Reduction of reaction mechanisms

Time-scale analysis

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Multiscale analysis in combustion

1938, Zeldovich and Frank-Kamenetskii (large activation energy, flame speeds)

1939, Frank-Kamenetskii (large activation energy, ignition limits)

1963, Friedlander and Keller (Damkohler number asymptotics)

1964, Blythe (activation energy asymptotics, “sudden freezing” in supersonic flow)

1970, Bush and Fendell (activation energy asymptotics, laminar flame speed)

1971, Linan and Williams (activation energy asymptotics, ignition time)

1971, Williams (activation energy asymptotics, laminar flame speed and diffusion flames)

1980s Peters, Williams, Rogg, Pitsch, Mauss, Sheshardi, Linian, Sivashinsky, Buckmaster, De Goey

Rate-ratio asymptotics

Williams, Physica D 20:21-34, 1986

Buckmaster, Physica D 20:91-108, 1986

Williams, Proc. Combust. Inst., 30:1-19, 2005

Refs

Reduced mechanisms: rate-ratio asymptotics

1985

NUMERICAL AND ASYMPTOTIC ANALYSIS OF SYSTEMATICALLY REDUCED REACTION SCHEMES FOR HYDROCARBON FLAMES

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Abstract

We intend to close the gap between the numerical description of hydrocarbon flames using a large number of elementary reactions and the asymptotic description using very few reaction steps. To proceed in this direction we first reduce the hydrocarbon chemistry to the smallest number of steps that still provides a realistic flame structure. For the example of methane oxidation these are the four reaction steps

$$CH_4 + 2H + H_2O = CO + 4H_2 \quad (I)$$

$$CO + H_2O = CO_2 + H_2 \quad (II)$$

$$2H + M = H_2 + M \quad (III)$$

$$O_2 + 3H_2 = 2H + 2H_2O \quad (IV)$$

Their rates are algebraicly complicated expressions that contain kinetic data from 9 elementary reactions. If standard values for these data are used, the flame velocity of a stoichiometric methane-air flame is calculated as 45.6 cm/sec . The reaction rates may be simplified to include only data from the five most important reactions

$$CH_4 + H \rightarrow CH_3 + H_2$$

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

$$CO + OH \rightleftharpoons CO_2 + H$$

$$O_2 + H + M \rightarrow HO_2 + M$$

$$O_2 + H \rightleftharpoons OH + O$$

where the rate expression of the fourth of these reactions is modified. This model is proposed for the asymptotic analysis of the flame structure.

N Peters, *Numerical Simulation of Combustion Phenomena: Proceedings of the Symposium Held at INRIA Sophia-Antipolis, France May 21–24, 1985*. Berlin, Heidelberg: Springer Berlin Heidelberg, 2005.

1. Non-physical reactions
2. Rates are linear combination of elementary reaction rates
3. Accompanied by a number of QSSAs

Reduced mechanisms: rate-ratio asymptotics

1987

COMBUSTION AND FLAME 68: 185–207 (1987)

The Asymptotic Structure of Stoichiometric Methane–Air Flames

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and

F. A. WILLIAMS

Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544

A C_1-chain mechanism for methane flames is systematically reduced through steady-state and partial-equilibrium assumptions to the three-step mechanism

I $CH_4 + O_2 \rightarrow CO + H_2 + H_2O$,

II $CO + H_2O \rightleftarrows CO_2 + H_2$,

III $O_2 + 2H_2 \rightarrow 2H_2O$,

with rates that still contain the kinetic information of the elementary mechanism.

1. Non-physical reactions
2. Rates are linear combination of elementary reaction rates
3. Accompanied by a number of QSSAs

Multiscale character of reacting proceses

QSSA (species)
rate of production =
rate of consumption

PEA (reactions)
forward rate =
backward rate

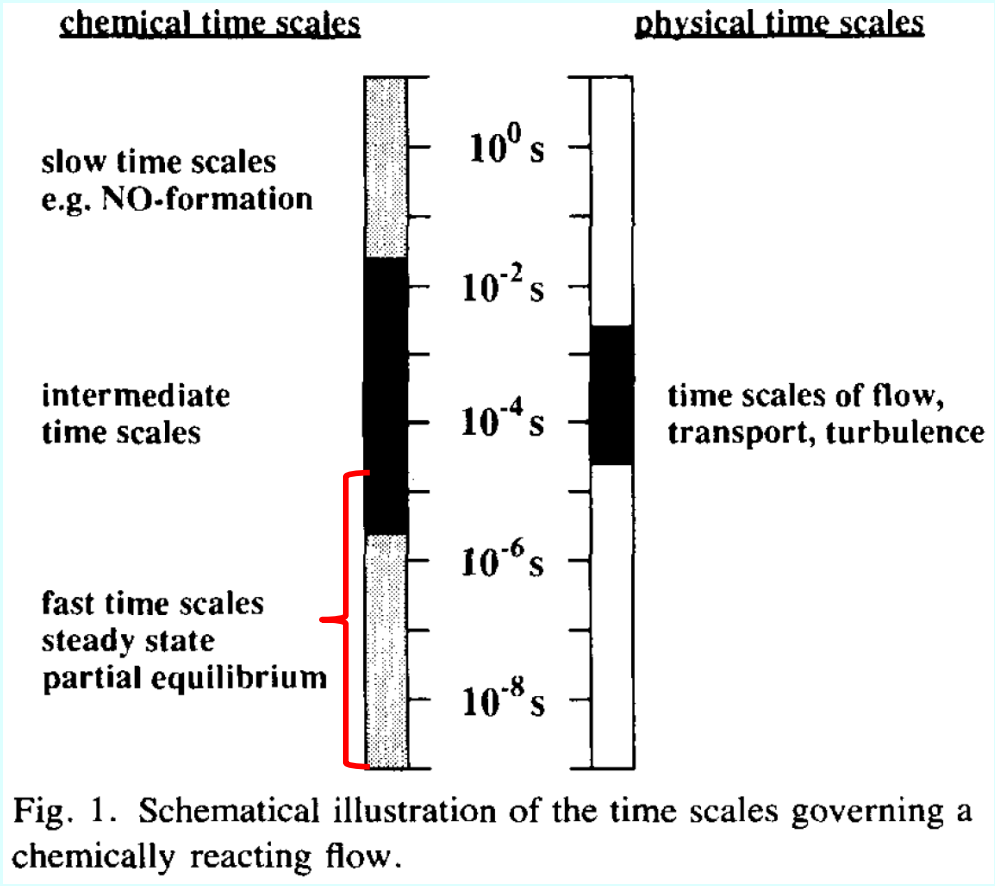


Fig. 1. Schematical illustration of the time scales governing a chemically reacting flow.

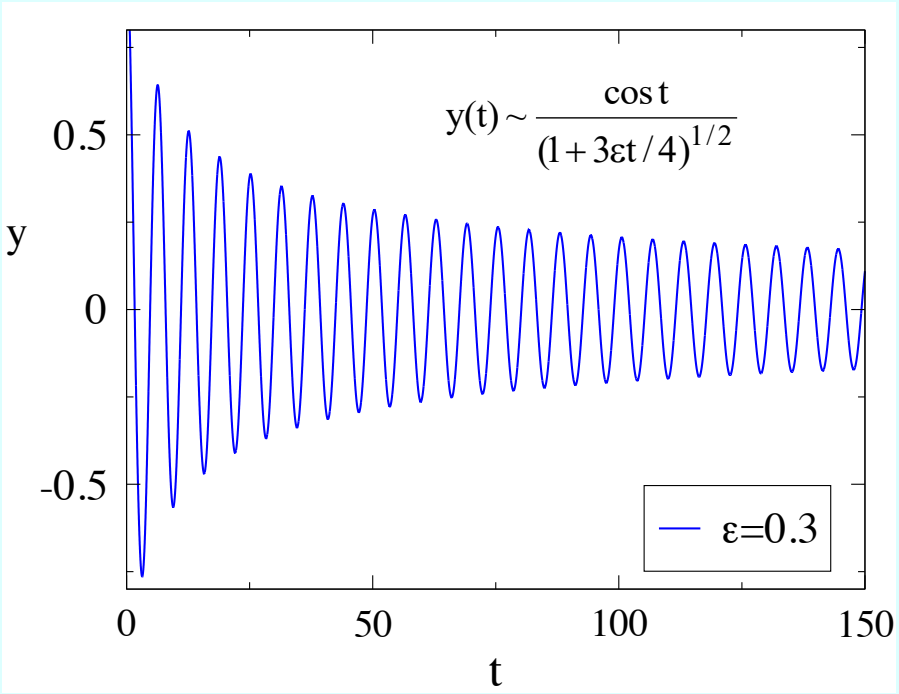
Maas & Pope, C&F 1992

Outline

1. Multiscale (fast/slow) dynamics
2. Time scales
3. Traditional reduction tools and their limitations
4. Alternative view for model reduction
5. Algorithmic model reduction; CSP
6. Various extensions; ILDM, REDIM, ISAT
7. Applications

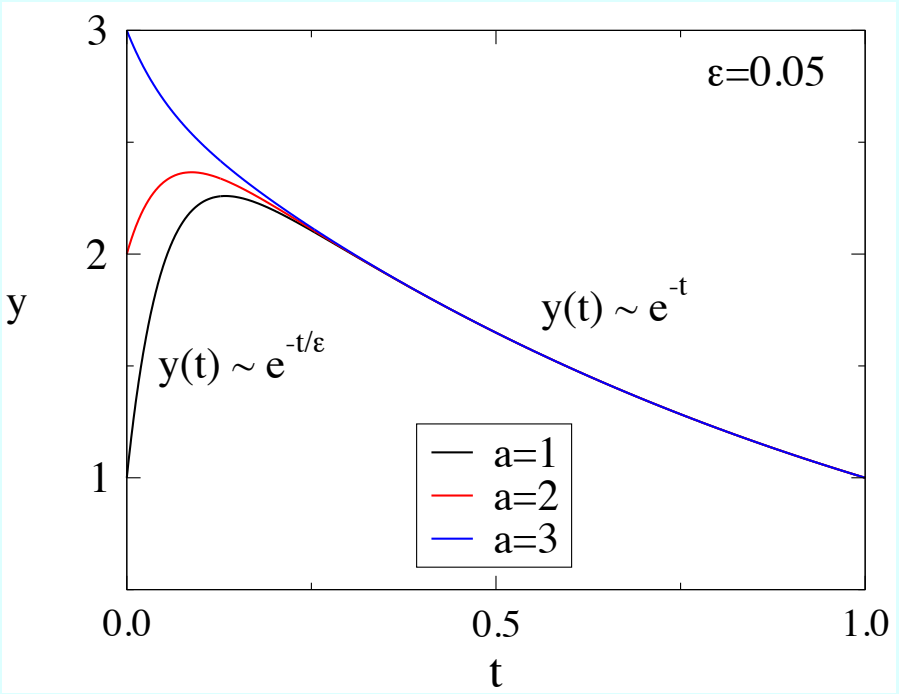
Fast / Slow systems

Multiple time scale problem



$$y'' + \varepsilon (y')^3 + y = 0$$
$$y(0) = 1 \qquad y'(0) = 0$$

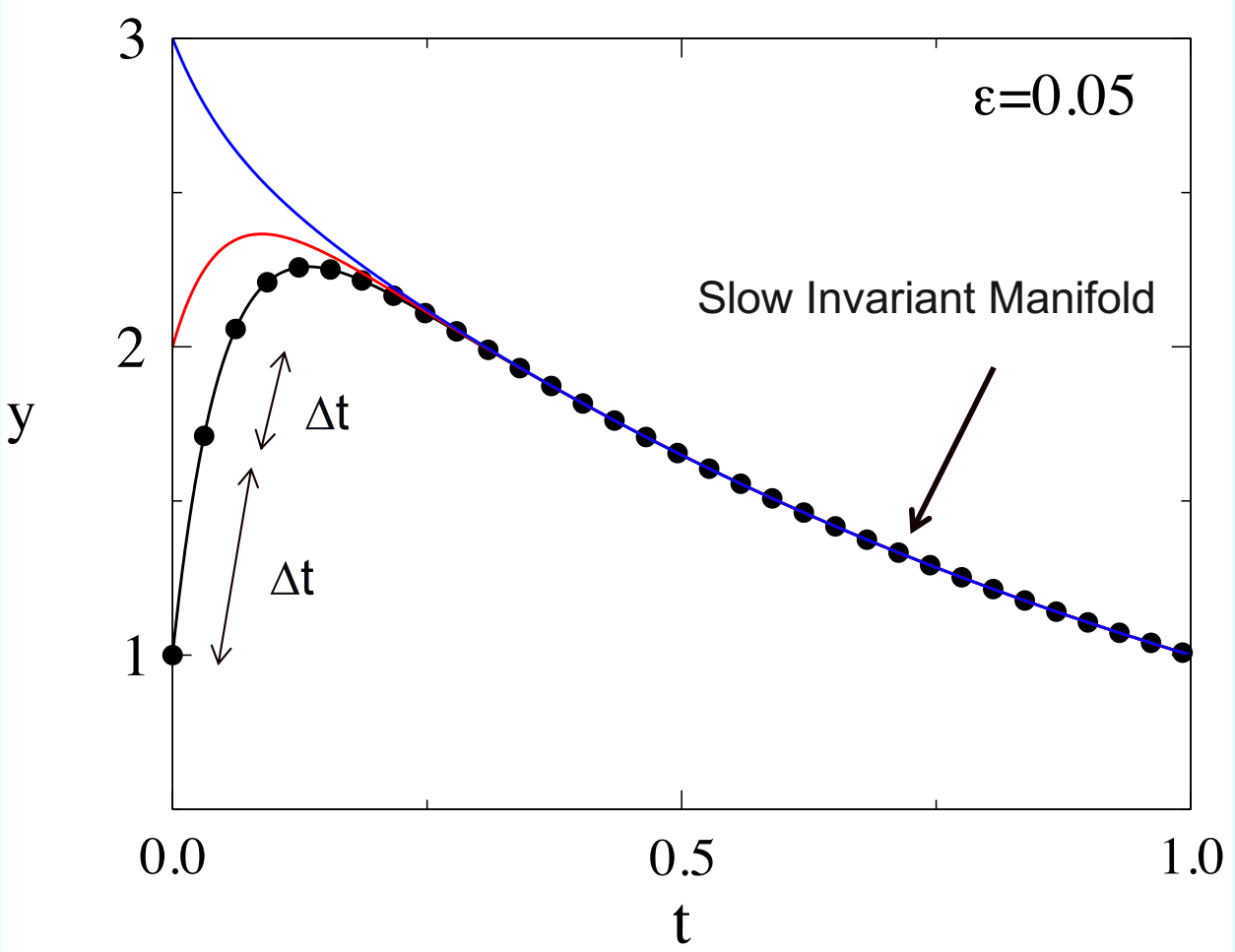
Boundary layer problem



$$\varepsilon y'' + (1+\varepsilon) y' + y = 0$$
$$y(0) = a \qquad y(1) = 1$$

Bender and Orszag 1978

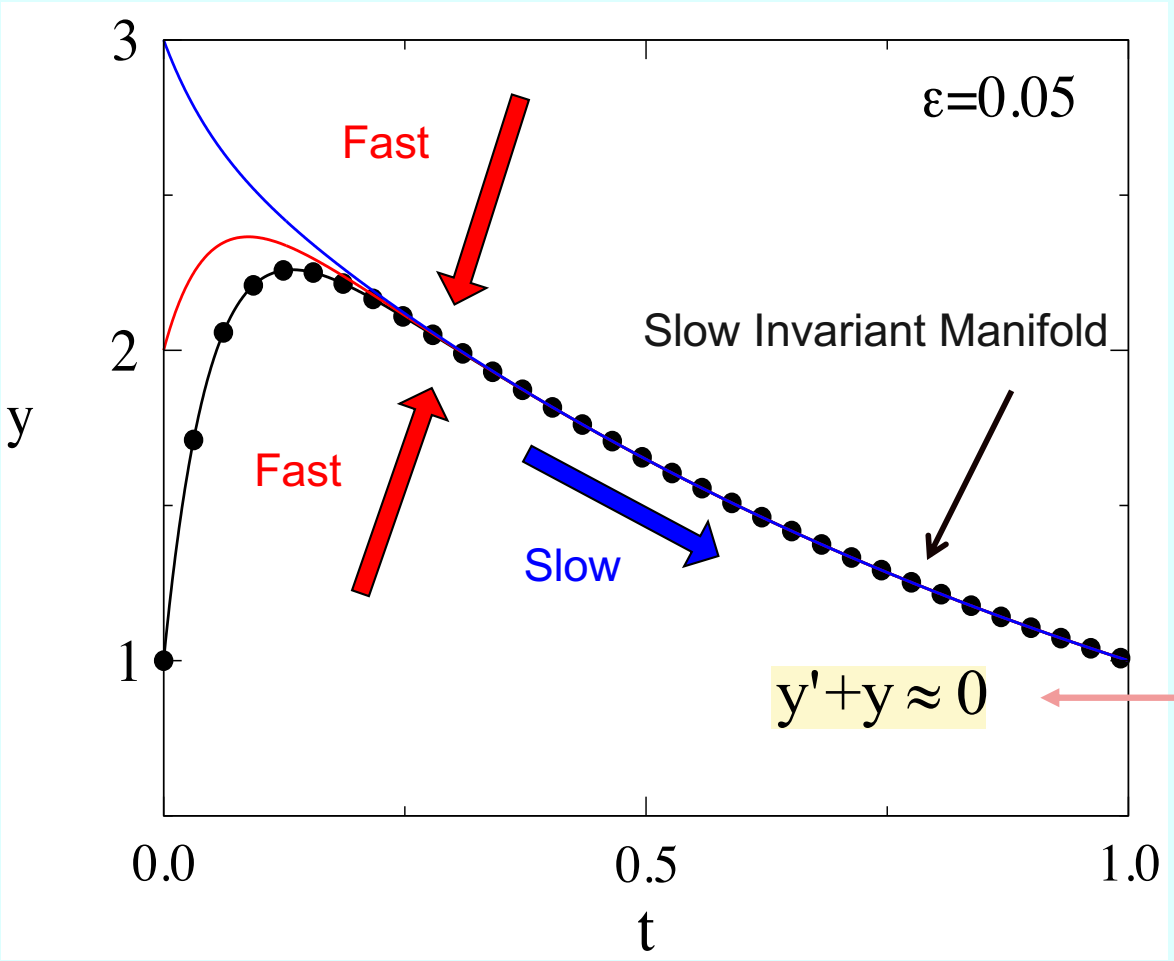
Boundary layer problem



$$\varepsilon y'' + (1+\varepsilon)y' + y = 0$$

$$y(0) = a \qquad y(1) = 1$$

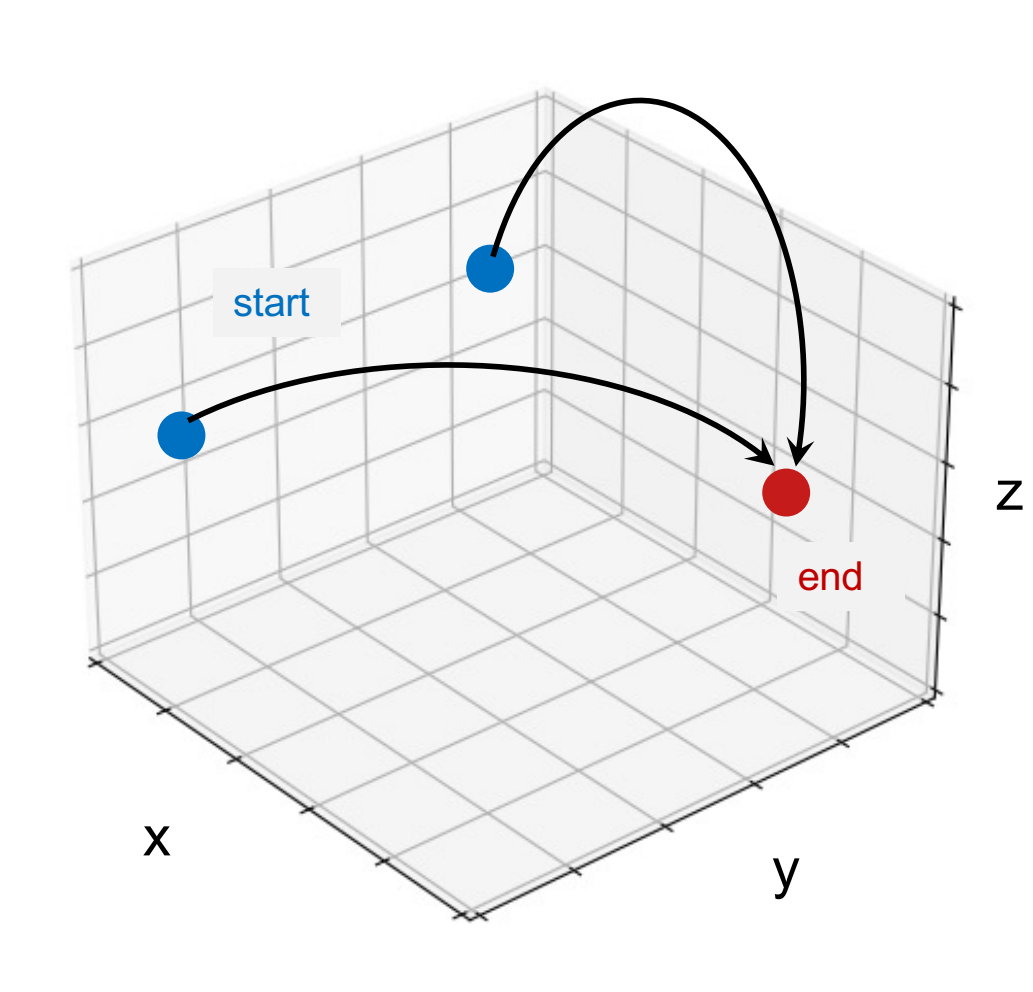
Fast and slow time scales



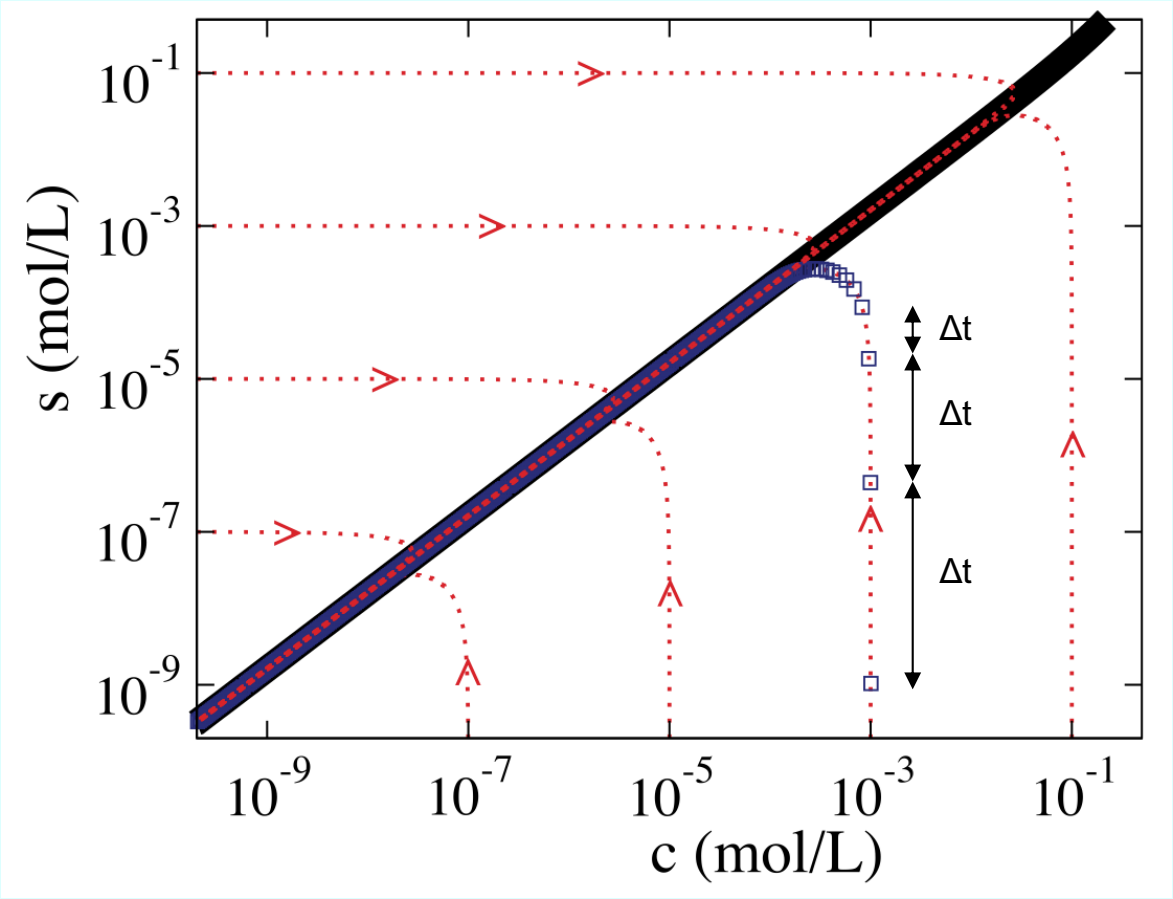
$$\varepsilon y'' + (1+\varepsilon)y' + y = 0$$

$$y(0) = a \qquad y(1) = 1$$

Distinct paths ?



Distinct paths ?



Michaelis – Menten model

$$E + S \underset{k_{1b}}{\overset{k_{1f}}{\Leftrightarrow}} C \overset{k_2}{\Rightarrow} E + P$$

$$\frac{d}{dt}\begin{bmatrix} s \\ c \end{bmatrix} = \mathbf{S}_1 R^1 + \mathbf{S}_2 R^2$$

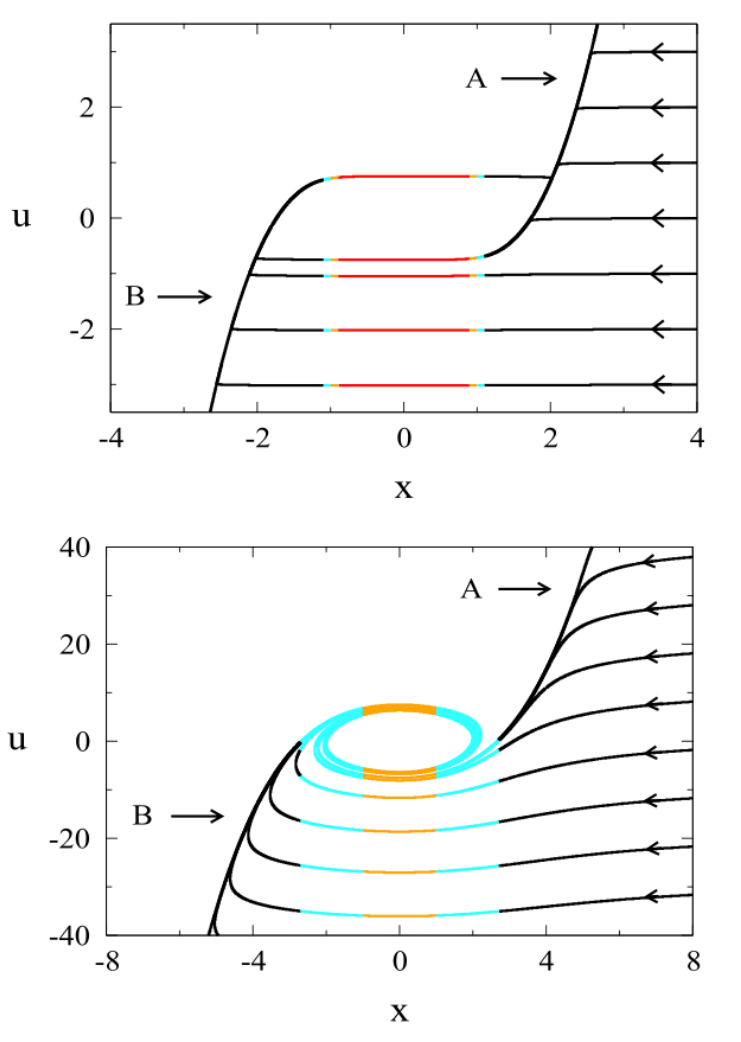
$$\mathbf{S}_1 = \begin{bmatrix} -1 \\ 1 \end{bmatrix} \quad \mathbf{S}_2 = \begin{bmatrix} 0 \\ -1 \end{bmatrix}$$

$$R^1 = k_{1f}(e_o - c)s - k_{1b}c$$

$$R^2 = k_2 c$$

$k_{1f} = 1\ L(mol\ s)^{-1} \quad k_{1b} = k_2 = 1\ s^{-1} \quad e_o = 1\ mol\ L^{-1}$

Distinct paths ?



$\epsilon = 10^{-2}$

$\epsilon = 10^{1}$

Van der Pol model

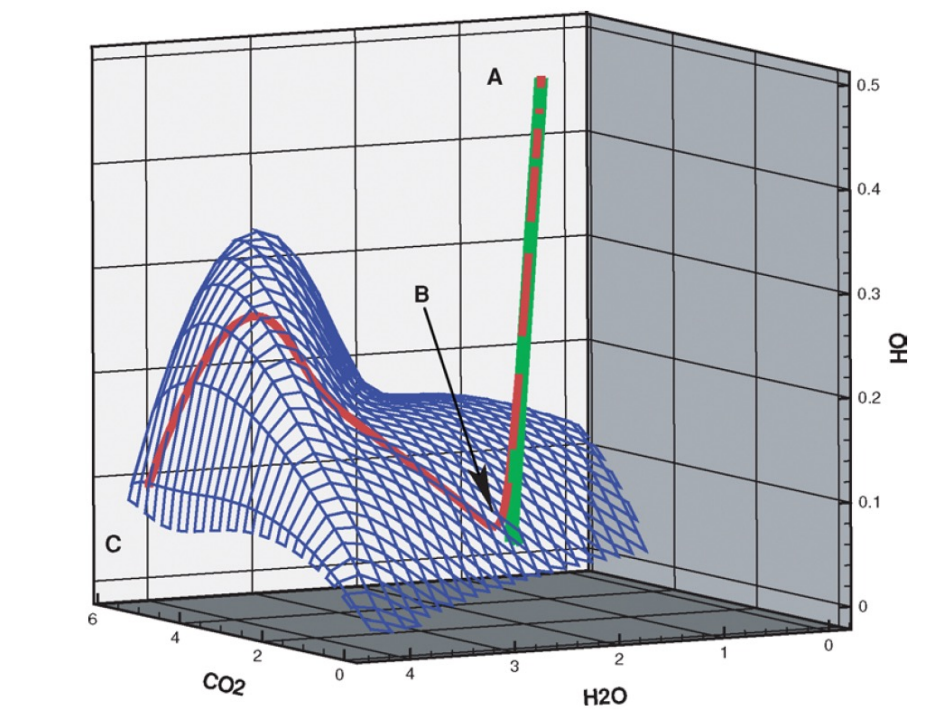
$$\frac{dx}{dt} = \frac{1}{\epsilon}(u - q(x))$$

$$\frac{du}{dt} = -x$$

$$q(x) = \frac{x^3}{3} - x$$

B. Van der Pol, *Radio Review* 1 (1920)

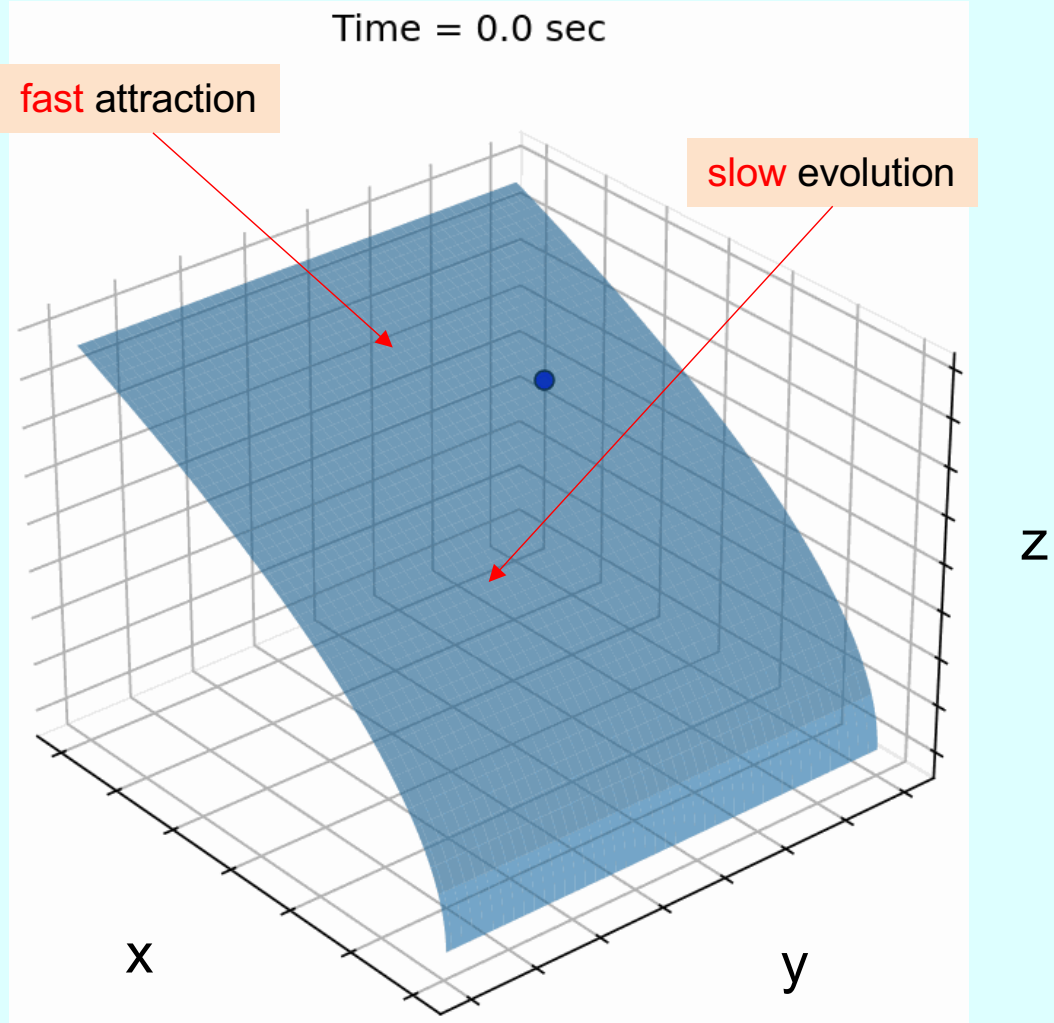
Distinct paths ?



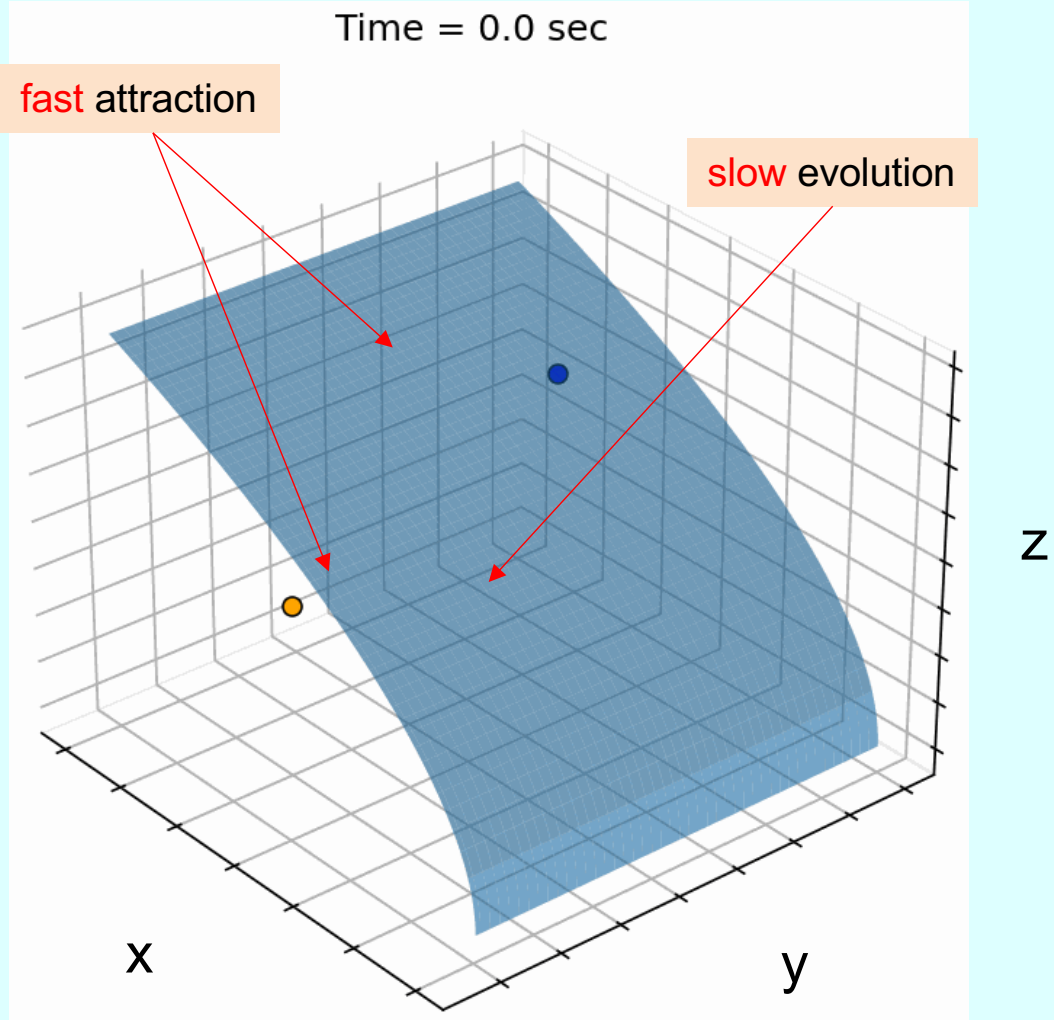
Homogeneous syngas/air system onto the $CO_2 - H_2O - OH$ space

Bykov & Maas, CTM 2007

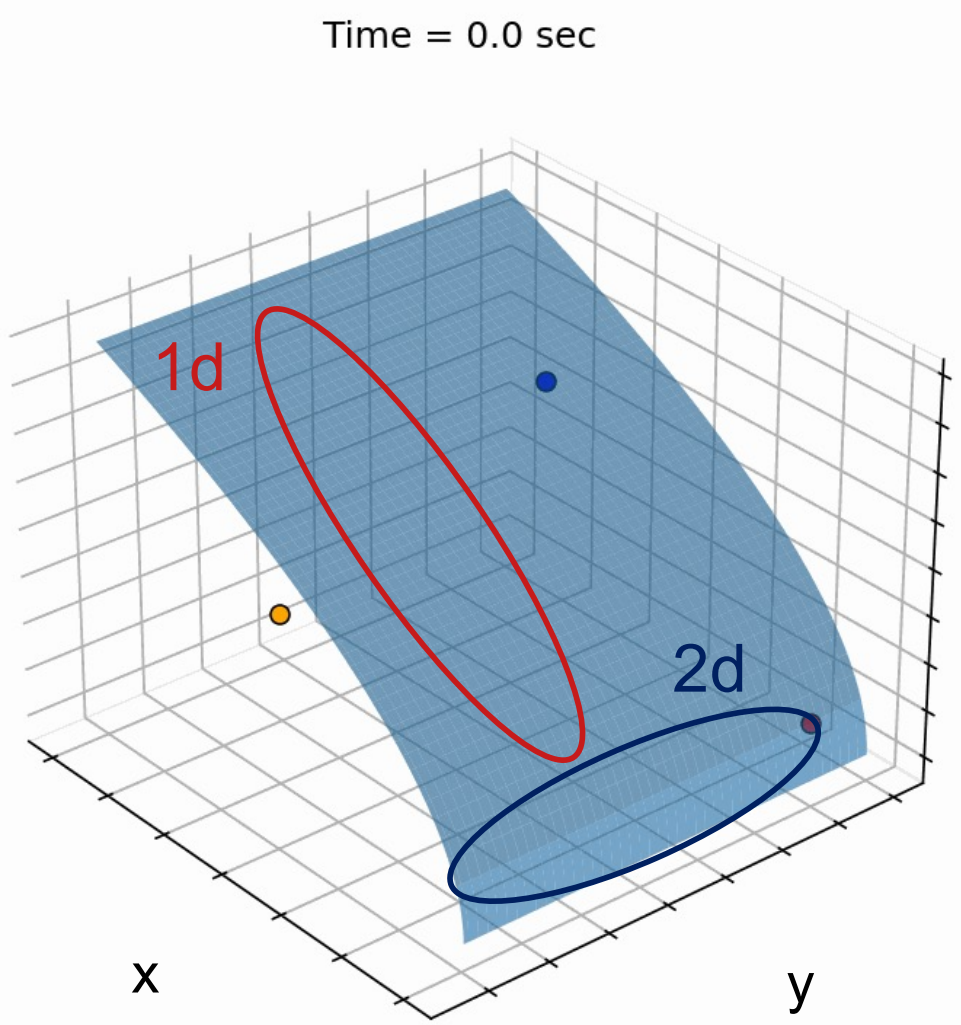
Fast-Slow transitions



Fast-Slow transitions



Fast-Slow transitions



Find:
(i) the constraints
(ii) the SIMPLE model that governs the slow evolution

Multi-scale analysis

Henri Poincaré

Celestial mechanics

"On curves defined by differential equations"
(1881–1882)

$$S + E \underset{k_{1b}}{\overset{k_{1f}}{\rightleftharpoons}} C \xrightarrow{k_2} E + P$$

Michaelis – Menten model

[1] V. Henri, Lois générales de l'action des diastases, Librairie Scientifique A. Hermann, 1903.

[2] A. J. Brown, Enzyme action, Journal of the Chemical Society, Transactions 81 (1902) 373–388.

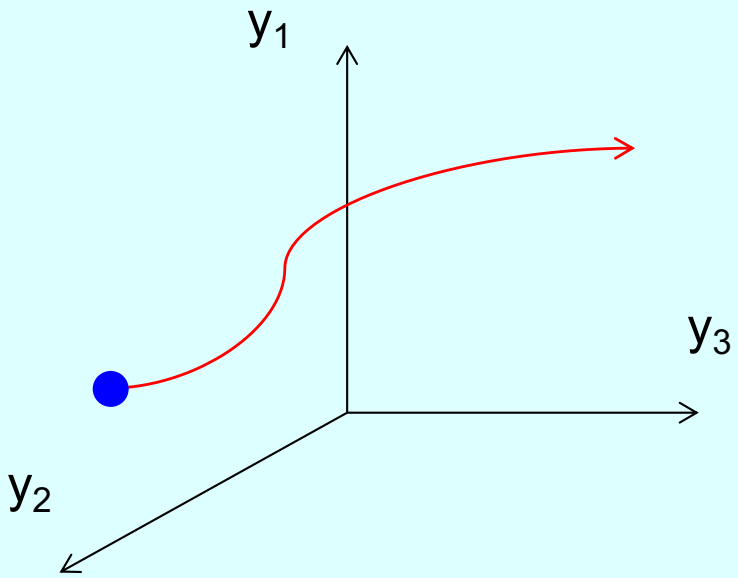
[3] L. Michaelis, M. L. Menten, Die kinetik der invertinwirkung, Biochem Z. 49 (1913) 333–369.

Methods of: Asymptotic expantions
Singular perturbations

Very tedious procedures
(most dreadful graduate course !!)

Most analyzed multi-scale model (2D)
1st global reduced model in 2018

Phase space



$$\frac{d}{dt}\begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix} = \begin{bmatrix} g_1(y_1, y_2, y_3) \\ g_2(y_1, y_2, y_3) \\ g_3(y_1, y_2, y_3) \end{bmatrix}$$

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y})$$

g(y): chemical kinetics source term:

$$\mathbf{g}(\mathbf{y}) = \mathbf{S}_1 R^1 + \mathbf{S}_2 R^2 + \ldots + \mathbf{S}_K R^K$$

y_i: concentration of i-th species

R^k: rate of k-th reaction

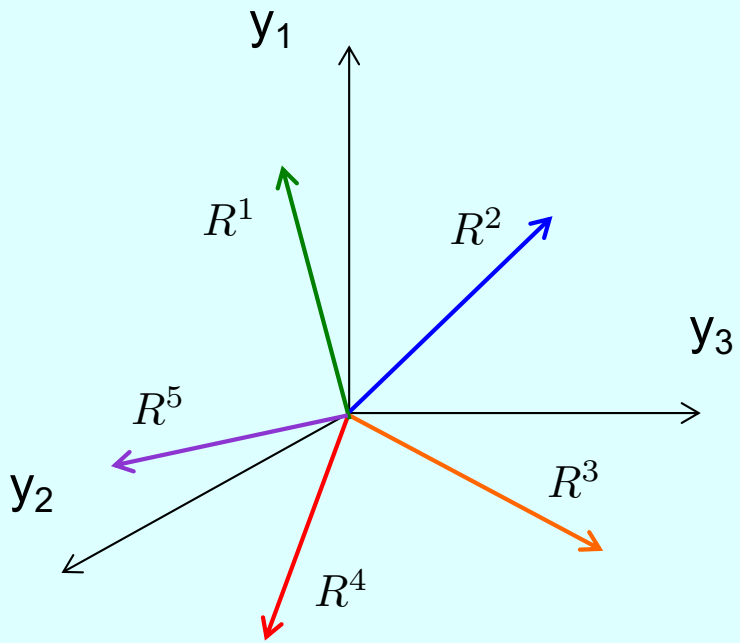
$\mathbf{S}_k$: stoichiometric vector of k-th reaction

$$H_2 + O \rightarrow H_2O$$

$$y_1 = [H_2],\ y_2 = [O],\ y_3 = [H_2O] \qquad \mathbf{S} = \begin{bmatrix} -1 \\ -1 \\ 1 \end{bmatrix}$$

$$R = k[H_2][O]$$

Stoichiometric vectors – Reaction rates



$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y})$$

$$\mathbf{g}(\mathbf{y}) = \mathbf{S}_1 R^1 + \mathbf{S}_2 R^2 + \ldots + \mathbf{S}_K R^K$$

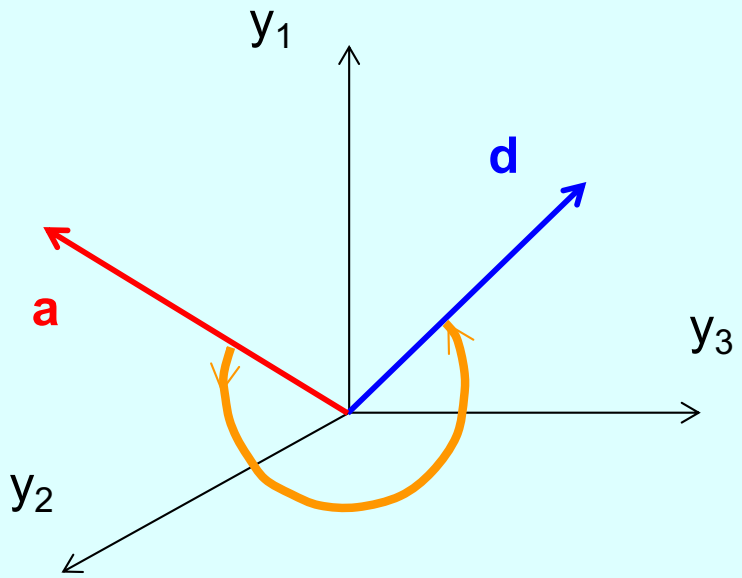
The i-th stoichiometric vector $\mathbf{S}_i$ points to the direction in which the i-th reaction tends to move the system

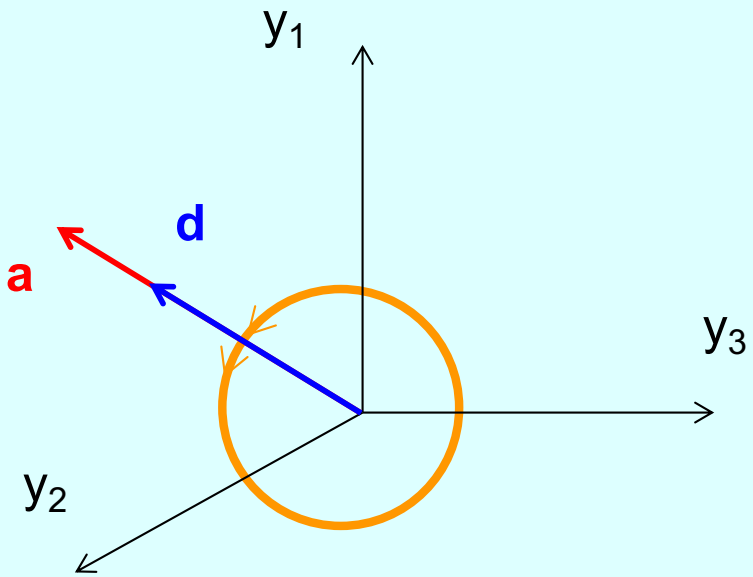
Which reactions drive the system or determine the characteristic time scale?

Which part of phase space is accessible by the trajectories?

Does the influence of the i-th reaction depends on the magnitude of its rate R^i ?

Eigenvalues and Eigenvectors





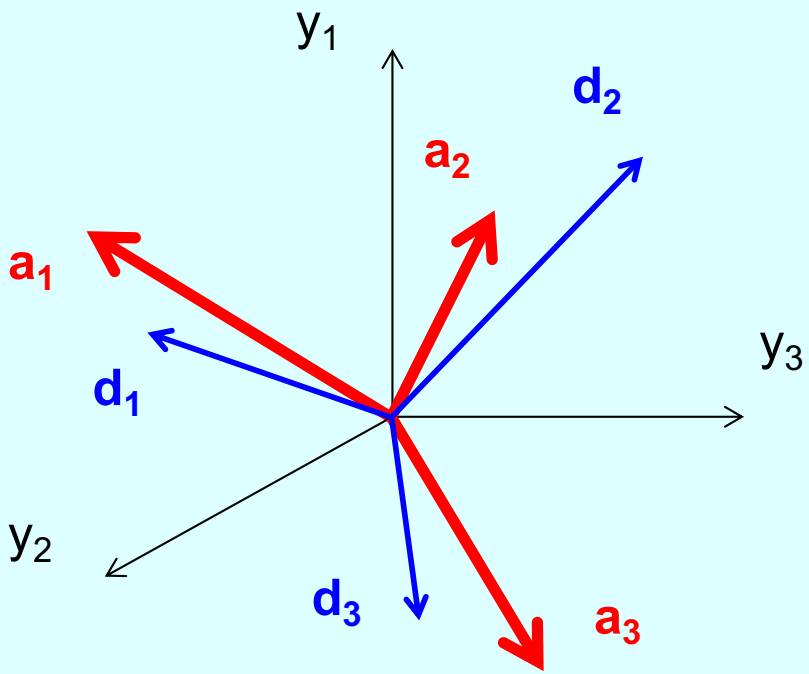
$$\begin{bmatrix} C_1^1 & C_2^1 & C_3^1 \\ C_1^2 & C_2^2 & C_3^2 \\ C_1^3 & C_2^3 & C_3^3 \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} = \begin{bmatrix} d_1 \\ d_2 \\ d_3 \end{bmatrix}$$

$$\mathbf{Ca} = \mathbf{d}$$

$$\begin{bmatrix} C_1^1 & C_2^1 & C_3^1 \\ C_1^2 & C_2^2 & C_3^2 \\ C_1^3 & C_2^3 & C_3^3 \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} = \begin{bmatrix} d_1 \\ d_2 \\ d_3 \end{bmatrix} = \lambda \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix}$$

$$\mathbf{Ca} = \mathbf{d} = \lambda\mathbf{a}$$

Eigenvalues and Eigenvectors



In general, given a NxN matrix there are N eigenvalues and N linearly independent eigenvectors

$$\mathbf{C}\mathbf{a}_n = \mathbf{d}_n = \lambda_n \mathbf{a}_n$$

Right (column) eigenvectors: $\mathbf{a} = \begin{bmatrix} \mathbf{a}_1 & \mathbf{a}_2 & \dots & \mathbf{a}_N \end{bmatrix}$ $\quad \mathbf{C}\mathbf{a}_n = \lambda_n \mathbf{a}_n$

Left (row) eigenvectors: $\mathbf{b} = \begin{bmatrix} \mathbf{b}^1 \\ \mathbf{b}^2 \\ \vdots \\ \mathbf{b}^N \end{bmatrix}$ $\quad \mathbf{b}^n \mathbf{C} = \lambda_n \mathbf{b}^n$

$$\mathbf{b}^i \cdot \mathbf{a}_j = \delta^i_j$$

Time scales

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}) \qquad \mathbf{y} = \mathbf{y}_o + \delta\mathbf{y} \qquad \frac{d\delta\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}_o) + \mathbf{J}(\mathbf{y}_o)\delta\mathbf{y}$$

$$\delta\mathbf{y}(0) = \mathbf{0}$$

$$\mathbf{J}(\mathbf{y}_o) = \nabla\mathbf{g}(\mathbf{y}_o)$$

$$\delta\mathbf{y} = \mathbf{a}_1\left(e^{\lambda_1 t} - 1\right)\frac{\mathbf{b}^1 \cdot \mathbf{g}(\mathbf{y}_o)}{\lambda_1} + \mathbf{a}_2\left(e^{\lambda_2 t} - 1\right)\frac{\mathbf{b}^2 \cdot \mathbf{g}(\mathbf{y}_o)}{\lambda_2} + \ldots$$

$\mathbf{a}_n$ Right eigenvector

$\mathbf{b}^n$ Left eigenvector

$$|\lambda_1| > |\lambda_2| > \ldots > |\lambda_N|$$

$$\tau_i = |\lambda_i|^{-1}$$

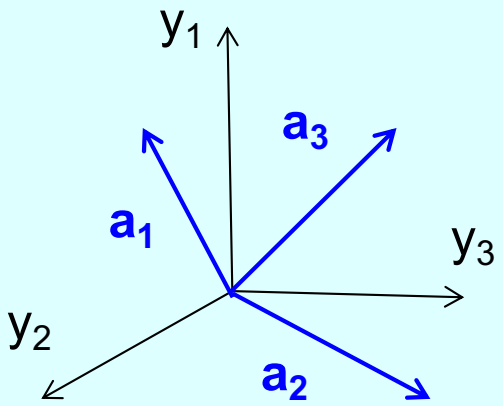
$\lambda_i < 0 \quad \tau_i : dissipative$

$\lambda_i > 0 \quad \tau_i : explosive$

When $\dfrac{\mathbf{b}^m \cdot \mathbf{g}(\mathbf{y}_o)}{\lambda_m} \approx 0 \qquad m = 1, \ldots, M$

Fast time scales: $\tau_m = |\lambda_m|^{-1} \qquad m = 1, \ldots, M$

Characteristic time scale: $\tau_{ch} = |\lambda_{M+1}|^{-1}$



Fast / slow directions

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}) \qquad \mathbf{y} = \mathbf{y}_o + \delta\mathbf{y} \qquad \frac{d\delta\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}_o) + \mathbf{J}(\mathbf{y}_o)\delta\mathbf{y}$$

$$\delta\mathbf{y}(0) = \mathbf{0}$$

$$\mathbf{J}(\mathbf{y}_o) = \nabla\mathbf{g}(\mathbf{y}_o)$$

$$\delta\mathbf{y} = \mathbf{a}_1\left(e^{\lambda_1 t} - 1\right)\frac{\mathbf{b}^1 \cdot \mathbf{g}(\mathbf{y}_o)}{\lambda_1} + \mathbf{a}_2\left(e^{\lambda_2 t} - 1\right)\frac{\mathbf{b}^2 \cdot \mathbf{g}(\mathbf{y}_o)}{\lambda_2} + \ldots$$

$\mathbf{a}_n$ Right eigenvector

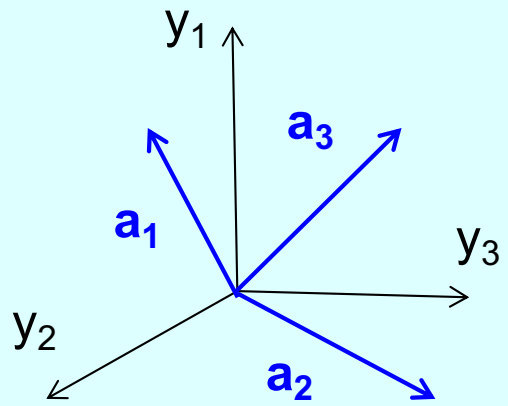
$\mathbf{b}^n$ Left eigenvector

$$|\lambda_1| > |\lambda_2| > \ldots > |\lambda_N|$$

Given the orthogonality condition: $\mathbf{I} = \mathbf{a}_1\mathbf{b}^1 + \mathbf{a}_2\mathbf{b}^2 + \ldots + \mathbf{a}_N\mathbf{b}^N$

it follows that the vector field can be decomposed as:

$$\mathbf{g}(\mathbf{y}_o) = \mathbf{a}_1\left(\mathbf{b}^1 \cdot \mathbf{g}(\mathbf{y}_o)\right) + \mathbf{a}_2\left(\mathbf{b}^2 \cdot \mathbf{g}(\mathbf{y}_o)\right) + \ldots + \mathbf{a}_N\left(\mathbf{b}^N \cdot \mathbf{g}(\mathbf{y}_o)\right)$$



When $\tau_m << \tau_{ch}$, i.e.: $\frac{\mathbf{b}^m \cdot \mathbf{g}(\mathbf{y}_o)}{\lambda_m} \approx 0 \qquad m = 1, \ldots, M$

The solution does not move along $\mathbf{a}_m \qquad m = 1, \ldots, M$

FAST directions

Fast / slow directions

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}) \qquad \mathbf{y} = \mathbf{y}_o + \delta\mathbf{y} \qquad \frac{d\delta\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}_o) + \mathbf{J}(\mathbf{y}_o)\delta\mathbf{y}$$

$$\delta\mathbf{y}(0) = \mathbf{0}$$

$$\mathbf{J}(\mathbf{y}_o) = \nabla\mathbf{g}(\mathbf{y}_o)$$

When $\tau_m << \tau_{ch}$, i.e.: $\dfrac{\mathbf{b}^m \cdot \mathbf{g}(\mathbf{y}_o)}{\lambda_m} \approx 0 \qquad m = 1, ..., M$

The solution moves along $\mathbf{a}_m \qquad m = M+1, ..., N$

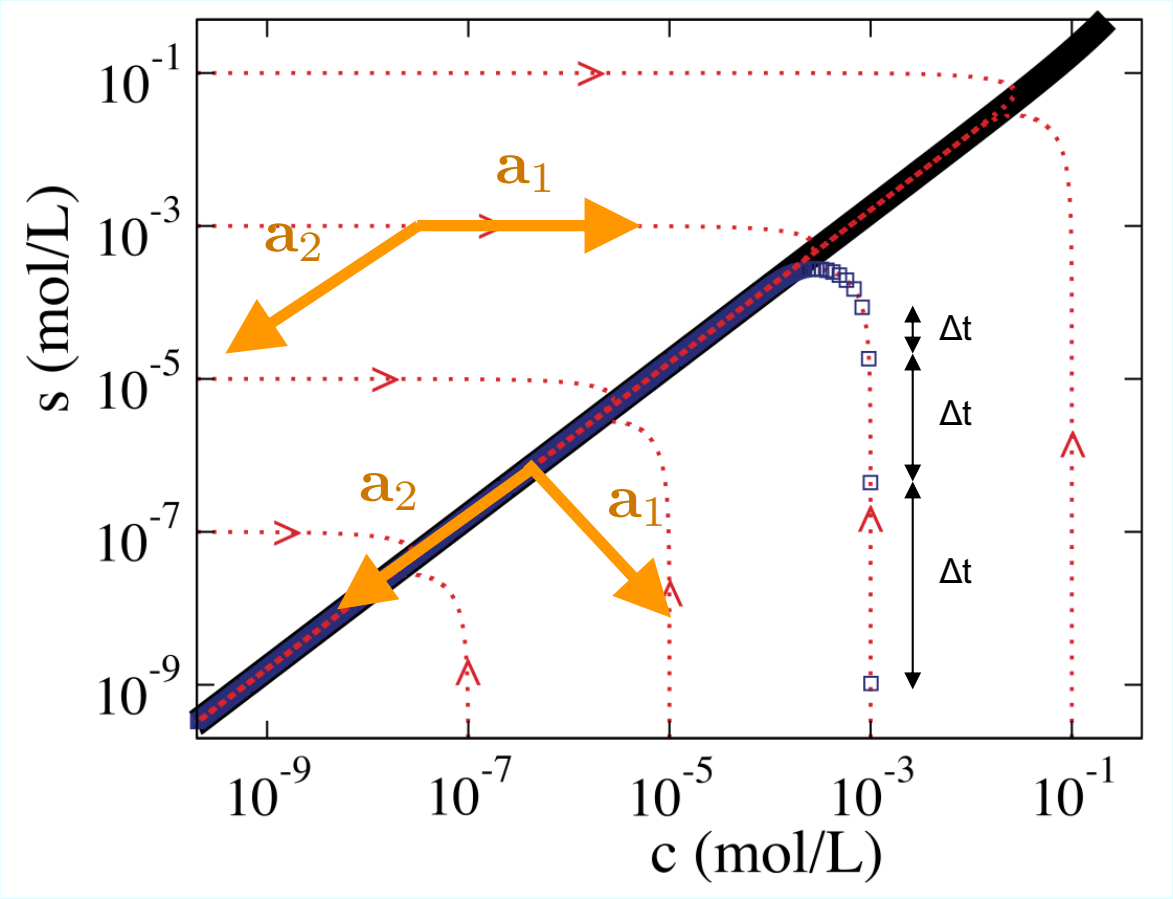
⇐ SLOW directions

$$\delta\mathbf{y} \approx \mathbf{a}_{M+1}\left(e^{\lambda_{M+1}t} - 1\right)\frac{\mathbf{b}^{M+1} \cdot \mathbf{g}(\mathbf{y}_o)}{\lambda_{M+1}} + \ldots + \mathbf{a}_N\left(e^{\lambda_N t} - 1\right)\frac{\mathbf{b}^N \cdot \mathbf{g}(\mathbf{y}_o)}{\lambda_N}$$

This is the solution of: $\dfrac{d\mathbf{y}}{dt} = \left[\mathbf{a}_{M+1}\mathbf{b}^{M+1} + \ldots + \mathbf{a}_N\mathbf{b}^N\right]\mathbf{g}(\mathbf{y})$

the components of **g** along the slow directions

Fast / slow dynamics



Michaelis – Menten model

$$E + S \underset{k_{1b}}{\overset{k_{1f}}{\Leftrightarrow}} C \overset{k_2}{\Rightarrow} E + P$$

$$\frac{d}{dt}\begin{bmatrix} s \\ c \end{bmatrix} = \mathbf{S}_1 R^1 + \mathbf{S}_2 R^2 = \mathbf{g}$$

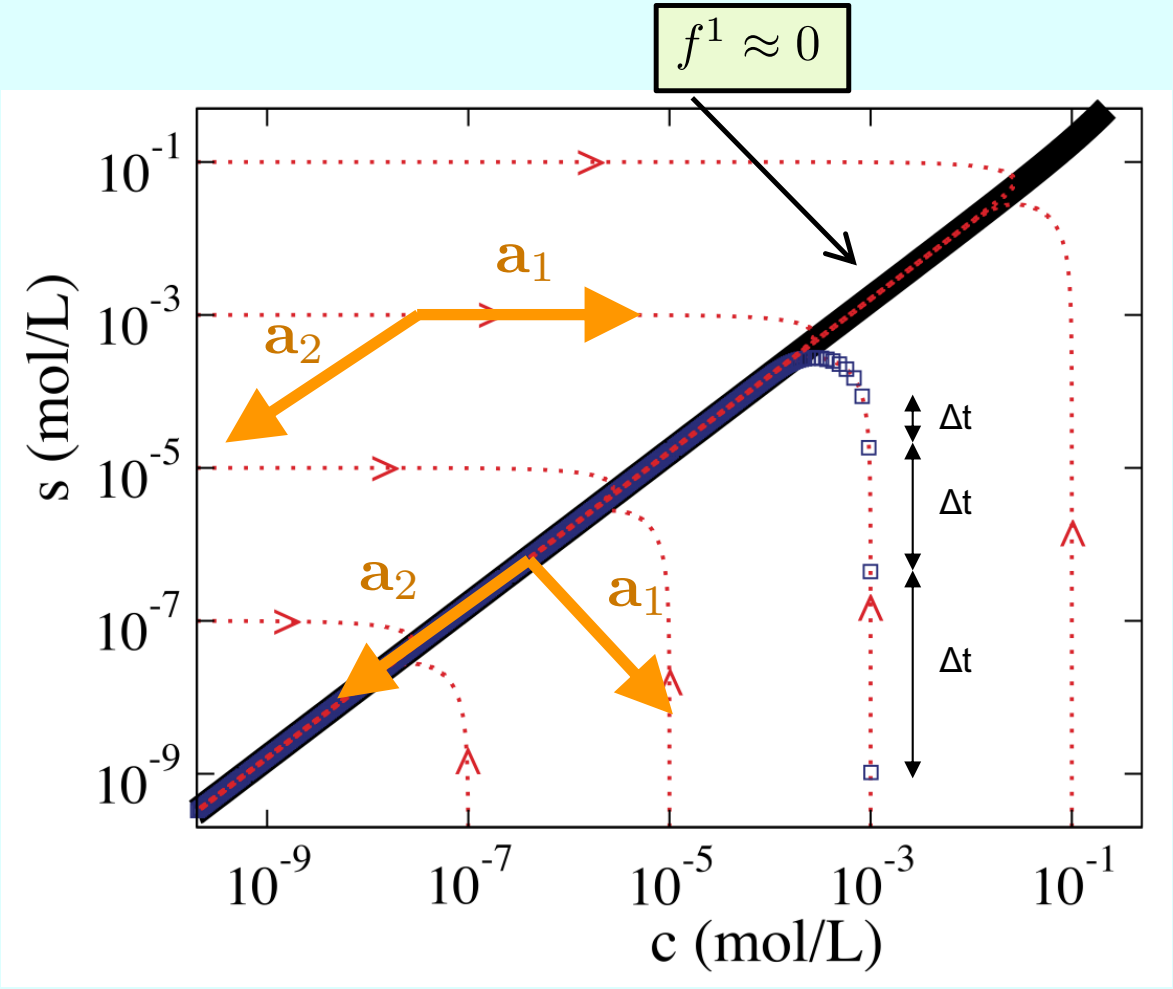
$$= \mathbf{a}_1 f^1 + \mathbf{a}_2 f^2$$

fast slow

$$f^i = \mathbf{b}^i \cdot \mathbf{g}$$

$$\mathbf{b}^i \cdot \mathbf{a}_j = \delta^i_j$$

Fast / slow dynamics



Michaelis – Menten model

$$E + S \underset{k_{1b}}{\overset{k_{1f}}{\Leftrightarrow}} C \overset{k_2}{\Rightarrow} E + P$$

$$\frac{d}{dt}\begin{bmatrix} s \\ c \end{bmatrix} = \mathbf{a}_1 f^1 + \mathbf{a}_2 f^2$$

fast slow

Fast transient

$$\frac{d}{dt}\begin{bmatrix} s \\ c \end{bmatrix} \approx \mathbf{a}_1 f^1 \quad (f^1 \gg f^2)$$

Slow reduced model

Slow evolution

$$\frac{d}{dt}\begin{bmatrix} s \\ c \end{bmatrix} \approx \mathbf{a}_2 f^2 \quad f^1 \approx 0$$

Conventional methodologies: QSSA and PEA

$$\frac{d}{dt}\begin{bmatrix} s \\ c \end{bmatrix} = \begin{bmatrix} -1 \\ 1 \end{bmatrix} R^1 + \begin{bmatrix} 0 \\ -1 \end{bmatrix} R^2 = \begin{bmatrix} g_s \\ g_c \end{bmatrix} \qquad R^1 = k_{1f}(e_o - c)s - k_{1b}c \qquad R^2 = k_2 c$$

$QSSA_{c,R^1}$ $\quad c,\ R^1 :\ fast \rightarrow\ g_c \approx 0 \qquad R^1 \approx R^2 \qquad \frac{ds}{dt} \approx -R^2$

$$c = \frac{k_{1f} e_o s}{(k_{1f}s + k_{1b} + k_2)}$$

$QSSA_{c,R^2}$ $\quad c,\ R^2 :\ fast \rightarrow\ g_c \approx 0 \qquad R^2 \approx R^1 \qquad \frac{ds}{dt} \approx -R^1$

$QSSA_{s,R^1}$ $\quad s,\ R^1 :\ fast \rightarrow\ g_s \approx 0 \qquad R^1 \approx 0 \qquad \frac{dc}{dt} = -R^2$

$$s = \frac{k_{1b} c}{k_{1f}(e_o - c)}$$

PEA_{R^1} $\quad R^1 :\ fast \rightarrow\ \frac{dR^1}{dt} \approx 0 \qquad R^1 \approx \frac{R^2}{1+\nu} \qquad \frac{ds}{dt} \approx -\frac{R^2}{1+\nu}$

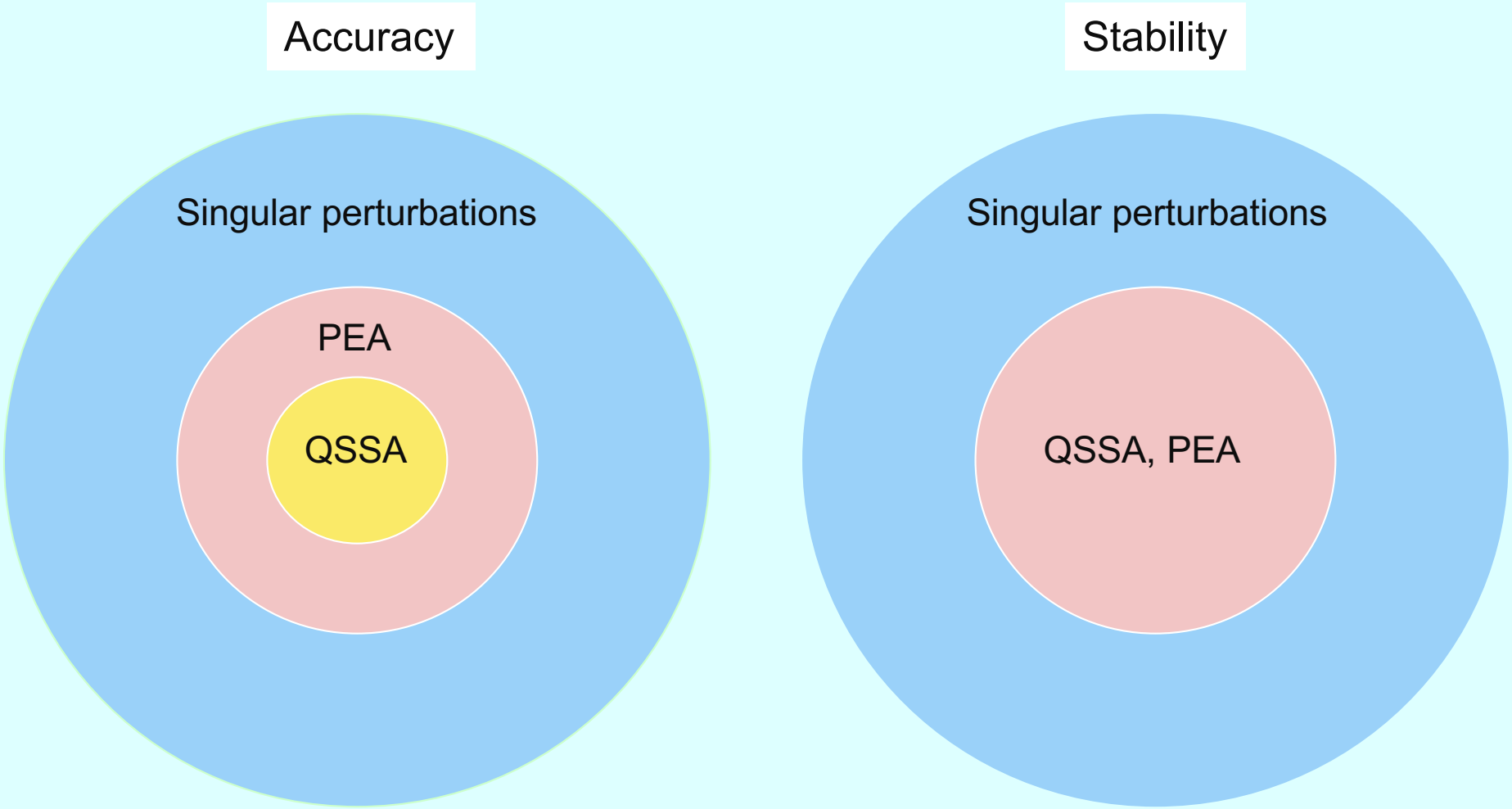
$$\frac{dc}{dt} \approx -\frac{\nu R^2}{1+\nu}$$

$\nu \rightarrow 0$
$QSSA_{c,R^1}$

$\nu \rightarrow \infty$
$QSSA_{s,R^1}$

$$\nu = \frac{e_o - c}{K_R + s} \qquad K_R = \frac{k_{1b}}{k_{1f}}$$

QSSA/PEA: stability and accuracy



Goussis, *CTM* 16 (2012)

Conventional methodologies: QSSA and PEA

$$\frac{d}{dt}\begin{bmatrix} s \\ c \end{bmatrix} = \begin{bmatrix} -1 \\ 1 \end{bmatrix} R^1 + \begin{bmatrix} 0 \\ -1 \end{bmatrix} R^2 = \begin{bmatrix} g_s \\ g_c \end{bmatrix} \qquad R^1 = k_{1f}(e_o - c)s - k_{1b}c \qquad R^2 = k_2 c$$

$QSSA_{c,R^1}$ $\quad c,\ R^1 :\ fast \rightarrow\ g_c \approx 0 \qquad R^1 \approx R^2 \qquad \frac{ds}{dt} \approx -R^2$

$$c = \frac{k_{1f} e_o s}{(k_{1f}s + k_{1b} + k_2)}$$

$QSSA_{c,R^2}$ $\quad c,\ R^2 :\ fast \rightarrow\ g_c \approx 0 \qquad R^2 \approx R^1 \qquad \frac{ds}{dt} \approx -R^1$

$QSSA_{s,R^1}$ $\quad s,\ R^1 :\ fast \rightarrow\ g_s \approx 0 \qquad R^1 \approx 0 \qquad \frac{dc}{dt} = -R^2$

$$s = \frac{k_{1b} c}{k_{1f}(e_o - c)}$$

PEA_{R^1} $\quad R^1 :\ fast \rightarrow\ \frac{dR^1}{dt} \approx 0 \qquad R^1 \approx \frac{R^2}{1+\nu} \qquad \frac{ds}{dt} \approx -\frac{R^2}{1+\nu}$

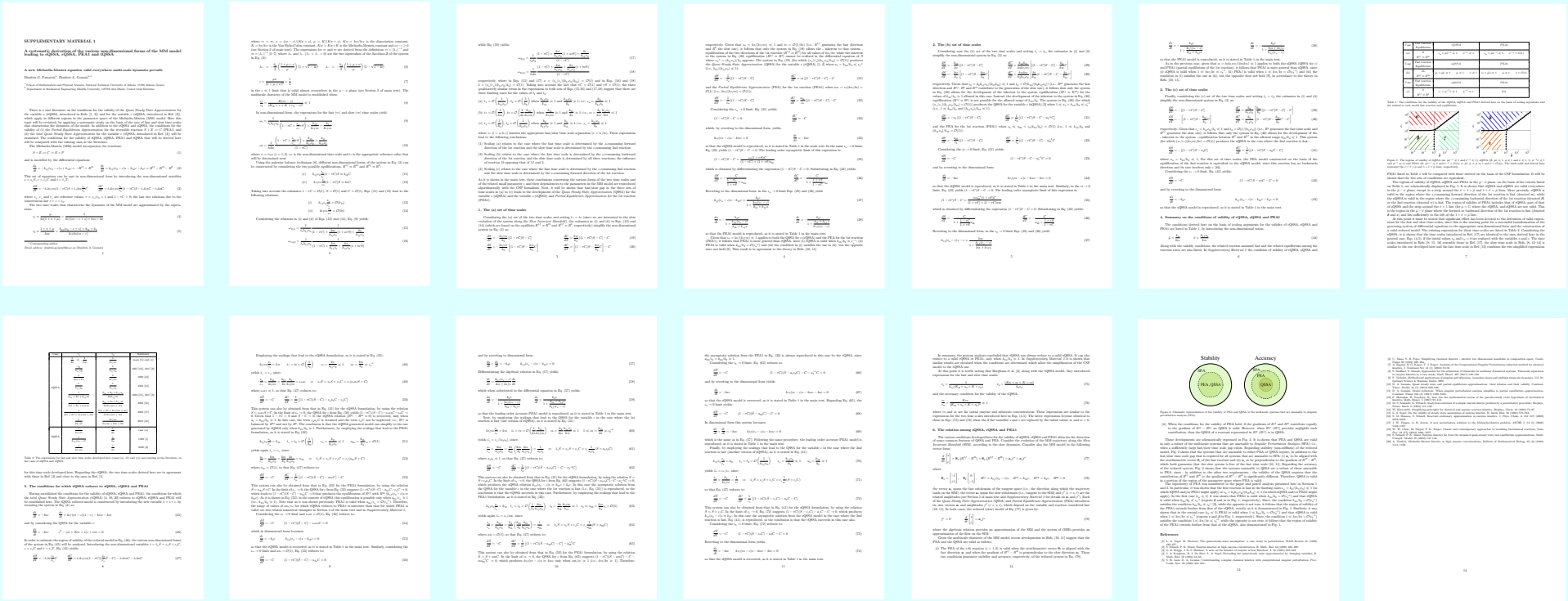
$$\frac{dc}{dt} \approx -\frac{\nu R^2}{1+\nu}$$

$\nu \rightarrow 0$
$QSSA_{c,R^1}$

$\nu \rightarrow \infty$
$QSSA_{s,R^1}$

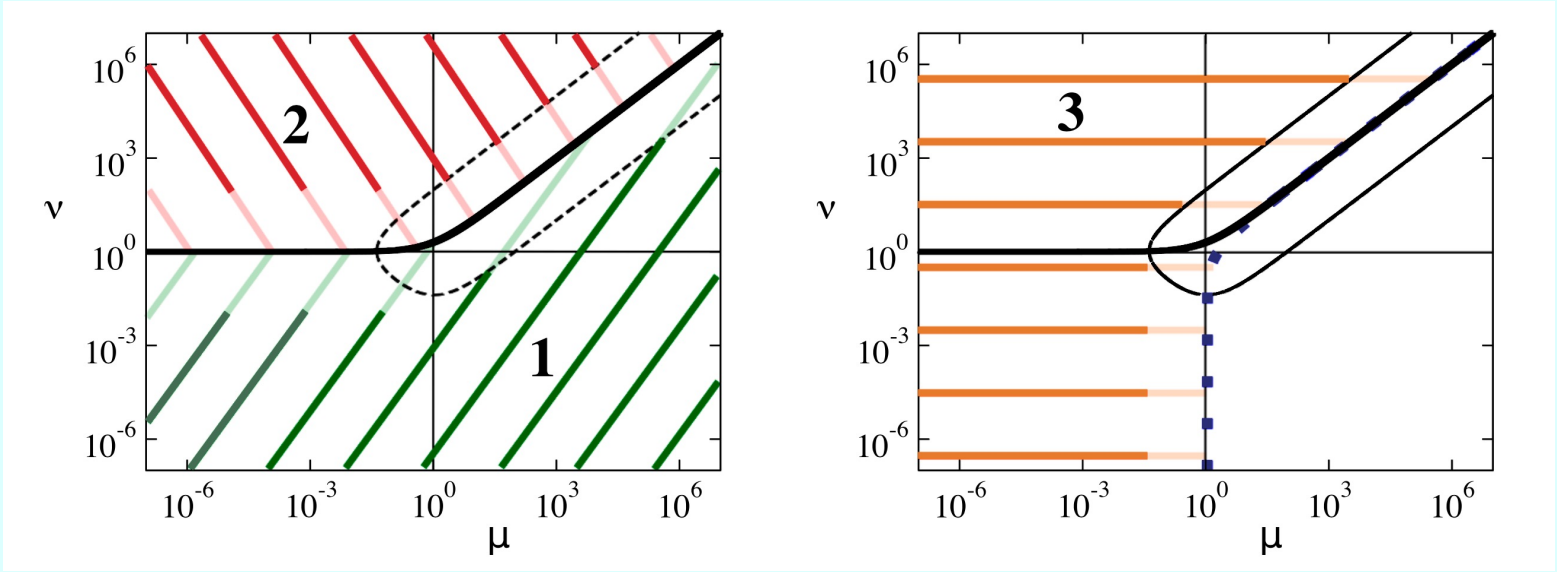
$$\nu = \frac{e_o - c}{K_R + s} \qquad K_R = \frac{k_{1b}}{k_{1f}}$$

Conventional methodologies in the MM model



Patsatzis & Goussis, *Math Biosc* 315 (2019)

Conventional methodologies in the MM model



$$\nu = \frac{e_o - c}{K_R + s} \qquad \mu = \frac{K}{K_R + s}$$

$$K_R = \frac{k_{1b}}{k_{1f}} \qquad K = \frac{k_2}{k_{1f}}$$

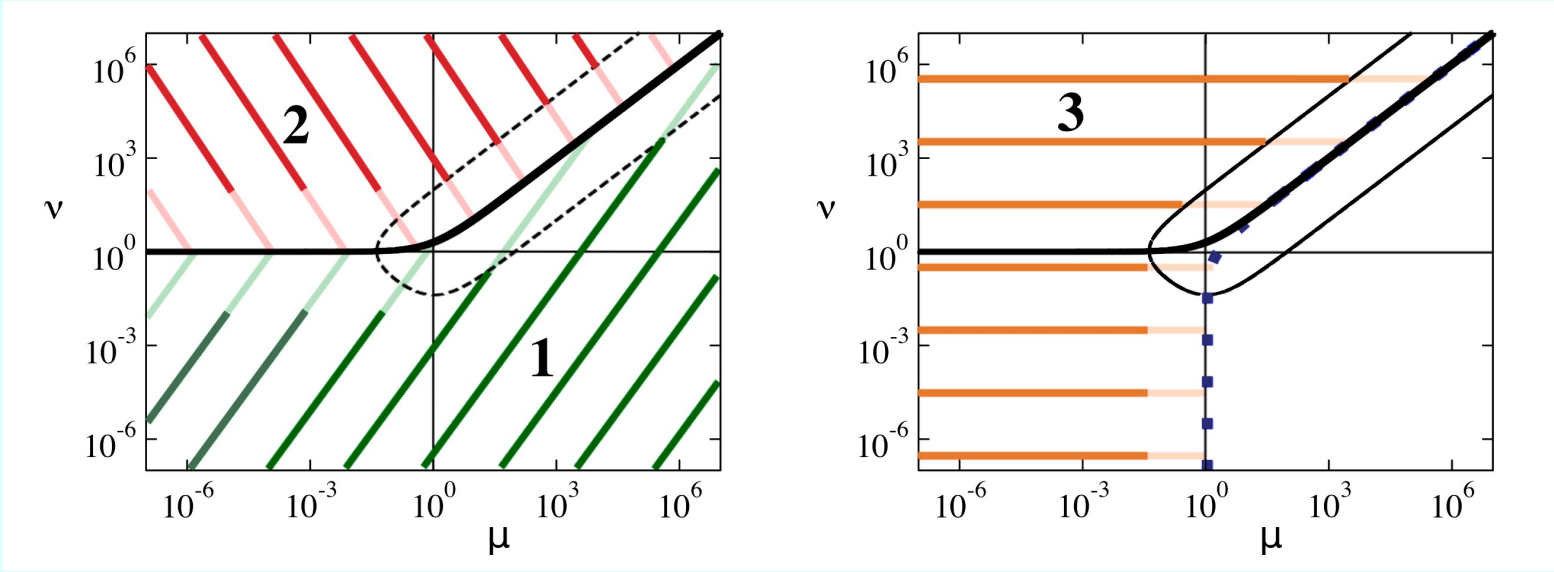
1 (left): $QSSA_{cR1}$

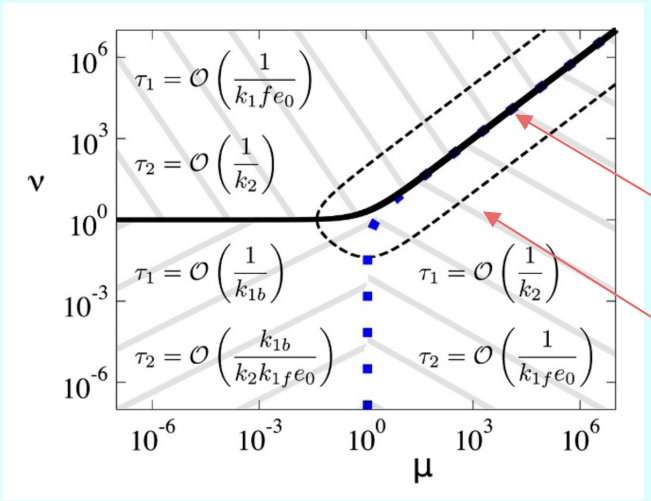
1 (right): $QSSA_{cR2}$

2 : $QSSA_{sR1}$

3 : PEA_{R1}

Conventional methodologies in the MM model





$$\epsilon = \frac{\tau_1}{\tau_2}$$

$\epsilon = 0.45$

$\epsilon = 10^{-2}$

1 (left): $QSSA_{cR1}$

1 (right): $QSSA_{cR2}$

2 : $QSSA_{sR1}$

3 : PEA_{R1}

Obstacles in conventional methodologies

Identification of:

i. Fast/slow/decoupled variables (e.g., species)

ii. Fast/slow/unimportant processes (e.g., reactions)

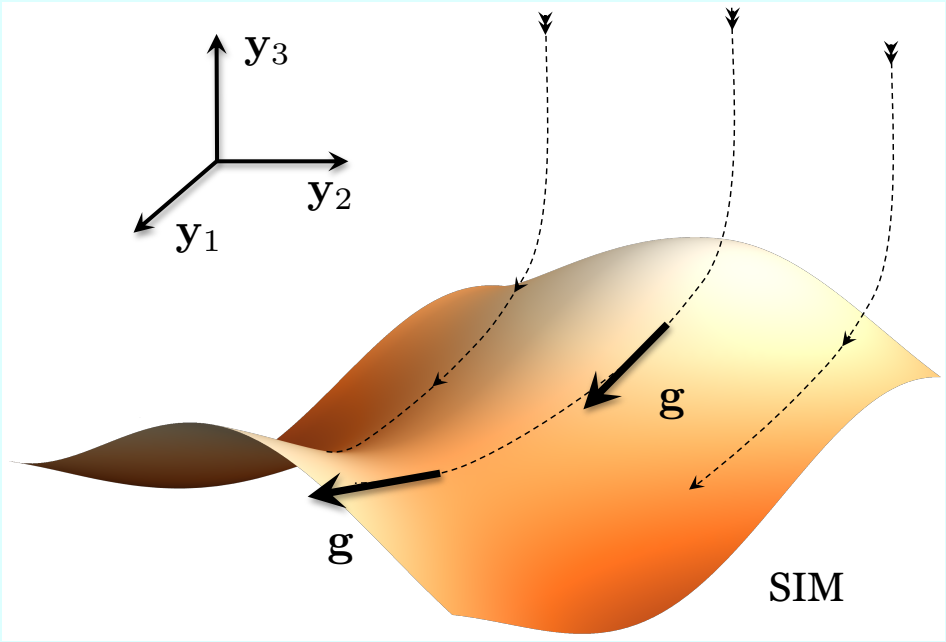
iii. Proper non-dimensional form of governing equations

iv. Small parameter ε; $\varepsilon \rightarrow 0$ yields the reduced model

Additional obstacles:

- Items in (i) and (ii) vary with time
- Number of items in (i) and (ii) vary with time
- Different sets of items in (i) and (ii) refer to different non-dimensional forms and ε.

Alternative view: Geometrical Singular Perturbations



Hirsch (1977), Fenichel (1979), Jones (1995)

Goals:

- Identify dynamical *structures* in phase space (SIM)
- Exploit their *properties*, such as fast/slow decomposition

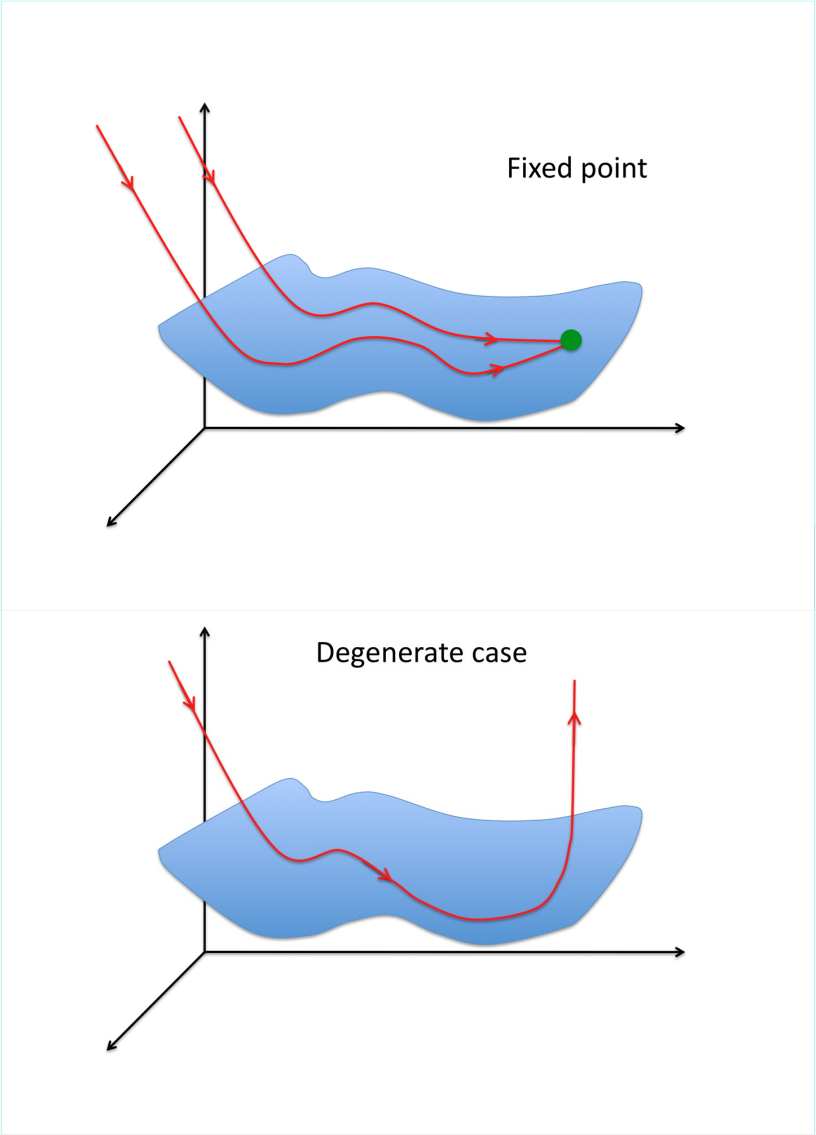
Basic tools:

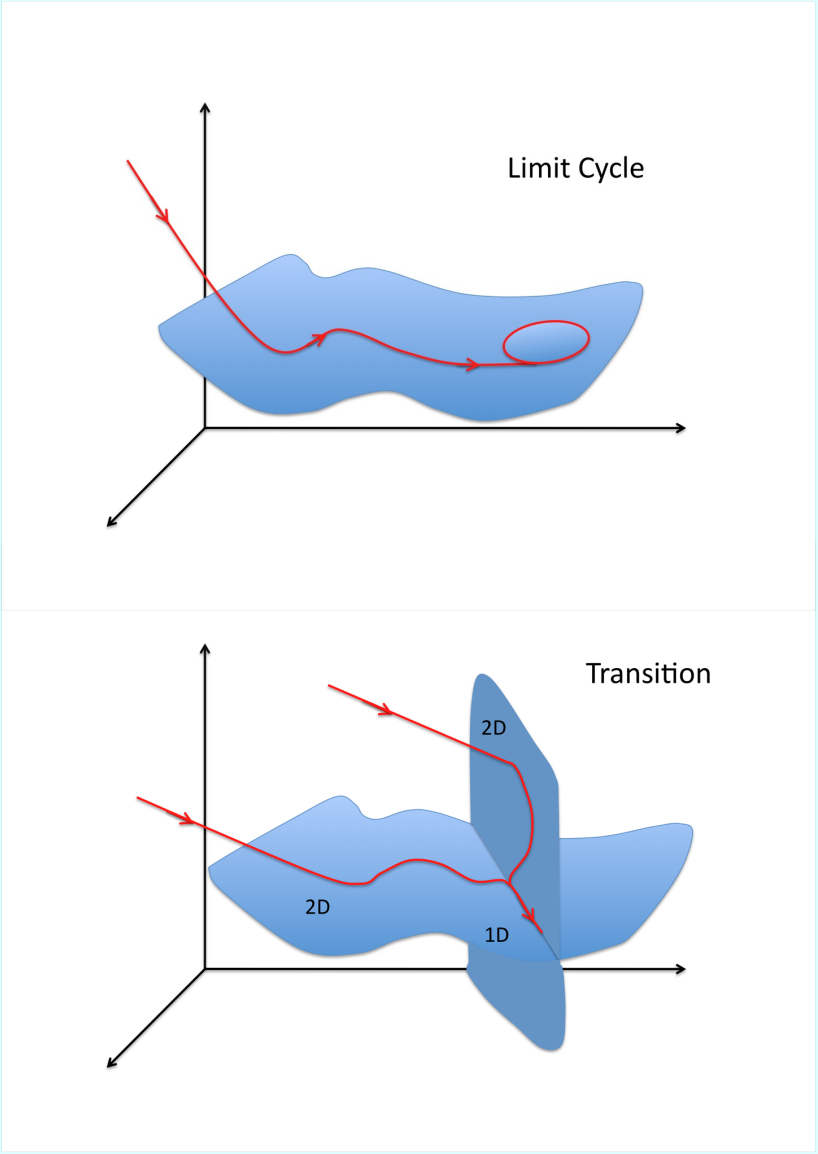
- The *tangent space* *(the tangent bundle)*
- Fast and slow *sub-domains* of tangent space

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y})$$

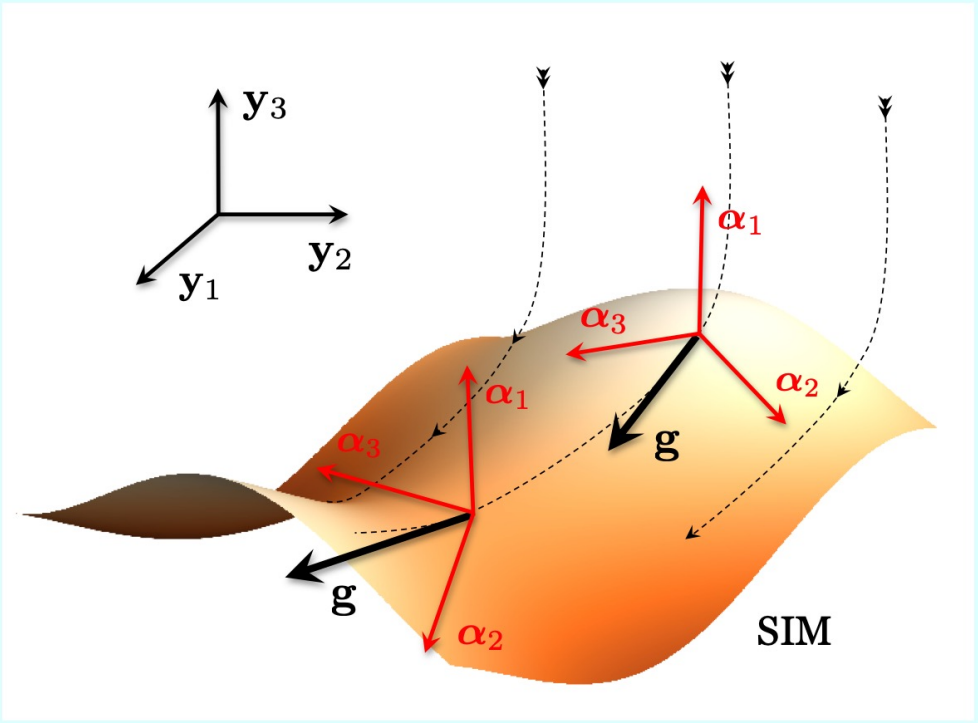
(Tasso Kaper 1999 - CKRT Jones 2006)

Structures in phase space





Alternative view: Computational Singular Perturbations (CSP)



$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y})$$

$$\frac{d\mathbf{y}}{dt} = \mathbf{a}_1 f^1 + \mathbf{a}_2 f^2 + \mathbf{a}_3 f^3$$

fast slow

Slow Invariant Manifold (SIM) $f^1 \approx 0$

Reduced (slow) model $\frac{d\mathbf{y}}{dt} \approx \mathbf{a}_2 f^2 + \mathbf{a}_3 f^3$

Lam & Goussis, *PCI* (1989)

Alternative view of conventional methodologies: $QSSA_{c,R1}$

$$\frac{d}{dt}\begin{bmatrix} s \\ c \end{bmatrix} = \begin{bmatrix} -1 \\ 1 \end{bmatrix} R^1 + \begin{bmatrix} 0 \\ -1 \end{bmatrix} R^2 = \begin{bmatrix} g_s \\ g_c \end{bmatrix} \qquad R^1 = k_{1f}(e_o - c)s - k_{1b}c \qquad R^2 = k_2 c$$

$QSSA_{c,R^1}$

$c,\ R^1 :\ fast \rightarrow\ g_c \approx 0 \qquad R^1 \approx R^2 \qquad \frac{ds}{dt} \approx -R^2$

$$\frac{d}{dt}\begin{bmatrix} s \\ c \end{bmatrix} = \mathbf{a}_1 f^1 + \mathbf{a}_2 f^2 \qquad f^i = \mathbf{b}^i \cdot \mathbf{g}$$

fast slow

$$\mathbf{a}_1 = \begin{bmatrix} -1 \\ 1 \end{bmatrix} \quad \mathbf{a}_2 = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad \mathbf{b}^1 = \begin{bmatrix} 0 & 1 \end{bmatrix} \quad \mathbf{b}^2 = \begin{bmatrix} 1 & 1 \end{bmatrix}$$

$$\frac{d}{dt}\begin{bmatrix} s \\ c \end{bmatrix} = \begin{bmatrix} -1 \\ 1 \end{bmatrix} (R^1 - R^2) - \begin{bmatrix} 1 \\ 0 \end{bmatrix} R^2$$

$f^1 \approx 0$

$R^1 - R^2 \approx 0$

$\frac{ds}{dt} \approx -R^2$

Alternative view of conventional methodologies

$$\frac{d}{dt}\begin{bmatrix} s \\ c \end{bmatrix} = \begin{bmatrix} -1 \\ 1 \end{bmatrix} R^1 + \begin{bmatrix} 0 \\ -1 \end{bmatrix} R^2 = \begin{bmatrix} g_s \\ g_c \end{bmatrix} \qquad R^1 = k_{1f}(e_o - c)s - k_{1b}c \qquad R^2 = k_2 c$$

$QSSA_{c,R^1}$

$$\mathbf{a}_1 = \begin{bmatrix} -1 \\ 1 \end{bmatrix} \quad \mathbf{a}_2 = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \mathbf{b}^1 = \begin{bmatrix} 0 & 1 \end{bmatrix} \quad \mathbf{b}^2 = \begin{bmatrix} 1 & 1 \end{bmatrix}$$

$QSSA_{c,R^2}$

$$\mathbf{a}_1 = \begin{bmatrix} 0 \\ -1 \end{bmatrix} \quad \mathbf{a}_2 = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \mathbf{b}^1 = \begin{bmatrix} 0 & -1 \end{bmatrix} \quad \mathbf{b}^2 = \begin{bmatrix} 1 & 0 \end{bmatrix}$$

$QSSA_{s,R^1}$

$$\mathbf{a}_1 = \begin{bmatrix} -1 \\ 1 \end{bmatrix} \quad \mathbf{a}_2 = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad \mathbf{b}^1 = \begin{bmatrix} -1 & 0 \end{bmatrix} \quad \mathbf{b}^2 = \begin{bmatrix} 1 & 1 \end{bmatrix}$$

PEA_{R^1}

$$\mathbf{a}_1 = \begin{bmatrix} -1 \\ 1 \end{bmatrix} \quad \mathbf{a}_2 = \begin{bmatrix} 1 \\ \nu \end{bmatrix} \quad \mathbf{b}^1 = \frac{1}{1+\nu}\begin{bmatrix} -\nu & 1 \end{bmatrix} \quad \mathbf{b}^2 = \frac{1}{1+\nu}\begin{bmatrix} 1 & 1 \end{bmatrix}$$

$\nu \to 0$
$QSSA_{c,R^1}$

$\nu \to \infty$
$QSSA_{s,R^1}$

CSP algorithm

$$\mathbf{y} = \begin{bmatrix} y^1 \\ : \\ y^N \end{bmatrix}$$

$$\frac{d\mathbf{y}}{dt} = \mathbf{S}_1 R^1 + \mathbf{S}_2 R^2 + \cdots + \mathbf{S}_K R^K$$

$$= \mathbf{a}_1 f^1 + \cdots + \mathbf{a}_M f^M + \mathbf{a}_{M+1} f^{M+1} + \cdots + \mathbf{a}_N f^N \qquad f^i = \mathbf{b}^i \cdot \mathbf{g}$$

$$\underbrace{\tau_1 \qquad \tau_M}_{\text{fast (dissipative)}} \ll \underbrace{\tau_{M+1} \qquad \tau_N}_{\text{slow}} \qquad \epsilon = \frac{\tau_{M+1}}{\tau_M} < 1$$

$$\mathbf{a}_f = \begin{bmatrix} \mathbf{a}_1 & \cdots & \mathbf{a}_M \end{bmatrix}$$

$$\mathbf{a}_s = \begin{bmatrix} \mathbf{a}_{M+1} & \cdots & \mathbf{a}_N \end{bmatrix}$$

$$\mathbf{b}^f = \begin{bmatrix} \mathbf{b}^1 \\ : \\ \mathbf{b}_M \end{bmatrix} \qquad \mathbf{b}^s = \begin{bmatrix} \mathbf{b}^{M+1} \\ : \\ \mathbf{b}_N \end{bmatrix}$$

Accuracy improvement; $x = x_0 + \varepsilon^1 x_1 + \varepsilon^2 x_2 + \ldots\ldots$

Fixed: $\mathbf{a}^f,\ \mathbf{b}^s$ Refined: $\mathbf{a}^s,\ \mathbf{b}^f$

Stability of reduced model

Refined: $\mathbf{a}^f,\ \mathbf{b}^s$ Fixed: $\mathbf{a}^s,\ \mathbf{b}^f$

Major drawback: M=M(t)

Leading order accuracy:
Left and right eigenvectors

CSP algorithm

$$\mathbf{y} = \begin{bmatrix} y^1 \\ : \\ y^N \end{bmatrix}$$

$$\frac{d\mathbf{y}}{dt} = \mathbf{S}_1 R^1 + \mathbf{S}_2 R^2 + \cdots + \mathbf{S}_K R^K$$

$$= \mathbf{a}_1 f^1 + \cdots + \mathbf{a}_M f^M + \mathbf{a}_{M+1} f^{M+1} + \cdots + \mathbf{a}_N f^N \qquad f^i = \mathbf{b}^i \cdot \mathbf{g}$$

$$\tau_1 \qquad \tau_M \ll \tau_{M+1} \qquad \tau_N \qquad\qquad \epsilon = \frac{\tau_{M+1}}{\tau_M} < 1$$

fast slow

Reduced model:

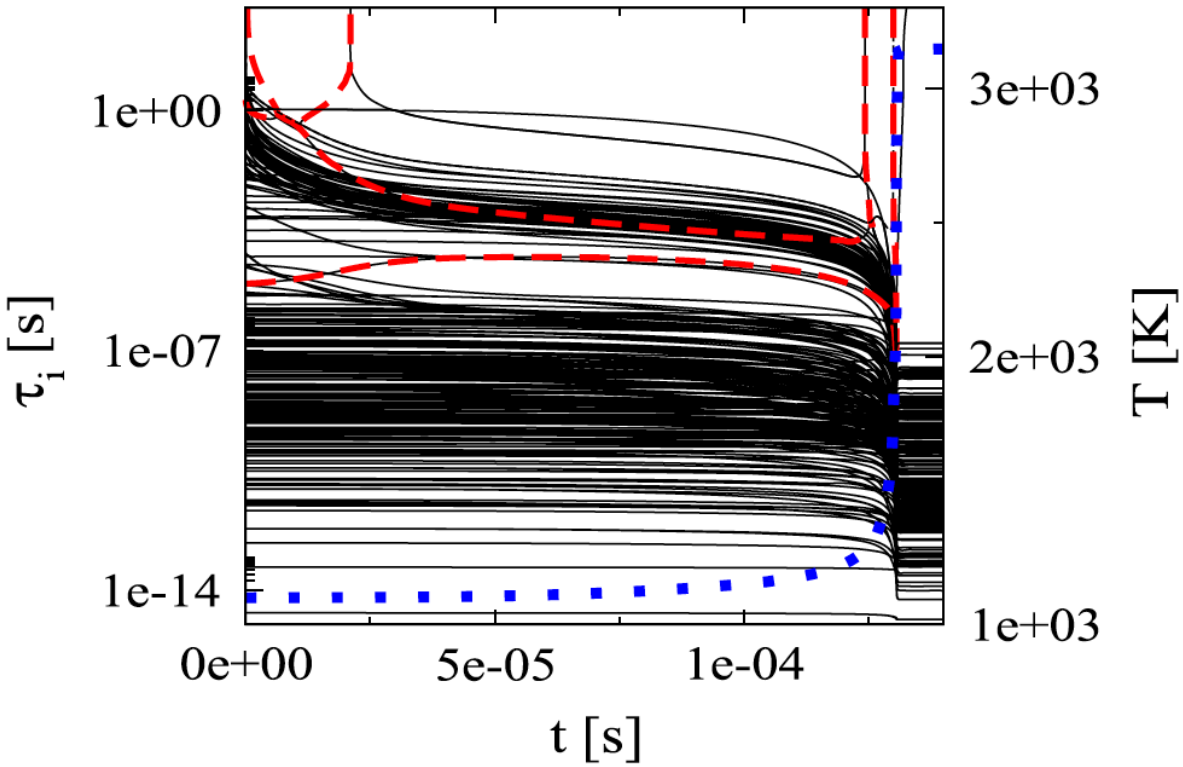
$$f^1 = f^2 = \cdots f^M = 0$$

$$\frac{d\mathbf{y}}{dt} = \mathbf{a}_{M+1} f^{M+1} + \cdots + \mathbf{a}_N f^N$$

$$\tau_{char} = \tau_{M+1}$$

Major drawback: M=M(t)

Number of fast time scales
homogeneous DME/air; T(0)=1100K



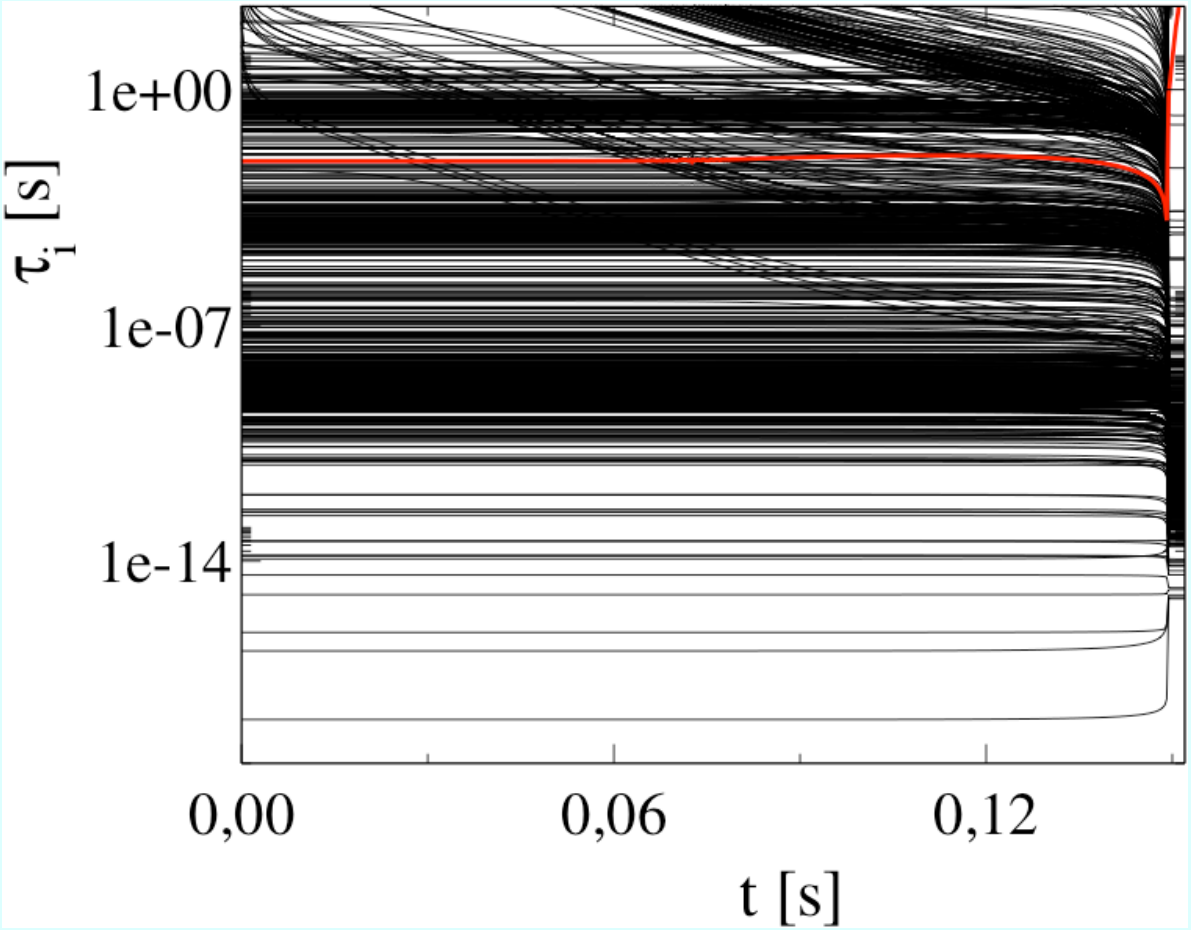
N=253 species

K=1542 reversible reactions

Explosive/Dissipative Temperature

Tigas et al C&F 2015

Number of fast time scales
homogeneous n-hexane/air; T(0)=600K



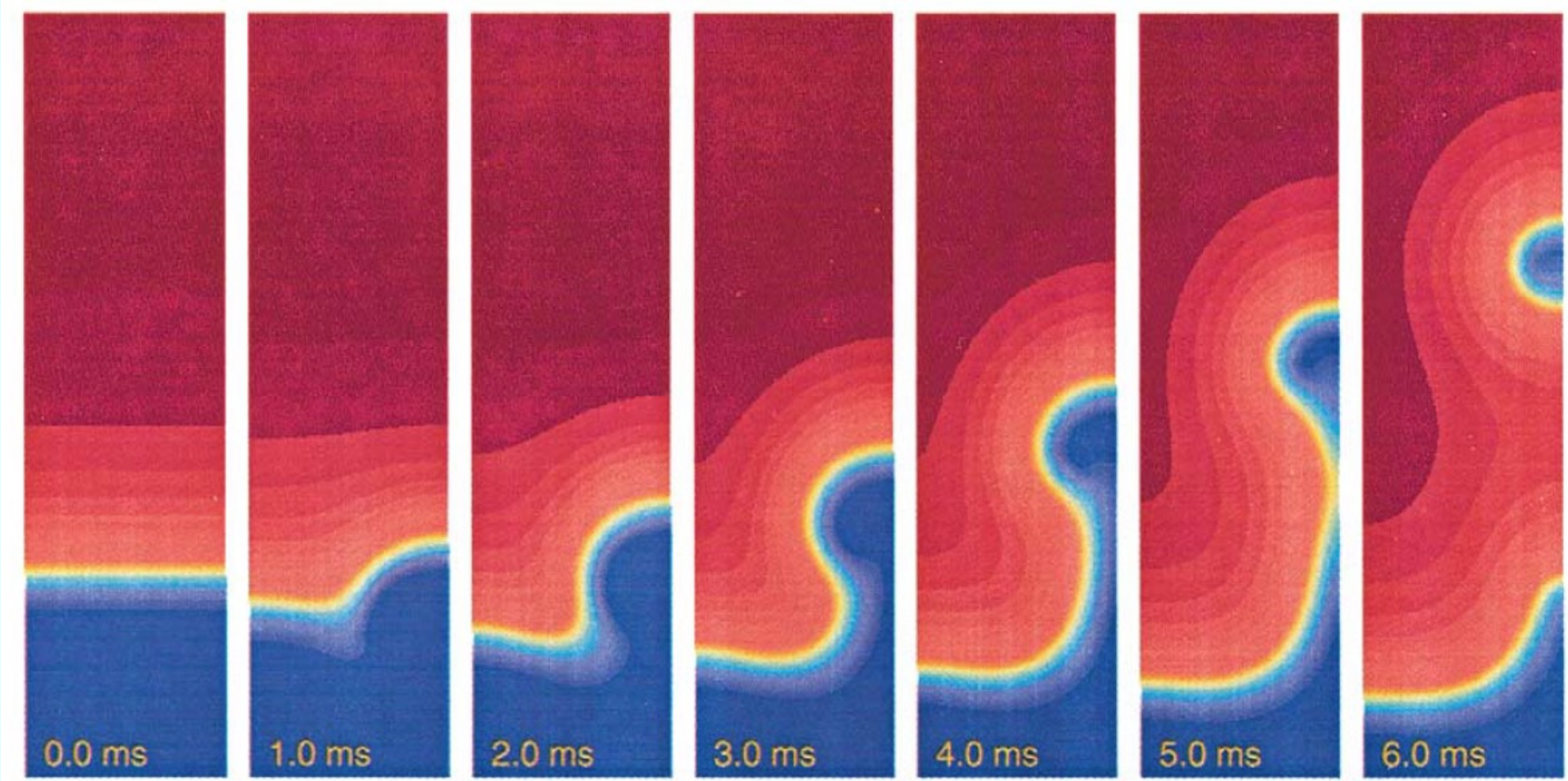
N=1118 species

K=4808 reversible reactions

Explosive/Dissipative

Tigas et al C&F 2018

Number of fast time scales
transient CH_4/air flame-vortex interaction



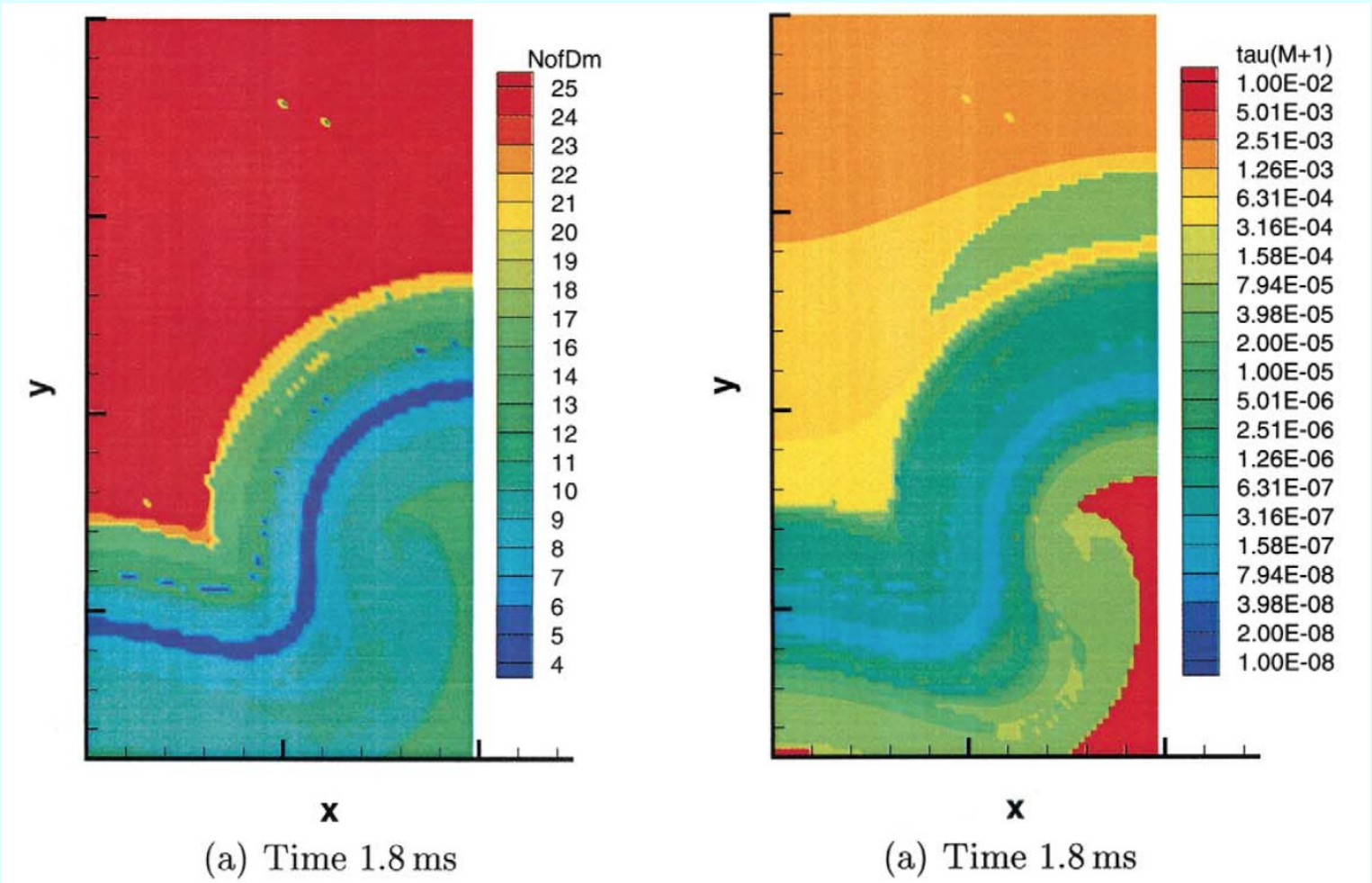
Temperature

Valorani et al, C&F 2003

Number of fast time scales
transient CH_4/air flame-vortex interaction

N=32

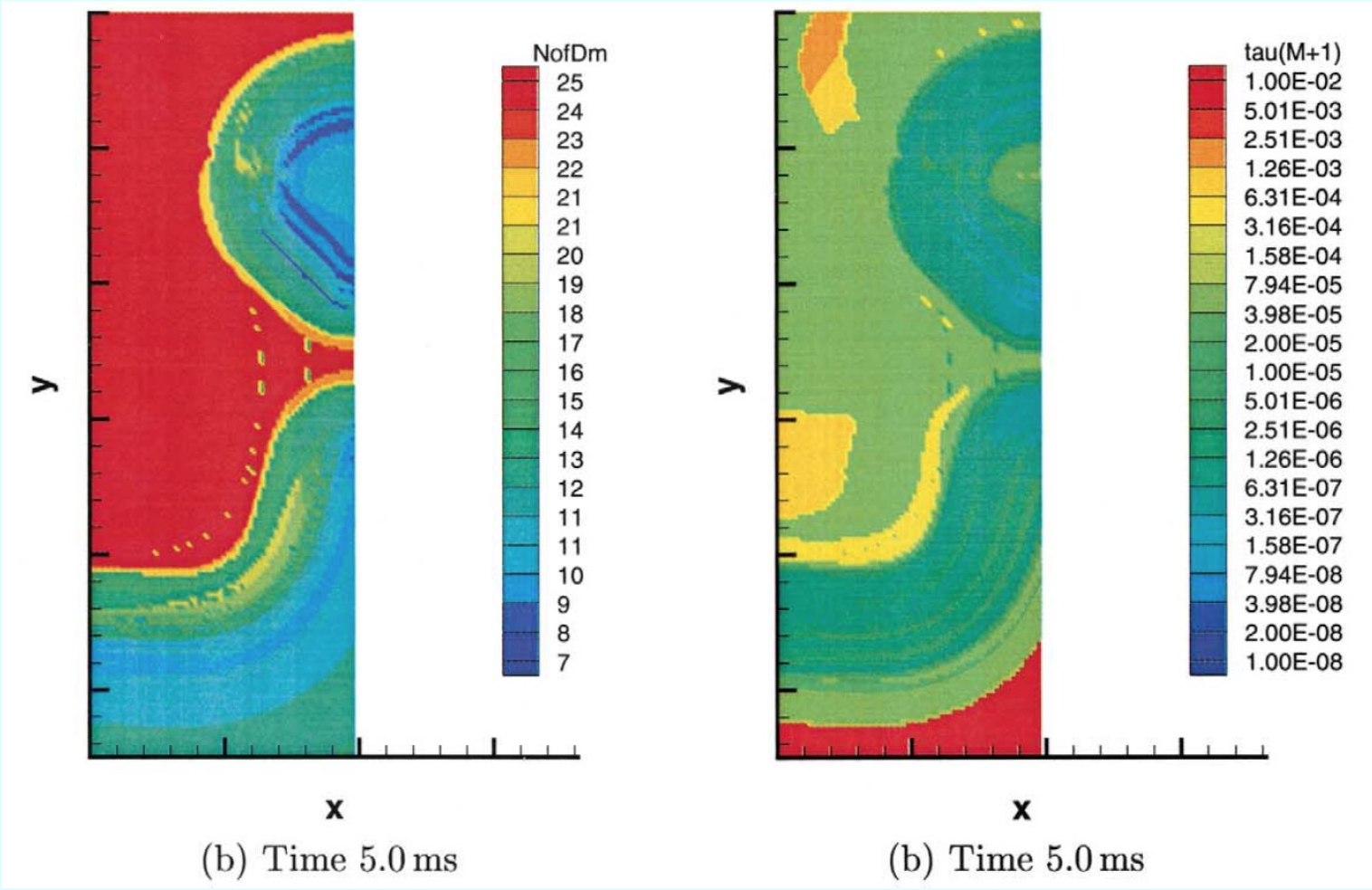
K=177



No. of fast time scales

Characteristic time scale

Number of fast time scales
transient CH_4/air flame-vortex interaction



No. of fast time scales

Characteristic time scale

The issue of transport

$$\frac{d\mathbf{y}}{dt} = \mathbf{S}_1 R^1 + \cdots + \mathbf{S}_K R^K + \mathbf{L}(\mathbf{y})$$

$$= \mathbf{a}_1 f^1 + \cdots + \mathbf{a}_M f^M + \mathbf{a}_{M+1} f^{M+1} + \cdots + \mathbf{a}_N f^N$$

$$\underbrace{\tau_1 \qquad \tau_M}_{\text{fast}} \ll \underbrace{\tau_{M+1} \qquad \tau_N}_{\text{slow}}$$

$$f^i = \mathbf{b}^i \cdot (\mathbf{S}_1 R^1 + \cdots + \mathbf{S}_K R^K + \mathbf{L}(\mathbf{y}))$$

τ_i	chemical time scales	$\tau_M \ll \tau_{M+1}$
τ_{trans}	transport time scale	$\tau_M \ll \tau_{trans}$

$$f^i = \mathbf{b}^i \cdot (\mathbf{S}_1 R^1 + \cdots + \mathbf{S}_K R^K) + \mathbf{b}^i \cancel{\mathbf{L}(\mathbf{y})} \quad \text{i=1,M}$$

transport independent

$$f^1 = f^2 = \cdots f^M = 0$$

Reduced model:

$$\frac{d\mathbf{y}}{dt} = \mathbf{a}_{M+1} f^{M+1} + \cdots + \mathbf{a}_N f^N$$

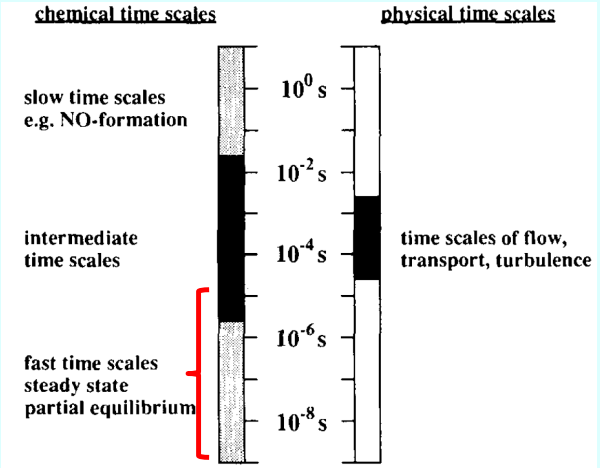


Fig. 1. Schematical illustration of the time scales governing a chemically reacting flow.

Various extensions of CSP; ILDM, REDIM, ISAT

1. Computational Singular Perturbation (CSP)
2. Intrinsic Low-Dimensional Manifolds (ILDM)
3. Reaction Diffusion Manifolds (REDIM)
4. In Situ Adaptive Tabulation (ISAT)

CSP: *Proc. Combust. Inst., 22:931-941 (1988), Int. J. Chem. Kinet., 26:461-486 (1994)*

ILDM: *Proc. Combust. Inst., 24:103-112 (1992), Proc. Combust. Inst., 25:1349-1356 (1994)*

REDIM: *Proc. Combust. Inst., 31:465-472 (2007), Proc. Combust. Inst., 34:197-203 (2013)*

ISAT: *Combust. Theory Model., 1:41-63 (1997), J. Comp. Phys., 228:361-386 (2009)*

ILDM

Full model:

$$\frac{d\mathbf{y}}{dt} = \mathbf{S}_1 R^1 + \cdots + \mathbf{S}_K R^K + \mathbf{L}(\mathbf{y})$$

$$= \mathbf{a}_1 f^1 + \cdots + \mathbf{a}_M f^M + \mathbf{a}_{M+1} f^{M+1} + \cdots + \mathbf{a}_N f^N$$

$$f^i = \mathbf{b}^i \cdot (\mathbf{S}_1 R^1 + \cdots + \mathbf{S}_K R^K + \mathbf{L}(\mathbf{y}))$$

Reduced model:

$$f^1 = f^2 = \cdots f^M = 0 \qquad (\mathbf{b}^i \cdot \mathbf{L} = 0)$$

$$\frac{d\mathbf{y}}{dt} = \mathbf{a}_{M+1} f^{M+1} + \cdots + \mathbf{a}_N f^N$$

1. Use right and left eigenvectors for $\mathbf{a}_i$ and $\mathbf{b}^i$
2. Parametrize variables $\boldsymbol{y_f = h(y_s)}$
3. Tabulate $f^i = 0$ (i=1,M) relations
4. Gov. equations for the N-M slow variables only

Major drawback: M=fixed

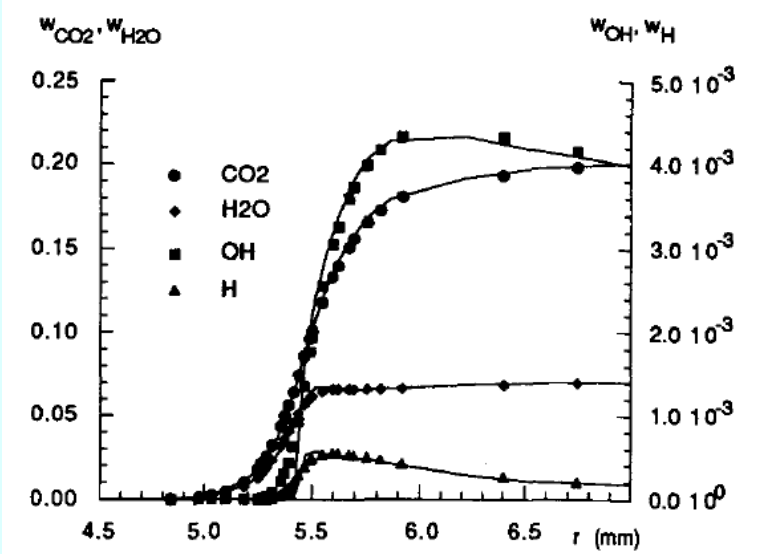


FIG. 4. Calculated structure of a syngas-air flame (points: reduced mechanism, lines: detailed mechanism).

Speed up by O(10)

Maas and Pope, Proc. CI, 1994

REDIM

Full model:

$$\frac{d\mathbf{y}}{dt} = \mathbf{S}_1 R^1 + \cdots + \mathbf{S}_K R^K + \mathbf{L}(\mathbf{y})$$

$$= \mathbf{a}_1 f^1 + \cdots + \mathbf{a}_M f^M + \mathbf{a}_{M+1} f^{M+1} + \cdots + \mathbf{a}_N f^N$$

$$f^i = \mathbf{b}^i \cdot (\mathbf{S}_1 R^1 + \cdots + \mathbf{S}_K R^K + \mathbf{L}(\mathbf{y}))$$

Reduced model:

$$f^1 = f^2 = \cdots f^M = 0 \qquad (\mathbf{b}^i \cdot \mathbf{L} = 0)$$

$$\frac{d\mathbf{y}}{dt} = \mathbf{a}_{M+1} f^{M+1} + \cdots + \mathbf{a}_N f^N$$

Issues to address:

1. $\mathbf{b}^i \cdot \mathbf{L} \neq 0$
2. Low temp domain

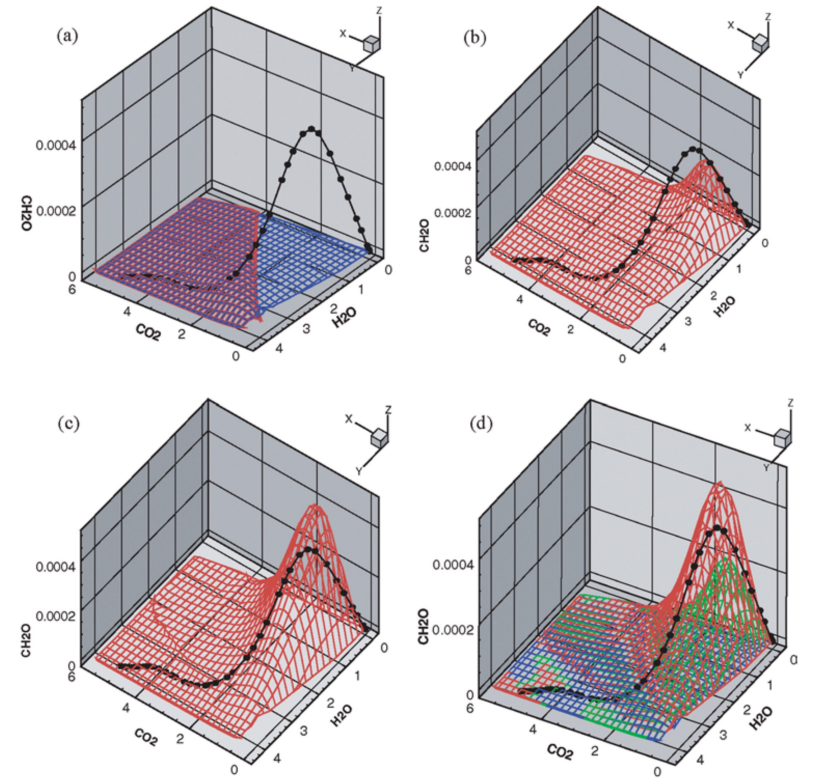


Figure 11. Two-dimensional relaxation, projection onto minor species. Manifolds: (a) extended ILDM; (b) after 10 iterations; (b) after 700 iterations; (d) combination of (a–c); black solid line is the detailed stationary solution.

syngas/air

Bykov and Maas CTM 2007

ISAT

Main obstacle in tabulation:

D=10 degrees of freedom
10 nodes in each direction

$10^D D = 10^{11}$ storage nodes

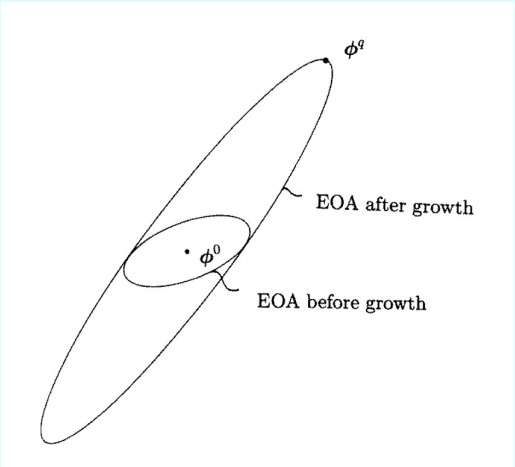
realizable vs accessed region

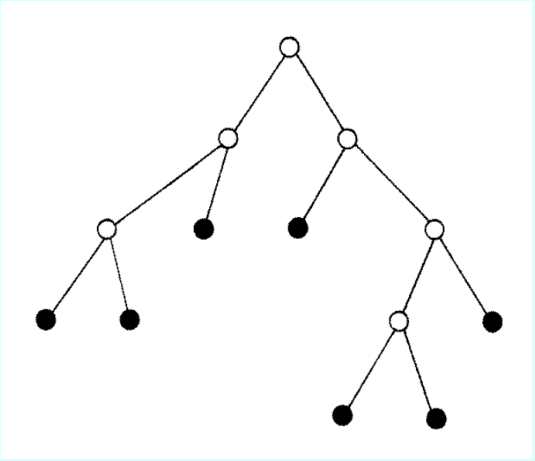
accessed region: low-dim. manifold

1 interpolation: $2^D D = 10^4$ op.

Table on accessed region:
Build up during the reactive flow calculation

Extrapolation when inside of EOA
Integration when outside of EOA

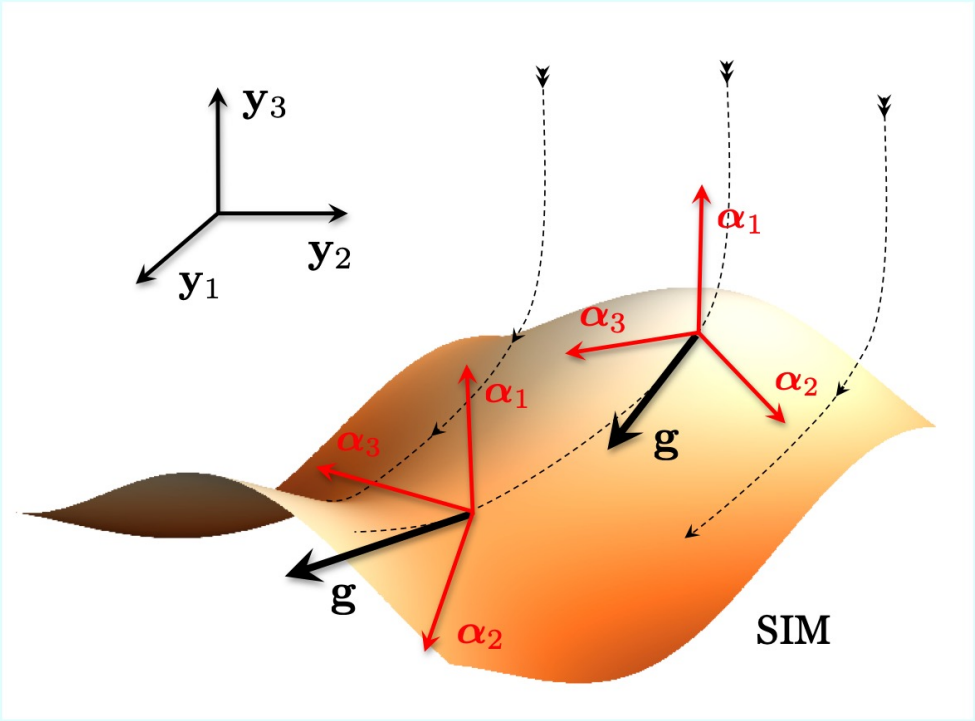


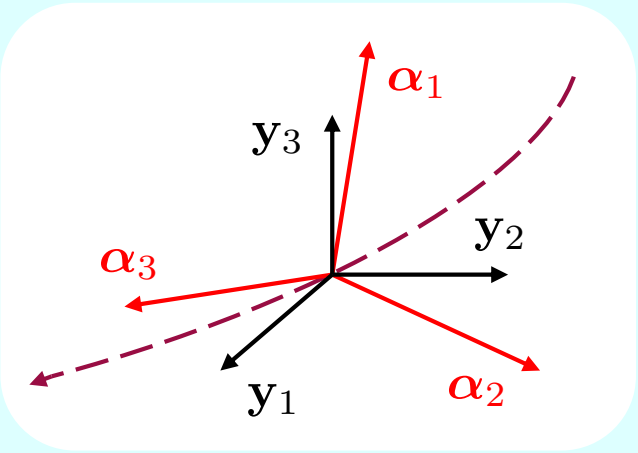


Speed up by $O(10^3)$

Pope, CST 1997

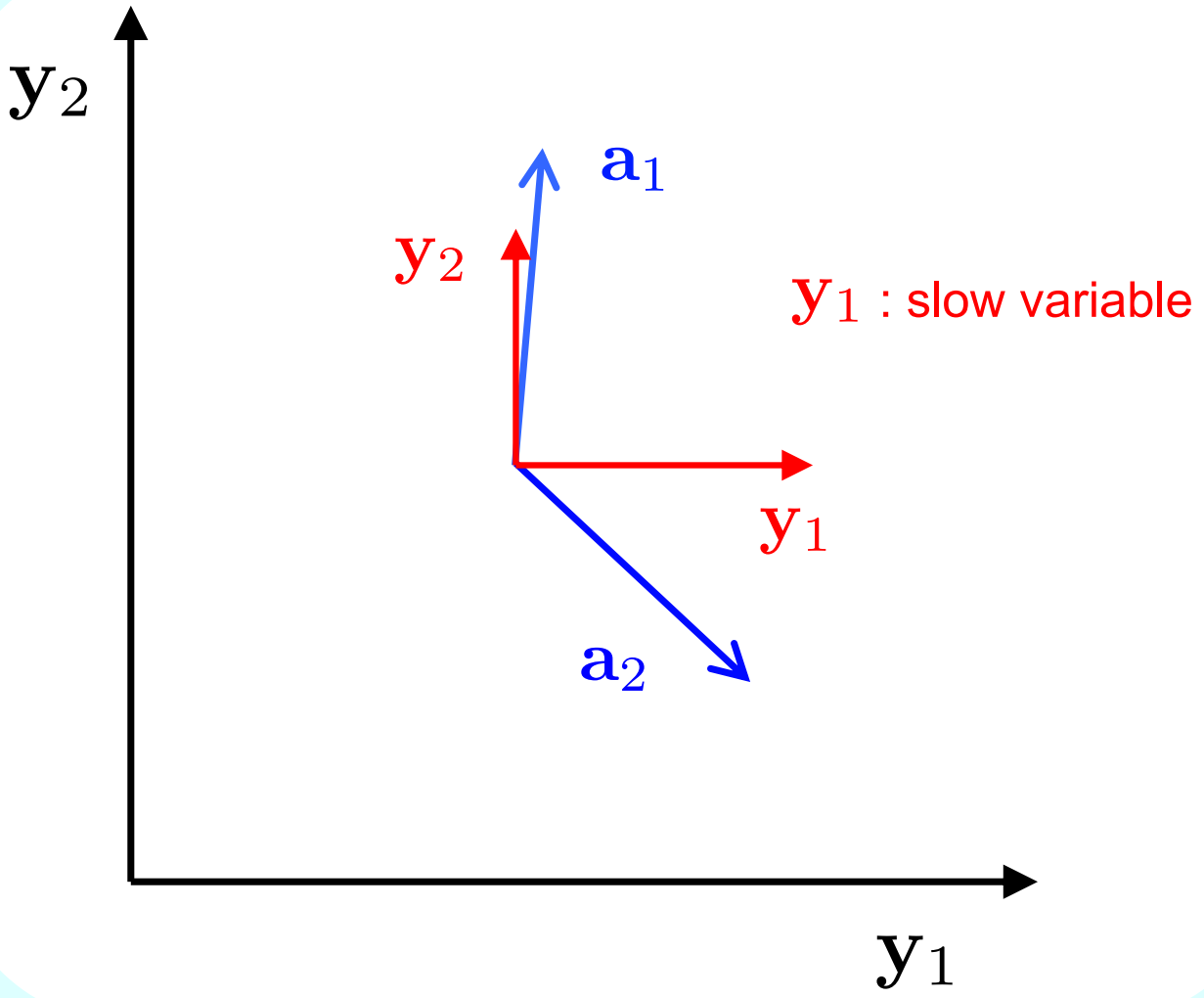
CSP Diagnostics



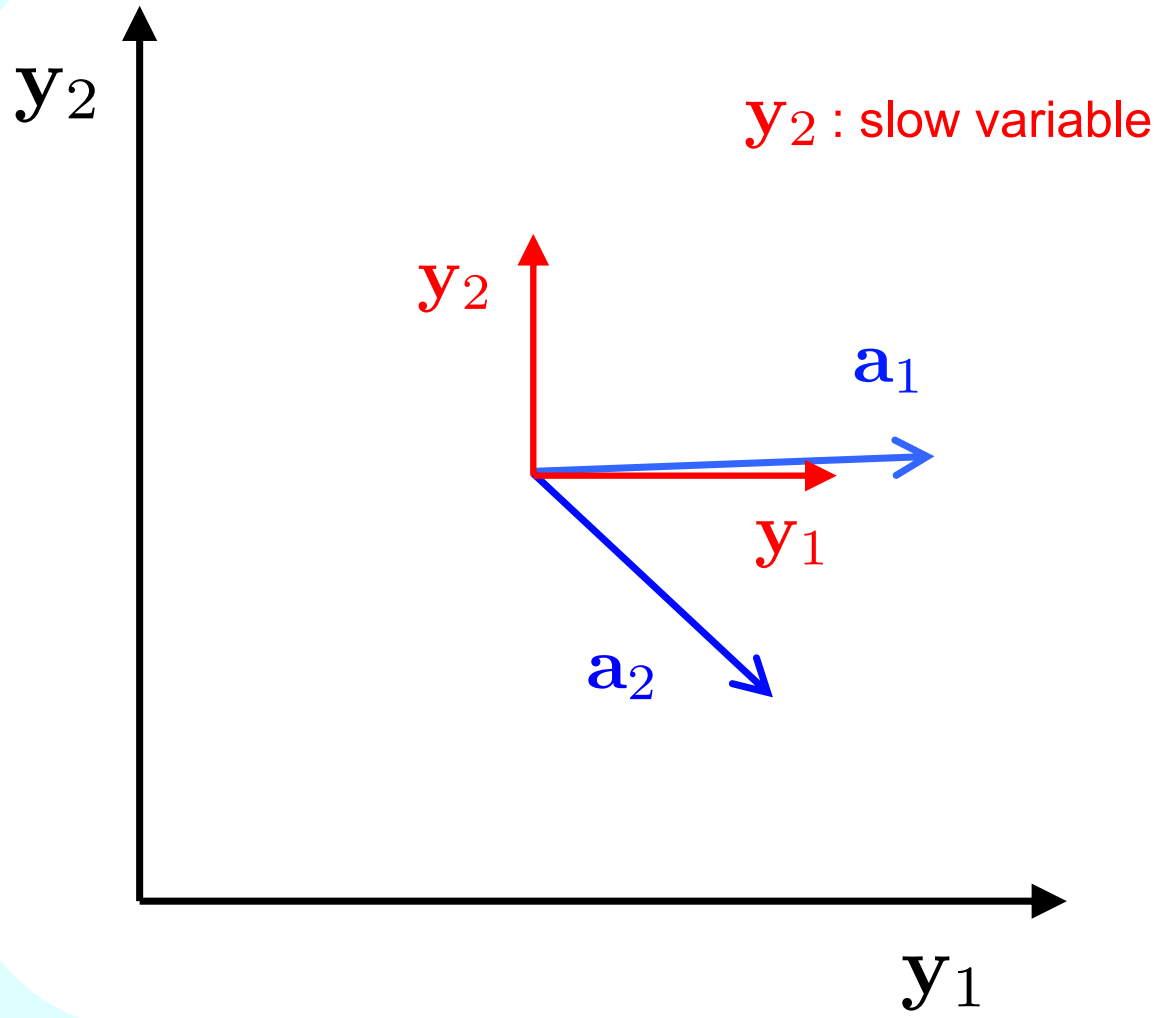


Which variables (species) relate the most to the evolution of the system ?

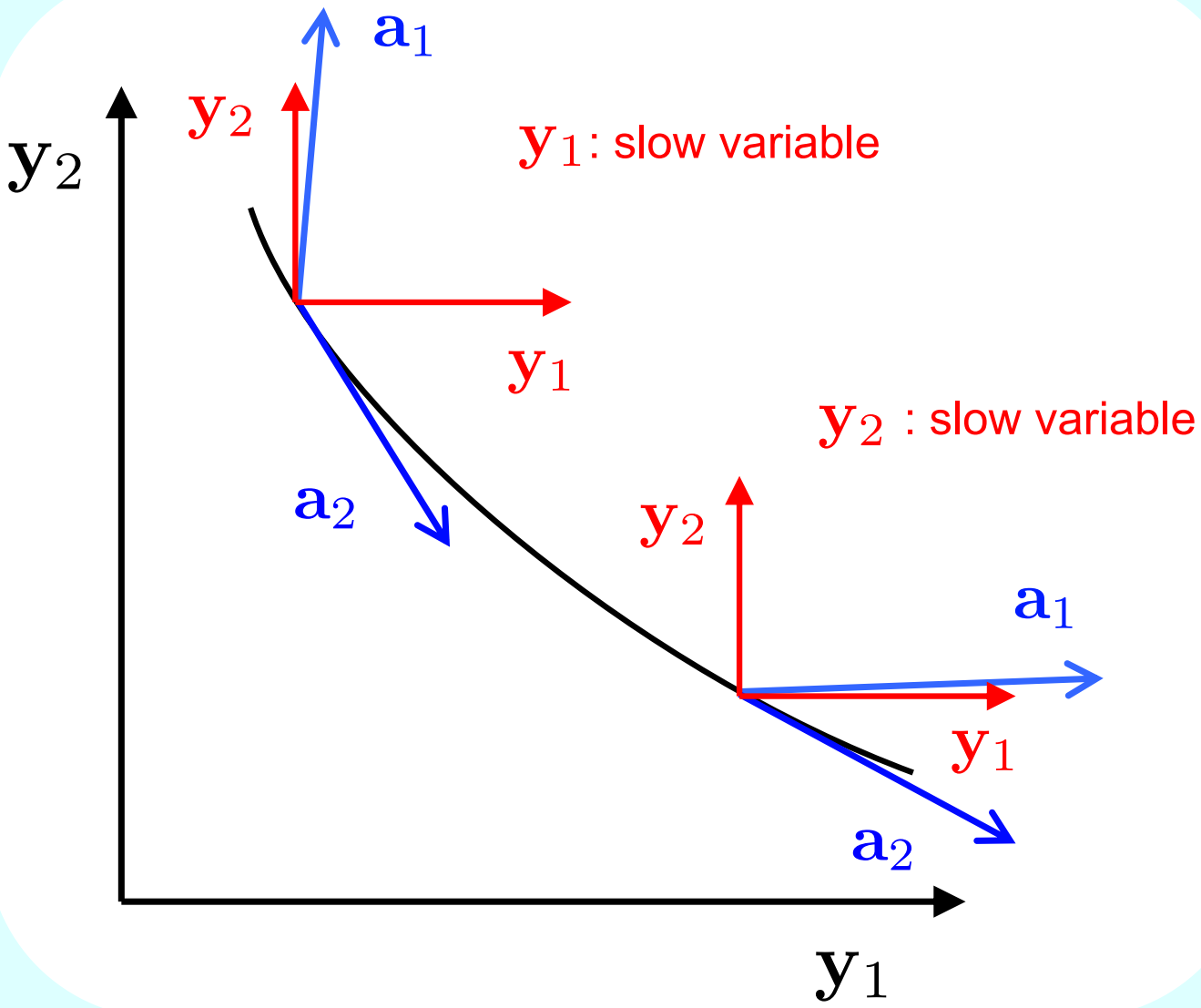
CSP Diagnostics: fast – slow variables



CSP Diagnostics: fast – slow variables



CSP Diagnostics: fast – slow variables



$$\mathbf{a}_1 = \begin{bmatrix} a_1^1 \\ a_1^2 \end{bmatrix}$$

$$\mathbf{b}^1 = \begin{bmatrix} b_1^1 & b_2^1 \end{bmatrix}$$

$$\mathbf{b}^1 \cdot \mathbf{a}_1 = 1$$

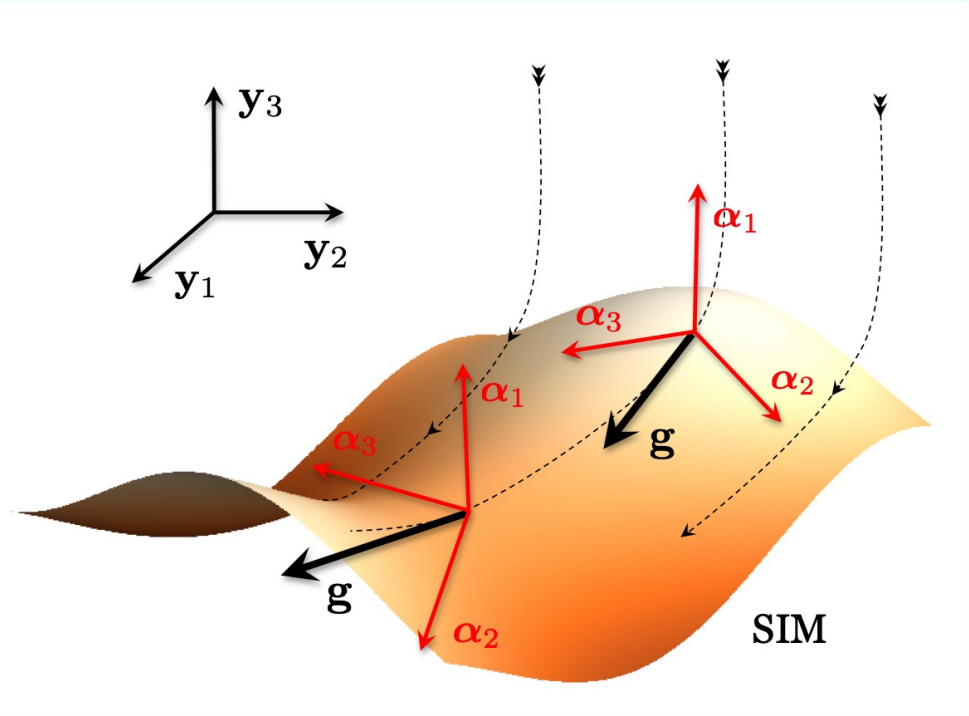
CSP Pointer

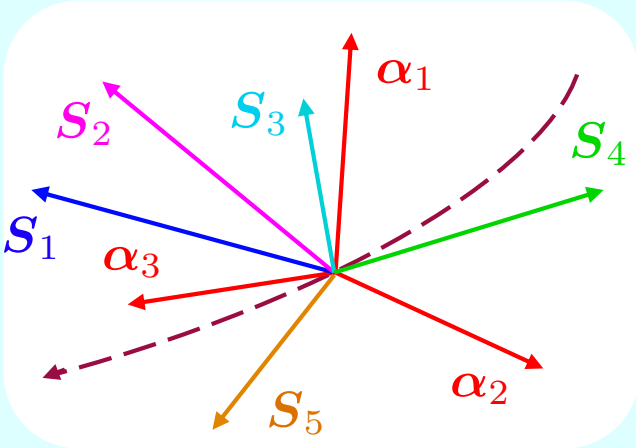
$$\mathbf{D}_1 = \begin{bmatrix} a_1^1 b_1^1 \\ a_1^2 b_2^1 \end{bmatrix}$$

$$a_1^1 b_1^1 + a_1^2 b_2^1 = 1$$

Manias et al, CNSNS 2025

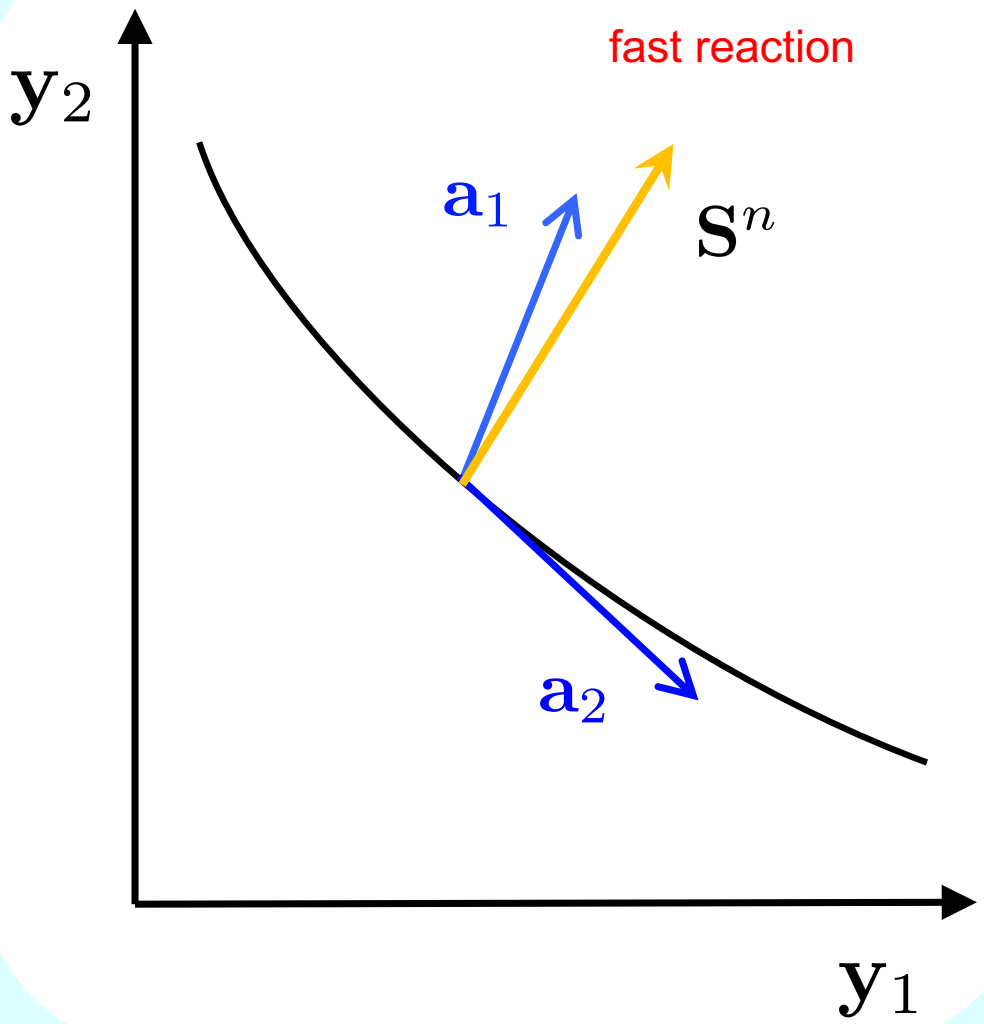
CSP Diagnostics





Which precesses (reactions, transport) drive the system ?

CSP Diagnostics: fast – slow reactions



$$\frac{d\mathbf{y}}{dt} = \mathbf{S}_1 R^1 + \cdots + \mathbf{S}_K R^K$$

$$\frac{d\mathbf{y}}{dt} = \mathbf{a}_1 f^1 + \cdots + \mathbf{a}_N f^N$$

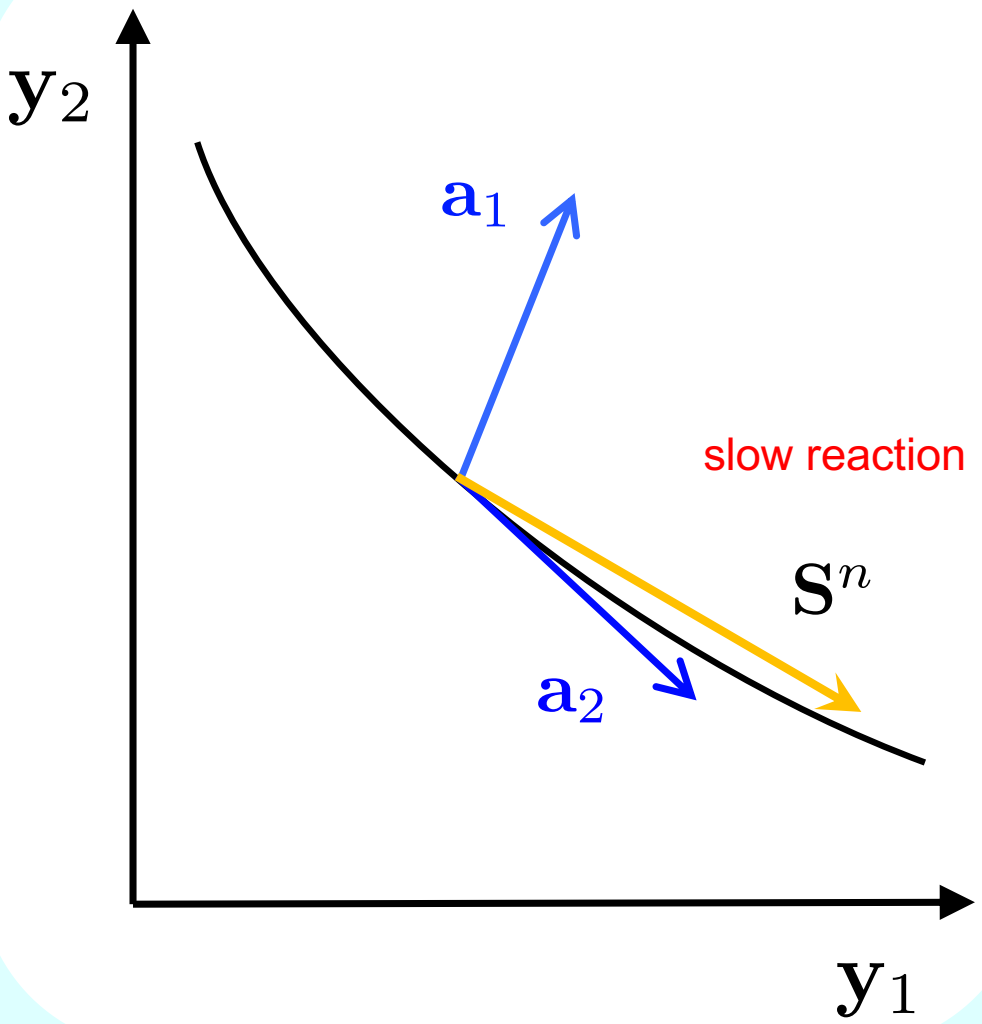
$$f^n = (\mathbf{b}^n.\mathbf{S}_1)R^1 + \cdots + (\mathbf{b}^n.\mathbf{S}_K)R^K$$

$$\mathbf{b}^i.\mathbf{a}_j = \delta^i_j$$

$$\frac{d\mathbf{y}}{dt} \approx \mathbf{a}_{M+1} f^{M+1} + \cdots + \mathbf{a}_N f^N$$

$$f^1, \cdots, f^M \approx 0$$

CSP Diagnostics: fast – slow reactions



$$\frac{d\mathbf{y}}{dt} = \mathbf{S}_1 R^1 + \cdots + \mathbf{S}_K R^K$$

$$\frac{d\mathbf{y}}{dt} = \mathbf{a}_1 f^1 + \cdots + \mathbf{a}_N f^N$$

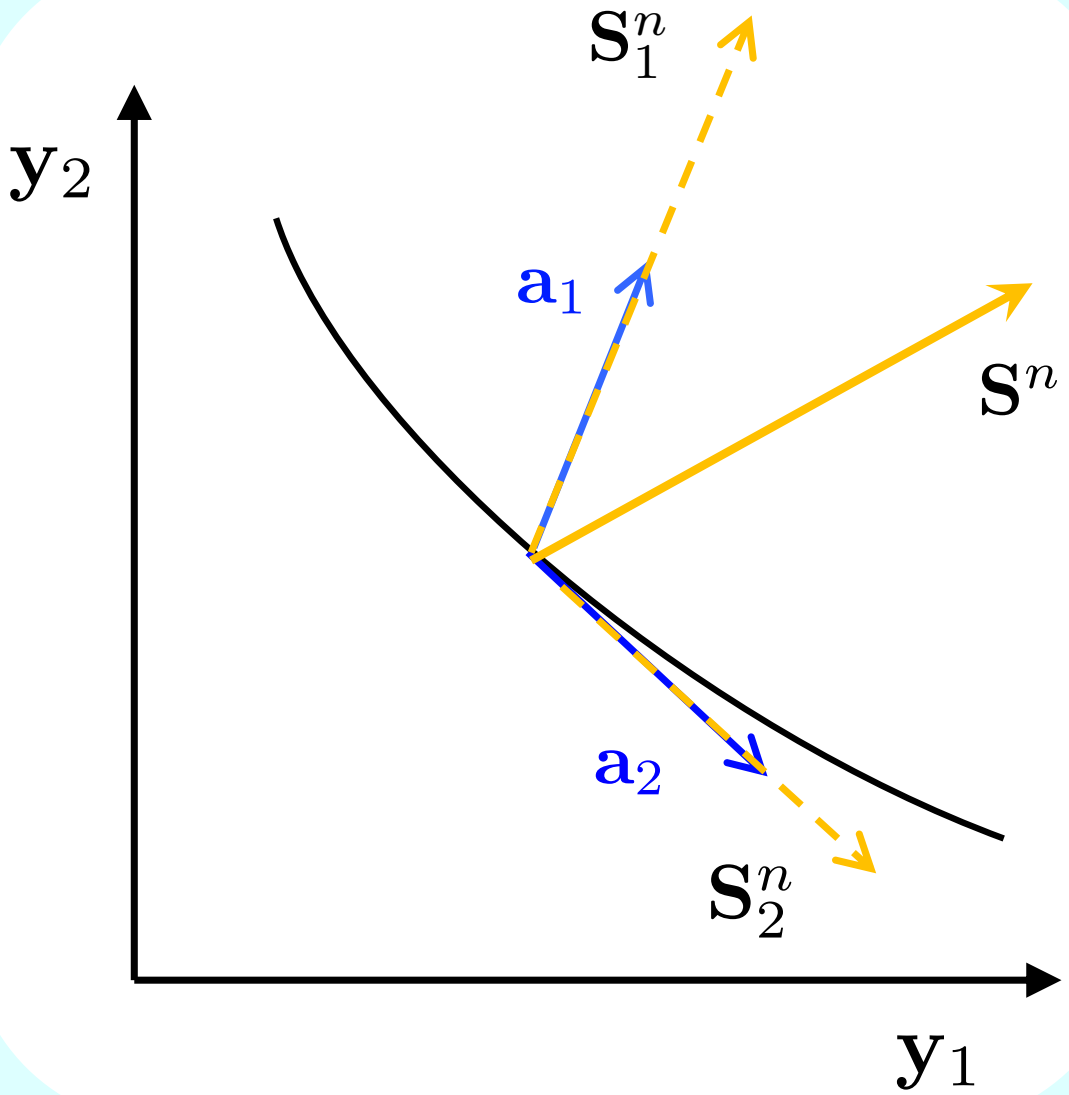
$$f^n = (\mathbf{b}^n.\mathbf{S}_1)R^1 + \cdots + (\mathbf{b}^n.\mathbf{S}_K)R^K$$

$$\mathbf{b}^i.\mathbf{a}_j = \delta^i_j$$

$$\frac{d\mathbf{y}}{dt} \approx \mathbf{a}_{M+1} f^{M+1} + \cdots + \mathbf{a}_N f^N$$

$$f^1, \cdots, f^M \approx 0$$

CSP Diagnostics: fast – slow components of a reaction



$$\mathbf{S}^n = \mathbf{S}_1^n + \mathbf{S}_2^n$$

On the manifold:

$\mathbf{S}_1^n$ has no influence

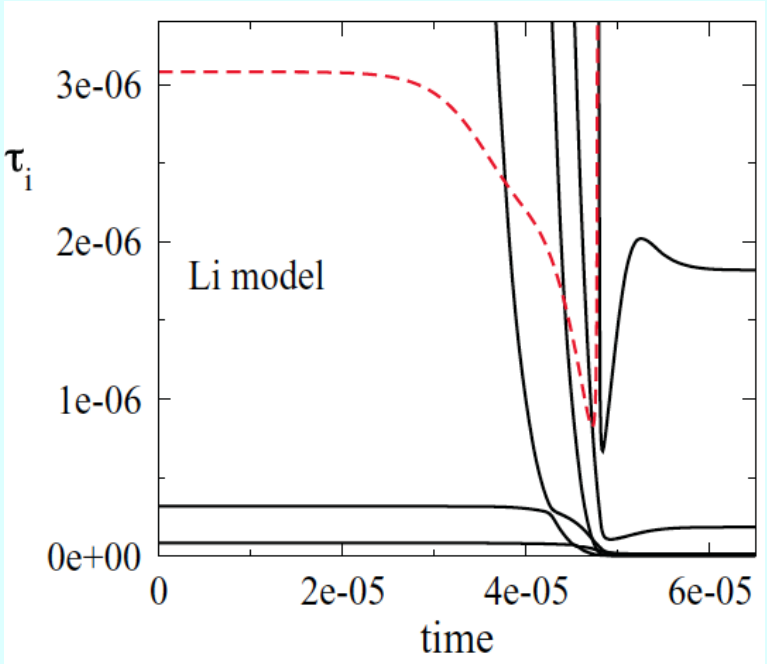
$\mathbf{S}^n$, $\mathbf{S}_2^n$ } increase y_1

$\mathbf{S}^n$ → increases y_2

$\mathbf{S}_2^n$ → decreases y_2

Michalaki et al, J Math Biol, 2018

CSP diagnostics: explosive mode in H_2/air autoignition



	$t = 0.0 \times 10^{-6}$ s $T = 1100$ K $\lambda = 3.245 \times 10^5$ s^{-1}	$t = 3.0 \times 10^{-6}$ s $T = 1100$ K $\lambda = 3.245 \times 10^5$ s^{-1}
TPI	$1f$: + 0.6273 $2f$: + 0.0739 $3f$: + 0.0183 $9f$: − 0.2792	$1f$: + 0.6273 $2f$: + 0.0739 $3f$: + 0.0183 $9f$: − 0.2792
API	$10b$: + 1.0000	$1f$: + 0.4987 $10b$: + 0.2100 $2f$: + 0.0543 $3f$: + 0.0138 $9f$: − 0.2220
Po	H: +0.79 O: +0.17 OH: +0.04	H: +0.79 O: +0.17 OH: +0.04

time scale

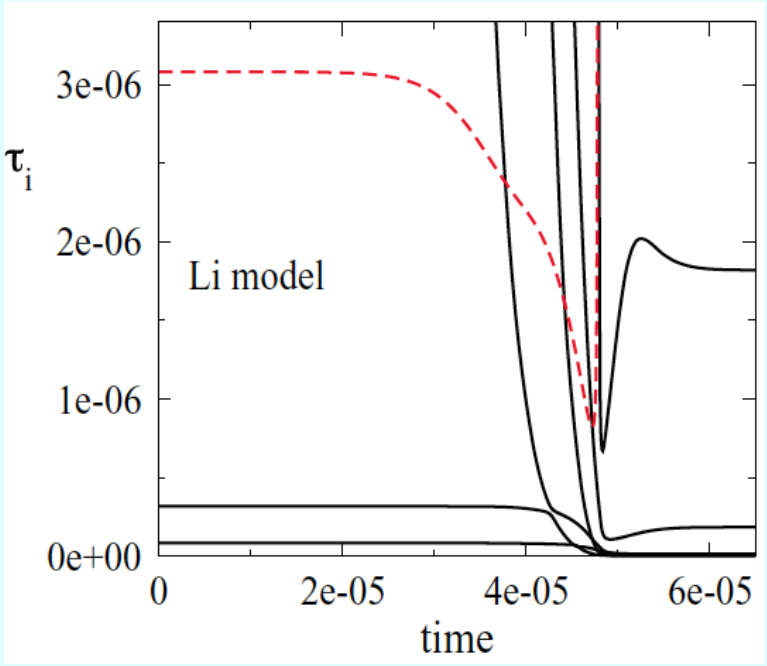
amplitude

variables

$1f-$EN	$H + O_2 \rightarrow O + OH$	$1b-$EX	$H + O_2 \leftarrow O + OH$
$2f-$EN	$O + H_2 \rightarrow H + OH$	$2b-$EX	$O + H_2 \leftarrow H + OH$
$3f-$EX	$OH + H_2 \rightarrow H + H_2O$	$3b-$EN	$OH + H_2 \leftarrow H + H_2O$
$8f-$EX	$H + OH(+M) \rightarrow H_2O(+M)$	$9f-$EX	$H + O_2(+M) \rightarrow HO_2(+M)$
$10f-$EX	$H + HO_2 \rightarrow H_2 + O_2$	$10b-$EN	$H + HO_2 \leftarrow H_2 + O_2$
$11f-$EX	$H + HO_2 \rightarrow OH + OH$		

Diamantis et al, CTM 2015

CSP diagnostics: explosive mode in H_2/air autoignition



	$t = 0.0 \times 10^{-6}$ s $T = 1100$ K $\lambda = 3.245 \times 10^5$ s^{-1}	$t = 3.0 \times 10^{-6}$ s $T = 1100$ K $\lambda = 3.245 \times 10^5$ s^{-1}
TPI	1*f*: + 0.6273 2*f*: + 0.0739 3*f*: + 0.0183 9*f*: − 0.2792	1*f*: + 0.6273 2*f*: + 0.0739 3*f*: + 0.0183 9*f*: − 0.2792
API	10*b*: + 1.0000	1*f*: + 0.4987 10*b*: + 0.2100 2*f*: + 0.0543 3*f*: + 0.0138 9*f*: − 0.2220
Po	H: +0.79 O: +0.17 OH: +0.04	H: +0.79 O: +0.17 OH: +0.04

time scale

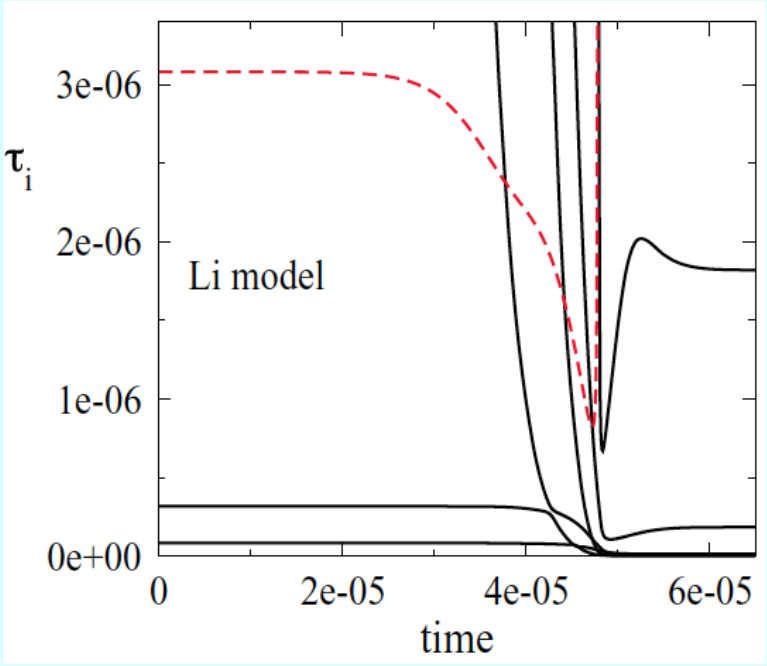
reactions

variables

$1f-\mathrm{EN}$	$H + O_2 \rightarrow O + OH$	$1b-\mathrm{EX}$	$H + O_2 \leftarrow O + OH$
$2f-\mathrm{EN}$	$O + H_2 \rightarrow H + OH$	$2b-\mathrm{EX}$	$O + H_2 \leftarrow H + OH$
$3f-\mathrm{EX}$	$OH + H_2 \rightarrow H + H_2O$	$3b-\mathrm{EN}$	$OH + H_2 \leftarrow H + H_2O$
$8f-\mathrm{EX}$	$H + OH(+M) \rightarrow H_2O(+M)$	$9f-\mathrm{EX}$	$H + O_2(+M) \rightarrow HO_2(+M)$
$10f-\mathrm{EX}$	$H + HO_2 \rightarrow H_2 + O_2$	$10b-\mathrm{EN}$	$H + HO_2 \leftarrow H_2 + O_2$
$11f-\mathrm{EX}$	$H + HO_2 \rightarrow OH + OH$		

Diamantis et al, CTM 2015

CSP diagnostics: explosive mode in H_2/air autoignition



	$t = 0.0 \times 10^{-6}$ s $T = 1100$ K $\lambda = 3.245 \times 10^5$ s^{-1}	$t = 3.0 \times 10^{-6}$ s $T = 1100$ K $\lambda = 3.245 \times 10^5$ s^{-1}
TPI	$1f$: + 0.6273 $2f$: + 0.0739 $3f$: + 0.0183 $9f$: − 0.2792	$1f$: + 0.6273 $2f$: + 0.0739 $3f$: + 0.0183 $9f$: − 0.2792
API	$10b$: + 1.0000	$1f$: + 0.4987 $10b$: + 0.2100 $2f$: + 0.0543 $3f$: + 0.0138 $9f$: − 0.2220
Po	H: +0.79 O: +0.17 OH: +0.04	H: +0.79 O: +0.17 OH: +0.04

time scale

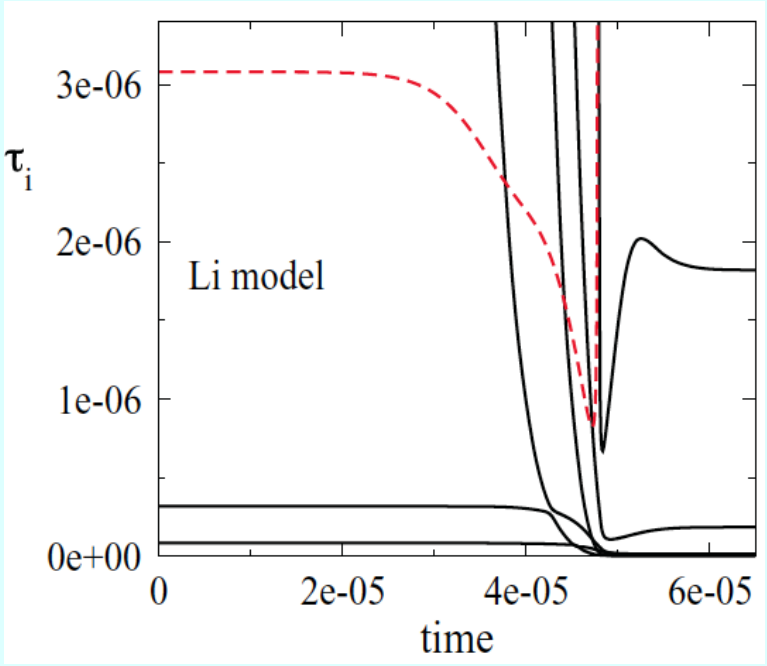
reactions

variables

$1f-$EN	$H + O_2 \rightarrow O + OH$	$1b-$EX	$H + O_2 \leftarrow O + OH$
$2f-$EN	$O + H_2 \rightarrow H + OH$	$2b-$EX	$O + H_2 \leftarrow H + OH$
$3f-$EX	$OH + H_2 \rightarrow H + H_2O$	$3b-$EN	$OH + H_2 \leftarrow H + H_2O$
$8f-$EX	$H + OH(+M) \rightarrow H_2O(+M)$	$9f-$EX	$H + O_2(+M) \rightarrow HO_2(+M)$
$10f-$EX	$H + HO_2 \rightarrow H_2 + O_2$	$10b-$EN	$H + HO_2 \leftarrow H_2 + O_2$
$11f-$EX	$H + HO_2 \rightarrow OH + OH$		

Diamantis et al, CTM 2015

CSP diagnostics: explosive mode in H_2/air autoignition



	$t = 0.0 \times 10^{-6}$ s $T = 1100$ K $\lambda = 3.245 \times 10^5$ s^{-1}	$t = 3.0 \times 10^{-6}$ s $T = 1100$ K $\lambda = 3.245 \times 10^5$ s^{-1}
TPI	$1f$: + 0.6273 $2f$: + 0.0739 $3f$: + 0.0183 $9f$: − 0.2792	$1f$: + 0.6273 $2f$: + 0.0739 $3f$: + 0.0183 $9f$: − 0.2792
API	$10b$: + 1.0000	$1f$: + 0.4987 $10b$: + 0.2100 $2f$: + 0.0543 $3f$: + 0.0138 $9f$: − 0.2220
Po	H: +0.79 O: +0.17 OH: +0.04	H: +0.79 O: +0.17 OH: +0.04

time scale

reactions

variables

$1f-$EN	$H + O_2 \rightarrow O + OH$	$1b-$EX	$H + O_2 \leftarrow O + OH$
$2f-$EN	$O + H_2 \rightarrow H + OH$	$2b-$EX	$O + H_2 \leftarrow H + OH$
$3f-$EX	$OH + H_2 \rightarrow H + H_2O$	$3b-$EN	$OH + H_2 \leftarrow H + H_2O$
$8f-$EX	$H + OH(+M) \rightarrow H_2O(+M)$	$9f-$EX	$H + O_2(+M) \rightarrow HO_2(+M)$
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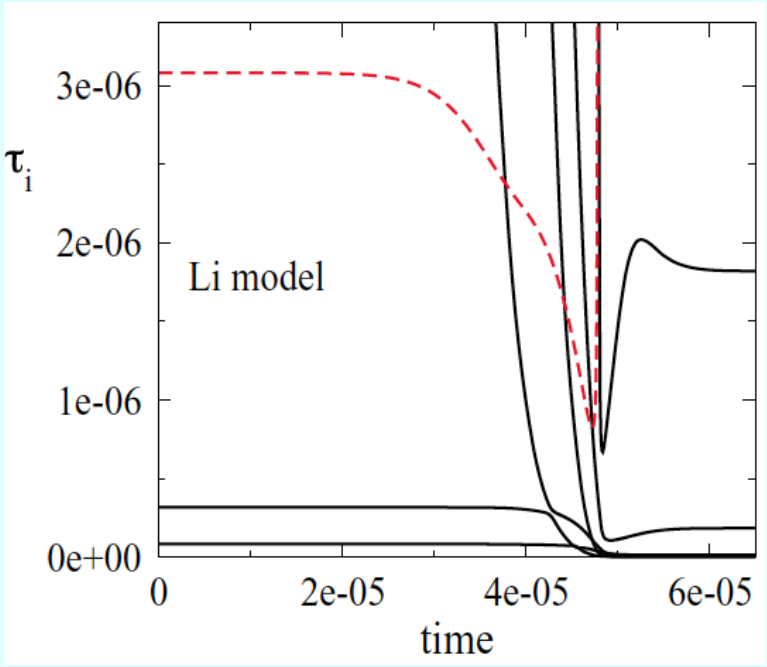
$11f-$EX	$H + HO_2 \rightarrow OH + OH$		

Diamantis et al, CTM 2015

CSP diagnostics: explosive mode in H_2/air autoignition



	$t = 2.000 \times 10^{-5}$ s $T = 1100$ K $\lambda = 3.251 \times 10^5$ s^{-1}	$t = 4.500 \times 10^{-5}$ s $T = 1168$ K $\lambda = 7.014 \times 10^5$ s^{-1}	$t = 4.782 \times 10^{-5}$ s $T = 1593$ K $\lambda = 3.043 \times 10^5$ s^{-1}
TPI	$1f$: + 0.6265 $2f$: + 0.0740 $3f$: + 0.0184 $9f$: − 0.2785	$1f$: + 0.5959 $2f$: + 0.1430 $3f$: + 0.0886 $11f$: + 0.0543 $10f$: − 0.0316 $1b$: − 0.0304 $8f$: − 0.0210	$1f$: + 0.2652 $2f$: + 0.1607 $3f$: + 0.0569 $8f$: + 0.0277 $1b$: − 0.1581 $2b$: − 0.1244 $3b$: − 0.0853
API	$1f$: + 0.6265 $2f$: + 0.0740 $3f$: + 0.0184 $9f$: − 0.2785	$1f$: + 0.5823 $2f$: + 0.1408 $3f$: + 0.0972 $11f$: + 0.0723 $10f$: − 0.0414 $1b$: − 0.0173 $8f$: − 0.0126	$1f$: + 0.3389 $2f$: + 0.1646 $3f$: + 0.1432 $9f$: + 0.0704 $8f$: + 0.0598 $1b$: − 0.0838 $2b$: − 0.0515 $3b$: − 0.0366
Po	H: + 0.79 O: + 0.17	H: + 0.65 T: + 0.19 O: + 0.13	T: + 3.50 O_2: −2.60 H_2O: −2.45

$1f-$EN	$H + O_2 \rightarrow O + OH$	$1b-$EX	$H + O_2 \leftarrow O + OH$
$2f-$EN	$O + H_2 \rightarrow H + OH$	$2b-$EX	$O + H_2 \leftarrow H + OH$
$3f-$EX	$OH + H_2 \rightarrow H + H_2O$	$3b-$EN	$OH + H_2 \leftarrow H + H_2O$
$8f-$EX	$H + OH(+M) \rightarrow H_2O(+M)$	$9f-$EX	$H + O_2(+M) \rightarrow HO_2(+M)$
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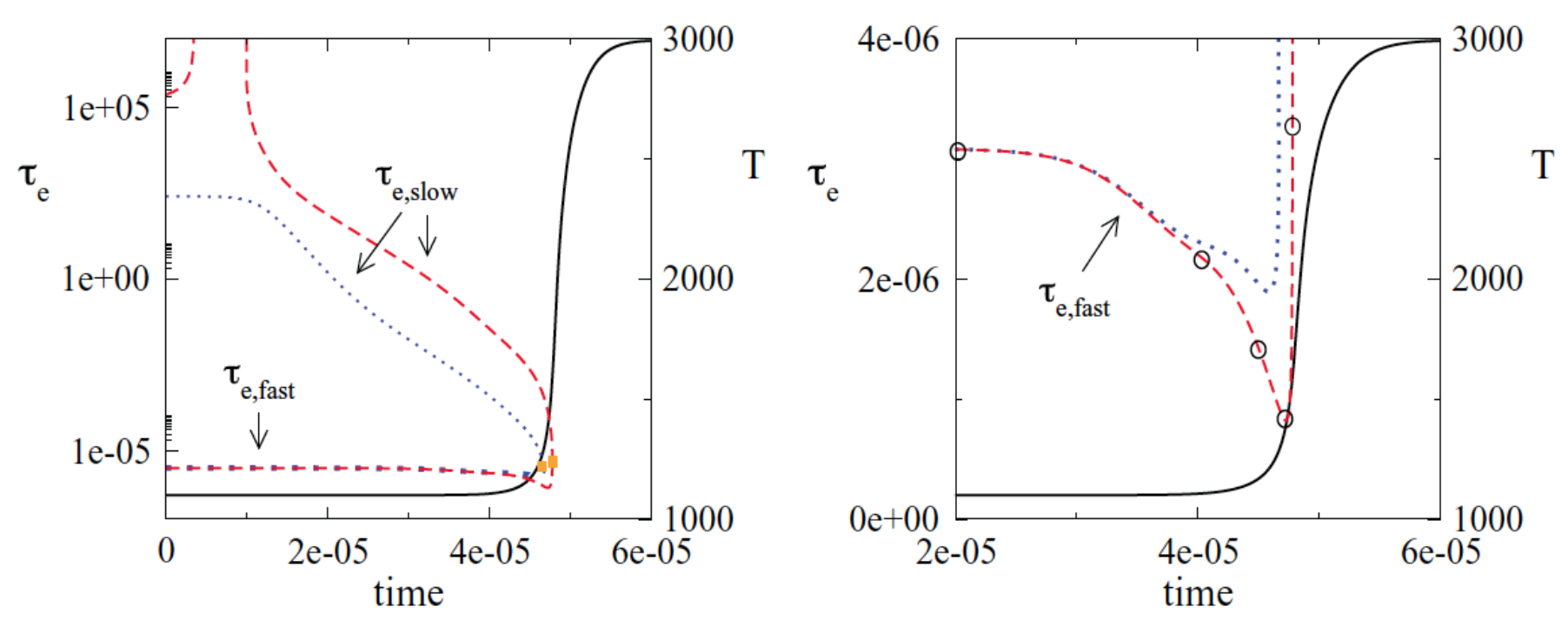
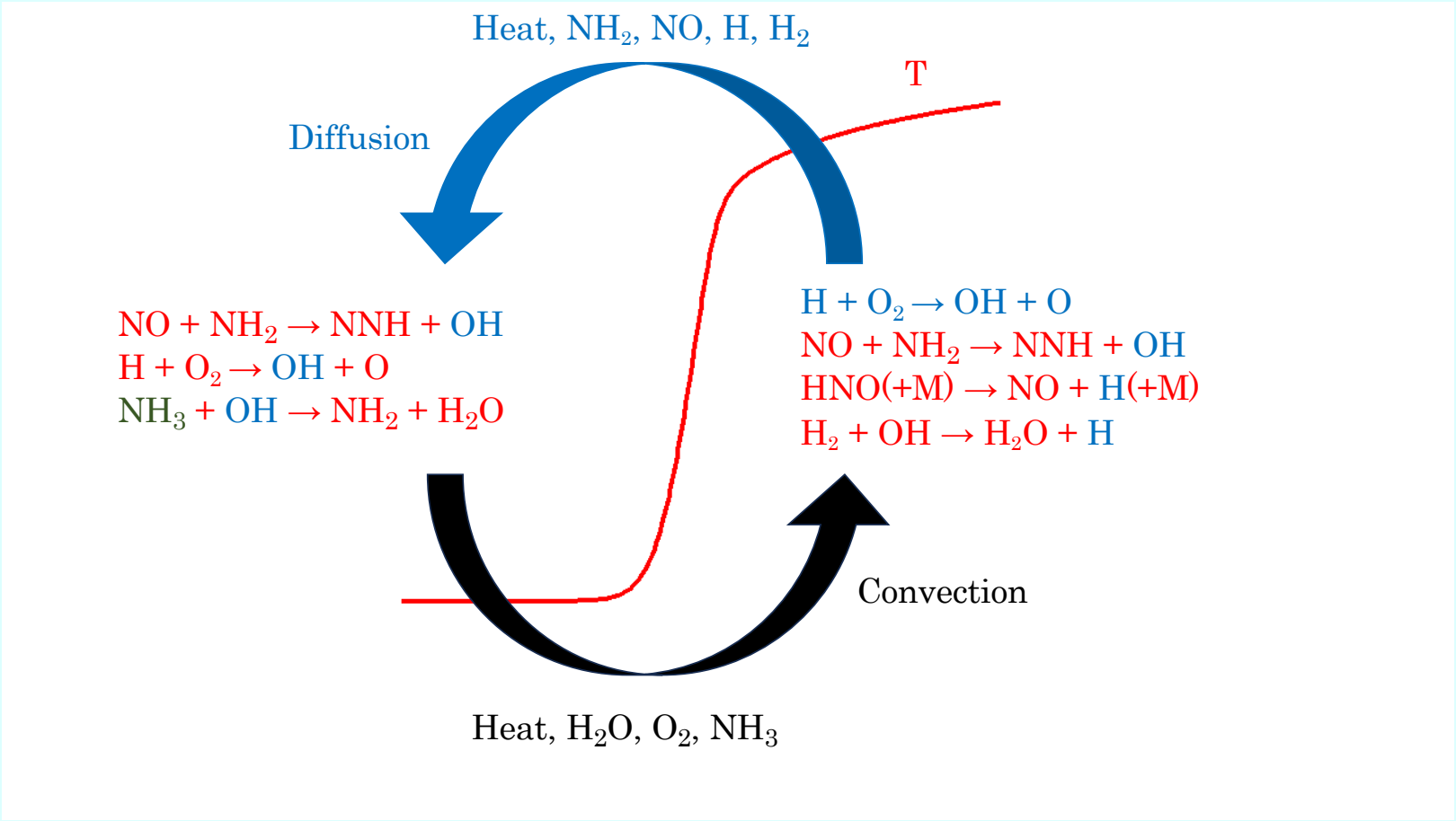
CSP diagnostics: explosive mode in H_2/air autoignition



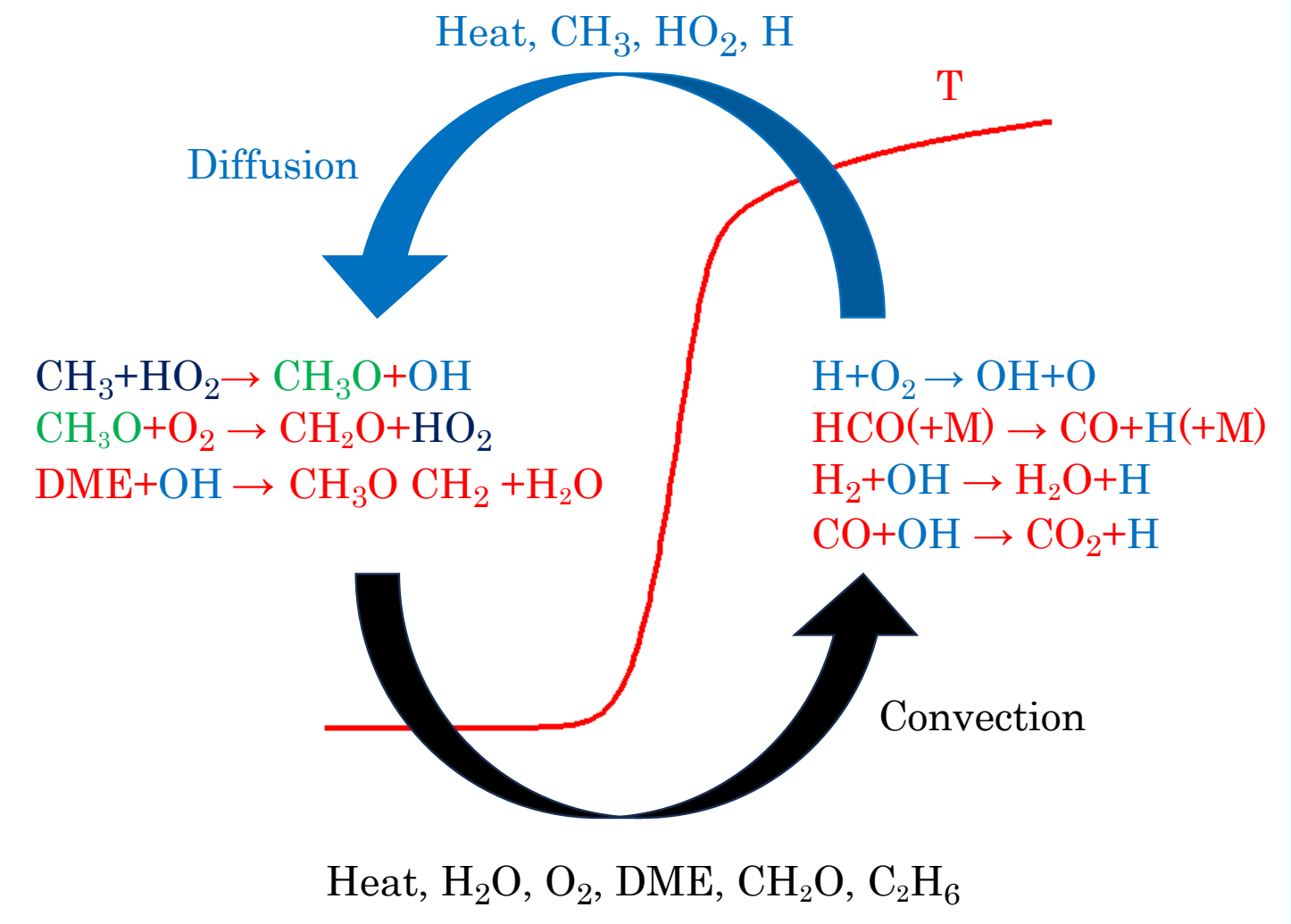
Chemical vs thermal runaway regime

Propagation mechanism of NH_3/air premixed flame



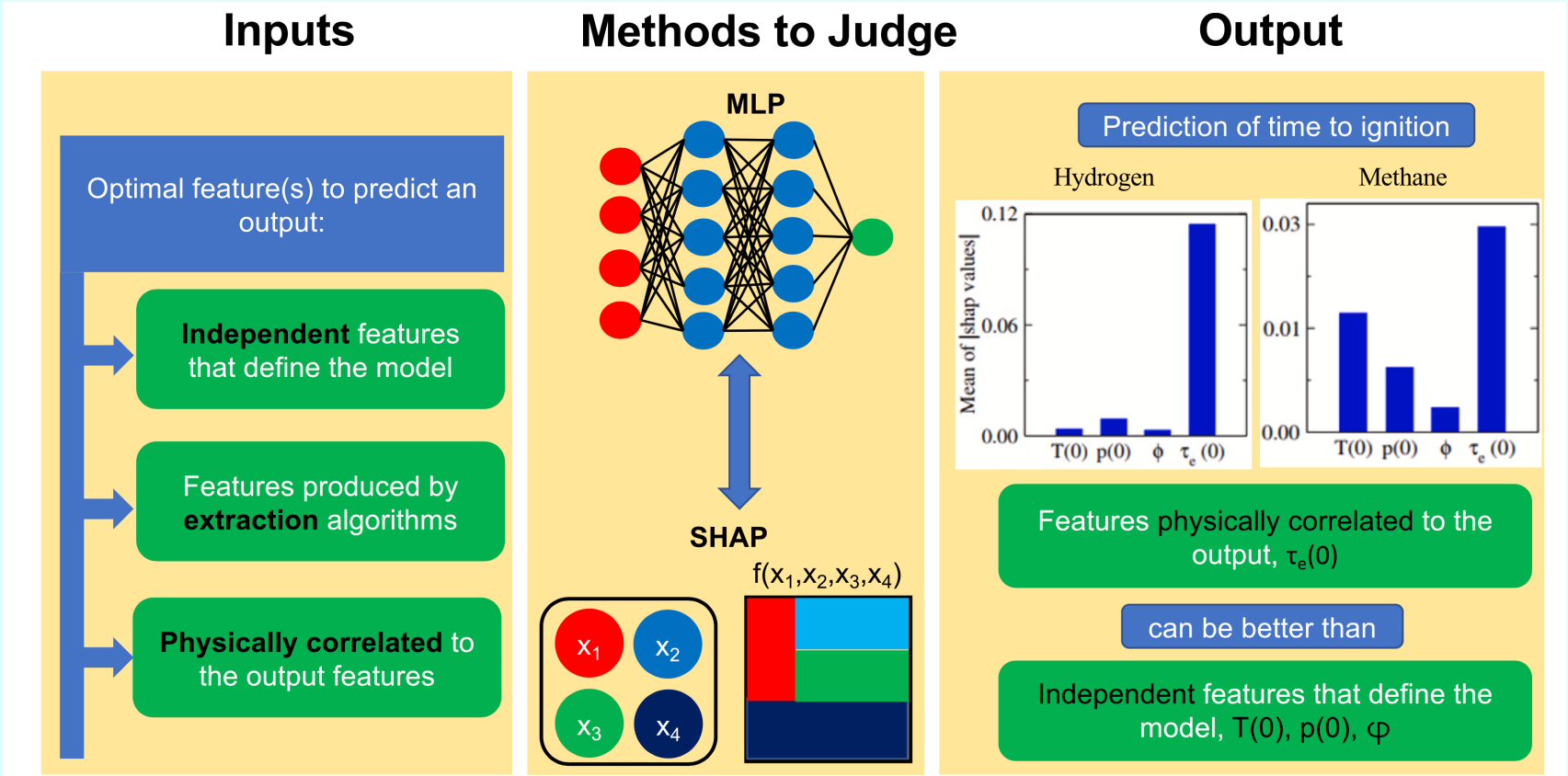
Tingas et al, IJHE 2024

Propagation mechanism of DME_3/air premixed flame



Radaideh et al, submitted

Optimal input in Machine Learning algorithms



HIGHLIGHTS

- Inputs to ML algorithms must convey the physics of the process.
- Time scale(s) are frequently employed to characterize the dynamics.
- The characteristic time is shown a excellent input.

Radaideh et al, Energy and AI, 2023

Optimal input in Machine Learning algorithms

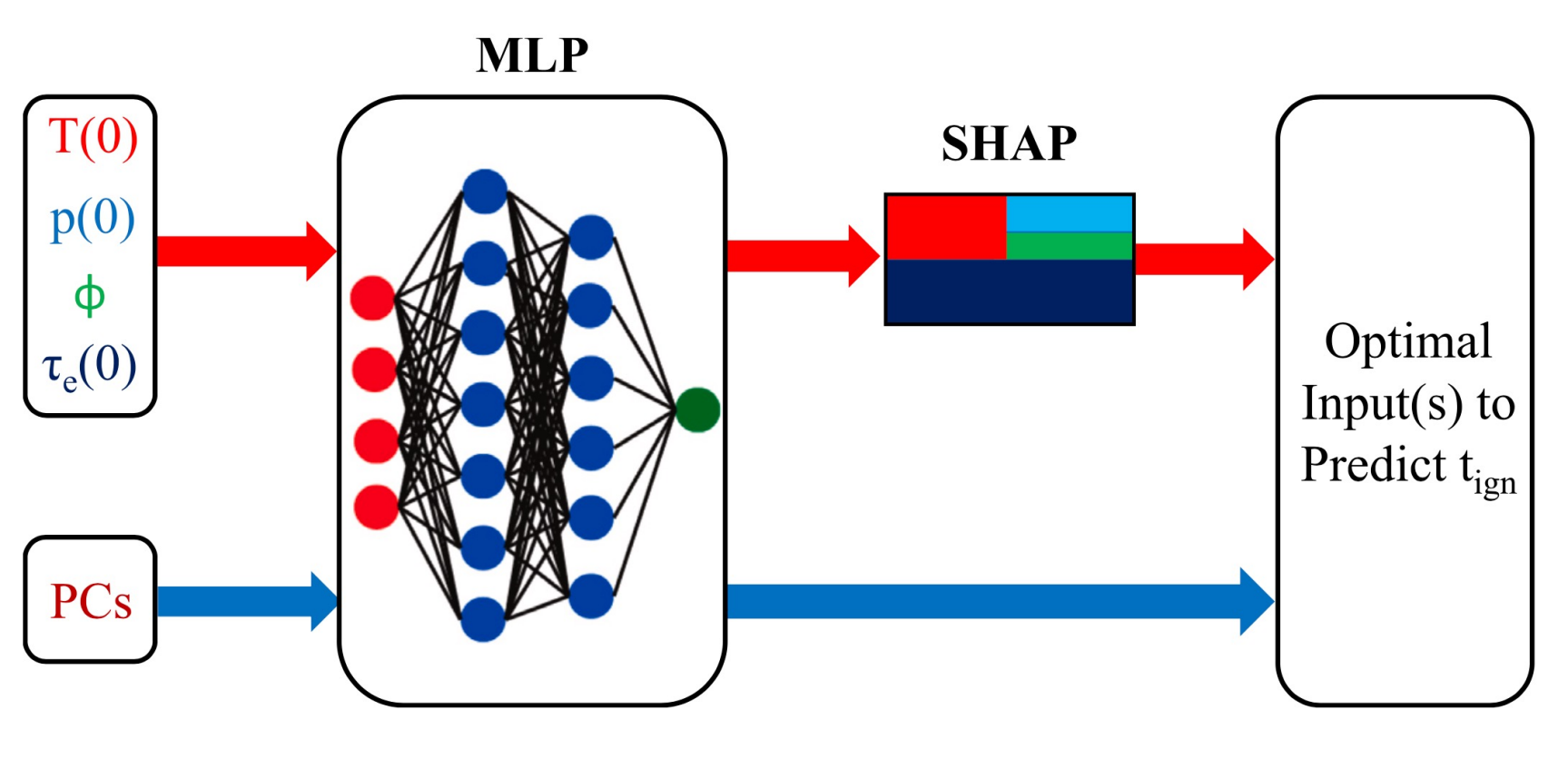
Homogeneous autoignition of H_2/air CH_4/air mixtures

System fully specified when T(0), p(0) and φ are known

Typical entries in the dataset for H_2/air mixtures.

$T(0)$ [K]	$p(0)$ [atm]	ϕ	$\tau_e(0)$ [s]	t_{ign} [s]
1100.00	1.00	0.50	4.94203973E−06	8.47149668E−05
1180.00	11.00	0.95	5.48137994E−06	3.50005334E−05
1260.00	7.00	1.70	5.23293601E−07	6.65079873E−06
:	:	:	:	:

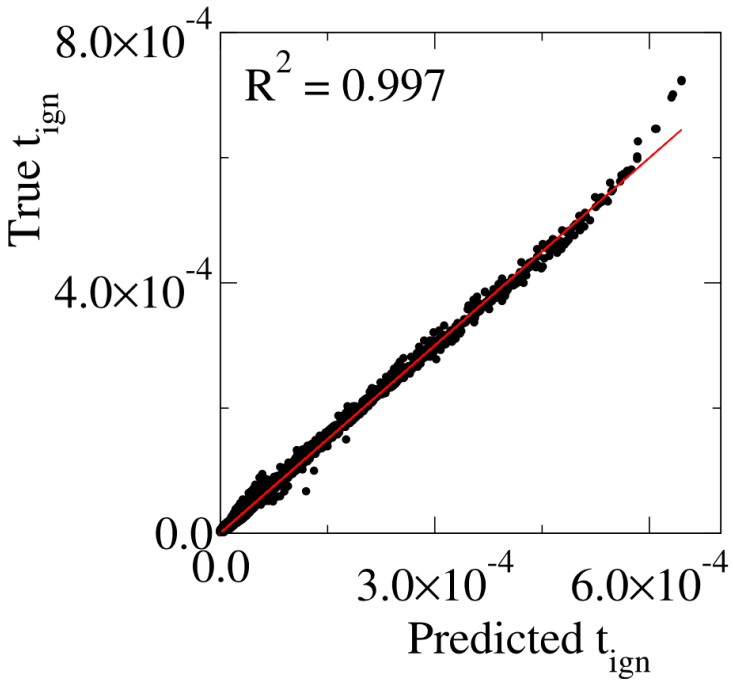
Optimal input in Machine Learning algorithms



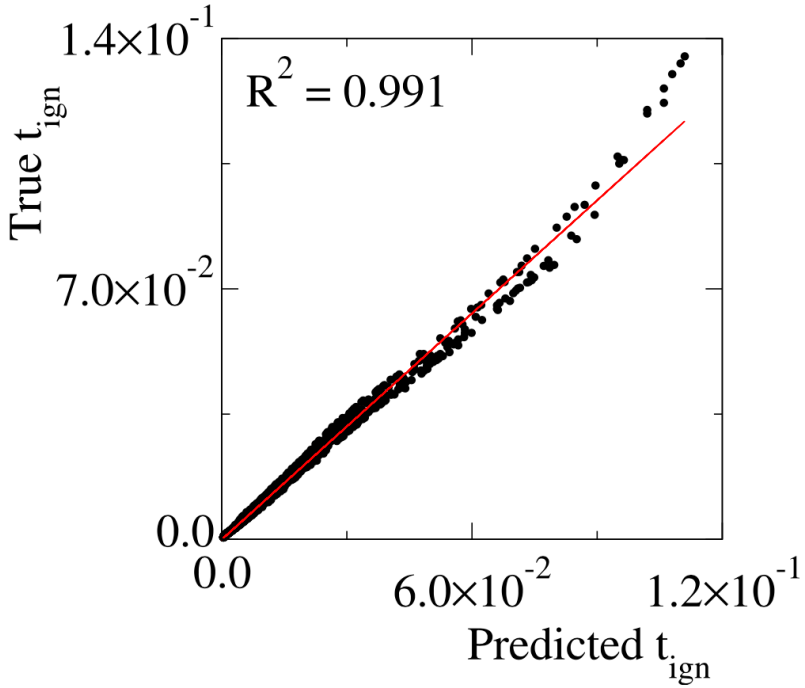
MLP: Multilayer Perceptron
SHAP: SHapley Additive exPlanations
PC: Principal Component

Optimal input in Machine Learning algorithms

H_2/air



CH_4/air

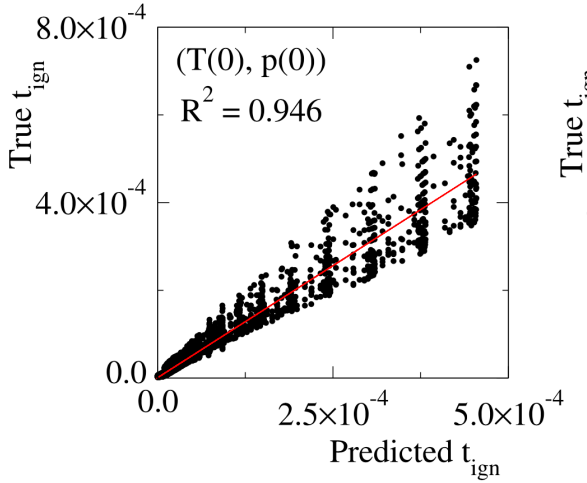


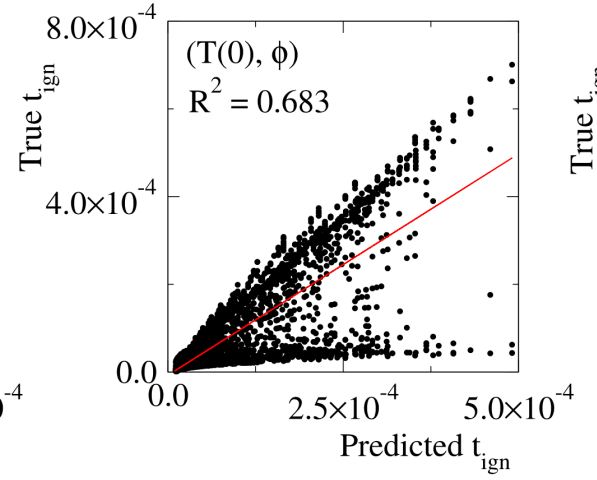
Input: T(0), p(0), φ

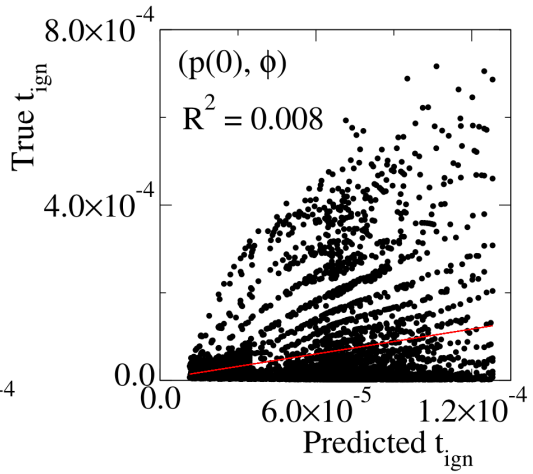
Optimal input in Machine Learning algorithms

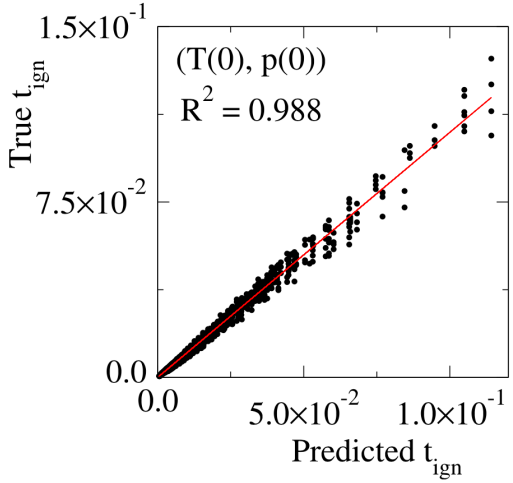
H_2/air

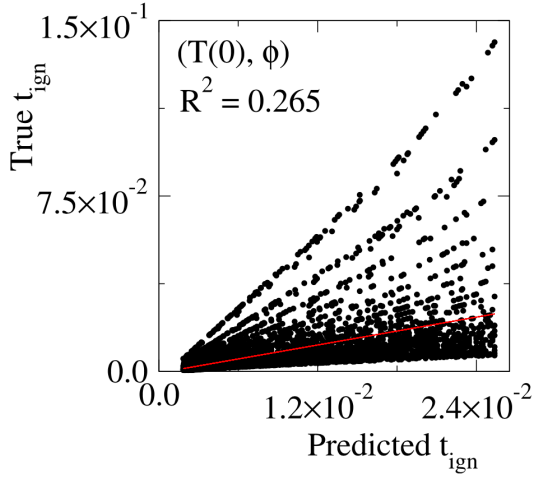
CH_4/air

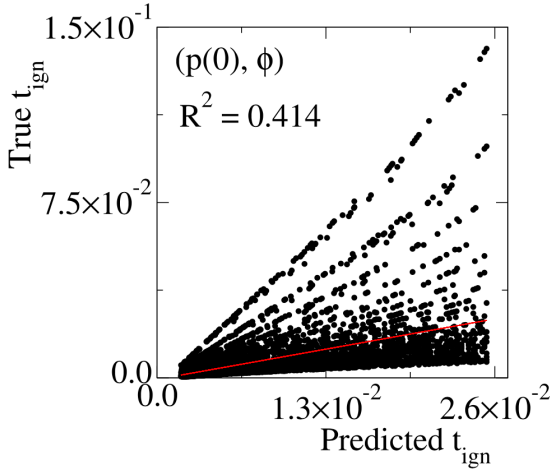












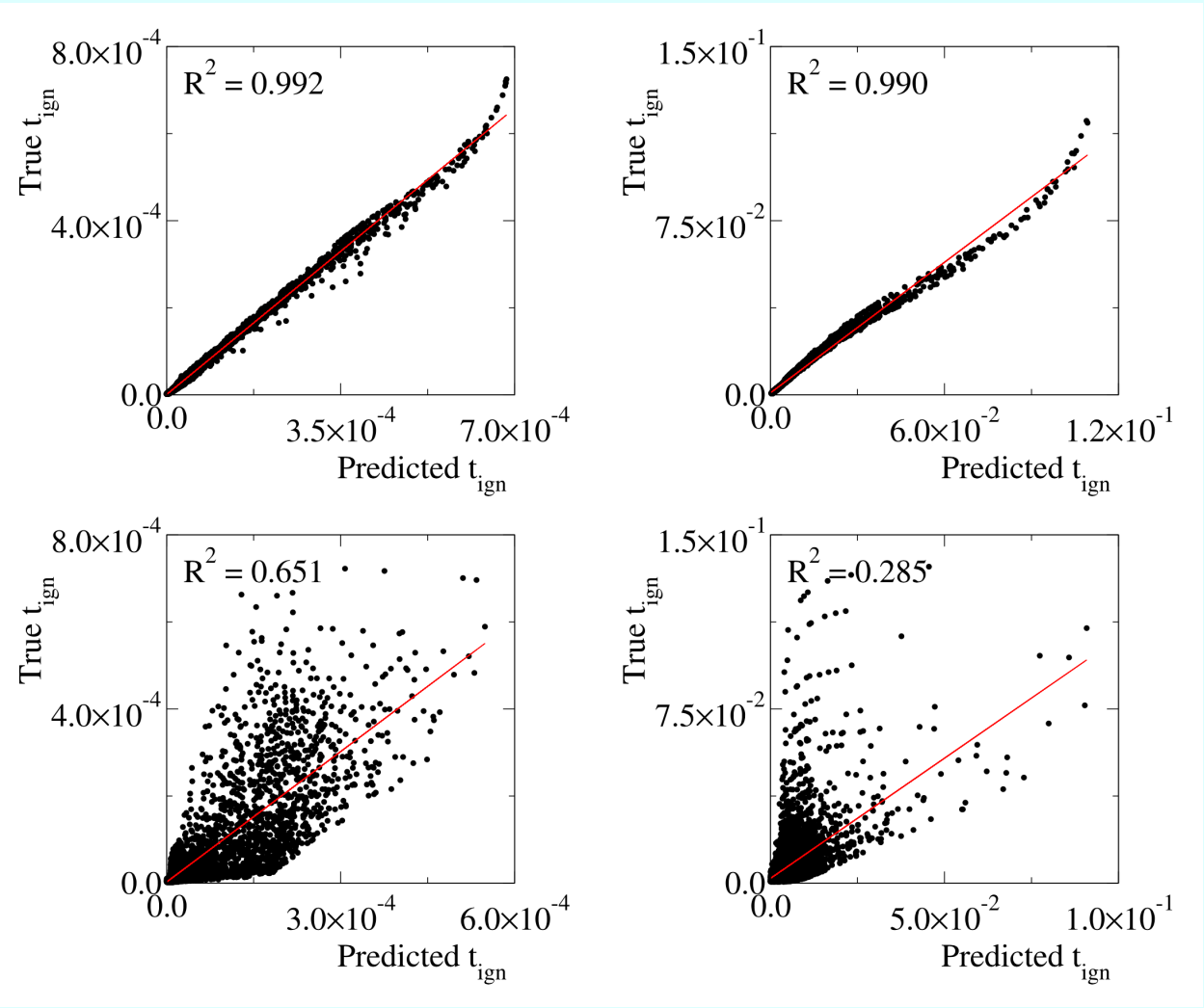
Optimal input in Machine Learning algorithms

H_2/air

CH_4/air

3 PCs

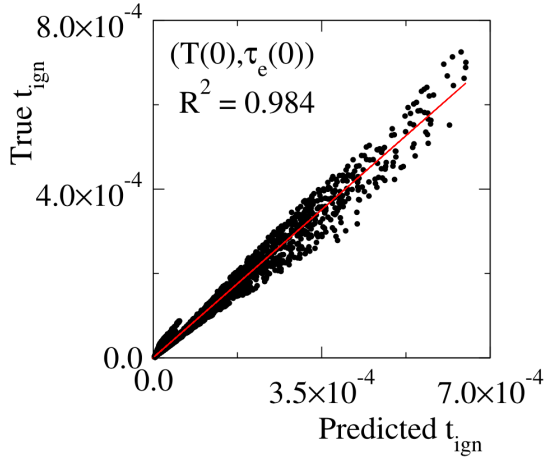
2 PCs

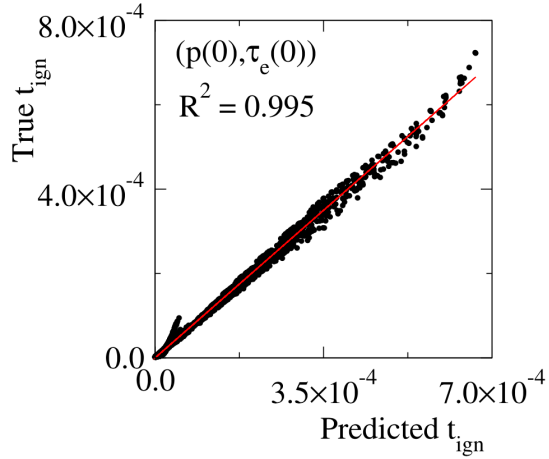


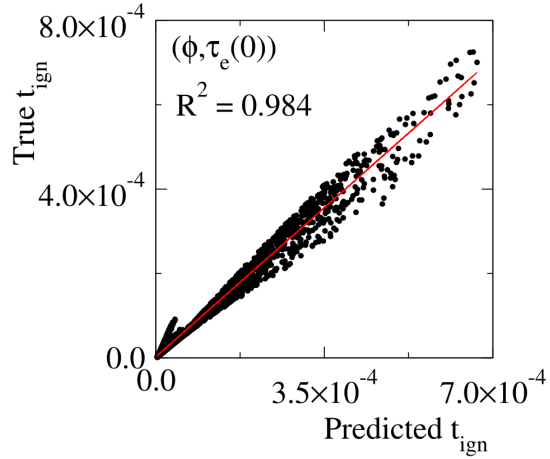
Optimal input in Machine Learning algorithms

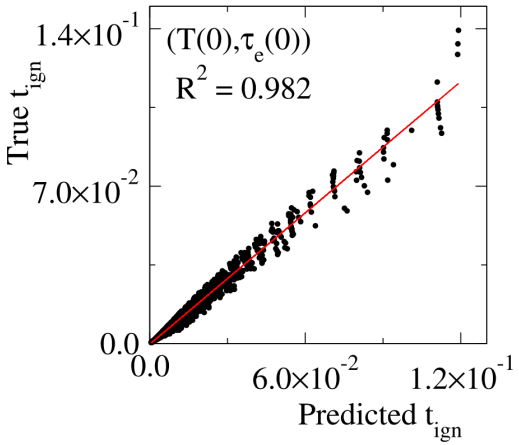
H_2/air

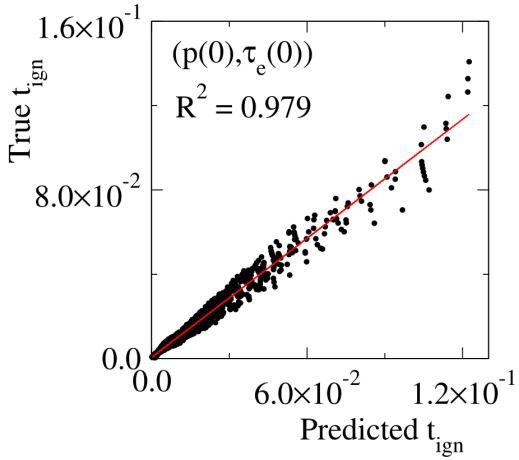
CH_4/air

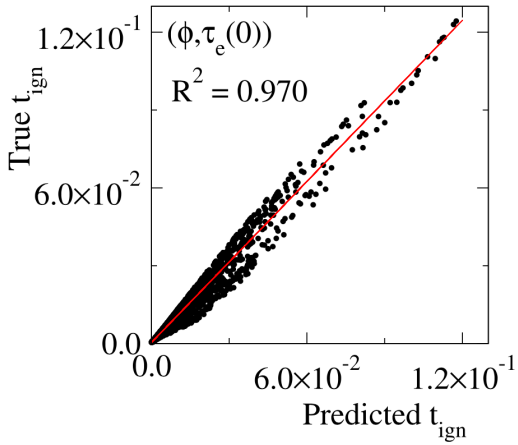




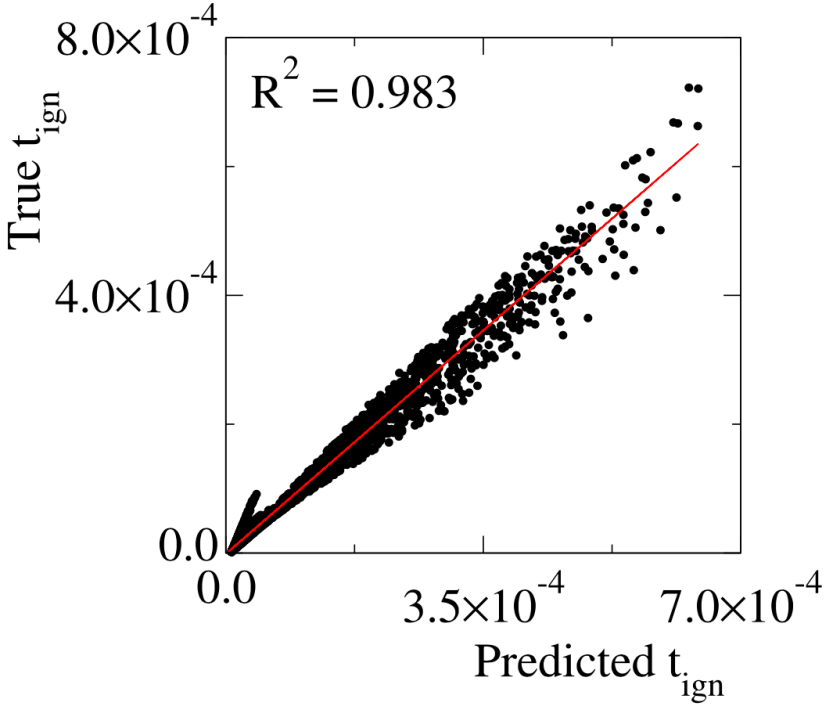


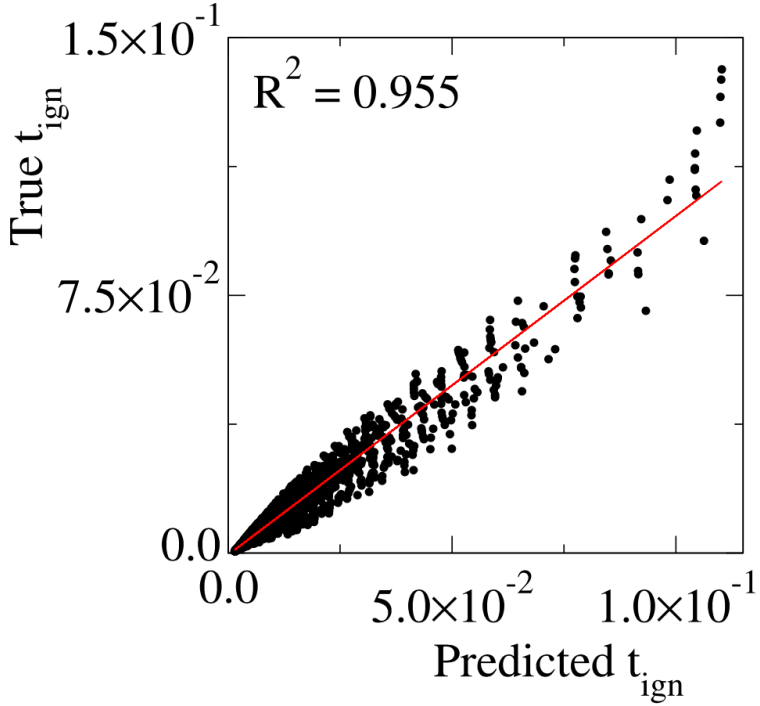






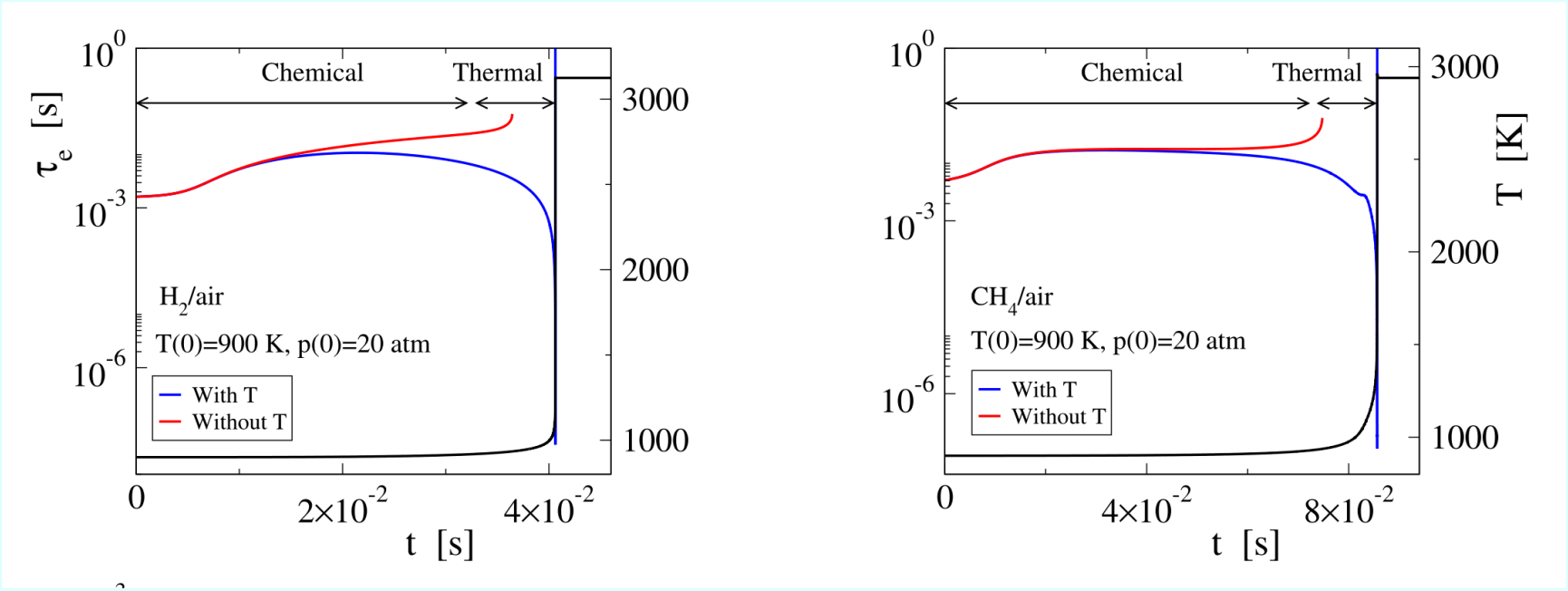
Optimal input in Machine Learning algorithms





$\tau_e(0)$ input

Optimal input in Machine Learning algorithms



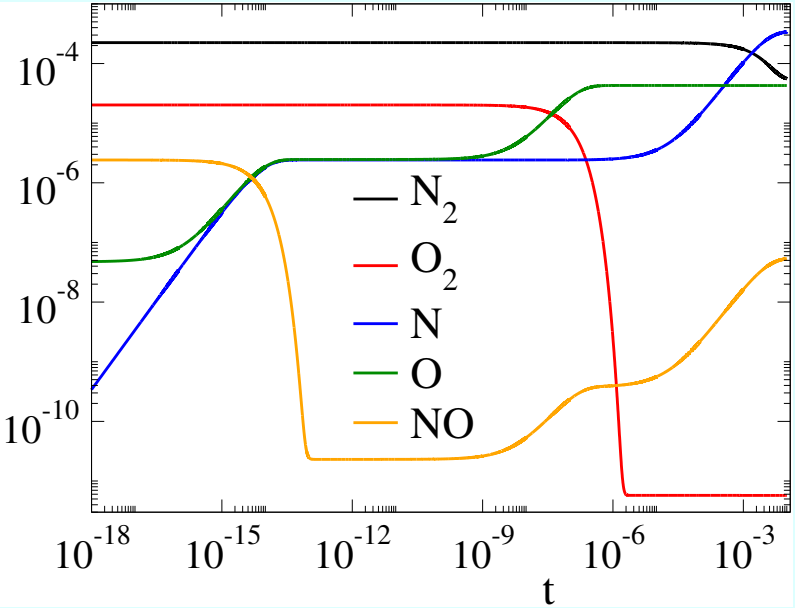
Sensitivity analysis: extended Zeldovich mechanism

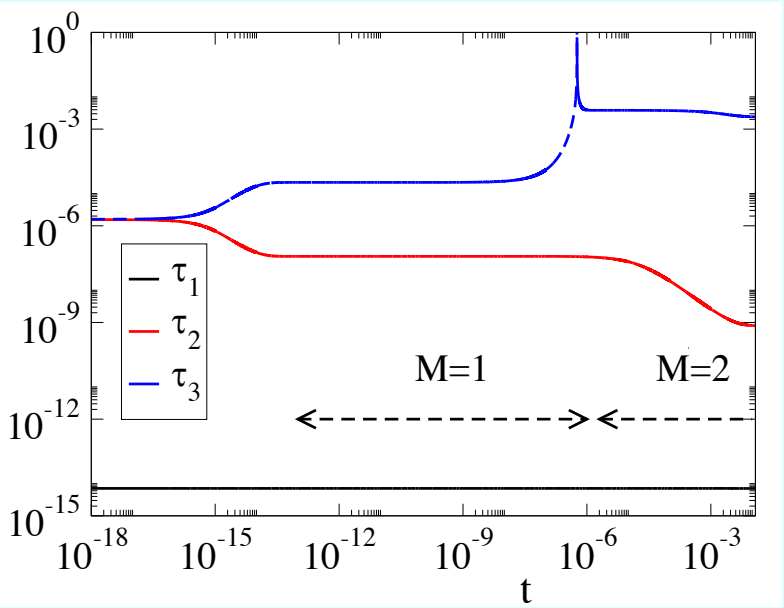
$(r_1) \quad N_2 + O \leftrightarrow N + NO$

$(r_2) \quad O_2 + N \leftrightarrow O + NO$

$(r_3) \quad N + O \leftrightarrow NO$

Initial conditions:
equilibrium of homogeneous, adiabatic constant volume autoignition of a NH_3/air mixture; φ = 0.6





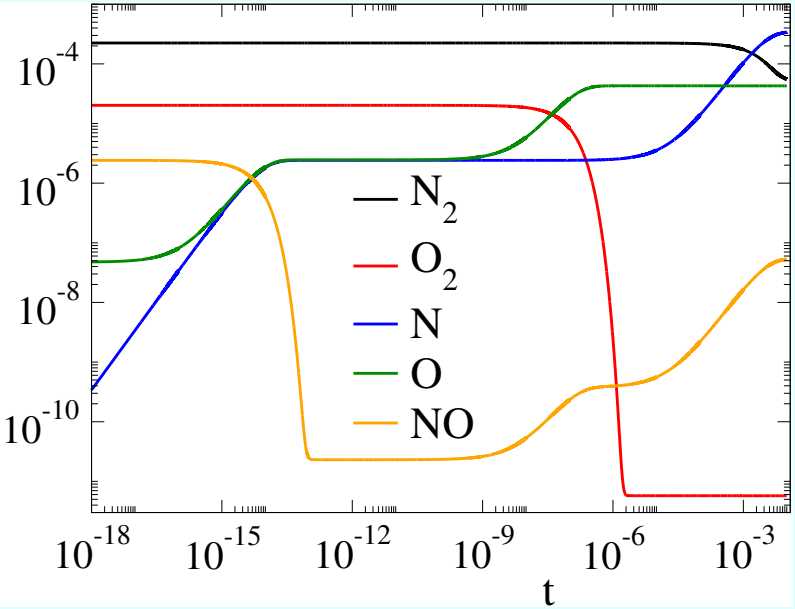
Tingas et al, submitted

Developing equilibria

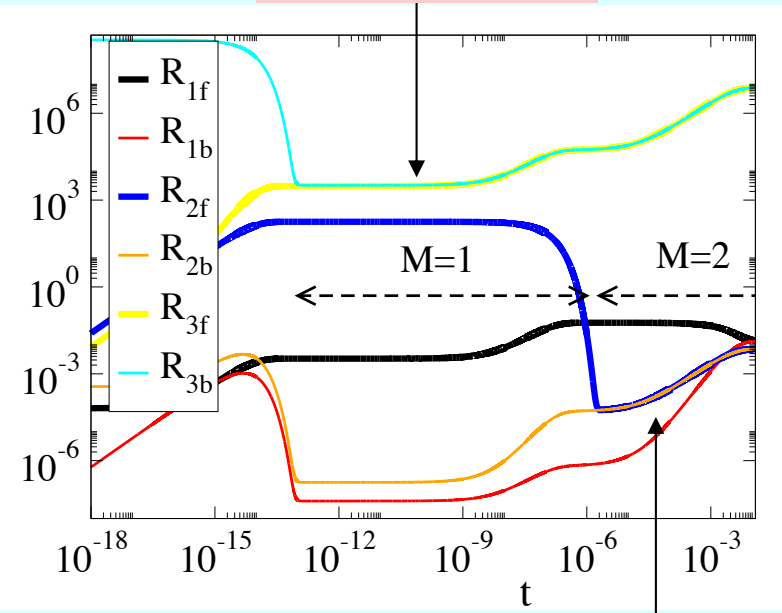
$$(r_1) \quad N_2 + O \leftrightarrow N + NO$$

$$(r_2) \quad O_2 + N \leftrightarrow O + NO$$

$$(r_3) \quad N + O \leftrightarrow NO$$



M=1: $R^{3f} = R^{3b}$



M=2: $R^{3f} = R^{3b}$, $R^{2f} = R^{2b}$

CSP diagnostics

$(r_1)\quad N_2 + O \leftrightarrow N + NO$

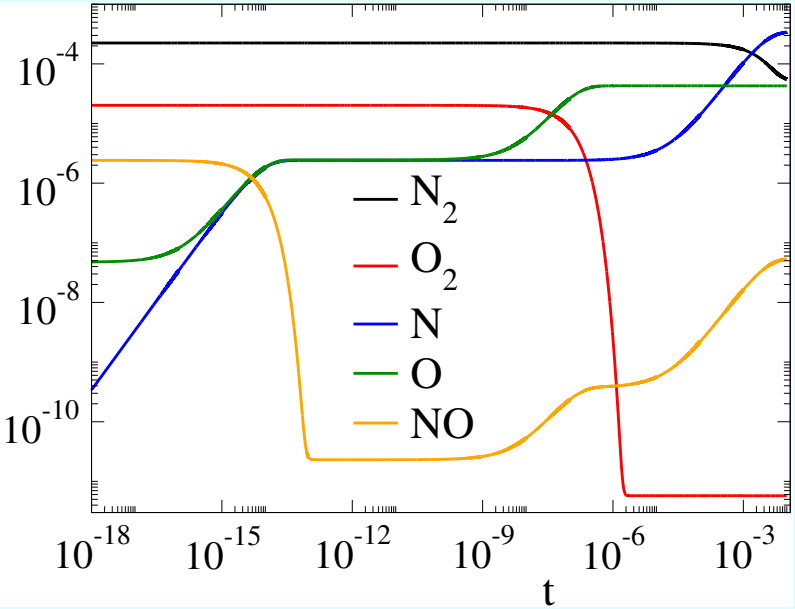
$(r_2)\quad O_2 + N \leftrightarrow O + NO$

$(r_3)\quad N + O \leftrightarrow NO$

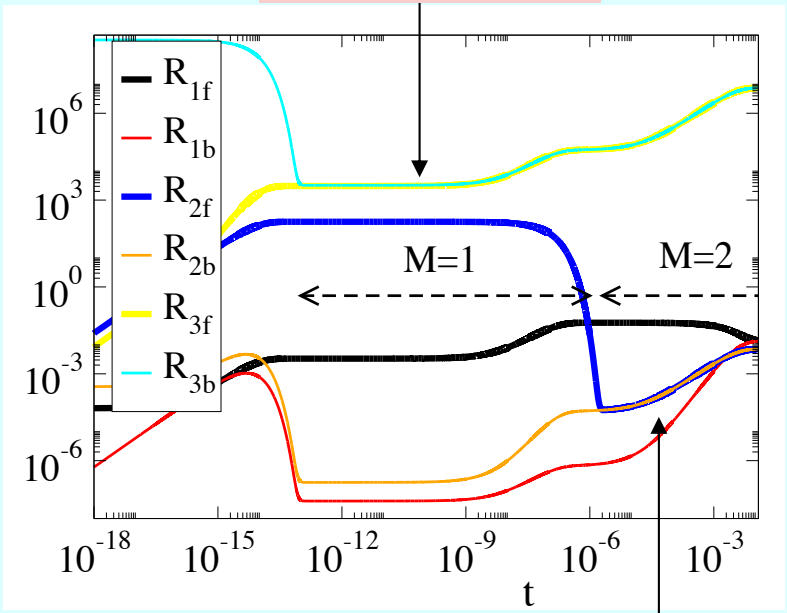
M=1: Fast reaction/species: 3b / NO, $R^{3f} - R^{3b} = 0$

M=2: Fast reaction/species: 3b / NO, $R^{3f} - R^{3b} = 0$

Fast reaction/species: 2f / O_2, $R^{2f} - R^{2b} = 0$



M=1: $R^{3f} = R^{3b}$



M=2: $R^{3f} = R^{3b}$, $R^{2f} = R^{2b}$

Phase space

$(r_1)\quad N_2 + O \leftrightarrow N + NO$

$(r_2)\quad O_2 + N \leftrightarrow O + NO$

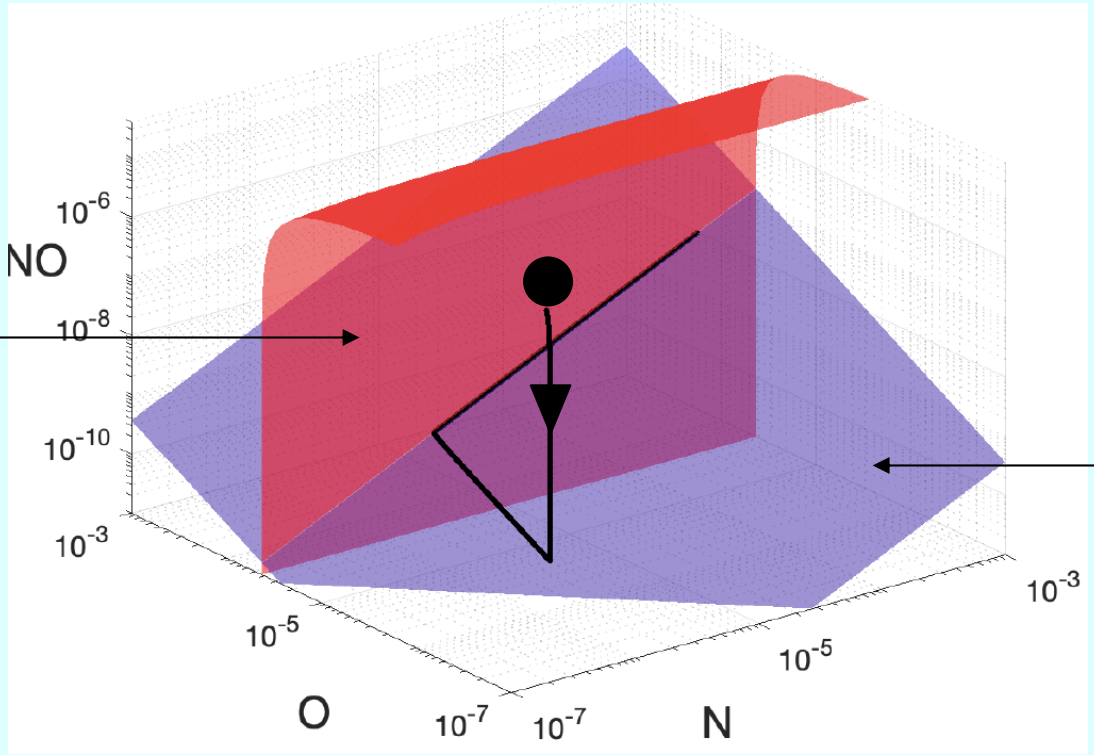
$(r_3)\quad N + O \leftrightarrow NO$

M=1: Fast reaction/species: 3b / NO, $R^{3f} - R^{3b} = 0$

M=2: Fast reaction/species: 3b / NO, $R^{3f} - R^{3b} = 0$

Fast reaction/species: 2f / O_2, $R^{2f} - R^{2b} = 0$

QSSA O_2



QSSA NO

Relations among the sensitivity coefficients

$(r_1)\quad N_2 + O \leftrightarrow N + NO$

$(r_2)\quad O_2 + N \leftrightarrow O + NO$

$(r_3)\quad N + O \leftrightarrow NO$

M=1: Fast reaction/species: 3b / NO, $R^{3f} - R^{3b} = 0$

$$k_{3f}[N][O] = k_{3b}[NO]$$

$k_{3f}\dfrac{\partial}{\partial k_{3f}}$

$k_{3b}\dfrac{\partial}{\partial k_{3b}}$

$$k_{3f}[N][O] + k_{3f}\frac{\partial[N]}{\partial lnk_{3f}}[O] + k_{3f}[N]\frac{\partial[O]}{\partial lnk_{3f}} = k_{3b}\frac{\partial[NO]}{\partial lnk_{3f}}$$

$$k_{3f}\frac{\partial[N]}{\partial lnk_{3b}}[O] + k_{3f}[N]\frac{\partial[O]}{\partial lnk_{3b}} = k_{3b}[NO] + k_{3b}\frac{\partial[NO]}{\partial lnk_{3b}}$$

$$k_{3f}\left(\frac{\partial[N]}{\partial lnk_{3f}} + \frac{\partial[N]}{\partial lnk_{3b}}\right)[O] + k_{3f}[N]\left(\frac{\partial[O]}{\partial lnk_{3f}} + \frac{\partial[O]}{\partial lnk_{3b}}\right) = k_{3b}\left(\frac{\partial[NO]}{\partial lnk_{3f}} + \frac{\partial[NO]}{\partial lnk_{3b}}\right)$$

Relations among the sensitivity coefficients

$$k_{3f}\left(\frac{\partial[N]}{\partial lnk_{3f}}+\frac{\partial[N]}{\partial lnk_{3b}}\right)[O]+k_{3f}[N]\left(\frac{\partial[O]}{\partial lnk_{3f}}+\frac{\partial[O]}{\partial lnk_{3b}}\right)$$
$$=k_{3b}\left(\frac{\partial[NO]}{\partial lnk_{3f}}+\frac{\partial[NO]}{\partial lnk_{3b}}\right)$$

$$k_{3f}\left(\frac{\partial[N]}{\partial lnk_{1f}}+\frac{\partial[N]}{\partial lnk_{1b}}+\frac{\partial[N]}{\partial lnk_{2f}}+\frac{\partial[N]}{\partial lnk_{2b}}+\frac{\partial[N]}{\partial lnk_{3f}}+\frac{\partial[N]}{\partial lnk_{3b}}\right)[O]+$$
$$k_{3f}[N]\left(\frac{\partial[O]}{\partial lnk_{1f}}+\frac{\partial[O]}{\partial lnk_{1b}}+\frac{\partial[O]}{\partial lnk_{2f}}+\frac{\partial[O]}{\partial lnk_{2b}}+\frac{\partial[O]}{\partial lnk_{3f}}+\frac{\partial[O]}{\partial lnk_{3b}}\right)=$$
$$k_{3b}\left(\frac{\partial[NO]}{\partial lnk_{1f}}+\frac{\partial[NO]}{\partial lnk_{1b}}+\frac{\partial[NO]}{\partial lnk_{2f}}+\frac{\partial[NO]}{\partial lnk_{2b}}+\frac{\partial[NO]}{\partial lnk_{3f}}+\frac{\partial[NO]}{\partial lnk_{3b}}\right)$$

Relations among the sensitivity coefficients

$(r_1)\quad N_2 + O \leftrightarrow N + NO$

$(r_2)\quad O_2 + N \leftrightarrow O + NO$

$(r_3)\quad N + O \leftrightarrow NO$

$$k_{3f}[N][O] = k_{3b}[NO]$$

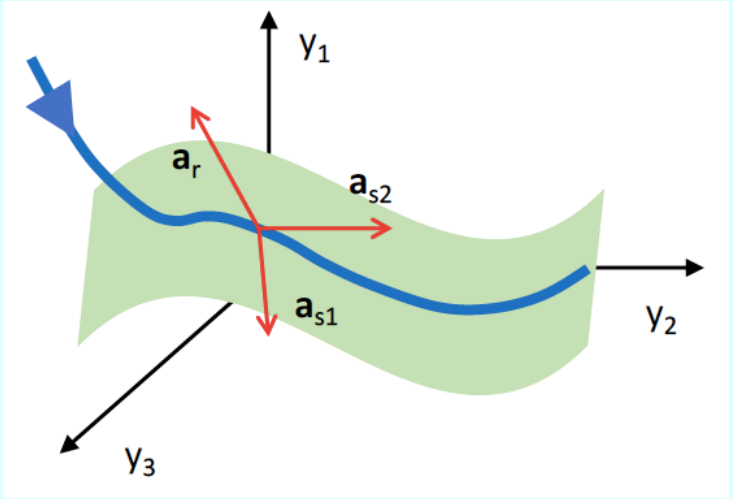
$$(k_{3f}[O])\eth[N] + (k_{3f}[N])\eth[O] - (k_{3b})\eth[NO] = 0$$

$$\eth = \left(\frac{\partial}{\partial lnk_{1f}} + \frac{\partial}{\partial lnk_{1b}} + \frac{\partial}{\partial lnk_{2f}} + \frac{\partial}{\partial lnk_{2b}} + \frac{\partial}{\partial lnk_{3f}} + \frac{\partial}{\partial lnk_{3b}}\right)$$

$$\underbrace{[0,\ 0,\ k_{3f}[O],\ k_{3f}[N],\ -k_{3b}]}\begin{bmatrix}\eth[N_2]\\ \eth[O_2]\\ \eth[N]\\ \eth[O]\\ \eth[NO]\end{bmatrix} = 0$$

Relations among the sensitivity coefficients

$$\mathbf{y} = \begin{bmatrix} [sp_1] \\ [sp_2] \\ [sp_3] \\ \vdots \end{bmatrix} \qquad \frac{d\mathbf{y}}{dt} = \mathbf{g}$$



$$\mathbf{G} = \begin{bmatrix} \eth[sp_1] \\ \eth[sp_2] \\ \eth[sp_3] \\ \vdots \end{bmatrix} \qquad \frac{d\mathbf{G}}{dt} = \mathbf{g} + \mathbf{JG}$$

$$\eth = \left(\frac{\partial}{\partial lnk_{1f}} + \frac{\partial}{\partial lnk_{1b}} + \frac{\partial}{\partial lnk_{2f}} + \cdots \right)$$

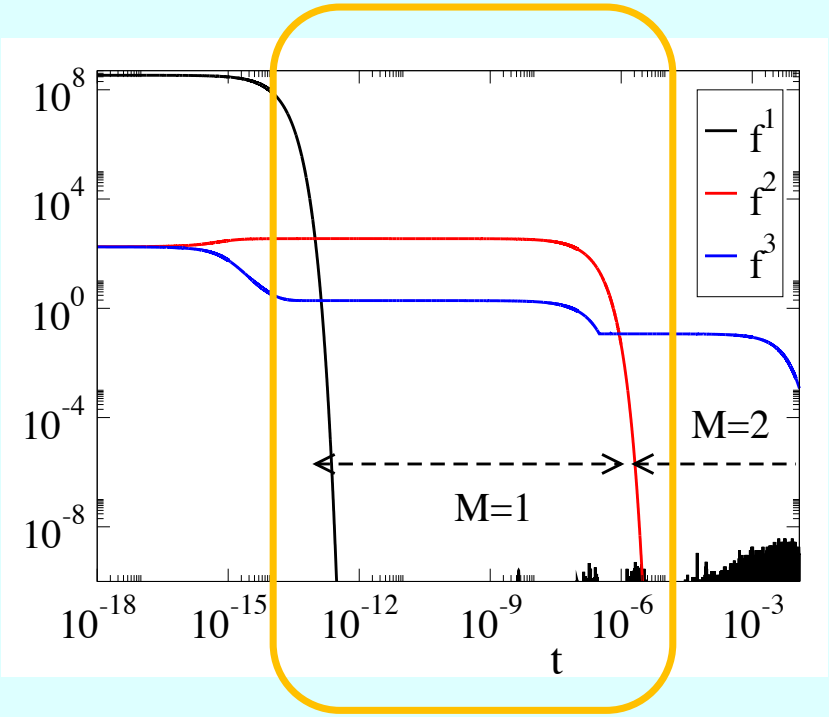
$$\mathbf{J} = \mathrm{grad}(\mathbf{g})$$

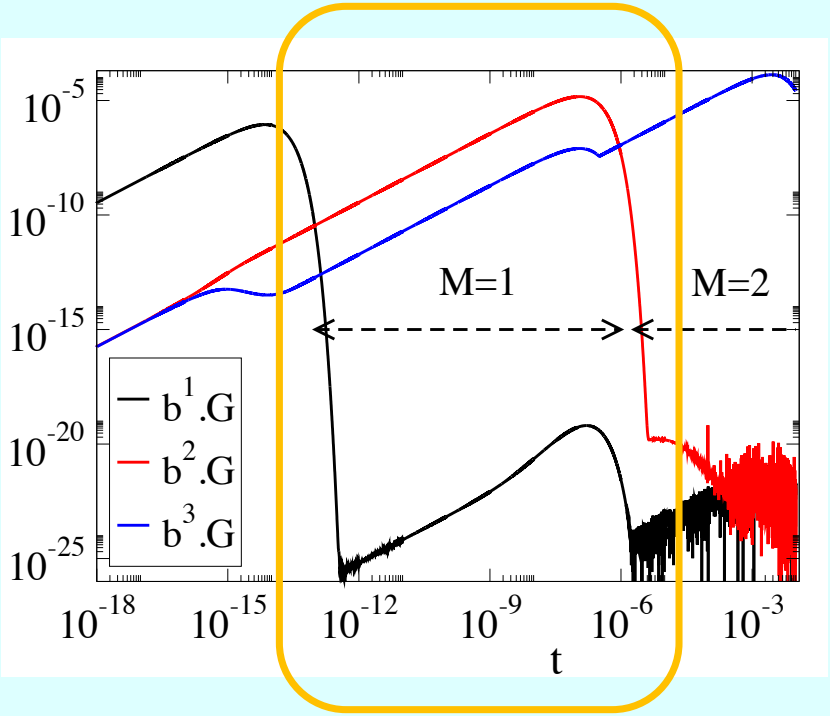
$$\mathbf{Q} = \mathbf{a}_{s1}\mathbf{b}^{s1} + \mathbf{a}_{s2}\mathbf{b}^{s2} \qquad \mathbf{b}^i.\mathbf{a}_j = \delta^i_j$$

$$\frac{d\mathbf{y}}{dt} = \mathbf{Qg} \qquad \mathbf{b}^r \cdot \mathbf{g} = 0$$

$$\frac{d\mathbf{G}}{dt} = \mathbf{Q}\left(\mathbf{g} + \mathbf{JG}\right) \qquad \mathbf{b}^r \cdot \mathbf{G} = 0$$

Relations among the sensitivity coefficients





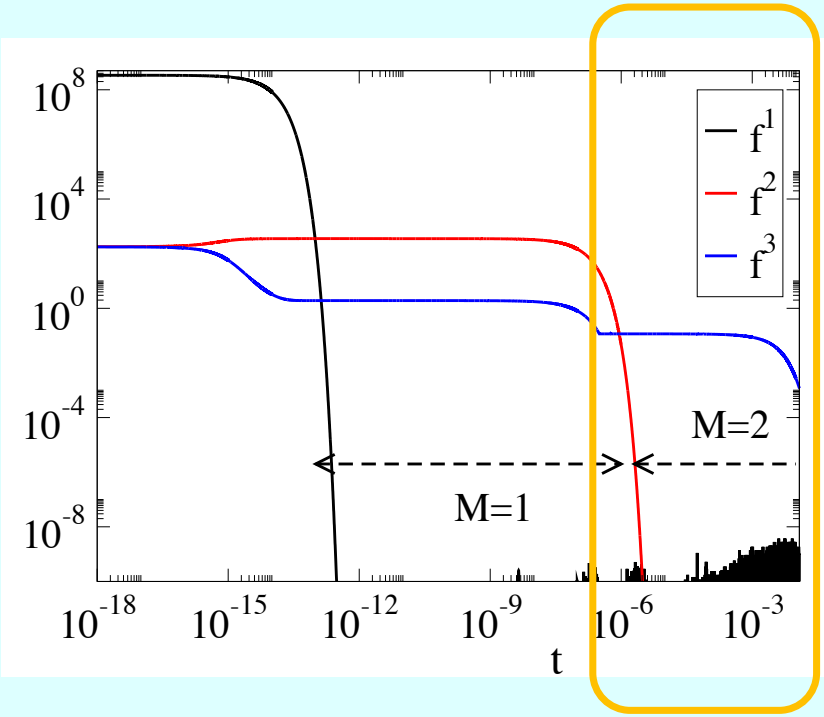
$$M = 1$$

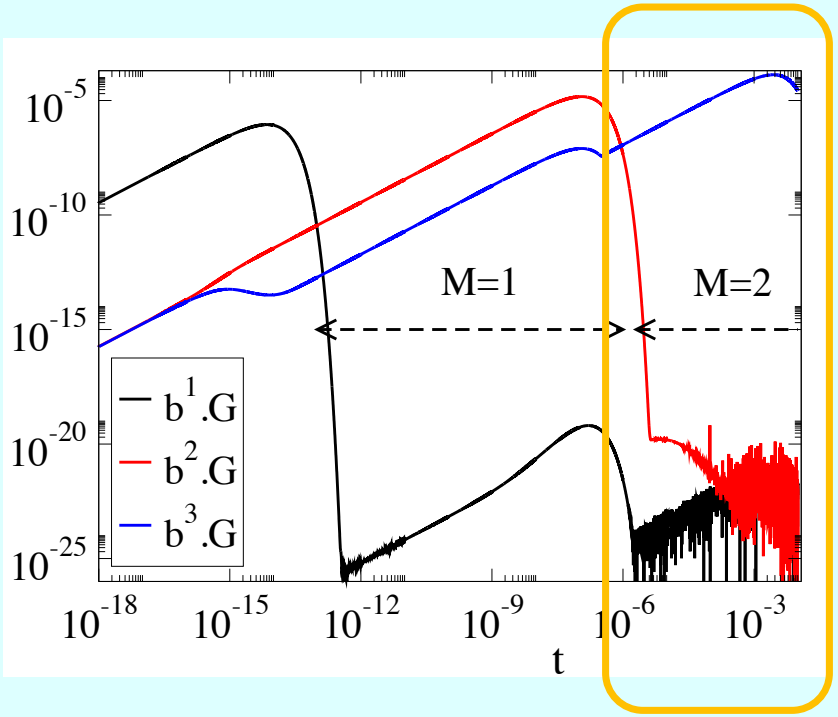
$$f^1 = \mathbf{b}^1 \cdot \mathbf{g} = \mathbf{b}^r \cdot \mathbf{g} \approx 0 \qquad \mathbf{b}^1 \cdot \mathbf{G} = \mathbf{b}^r \cdot \mathbf{G} \approx 0$$

$$f^2 = \mathbf{b}^2 \cdot \mathbf{g} = \mathbf{b}^{s1} \cdot \mathbf{g} \qquad \mathbf{b}^2 \cdot \mathbf{G} = \mathbf{b}^{s1} \cdot \mathbf{G}$$

$$f^3 = \mathbf{b}^3 \cdot \mathbf{g} = \mathbf{b}^{s2} \cdot \mathbf{g} \qquad \mathbf{b}^3 \cdot \mathbf{G} = \mathbf{b}^{s2} \cdot \mathbf{G}$$

Relations among the sensitivity coefficients





$$M = 2$$

$$f^1 = \mathbf{b}^1 \cdot \mathbf{g} = \mathbf{b}^{r1} \cdot \mathbf{g} \approx 0$$

$$f^2 = \mathbf{b}^2 \cdot \mathbf{g} = \mathbf{b}^{r2} \cdot \mathbf{g} \approx 0$$

$$f^3 = \mathbf{b}^3 \cdot \mathbf{g} = \mathbf{b}^s \cdot \mathbf{g}$$

$$\mathbf{b}^1 \cdot \mathbf{G} = \mathbf{b}^{r1} \cdot \mathbf{G} \approx 0$$

$$\mathbf{b}^2 \cdot \mathbf{G} = \mathbf{b}^{r2} \cdot \mathbf{G} \approx 0$$

$$\mathbf{b}^3 \cdot \mathbf{G} = \mathbf{b}^s \cdot \mathbf{G}$$

M=1: Physical understanding

$(r_1)\quad N_2 + O \leftrightarrow N + NO$

$(r_2)\quad O_2 + N \leftrightarrow O + NO$

$(r_3)\quad N + O \leftrightarrow NO$

CSP Fast reaction: 3b

Fast species: NO

Equilibrium: $QSSA_{NO}$ $R^{3f} - R^{3b} = 0$

LSA Fast variable: $\eth[NO]$

Equilibrium: $$\frac{\partial[NO]}{\partial lnk_{3f}} + \frac{\partial[NO]}{\partial lnk_{3b}} = 0$$

Fast species

Fast reaction

M=2: Physical understanding

$(r_1)\quad N_2 + O \leftrightarrow N + NO$

$(r_2)\quad O_2 + N \leftrightarrow O + NO$

$(r_3)\quad N + O \leftrightarrow NO$

CSP Fast reaction: 2f

Fast species: O_2,

Equilibrium: QSSA O_2, $R^{2f} - R^{2b} = 0$

LSA Fast variable: $\partial[O_2]$

Equilibrium: $$\frac{\partial[O_2]}{\partial lnk_{2f}} + \frac{\partial[O_2]}{\partial lnk_{2b}} = 0$$

Fast species

Fast reaction

Appendix A

Lindemann Mechanism

The traditional method (asymptotics): Lindemann mechanism

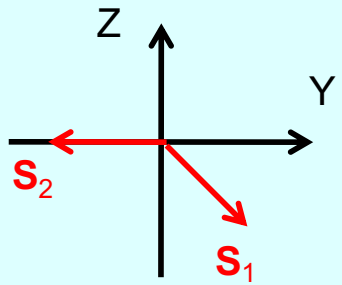
$$A + A \underset{k_{1b}}{\overset{k_{1f}}{\Leftrightarrow}} B + A \qquad B \overset{k_2}{\Rightarrow} \text{Products}$$

$$\frac{d}{dt}\begin{bmatrix} Y \\ Z \end{bmatrix} = \begin{bmatrix} +1 \\ -1 \end{bmatrix} k_{1f} Z^2 + \begin{bmatrix} -1 \\ +1 \end{bmatrix} k_{1b} YZ + \begin{bmatrix} -1 \\ 0 \end{bmatrix} k_2 Y$$

$$[B] = Y$$

$$[A] = Z$$

$$\frac{dy}{dt} = \mathbf{S}_1 (R^{1f} - R^{1b}) + \mathbf{S}_2 R^2$$



First steps in asymptotic analysis: 1) get the system in non-dimensional form

2) define the small parameter ε

Three different non-dimensional systems

1st system

$$\frac{dy}{dt} = \frac{z^2}{\varepsilon} - \frac{yz}{\varepsilon} - y \qquad \frac{dz}{dt} = -r\left(\frac{z^2}{\varepsilon} - \frac{yz}{\varepsilon}\right) \qquad \varepsilon = \frac{k_2}{k_{1b}A_o} << 1$$

2nd system

$$\frac{dy}{dt} = z^2 - yz - y \qquad \frac{dz}{dt} = -r(z^2 - yz) \qquad \varepsilon = \frac{k_2}{k_{1b}A_o} = O(1)$$

3rd system

$$\frac{dy}{dt} = \frac{z^2}{\varepsilon} - yz - \frac{y}{\varepsilon} \qquad \frac{dz}{dt} = -r(z^2 - \varepsilon yz) \qquad \varepsilon = \frac{k_{1b}A_o}{k_2} << 1$$

$$r = \frac{k_{1f}}{k_{1b}} \qquad [A] = A_o z$$

Three non-dimensional systems

1st system

$$\frac{dy}{dt} = \frac{z^2}{\varepsilon} - \frac{yz}{\varepsilon} - y \qquad \frac{dz}{dt} = -r\left(\frac{z^2}{\varepsilon} - \frac{yz}{\varepsilon}\right)$$

PEA-1

r=O(1), ε<<1

2nd system

$$\frac{dy}{dt} = z^2 - yz - y \qquad \frac{dz}{dt} = -r(z^2 - yz)$$

QSSA-z

r>>1, ε=O(1)

3rd system

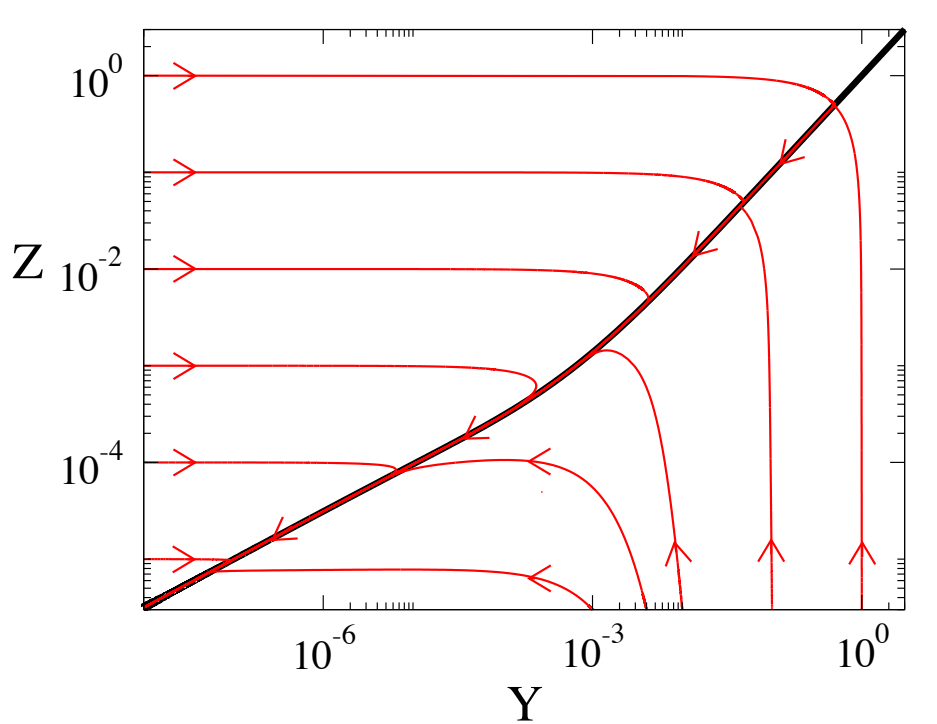
$$\frac{dy}{dt} = \frac{z^2}{\varepsilon} - yz - \frac{y}{\varepsilon} \qquad \frac{dz}{dt} = -r(z^2 - \varepsilon yz)$$

QSSA-y

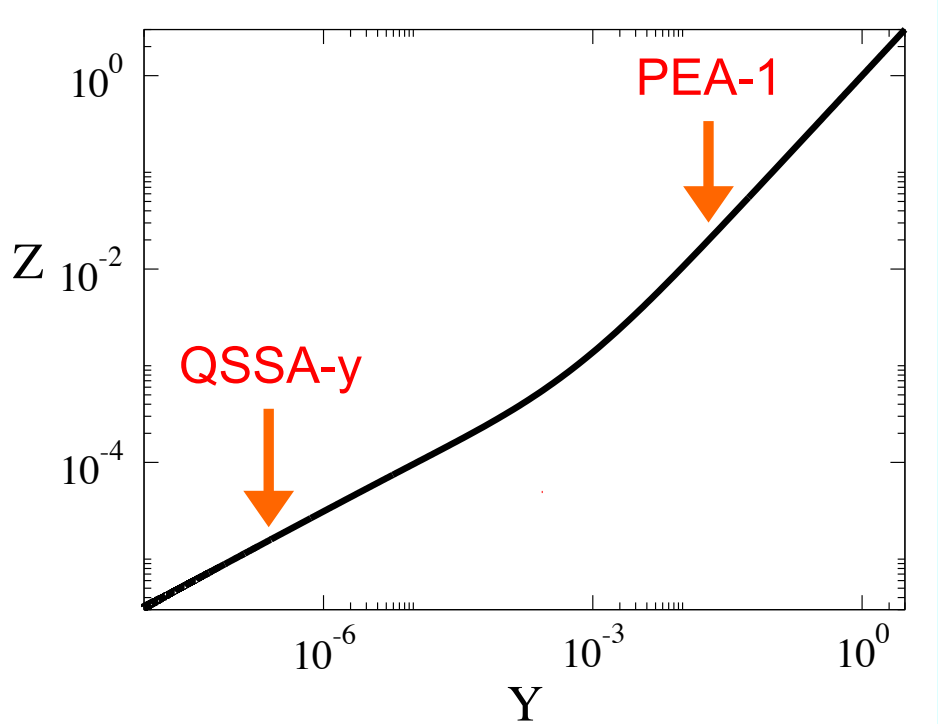
r=O(1), ε<<1

:
:

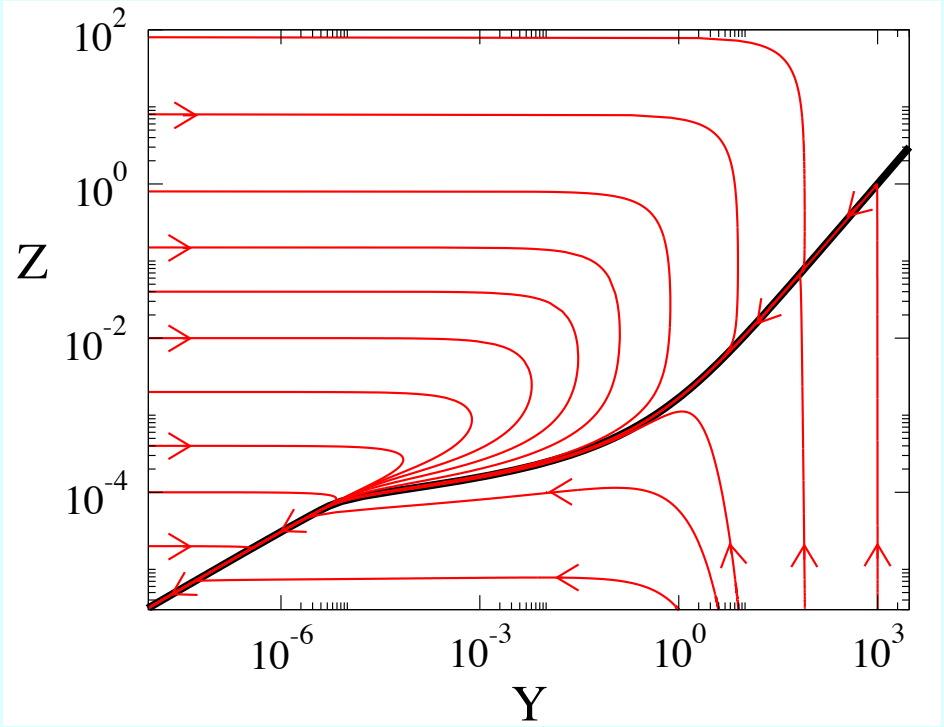
Trajectories: $k_{1f}=10^3$ $k_{1b}=10^3$ $k_2=1$



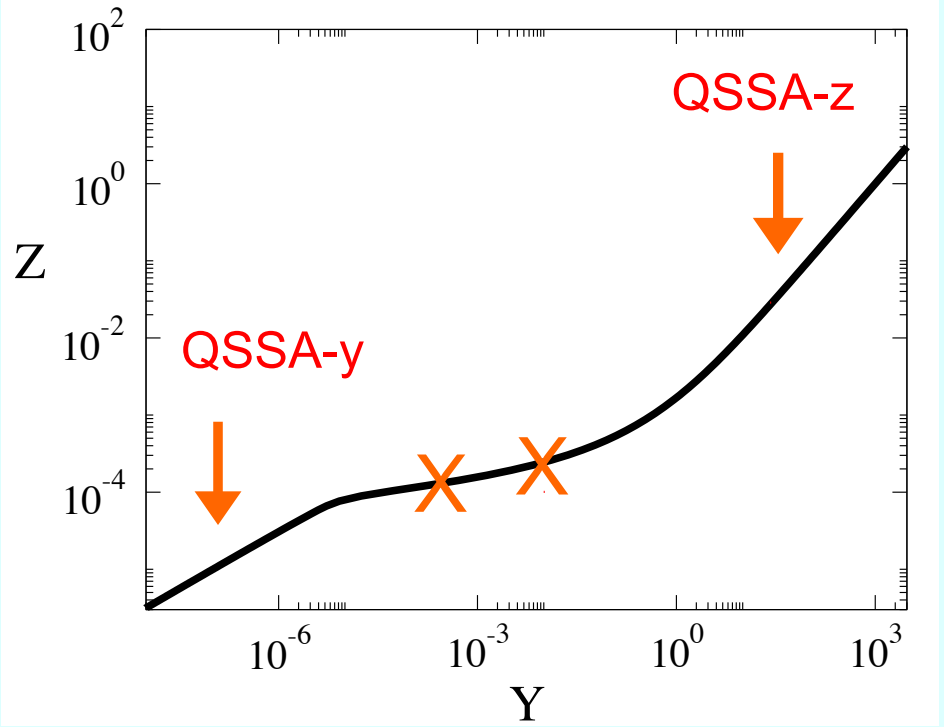
Leading order asymptotics



Trajectories: $k_{1f}=10^3$ $k_{1b}=1$ $k_2=1$

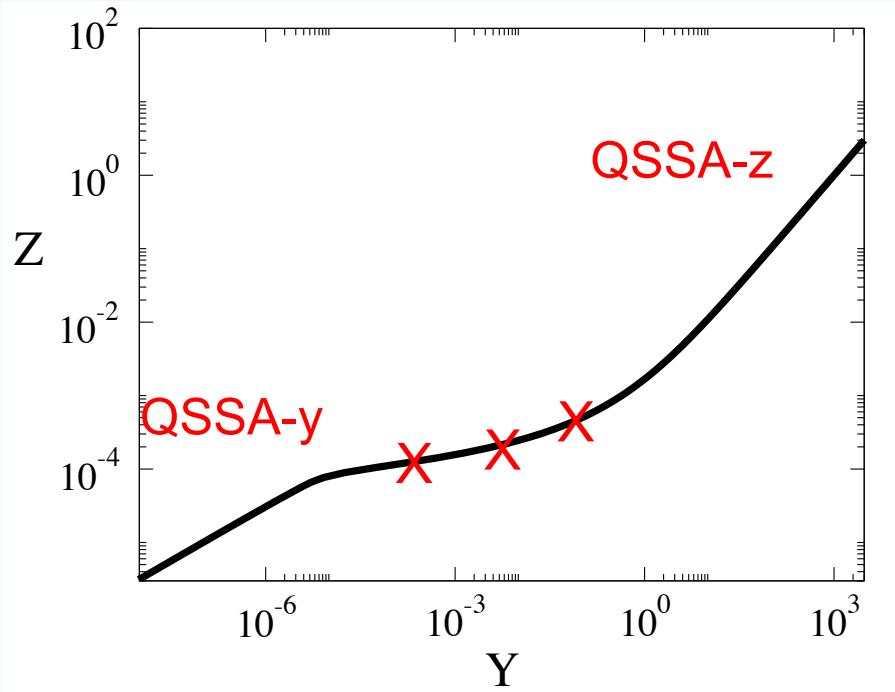


Leading order asymptotics

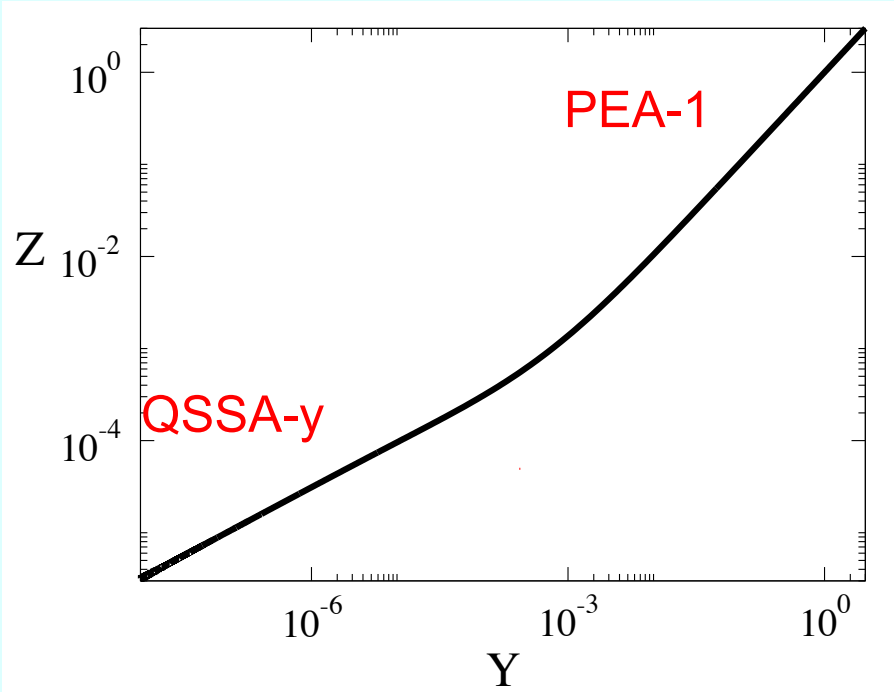


Long term (global) behavior: 3 different approximations

$k_{1f}=10^3$ $k_{1b}=1$ $k_2=1$

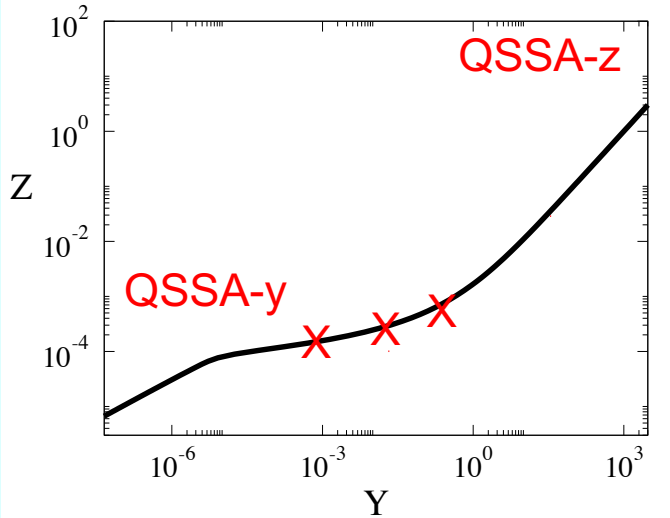


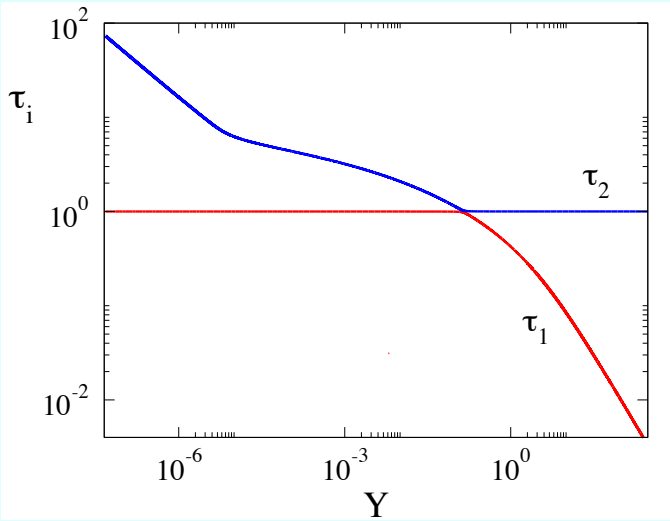
$k_{1f}=10^3$ $k_{1b}=10^3$ $k_2=1$



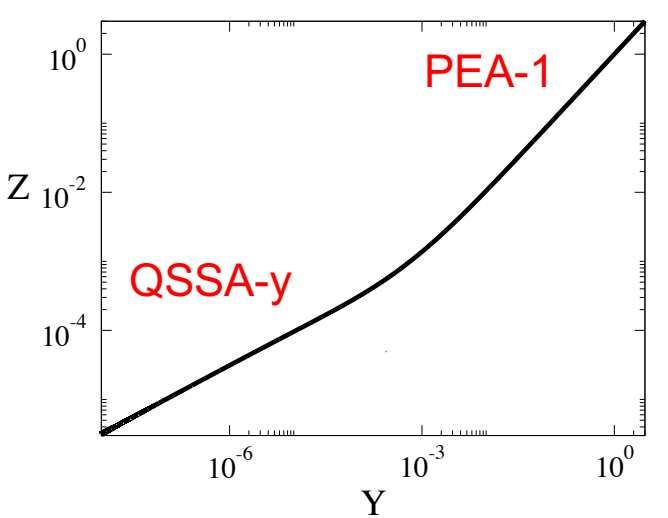
Long term (global) behavior: 3 different approximations

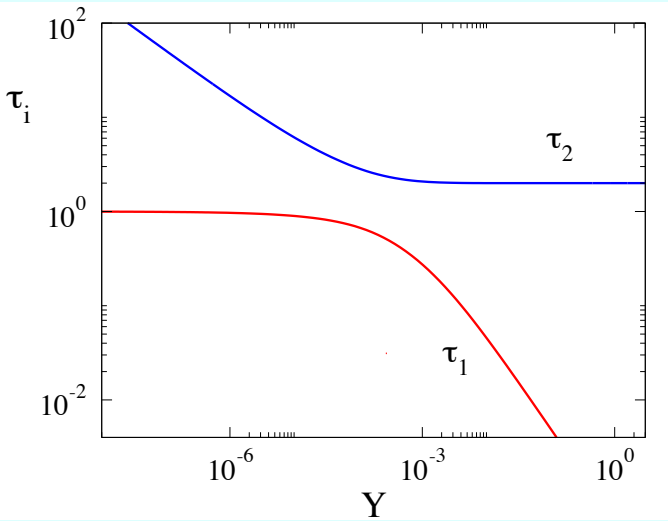
$k_{1f}=10^3$ $k_{1b}=1$ $k_2=1$





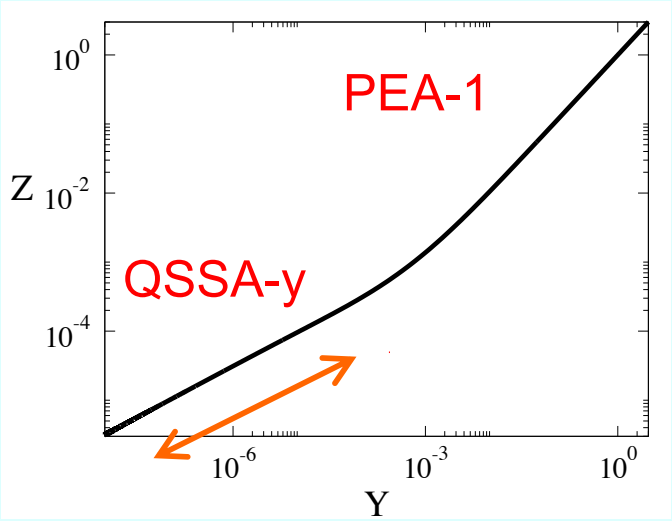
$k_{1f}=10^3$ $k_{1b}=10^3$ $k_2=1$





Long term behavior: QSSA - y

$k_{1f}=10^3$ $k_{1b}=10^3$ $k_2=1$



Normal form

$$\varepsilon\frac{dy}{dt}=z^2-yz-\varepsilon y \qquad y=y_0+\varepsilon y_1+\ldots$$

$$\frac{dz}{dt}=-z^2+\varepsilon yz \qquad z=z_0+\varepsilon z_1+\ldots$$

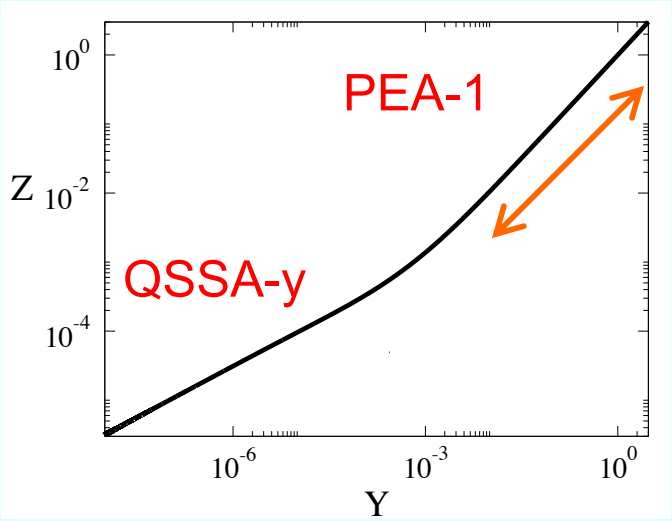
$$y_0=z_0^2$$

$$\frac{dz_0}{dt}=-z_0^2$$

Fine !

Long term behavior: PEA-1

$k_{1f}=10^3$ $k_{1b}=10^3$ $k_2=1$



Not in normal form

$$\varepsilon\frac{dy}{dt}=z^2-yz-\varepsilon y \qquad y=y_0+\varepsilon y_1+\ldots$$

$$\varepsilon\frac{dz}{dt}=-z^2+yz \qquad z=z_0+\varepsilon z_1+\ldots$$

$$y_0=z_0$$

$$y_0=z_0$$

Problem !

Getting the non-dimensional system in normal form

$$\varepsilon\frac{dy}{dt} = z^2 - yz - \varepsilon y$$

$$\varepsilon\frac{dz}{dt} = -z^2 + yz$$

$w = y + z$

$$\varepsilon\frac{dy}{dt} = (w-y)(w-2y) - \varepsilon y$$

$$\frac{dw}{dt} = -y$$

$y = y_0 + \varepsilon y_1 + \ldots$ $\qquad$ $w = w_0 + \varepsilon w_1 + \ldots$

$$w_0 = 2y_0$$

$$\frac{dw_0}{dt} = -y_0$$

$z = w - y$

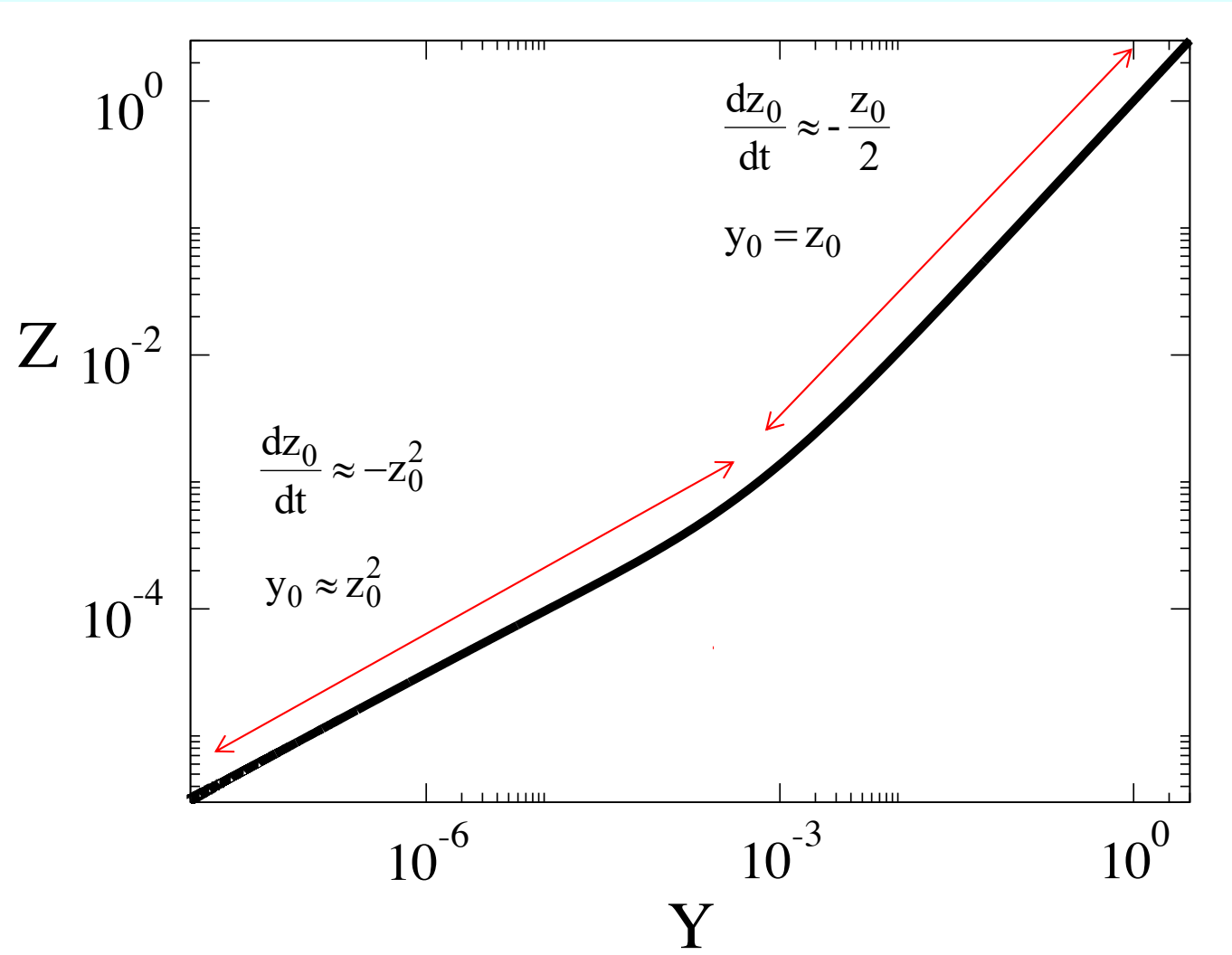
$$y_0 = z_0$$

$$\frac{dz_0}{dt} = -\frac{y_0}{2}$$

Fine !

Long term (global) behavior: 3 different models

$k_{1f}=10^3 \quad k_{1b}=10^3 \quad k_2=1$



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