Mechanism reduction methods based on time scale separation

1st part

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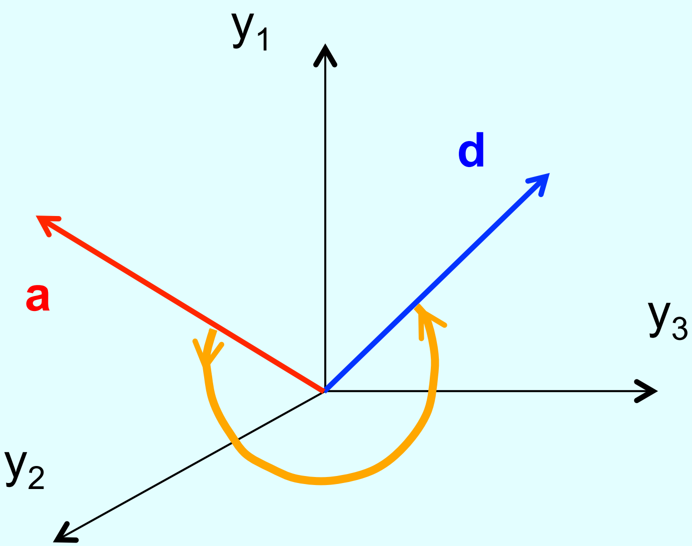
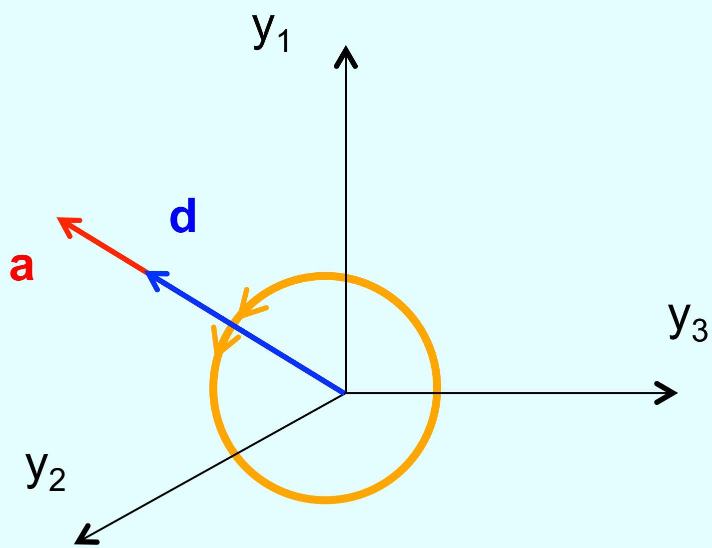
Outline

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.

Eigenvalues and Eigenvectors





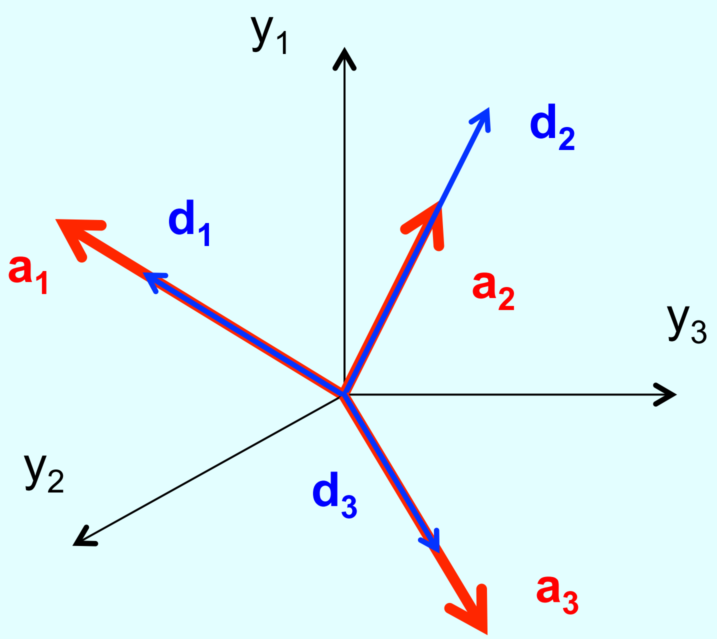
$$\begin{bmatrix} C_1^1 & C_2^1 & C_3^1 \\ C_1^2 & C_2^2 & C_3^2 \\ C_1^3 & C_2^3 & C_3^3 \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} = \begin{bmatrix} d_1 \\ d_2 \\ d_3 \end{bmatrix}$$

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

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

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

Eigenvalues and Eigenvectors



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

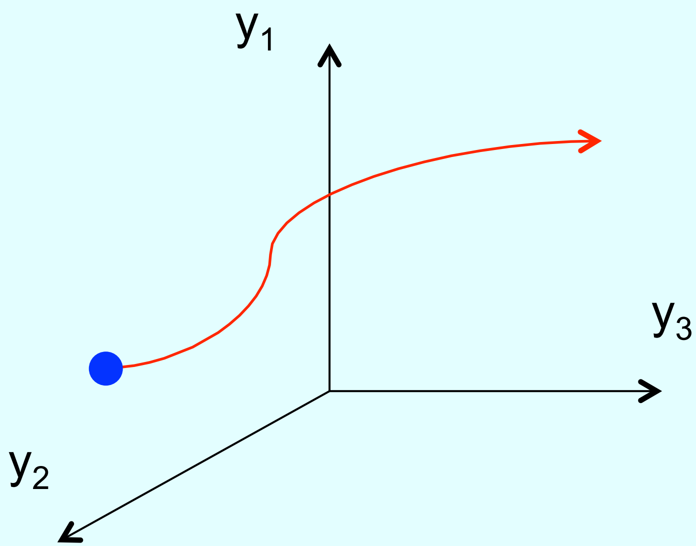
$$\mathbf{C}\mathbf{a}_n = \mathbf{d}_n = \lambda_n \mathbf{a}_n$$

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

$$\mathbf{b}^i \cdot \mathbf{a}_j = \delta^{\mathrm{i}}_{\mathrm{j}}$$

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

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

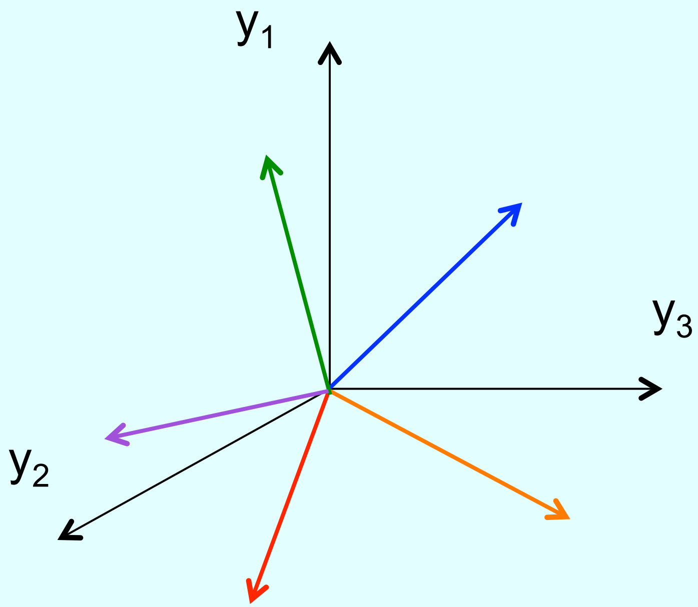
$\mathbf{S}_k$: stoichiometric vector of k-th reaction

$$H_2 + O \rightarrow H_2O$$

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

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

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

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

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

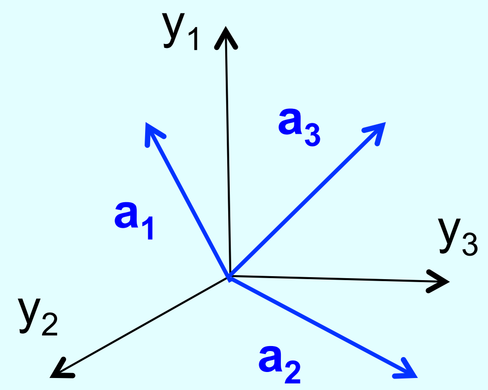
$$|\lambda_1| > |\lambda_2| > \ldots > |\lambda_N|$$

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

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

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

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



Fast / slow directions

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

$$\delta\mathbf{y}(0) = \mathbf{0} \qquad \mathbf{J}(\mathbf{y}_o) = \nabla\mathbf{g}(\mathbf{y}_o)$$

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

$\mathbf{a}_n$ Right eigenvector

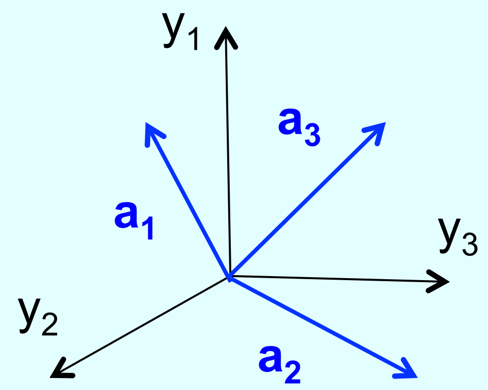
$\mathbf{b}^n$ Left eigenvector

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

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

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

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

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

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

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

A simple example

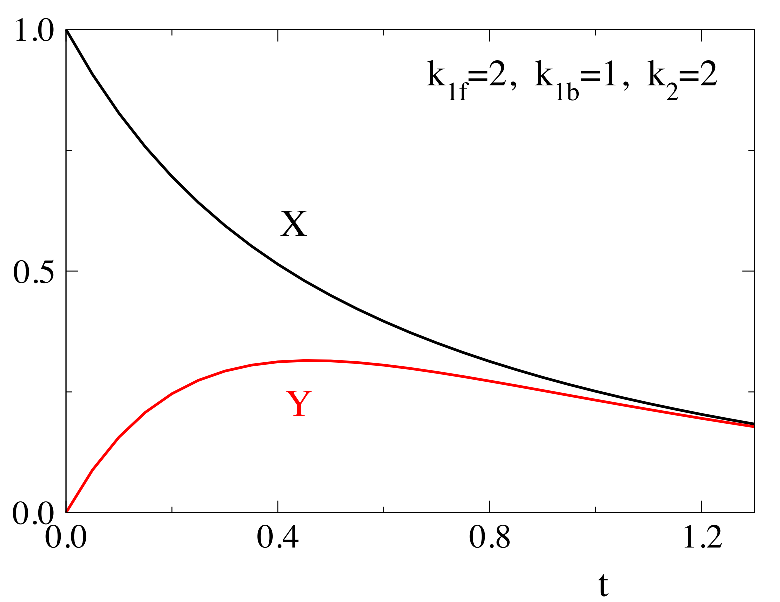
$$x \underset{k_{1b}}{\overset{k_{1f}}{\leftrightarrow}} y \qquad y \overset{k_2}{\rightarrow} \text{products}$$

1. Homogeneous
2. Const. temperature

$$\frac{d}{dt}\begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} -1 \\ +1 \end{bmatrix} k_{1f}\, X + \begin{bmatrix} +1 \\ -1 \end{bmatrix} k_{1b}\, Y + \begin{bmatrix} 0 \\ -1 \end{bmatrix} k_2\, Y$$

$$X(0) = 1$$

$$Y(0) = 0$$



Reference case

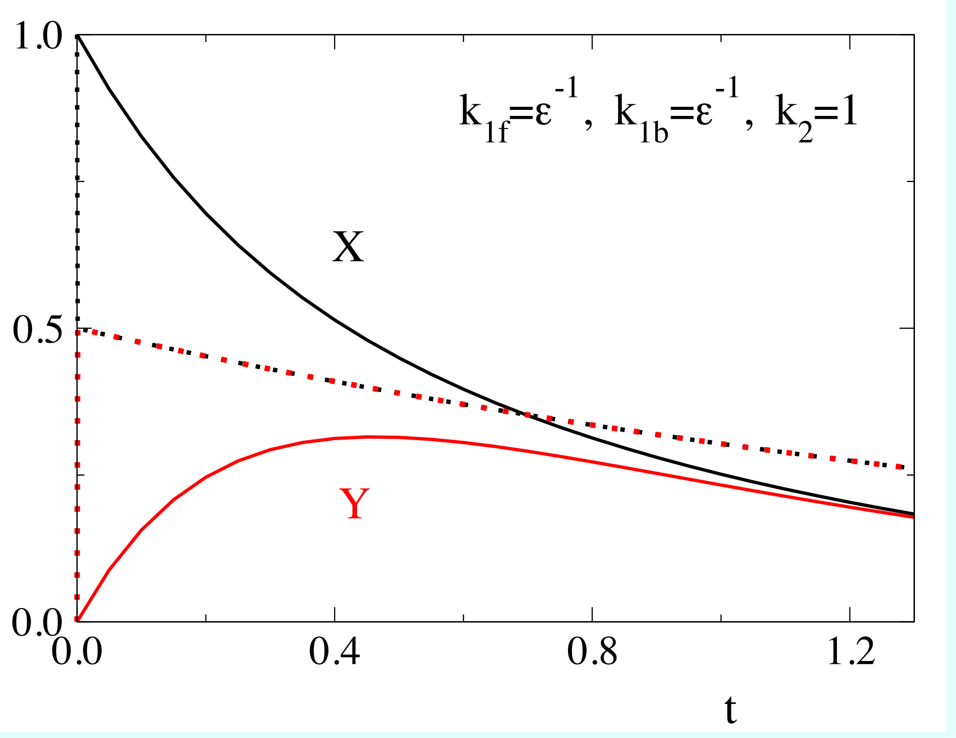
A simple example

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

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

$$\frac{d}{dt}\begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} -1 \\ +1 \end{bmatrix} \frac{X - Y}{\varepsilon} + \begin{bmatrix} 0 \\ -1 \end{bmatrix} Y$$

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



A simple example

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

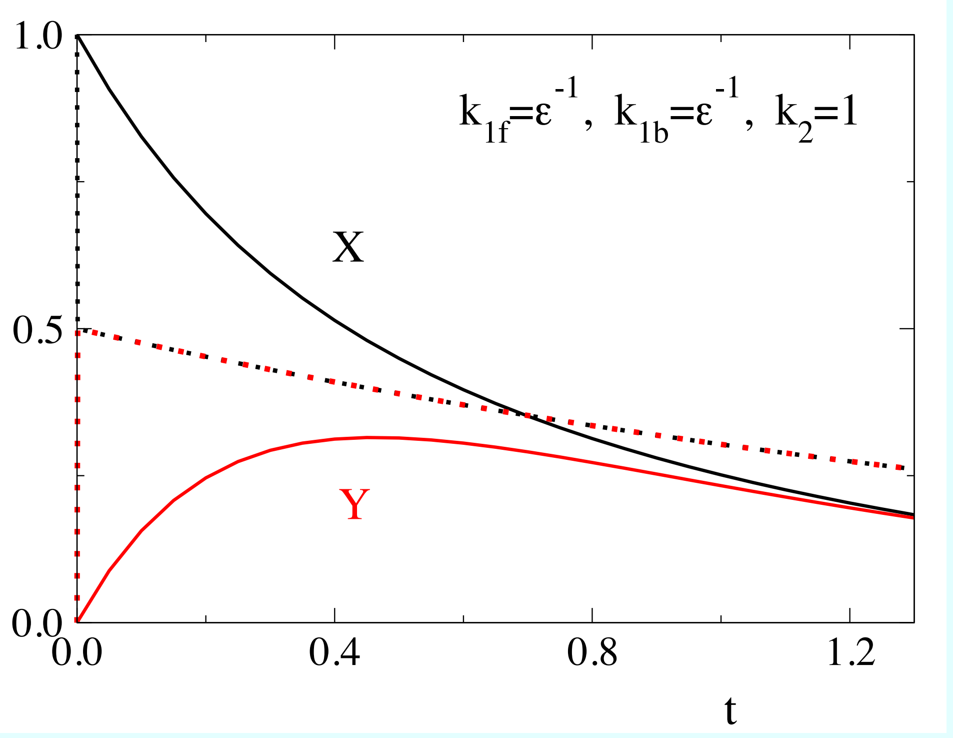
$$\frac{d}{dt}\begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} -1 \\ +1 \end{bmatrix}\frac{1}{\varepsilon}X + \begin{bmatrix} +1 \\ -1 \end{bmatrix}\frac{1}{\varepsilon}Y + \begin{bmatrix} 0 \\ -1 \end{bmatrix}Y \qquad \varepsilon = 10^{-6}$$

$$X - Y = O(\varepsilon) \rightarrow \frac{d(X-Y)}{dt} = O(\varepsilon)$$

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

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

Partial Equilibrium Approximation



A simple example

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

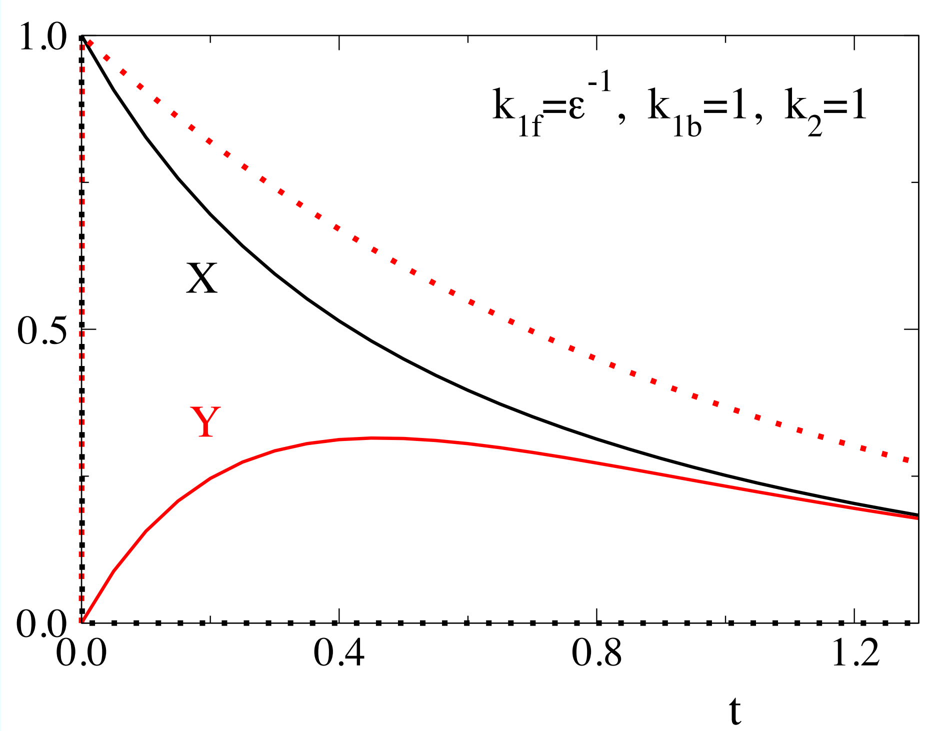
$$\frac{d}{dt}\begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} -1 \\ +1 \end{bmatrix}\frac{1}{\varepsilon}X + \begin{bmatrix} +1 \\ -1 \end{bmatrix}Y + \begin{bmatrix} 0 \\ -1 \end{bmatrix}Y \qquad \varepsilon = 10^{-6}$$

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

$$\frac{dZ}{dt} = \frac{-Z+Y}{\varepsilon} \qquad \frac{dY}{dt} = Z - 2Y$$

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

Quasi Steady-State Approximation for X



A simple example

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

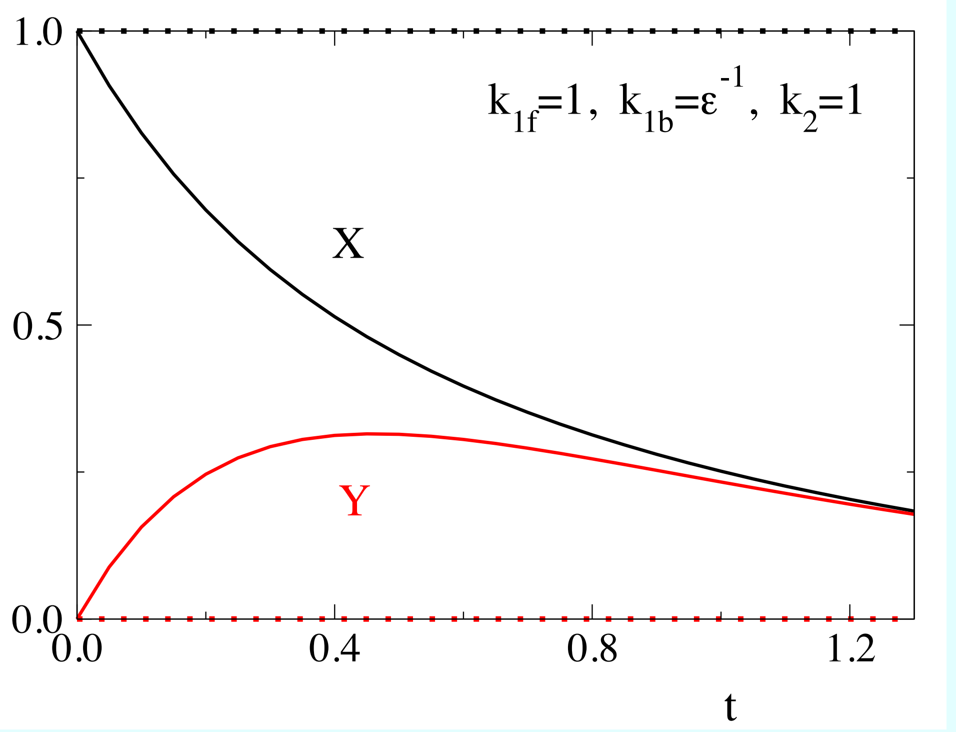
$$\frac{d}{dt}\begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} -1 \\ +1 \end{bmatrix} X + \begin{bmatrix} +1 \\ -1 \end{bmatrix} \frac{1}{\varepsilon} Y + \begin{bmatrix} 0 \\ -1 \end{bmatrix} Y \qquad \varepsilon = 10^{-6}$$

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

$$\frac{dX}{dt} = -X + Z \qquad \frac{dZ}{dt} = \frac{X - Z - \varepsilon Z}{\varepsilon}$$

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

Quasi Steady-State Approximation for Y



A simple example

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

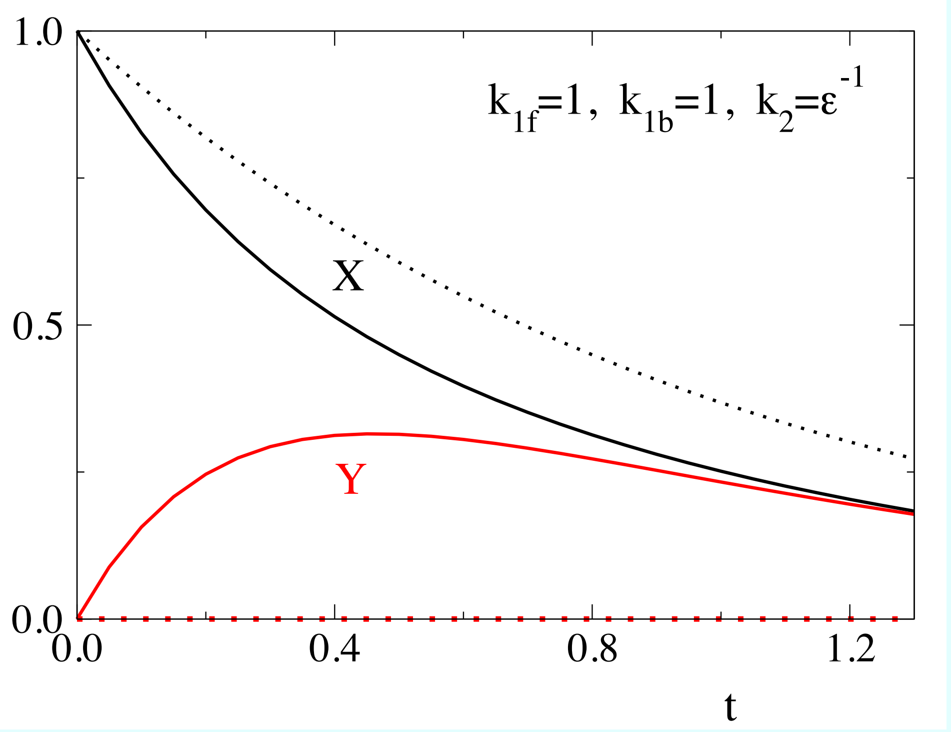
$$\frac{d}{dt}\begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} -1 \\ +1 \end{bmatrix} X + \begin{bmatrix} +1 \\ -1 \end{bmatrix} Y + \begin{bmatrix} 0 \\ -1 \end{bmatrix} \frac{1}{\varepsilon} Y \qquad \varepsilon = 10^{-6}$$

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

$$\frac{dX}{dt} = -X + \varepsilon Z \qquad \frac{dZ}{dt} = \frac{X - \varepsilon Z - Z}{\varepsilon}$$

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

Quasi Steady-State Approximation for Y

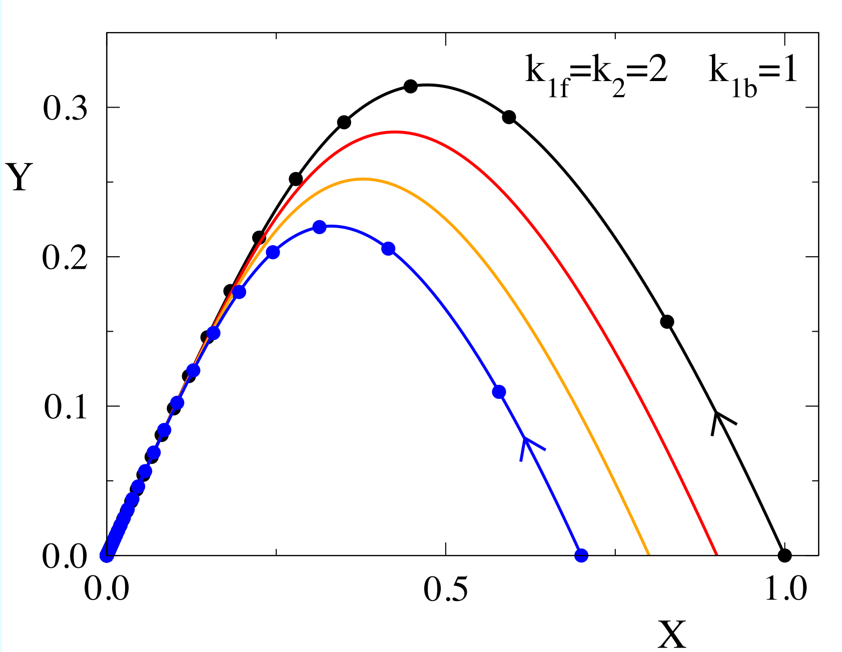


What is a time scale ? (Ref. case)

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

$$\frac{d}{dt}\begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} -1 \\ +1 \end{bmatrix}(2X - Y) + \begin{bmatrix} 0 \\ -1 \end{bmatrix} 2Y$$

$$\begin{bmatrix} X/X_o \\ Y/X_o \end{bmatrix} = \frac{1}{3}\begin{bmatrix} +1 \\ -2 \end{bmatrix} e^{-4t} + \frac{2}{3}\begin{bmatrix} +1 \\ +1 \end{bmatrix} e^{-t}$$



Time scales

$$\tau_1 = |4|^{-1} \qquad \tau_2 = |1|^{-1}$$

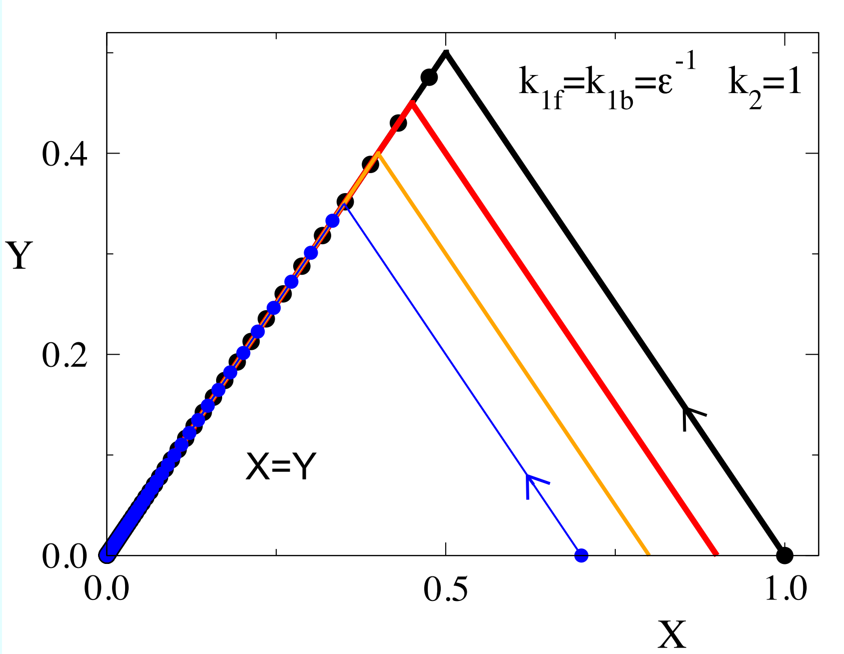
$$\frac{\tau_1}{\tau_2} = 0.25$$

What is a time scale ? (PEA)

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

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

$$\begin{bmatrix} X/X_o \\ Y/X_o \end{bmatrix} = \frac{1}{2}\begin{bmatrix} +1 \\ -1 \end{bmatrix} e^{-\frac{2}{\varepsilon}t} + \frac{1}{2}\begin{bmatrix} +1 \\ +1 \end{bmatrix} e^{-\frac{1}{2}t} + O(\varepsilon)$$



Time scales

$$\tau_1 = \frac{\varepsilon}{2} \qquad \tau_2 = 2$$

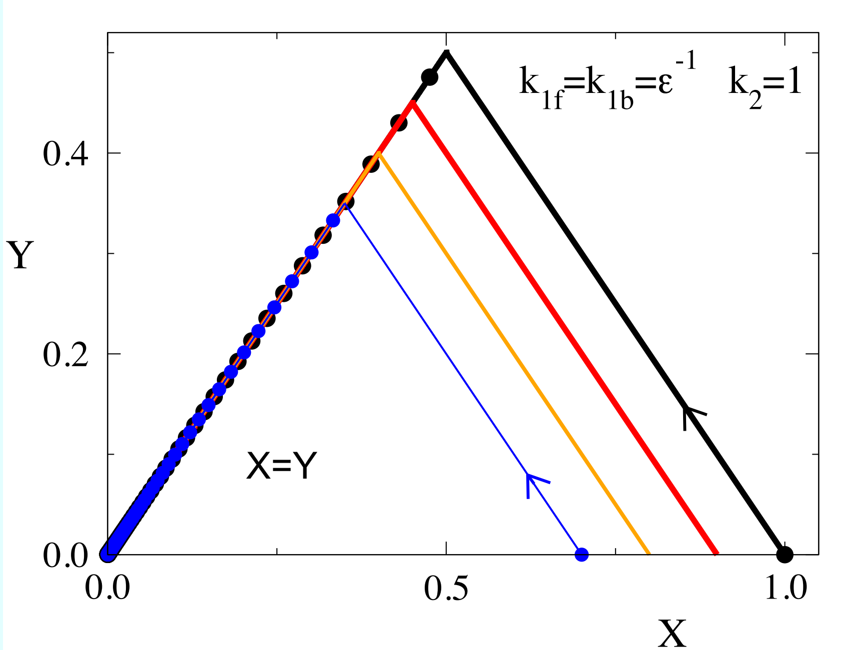
$$\frac{\tau_1}{\tau_2} = \frac{\varepsilon}{4} << 1$$

What is a time scale ? (PEA)

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

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

$$\begin{bmatrix} X/X_o \\ Y/X_o \end{bmatrix} = \frac{1}{2}\begin{bmatrix} +1 \\ -1 \end{bmatrix} e^{-\frac{2}{\varepsilon}t} + \frac{1}{2}\begin{bmatrix} +1 \\ +1 \end{bmatrix} e^{-\frac{1}{2}t} + O(\varepsilon)$$



$$e^{-\frac{2}{\varepsilon}t}(t=0)=1 \qquad e^{-\frac{2}{\varepsilon}t}(t=k\varepsilon)=e^{-2k} << 1$$

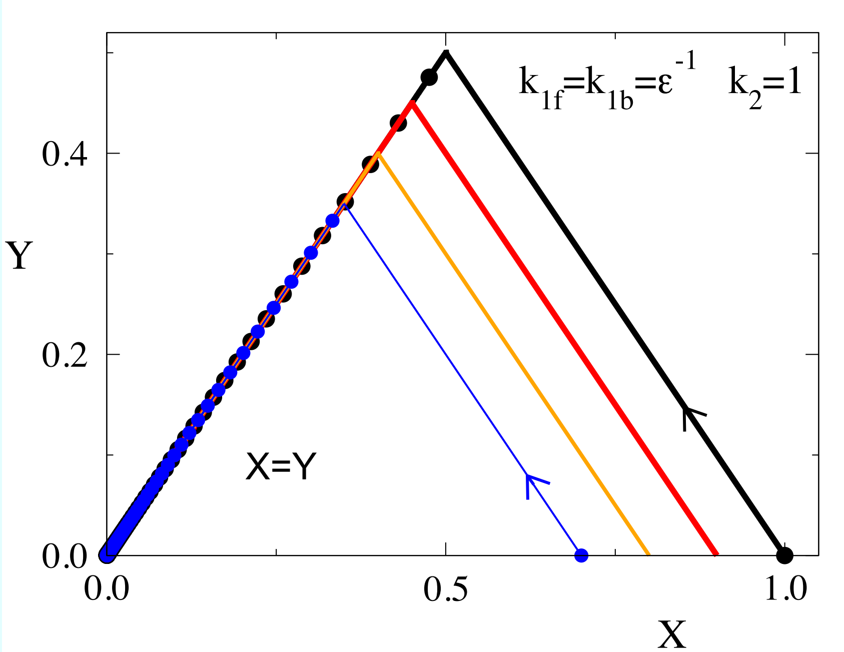
$$e^{-\frac{1}{2}t}(t=0)=1 \qquad e^{-\frac{1}{2}t}(t=k\varepsilon)=e^{-k\varepsilon/2} \approx 1$$

What is a time scale ? (PEA)

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

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

$$\begin{bmatrix} X/X_o \\ Y/X_o \end{bmatrix} = \frac{1}{2}\begin{bmatrix} +1 \\ -1 \end{bmatrix} e^{-\frac{2}{\varepsilon}t} + \frac{1}{2}\begin{bmatrix} +1 \\ +1 \end{bmatrix} e^{-\frac{1}{2}t} + O(\varepsilon)$$



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

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

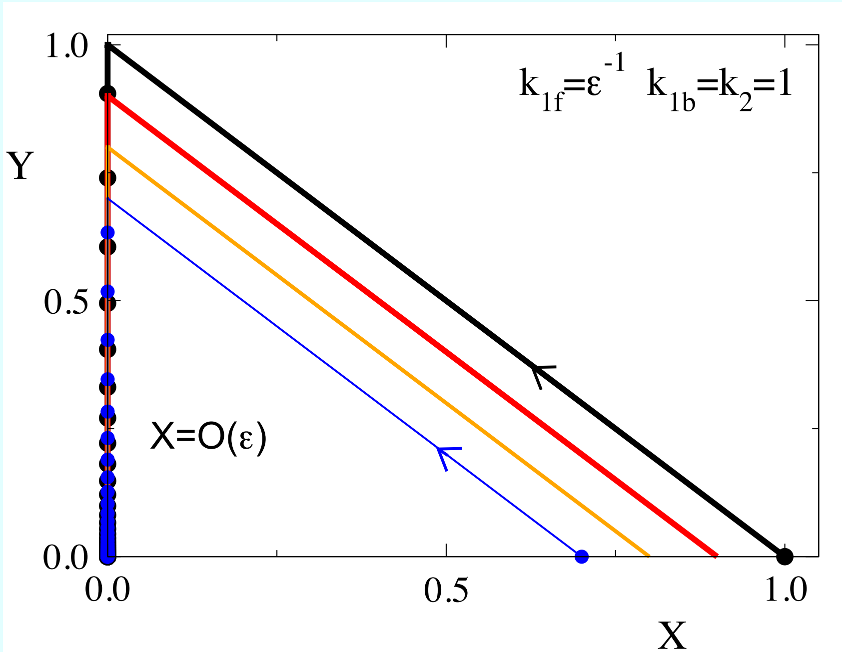
Partial Equilibrium Approximation

What is a time scale ? (QSSA-x)

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

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

$$\begin{bmatrix} X/X_o \\ Y/X_o \end{bmatrix} = \begin{bmatrix} +1 \\ -1 \end{bmatrix} e^{-\frac{1}{\varepsilon}t} + \frac{1}{2}\begin{bmatrix} 0 \\ +1 \end{bmatrix} e^{-t} + O(\varepsilon)$$



Time scales

$$\tau_1 = \varepsilon \qquad \tau_2 = 1$$

$$\frac{\tau_1}{\tau_2} = \varepsilon \ll 1$$

What is a time scale ? (QSSA-x)

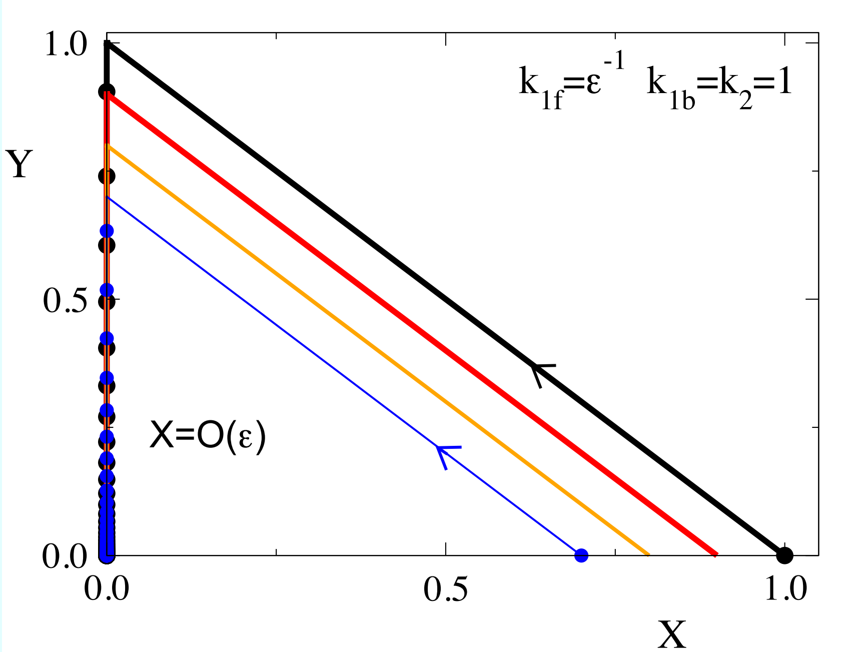
$$x \underset{k_{1b}}{\overset{k_{1f}}{\leftrightarrow}} y \qquad y \xrightarrow{k_2} \text{products}$$

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

$$\begin{bmatrix} X/X_o \\ Y/X_o \end{bmatrix} = \begin{bmatrix} +1 \\ -1 \end{bmatrix} e^{-\frac{1}{\varepsilon}t} + \frac{1}{2}\begin{bmatrix} 0 \\ +1 \end{bmatrix} e^{-t} + O(\varepsilon)$$

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

Quasi Steady-State Approximation for X

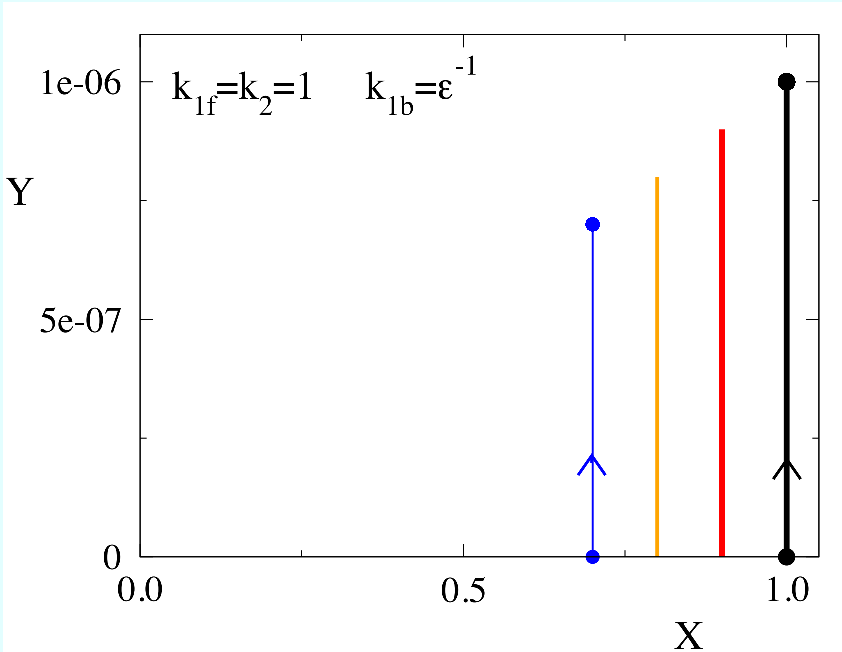


What is a time scale ? (QSSA-y 1st)

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

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

$$\begin{bmatrix} X/X_o \\ Y/X_o \end{bmatrix} = \begin{bmatrix} +1 \\ -1 \end{bmatrix} \varepsilon e^{-\frac{1}{\varepsilon}t} + \begin{bmatrix} 1 \\ \varepsilon^2 \end{bmatrix} e^{-\varepsilon t} + O(\varepsilon)$$



Time scales

$$\tau_1 = \varepsilon \qquad \tau_2 = \varepsilon^{-1}$$

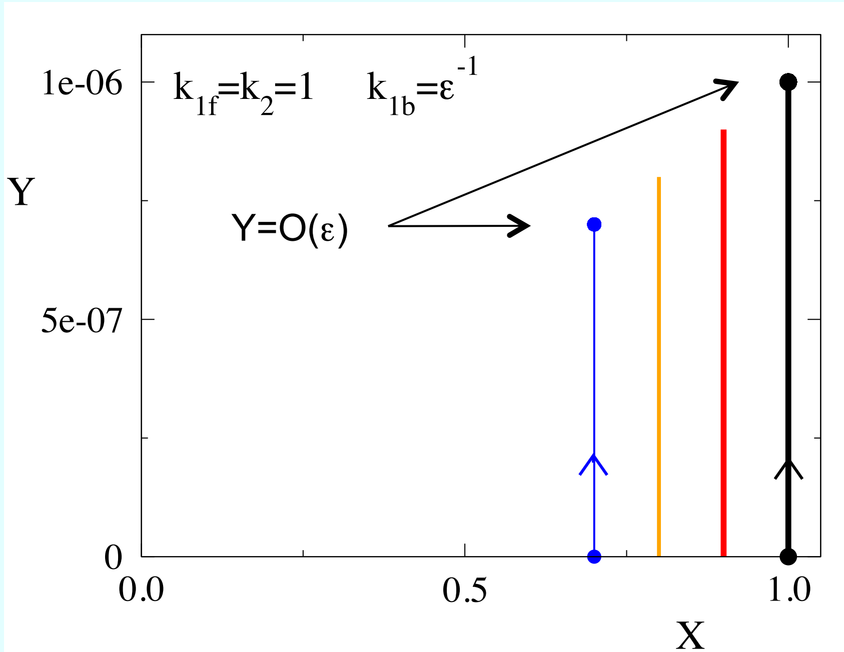
$$\frac{\tau_1}{\tau_2} = \varepsilon^2 << 1$$

What is a time scale ? (QSSA-y 1st)

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

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

$$\begin{bmatrix} X/X_o \\ Y/X_o \end{bmatrix} = \begin{bmatrix} +1 \\ -1 \end{bmatrix} \varepsilon e^{-\frac{1}{\varepsilon}t} + \begin{bmatrix} 1 \\ \varepsilon^2 \end{bmatrix} e^{-\varepsilon t} + O(\varepsilon)$$



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

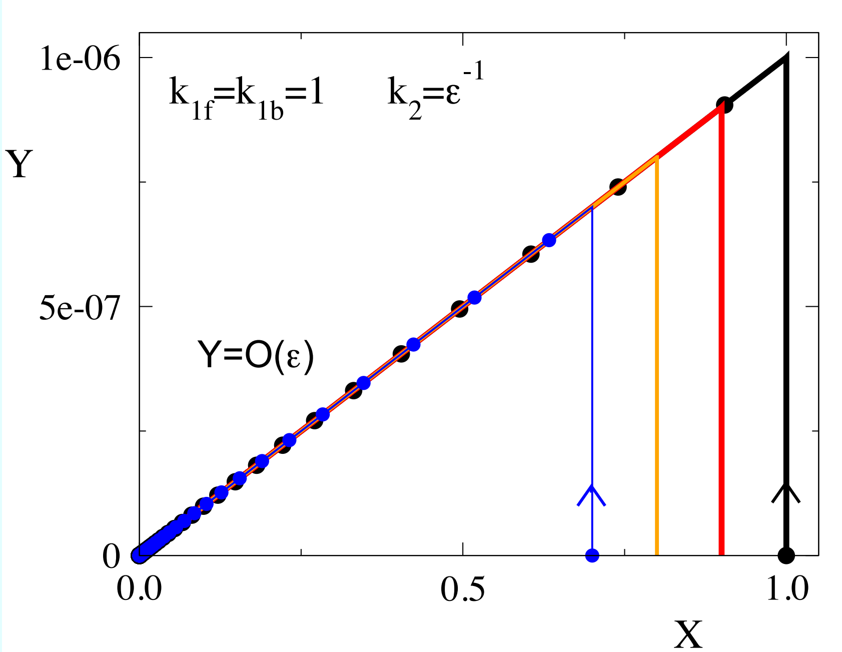
Quasi Steady-State Approximation for Y

What is a time scale ? (QSSA-y 2nd)

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

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

$$\begin{bmatrix} X/X_o \\ Y/X_o \end{bmatrix} = \begin{bmatrix} +\varepsilon \\ -1 \end{bmatrix}\varepsilon e^{-\frac{1}{\varepsilon}t} + \begin{bmatrix} 1 \\ \varepsilon^2 \end{bmatrix} e^{-t} + O(\varepsilon)$$



Time scales

$$\tau_1 = \varepsilon \qquad \tau_2 = 1$$

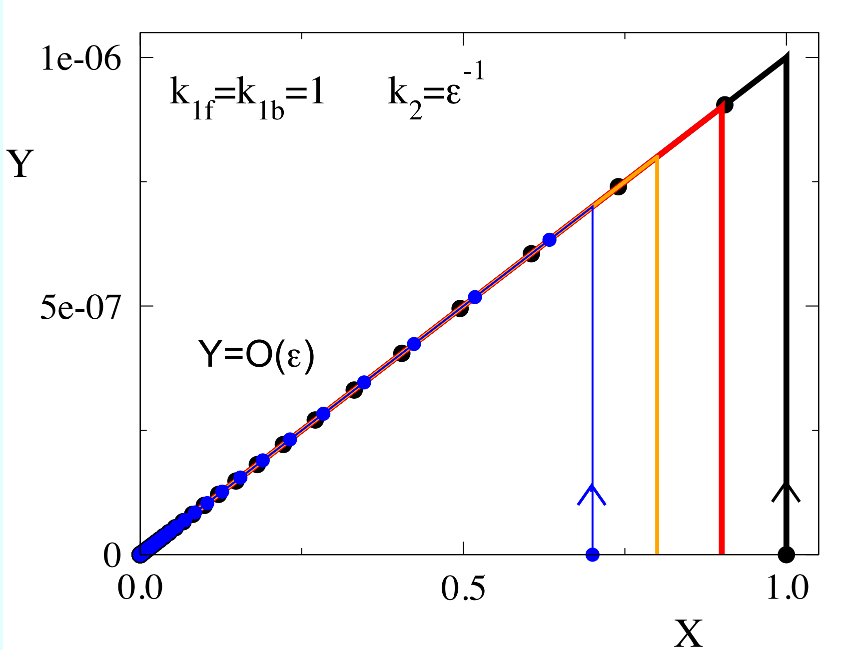
$$\frac{\tau_1}{\tau_2} = \varepsilon << 1$$

What is a time scale ? (QSSA-y 2nd)

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

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

$$\begin{bmatrix} X/X_o \\ Y/X_o \end{bmatrix} = \begin{bmatrix} +\varepsilon \\ -1 \end{bmatrix}\varepsilon e^{-\frac{1}{\varepsilon}t} + \begin{bmatrix} 1 \\ \varepsilon^2 \end{bmatrix} e^{-\varepsilon t} + O(\varepsilon)$$



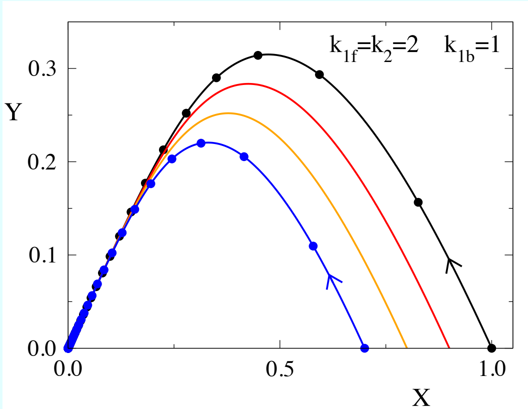
$$\frac{dX}{dt} = -X + O(\varepsilon) \qquad X - \frac{Y}{\varepsilon} = O(\varepsilon)$$

Quasi Steady-State Approximation for Y

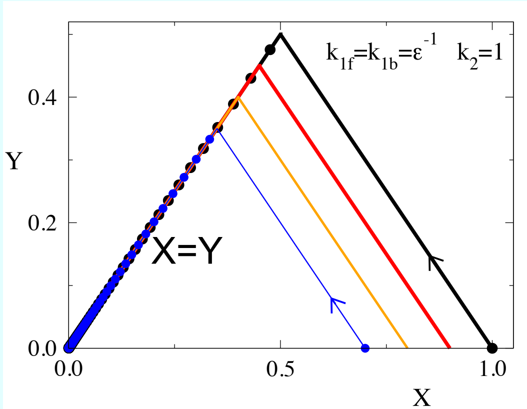
Some common features

$\varepsilon = 10^{-6}$

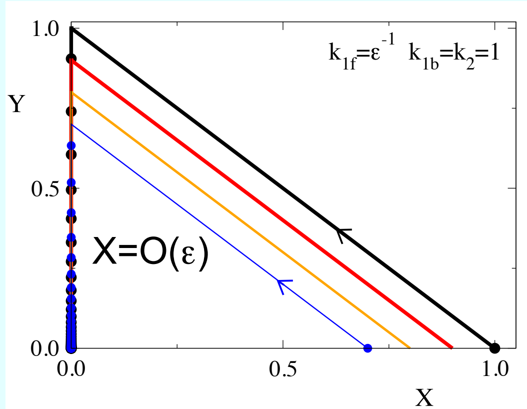
$\tau_1 / \tau_2 = 0.25$ $\lambda_1 = -4$



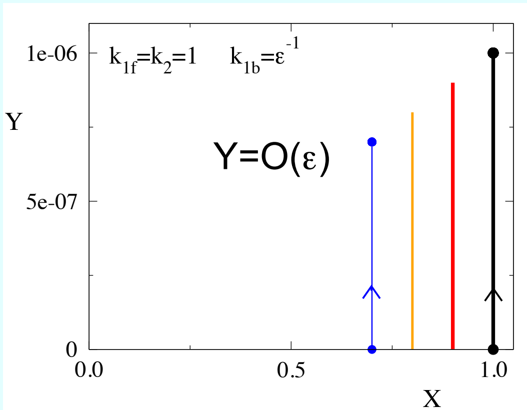
$\tau_1 / \tau_2 = \varepsilon / 4$ $\lambda_1 = -2/\varepsilon$



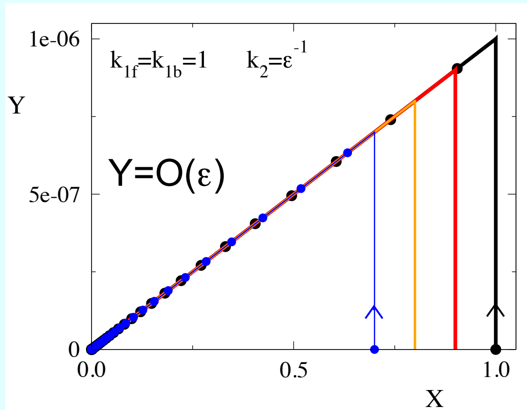
$\tau_1 / \tau_2 = \varepsilon$ $\lambda_1 = -1/\varepsilon$



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



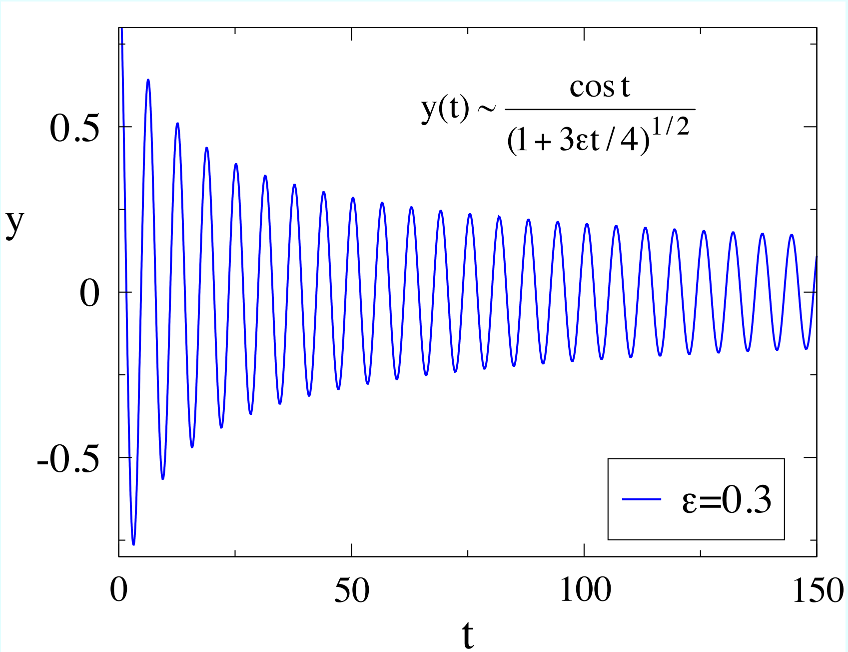
$\tau_1 / \tau_2 = \varepsilon$ $\lambda_1 = -1/\varepsilon$



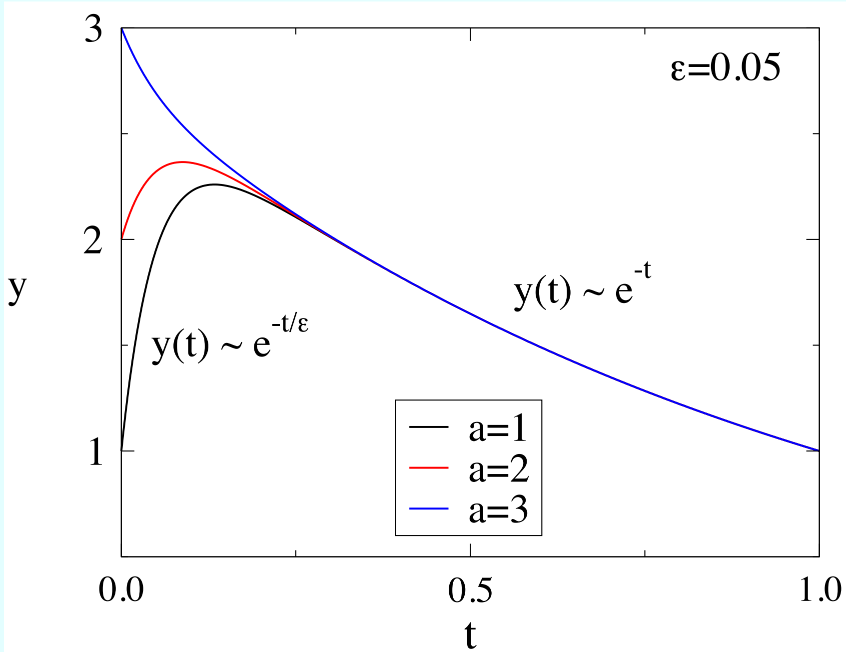
1. Time scale gaps
2. Dissipative time scales
3. Fast/slow behavior
4. Structures in phase space

Fast / Slow systems

Multiple time scale problem



Boundary layer problem

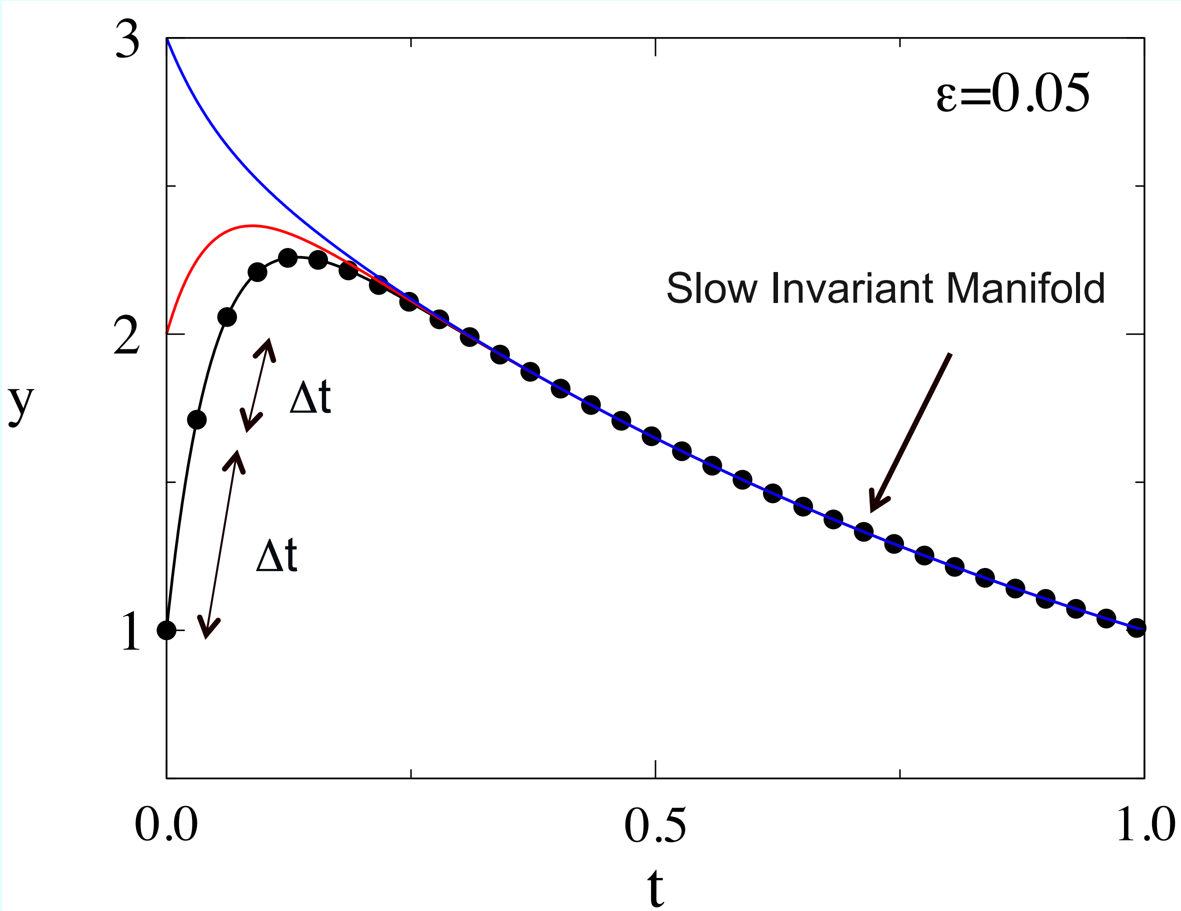


$$y'' + \varepsilon (y')^3 + y = 0$$
$$y(0) = 1 \qquad y'(0) = 0$$

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

Bender and Orszag 1978

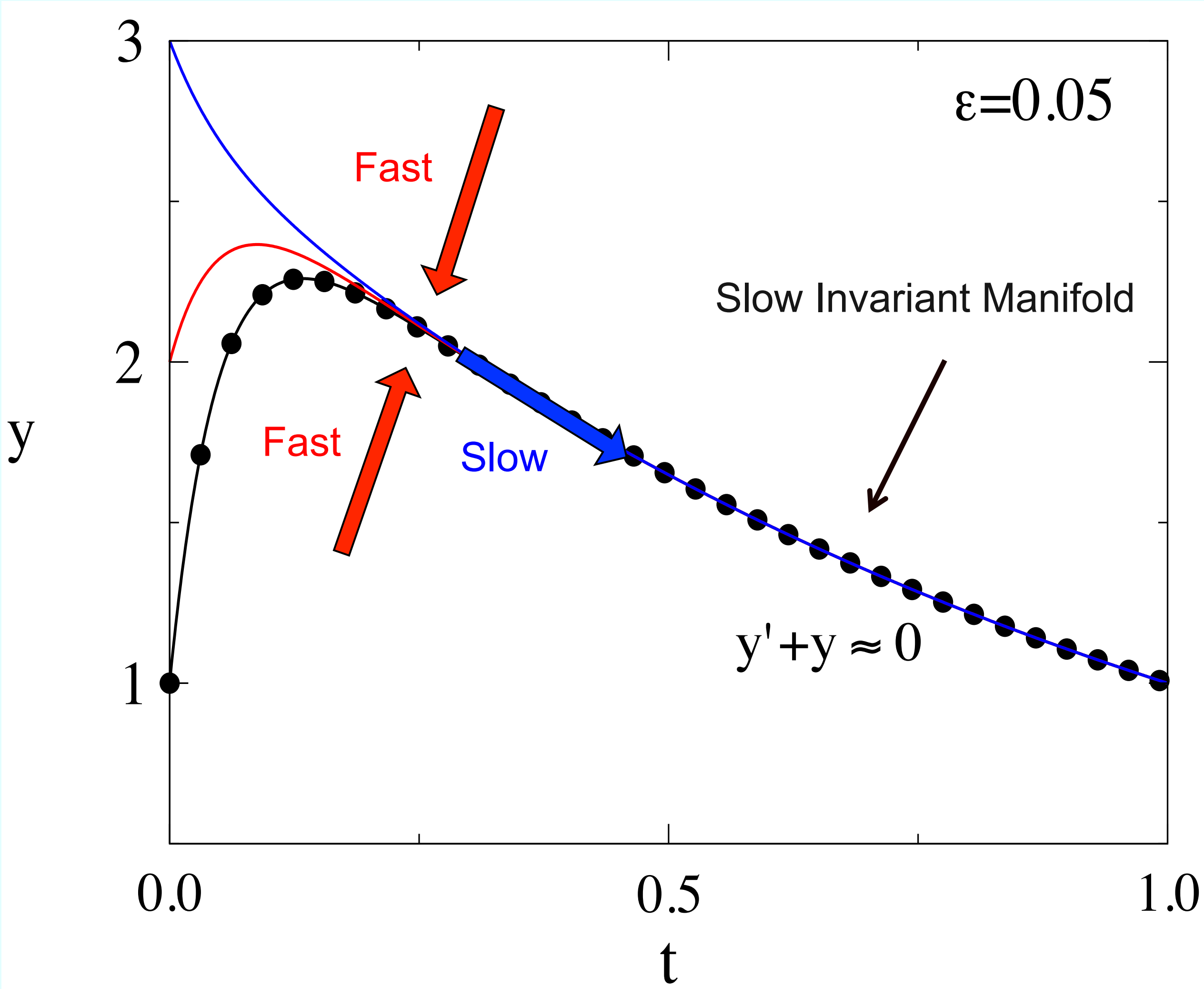
Boundary layer problem



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

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

Fast and slow time scales



The traditional method (asymptotics): Lindemann mechanism

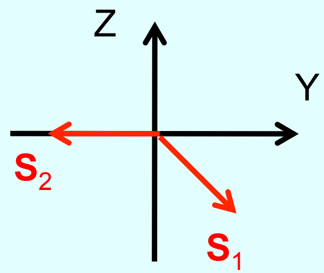
$$A + A \underset{k_{1b}}{\overset{k_{1f}}{\Leftrightarrow}} B + A \qquad\qquad B \overset{k_2}{\Rightarrow} \text{Products}$$

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

$[B] = Y$

$[A] = Z$

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



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

$r=O(1)$, $\varepsilon<<1$

2nd system

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

QSSA-z

$r>>1$, $\varepsilon=O(1)$

3rd system

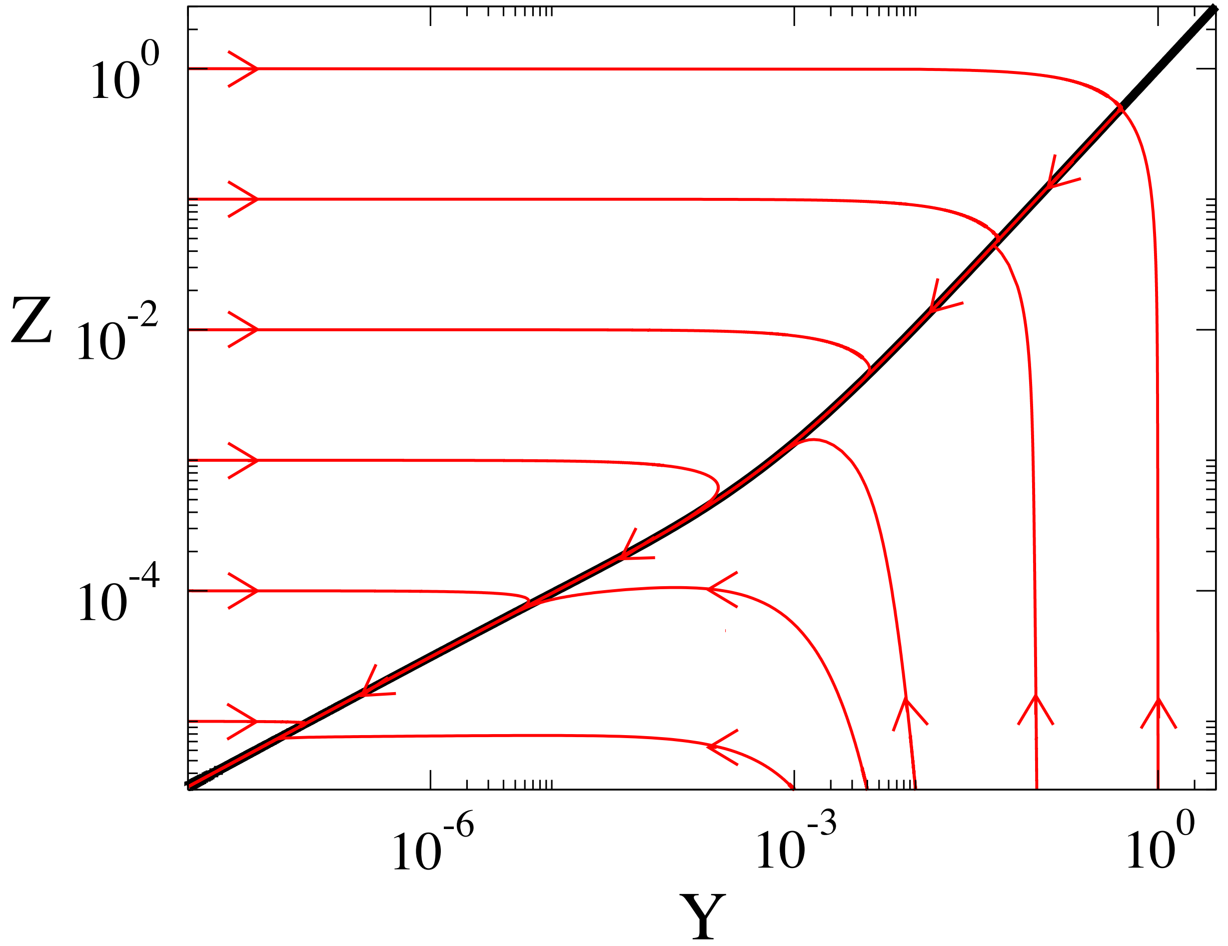
$$\frac{dy}{dt} = \frac{z^2}{\varepsilon} - yz - \frac{y}{\varepsilon} \qquad \frac{dz}{dt} = -r(z^2 - \varepsilon yz)$$

QSSA-y

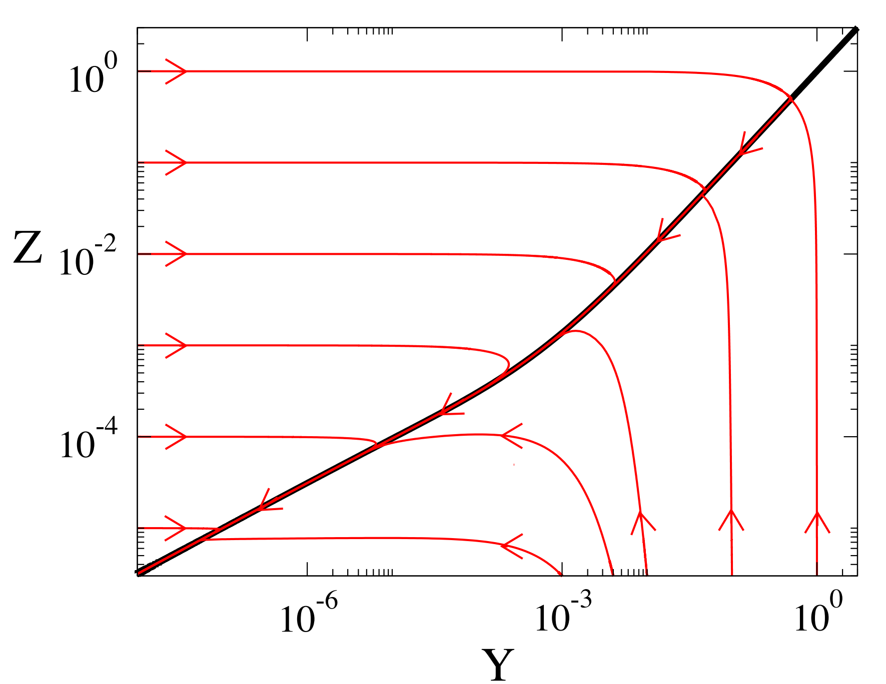
$r=O(1)$, $\varepsilon<<1$

:
:

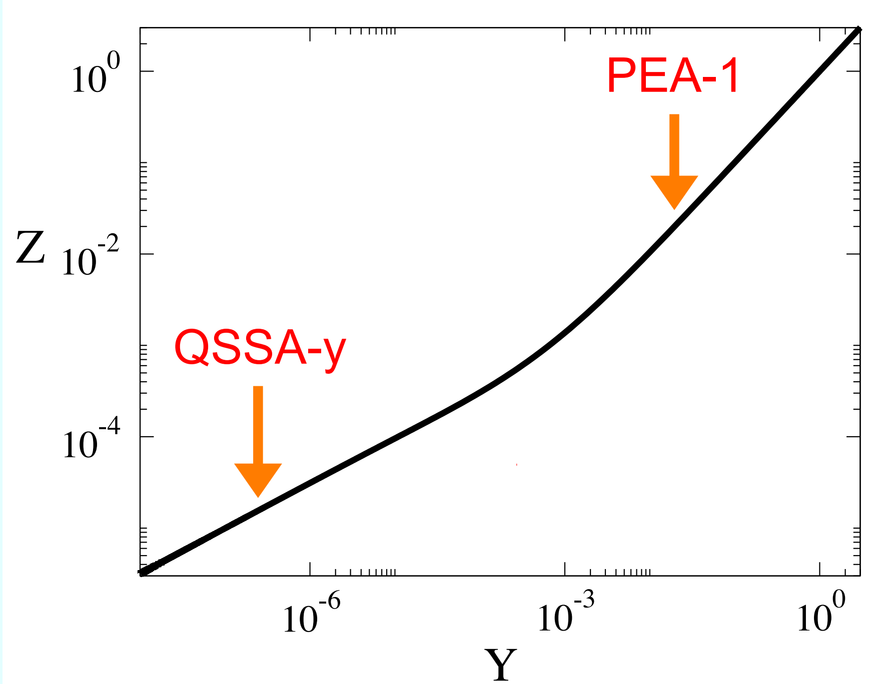
Trajectories: $k_{1f}=10^3$ $k_{1b}=10^3$ $k_2=1$



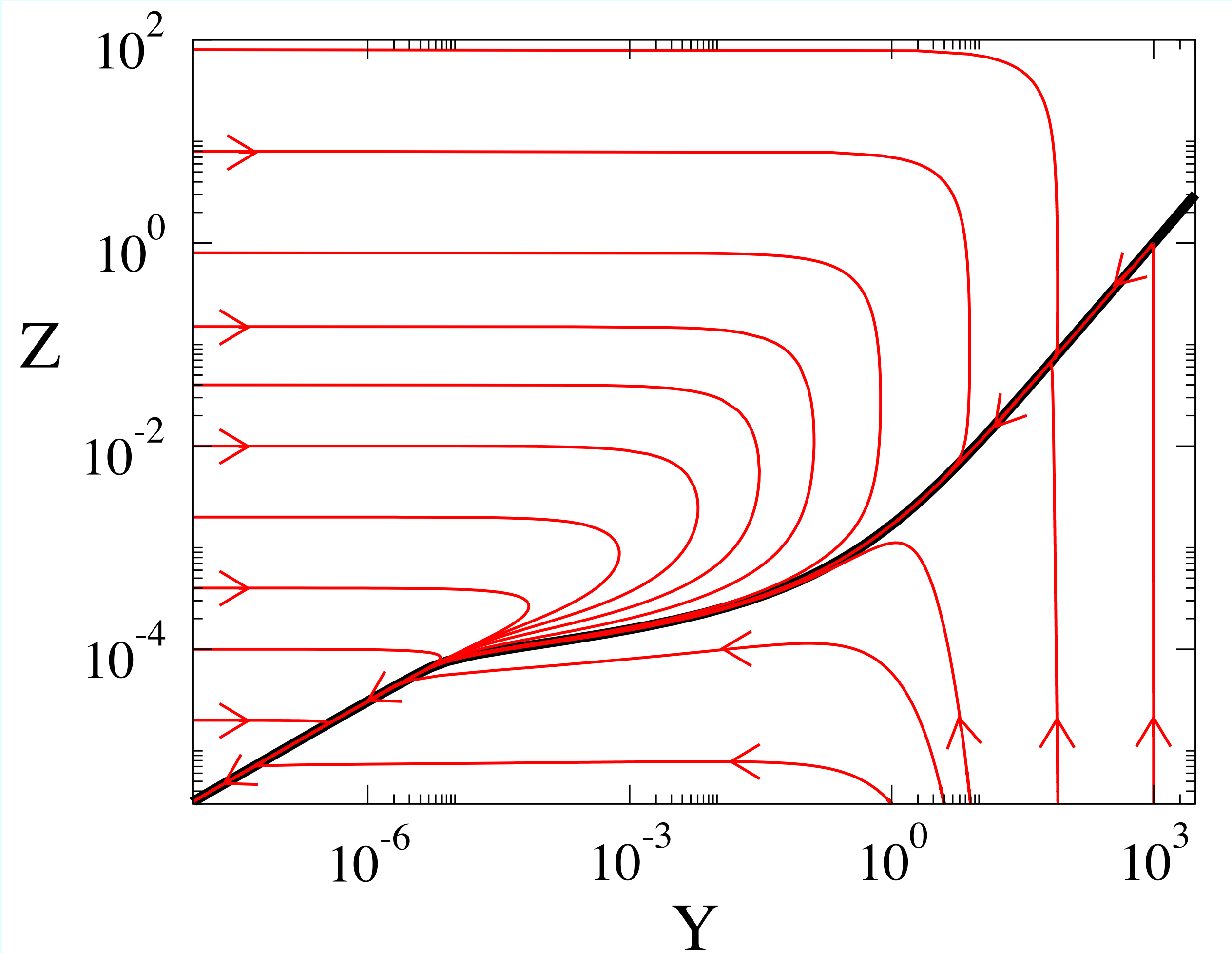
Trajectories: $k_{1f}=10^3$ $k_{1b}=10^3$ $k_2=1$



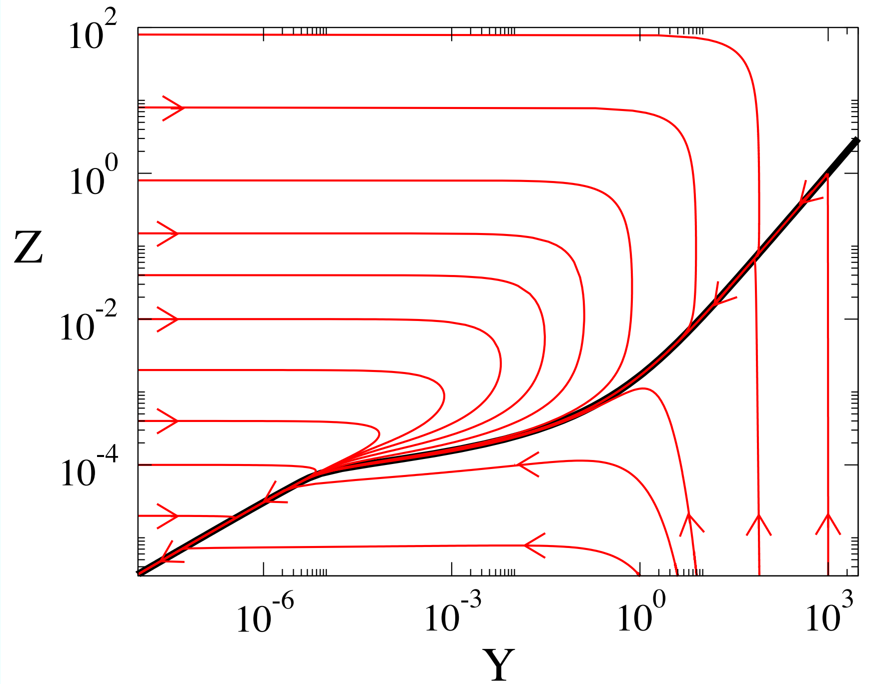
Leading order asymptotics



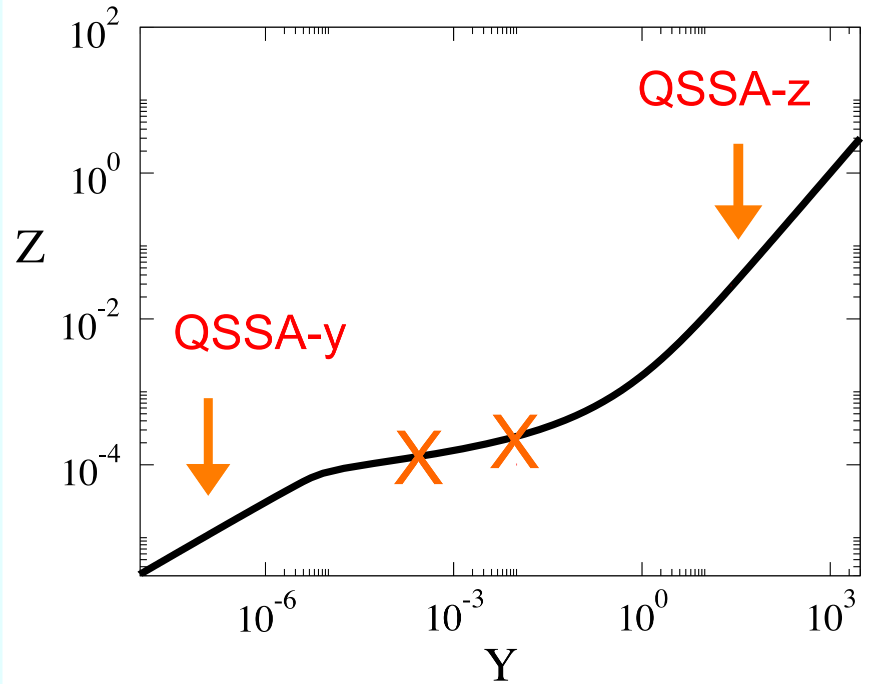
Trajectories: $k_{1f}=10^3$ $k_{1b}=1$ $k_2=1$



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

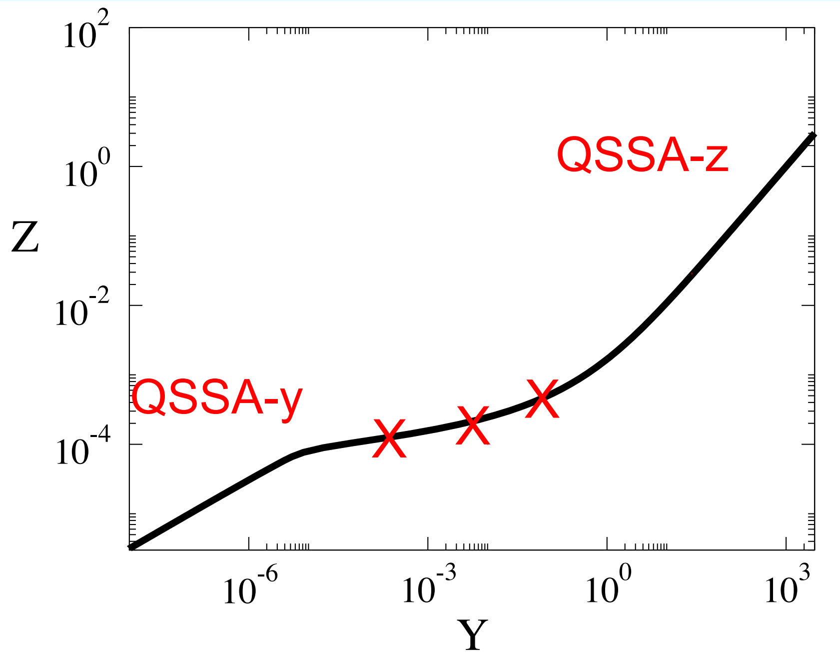


Leading order asymptotics

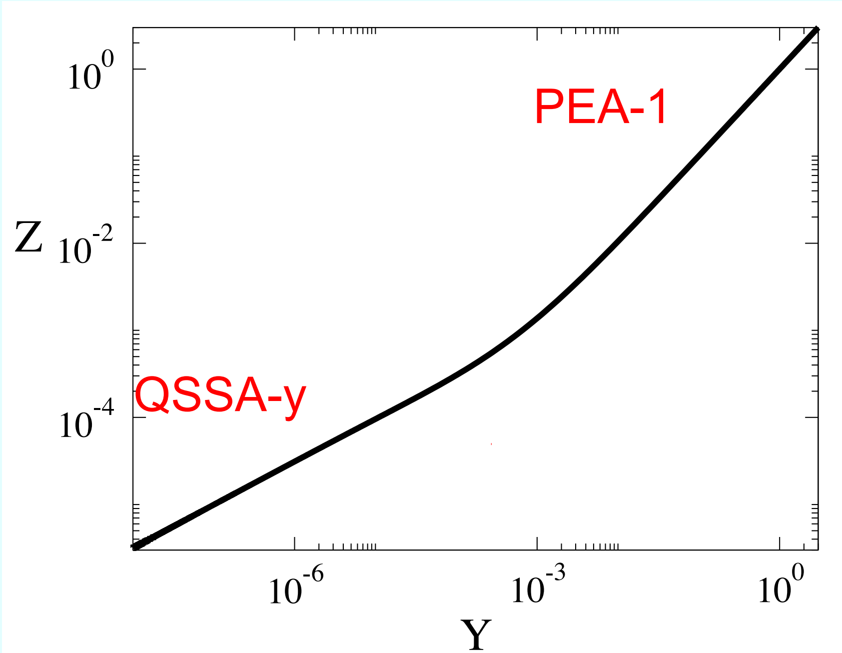


Long term (global) behavior: 3 different approximations

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

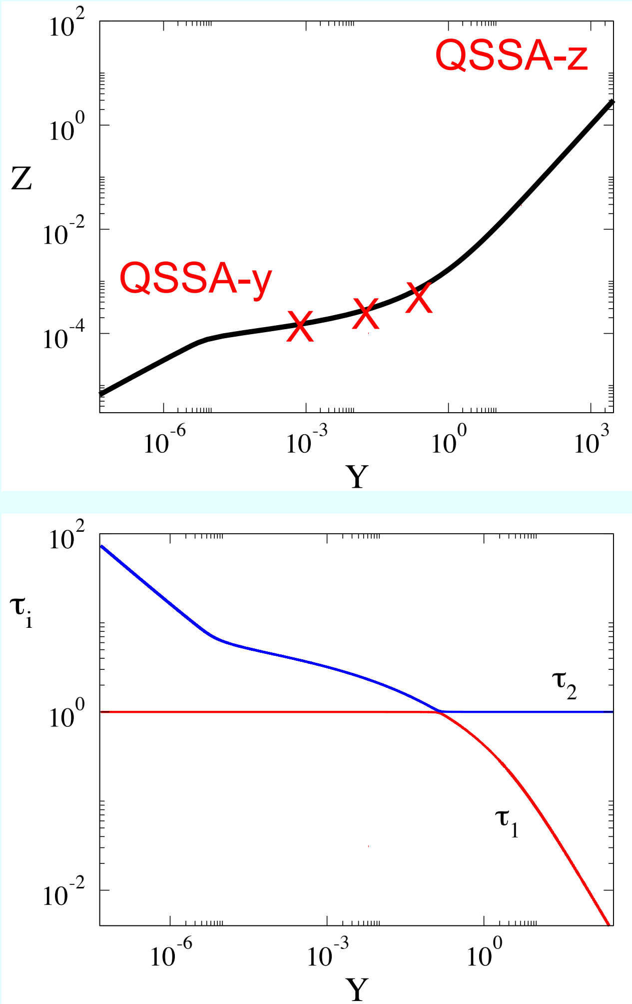


$k_{1f}=10^3$ $k_{1b}=10^3$ $k_2=1$

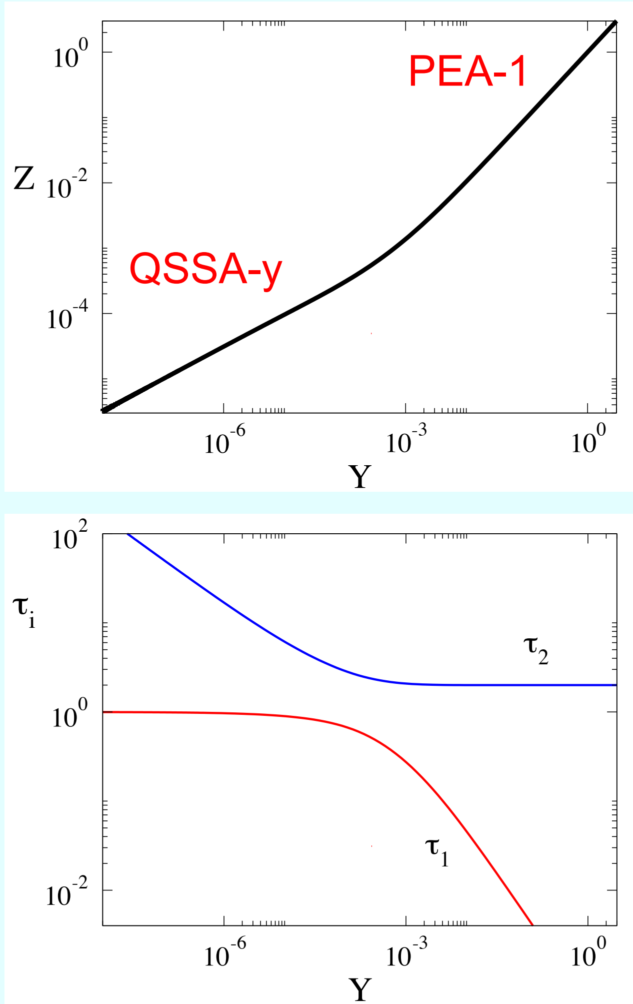


Long term (global) behavior: 3 different approximations

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

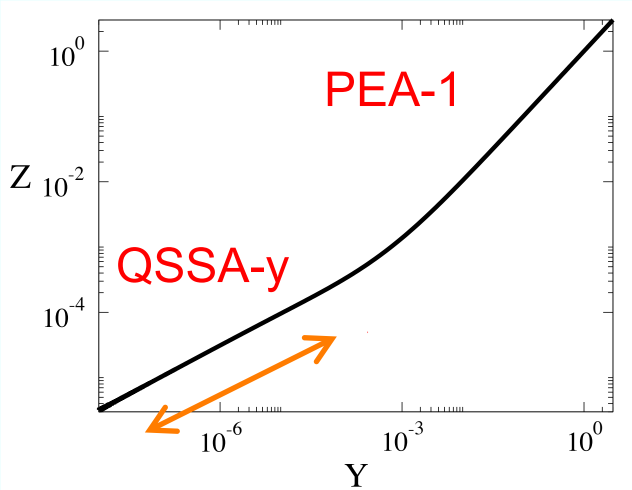


$k_{1f}=10^3 \quad k_{1b}=10^3 \quad k_2=1$



Long term behavior: QSSA - y

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



Normal form

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

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

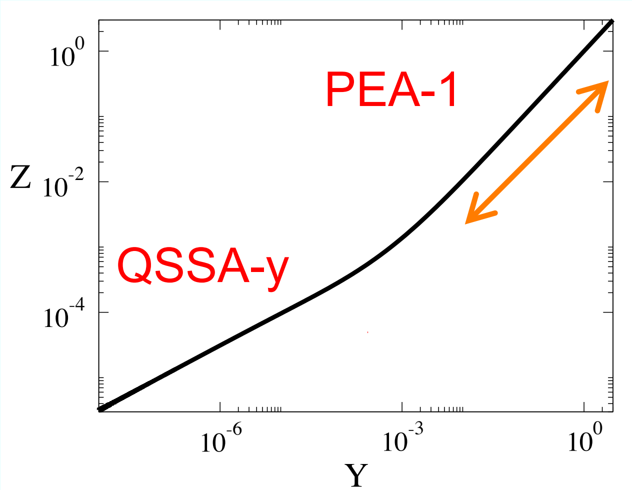
$$y_0 = z_0^2$$

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

Fine !

Long term behavior: PEA-1

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



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

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

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

$w = y + z$ →

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

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

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

$$w_0 = 2y_0$$

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

$z = w - y$ →

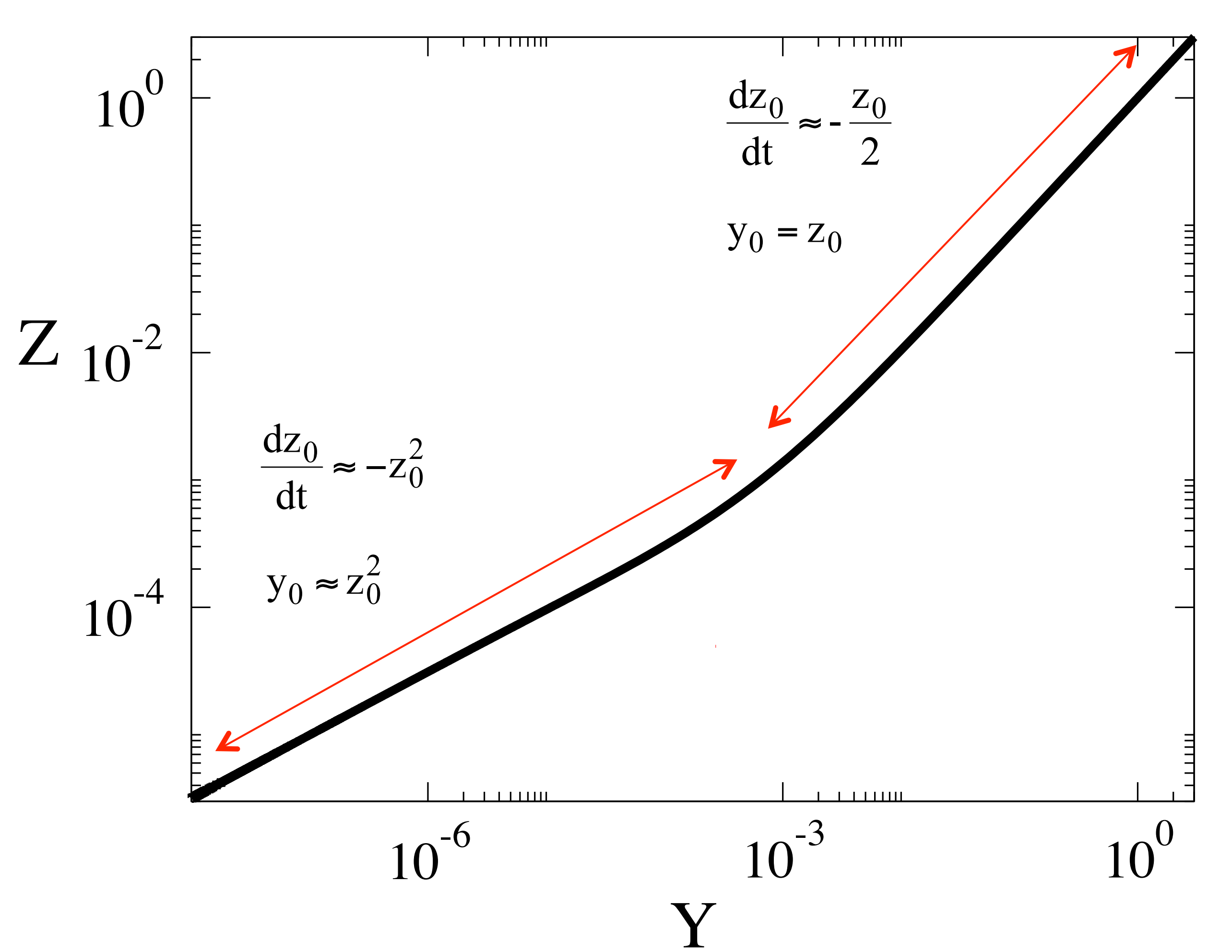
$$y_0 = z_0$$

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

Fine !

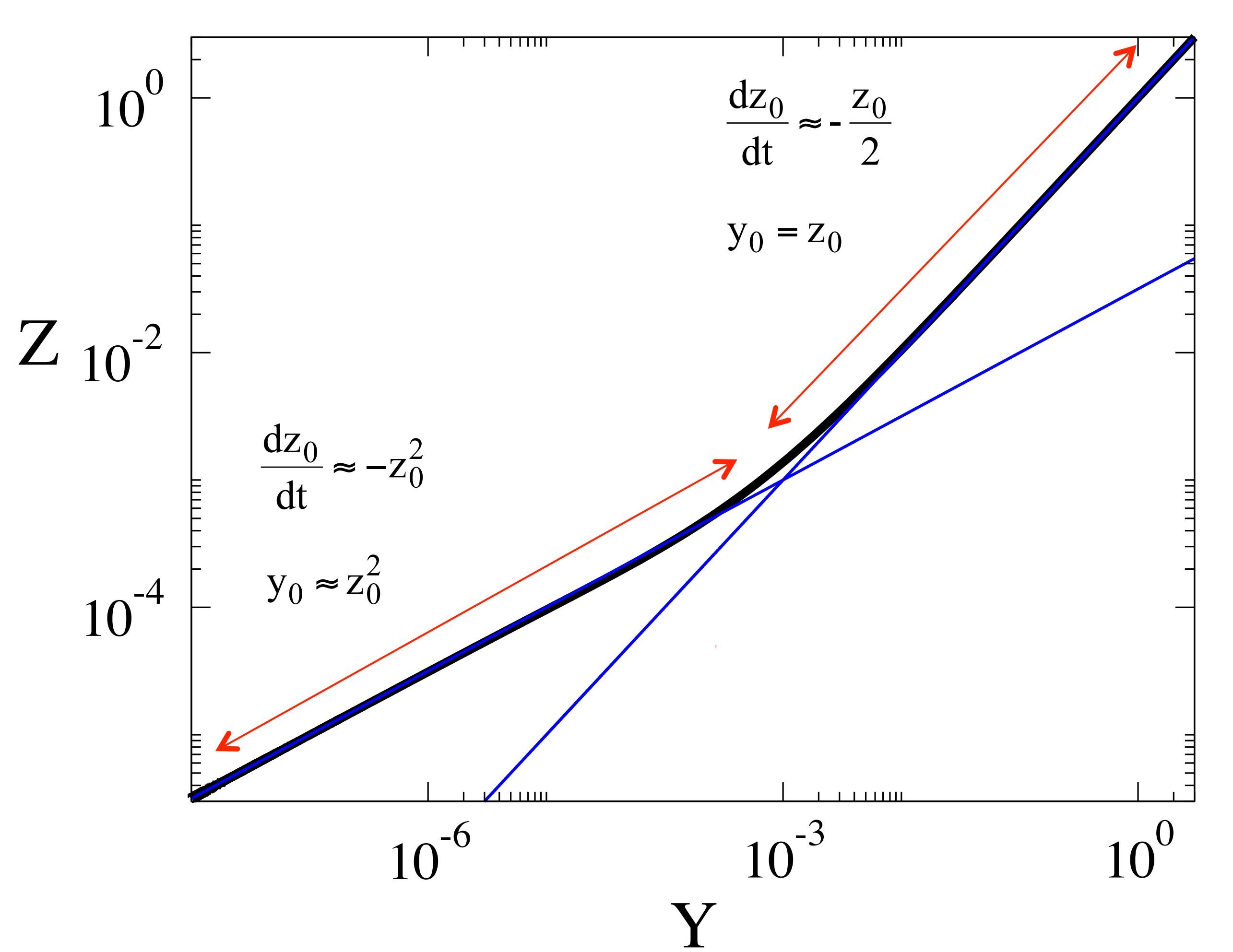
Long term (global) behavior: 3 different models

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



Long term (global) behavior: 3 different models

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



Obstacles for a successful asymptotic analysis

Given a system in dimensional form: $$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y};\mathbf{k})$$

When using the traditional tools a researcher must:

1. find all applicable *non-dimensional forms* of the system
2. transform all systems in *normal form*
3. determine the *sub-domain in phase space* where each system is valid
4. proceed with the *proper expansion* of variables
5. find a way to *match* the solution of the various systems

Asymptotic 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)

Williams, Physica D 20:21-34, 1986

Buckmaster, Physica D 20:91-108, 1986

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

NEXT

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.