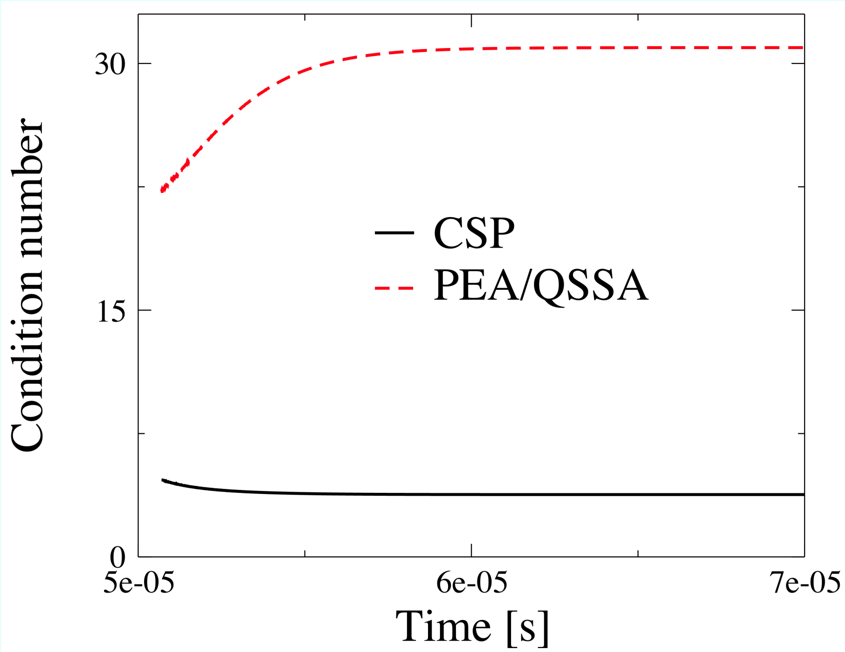


Asymptotics: OK

PEA accuracy ok

PEA->QSSA not ok

Region II (M=4), QSSA/PEA: stability



QSSA/PEA stability	not ok
PEA accuracy	ok
PEA->QSSA	not ok

Conclusions

There exist algorithms that can identify:

1. The number of fast time scales
2. The fast variables
3. The fast reactions
4. The possible validity of the QSSA/PEA