Karlsruhe Institute of Technology

# Mechanisms of chemical kinetics: detailed modelling and model reduction

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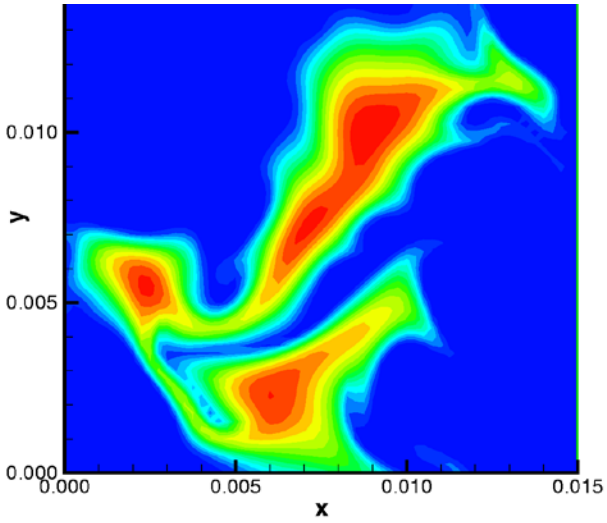
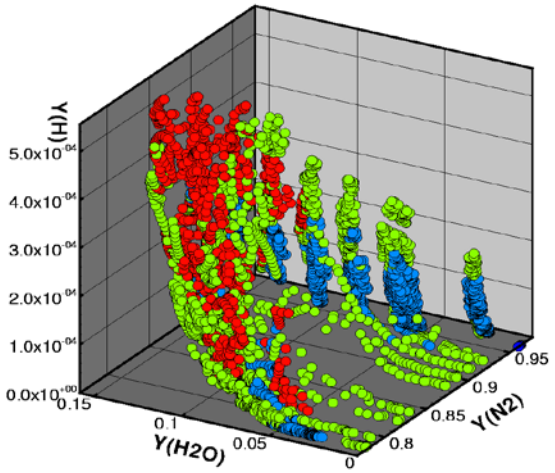
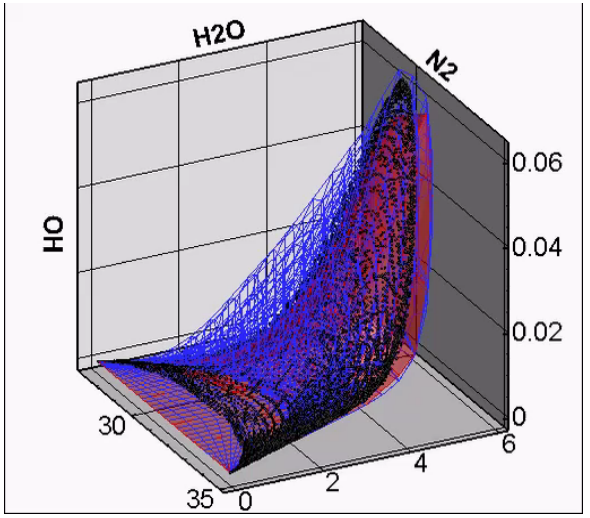


# Outline

- Introduction
  - mechanisms of chemical kinetics of combustion
- Problem statement of model reduction
  - dimensionality, non-linearity, stiffness
- Methodology
  - empirical standard / conventional methods
  - local and global multiple time-scales analysis
  - system degeneration, time scale separation, Global Quasi-Linearization (GQL)
- Implementation example
  - Auto-ignition problem of hydrogen/oxygen combustion system
- Summary, acknowledgments and future work

# Problem Statement: $2H_2+O_2 = 2H_2O$

- Modelling of combustion wave, $p$ = const
- Mass balance $\rho_\infty v_\infty = \rho_0 v_0$
- Energy balance $h_\infty = h_0$
- Calculation of the temperature:

$$h_{H_2O}(T_\infty) = h_\infty = h_0 = w_{H_2} h_{H_2}(T_0) + w_{O_2} h_{O_2}(T_0)$$

- Problem: Model: $T$ = 4800 K, only $H_2O$ present in Products
- Reality: $T$ = 3090 K, $H_2O$, $O_2$, $H_2$, OH, H, O in Products
- Meaning: no information how chemical reaction occurs
  no information on the composition of the mixture
- What to do in order to improve this situation?

# Radicals chain reactions of $H_2$-$O_2$ - combustion system

- $H_2 + O_2 = OH + OH$ chain initiation

- $OH + H_2 = H_2O + H$ chain branching
- $H + O_2 = OH + O$ chain branching
- $O + H_2 = OH + H$ chain branching

- $H = 1/2\ H_2$ chain termination (e.g. on the wall)
- $H + O_2 + M = HO_2 + M$ chain termination (homogenous)

- For $T < 1100$ K additional channel has to be accounted for!

- $HO_2 + H_2 = H_2O_2 + H$
- $H_2O_2 + M = OH + OH + M$

# Mechanisms of detailed chemical kinetics - Example

$H_2$ / $O_2$ Mechanism

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $O_2$ | + | H | | = | OH | + | O |
| $H_2$ | + | O | | = | OH | + | H |
| $H_2$ | + | OH | | = | $H_2O$ | + | H |
| OH | + | OH | | = | $H_2O$ | + | O |
| H | + | H | + M | = | $H_2$ | + | M |
| H | + | OH | + M | = | $H_2O$ | + | M |
| O | + | O | + M | = | $O_2$ | + | M |
| H | + | $O_2$ | + M | = | $HO_2$ | + | M |
| $HO_2$ | + | H | | = | OH | + | OH |
| $HO_2$ | + | H | | = | $H_2$ | + | $O_2$ |
| $HO_2$ | + | H | | = | $H_2O$ | + | O |
| $HO_2$ | + | O | | = | OH | + | $O_2$ |
| $HO_2$ | + | OH | | = | $H_2O$ | + | $O_2$ |
| $HO_2$ | + | $HO_2$ | | = | $H_2O_2$ | + | $O_2$ |
| OH | + | OH | + M | = | $H_2O_2$ | + | M |
| $H_2O_2$ | + | H | | = | $H_2$ | + | $HO_2$ |
| $H_2O_2$ | + | H | | = | $H_2O$ | + | OH |
| $H_2O_2$ | + | O | | = | OH | + | $HO_2$ |
| $H_2O_2$ | + | OH | | = | $H_2O$ | + | $HO_2$ |

**see e.g.: Warnatz, Maas, Dibble: Combustion, Springer 2004**

- Hydrogen/air combustion mechanism consists of 19 elementary reactions ($n_r = 19$) between 9 species ($n_s = 9$)
  - Even for simplest possible combustion system the dimension is quite high

$$\frac{d[H_2]}{dt} = -R_2 - R_3 + R_5 + \dots$$

$$\dots$$

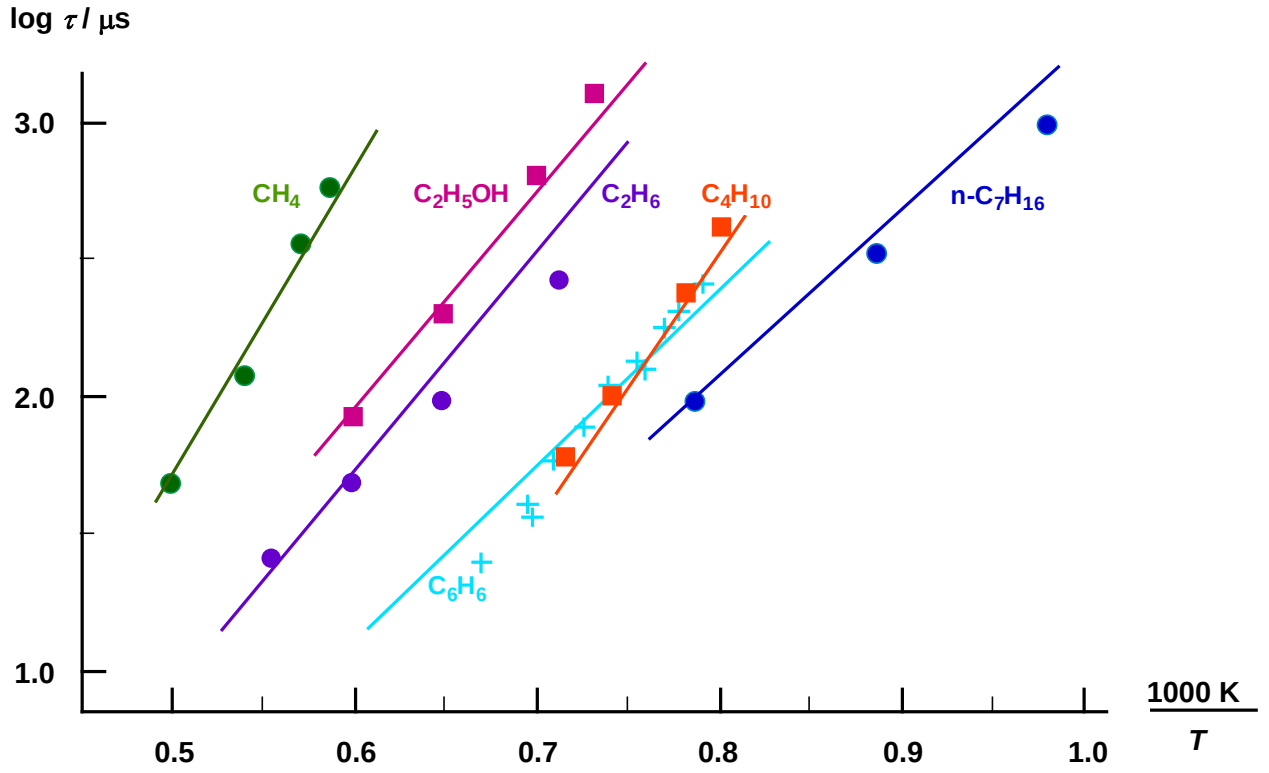
$$\frac{d[H_2O_2]}{dt} = R_{15} + R_{16} - \dots$$

$$R_2(\psi) = A_2^+ e^{-\frac{E_2^+}{RT}}[H_2][O] - A_2^- e^{-\frac{E_2^-}{RT}}[OH][H]$$

$$\frac{d\psi}{dt} = \begin{pmatrix} s_{1,1} & s_{1,2} & \dots & s_{1,n_r} \\ \dots & \dots & \dots & \dots \\ s_{n_s,1} & s_{n_s,2} & \dots & s_{n_s,n_r} \end{pmatrix} \cdot \begin{pmatrix} R_1(\psi) \\ R_2(\psi) \\ \dots \\ R_{n_r}(\psi) \end{pmatrix} = \begin{pmatrix} F_1(\psi) \\ F_2(\psi) \\ \dots \\ F_n(\psi) \end{pmatrix}$$

# Predictions of the thermodynamics of the chemical kinetics

- Composition of the products:
  - $H_2$-$O_2$ – combustion system
  - $T_\infty$ = 3080 K, 57 % $H_2O$, 5 % $O_2$,16 % $H_2$, 10 % OH, 8 % H, 4 % O
- Reaction times
- Ignition delay times

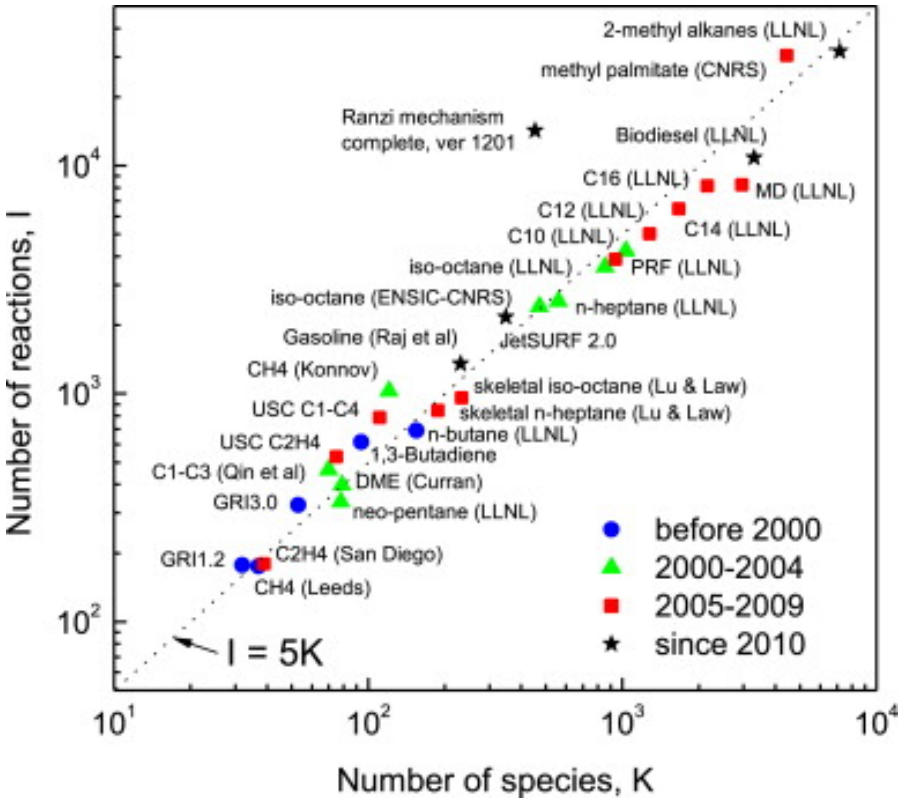



- Ref.: Warnatz, Maas, Dibble: Combustion

# Mechanisms of detailed chemical kinetics - dimenisonality

- Overall dimension of a reacting system is defined by a number of species minus number of conserved quantities

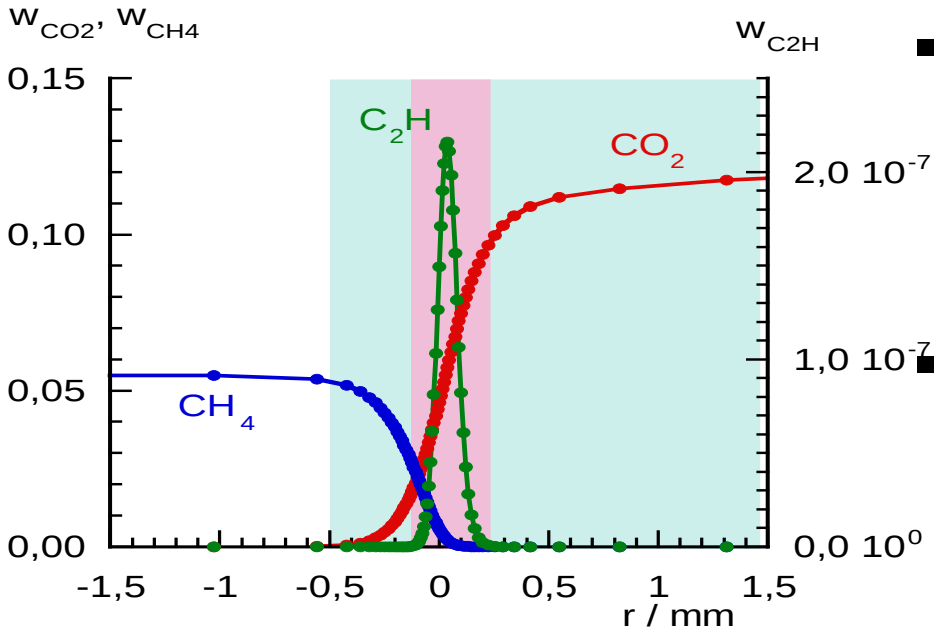
$$n_s \sim O(100), \quad n_r \sim O(1000)$$




- Do we really need so many parameters to describe the process with prescribed accuracy?

- Ref.: F.N. Egolfopoulos, N. Hansen, Y. Ju, K. Kohse-Höinghaus, C.K. Law, F. Qi
Advances and challenges in laminar flame experiments and implications for combustion chemistry, Progress in Energy and Combustion Science, Volume 43, August 2014, Pages 36-67.

# Mechanisms of detailed chemical kinetics - Stiffness




- Non-linear chemical source term leads to stiffness of the governing equations system
- Furthermore, different chemical time scales do not only introduce stiffness, but also cause the existence of very small length scales

1-dimensional cut through a $CH_4$-air flame ($n_s$ =33)

# Mechanisms of detailed chemical kinetics

- Brief overview

  - “too many” species are involved in accurate modeling of combustion process participating in
  - several thousand elementary reactions with a little known about their rates

leading to

  - stiffness of system of governing equations

and

  - high dimensionality of thermo-kinetic state of combustion system

# Solution I: skeletal mechanisms

- The model is reduced by removing (neglecting) particular elementary reactions or species

- If a specific set of system parameters and conditions is considered, then

  - Hydrogen, Syngas ~10
  - Methane ~30
  - Heptane ~50
  - etc.

**Binomial[300,30]** =173193226149263513034110205899732811401360= $1.73193 \times 10^{41}$

- More sophisticated methodologies have to be developed to proceed beyond these limits!

# Solution II: standard approaches – QSSA

- The decomposition can be represented by species

$$\frac{d\psi}{dt} = \begin{pmatrix} s_{1,1} & s_{1,2} & \dots & s_{1,n_r} \\ \dots & \dots & \dots & \dots \\ s_{n_s,1} & s_{n_s,2} & \dots & s_{n_s,n_r} \end{pmatrix} \cdot \begin{pmatrix} R_1(\psi) \\ R_2(\psi) \\ \dots \\ R_{n_r}(\psi) \end{pmatrix} = \begin{pmatrix} F_1(\psi) \\ F_2(\psi) \\ \dots \\ F_n(\psi) \end{pmatrix}$$

- Some species are assumed to be at quasi-steady states (QSS)

$$M^{0}_{QSSA} = \left\{ F_{j_1}(\psi) = 0, \dots, F_{j_{n-m}}(\psi) = 0 \right\}$$
$$M^{0,\,fast}_{QSSA} = \left\{ \psi_{j_1} = const, \dots, \psi_{j_{n-m}} = const \right\}$$

$$\frac{d[H_2]}{dt} = F_1(\psi) = -R_2 - R_3 + R_5 + \dots$$

...

$$\frac{d[H_2O_2]}{dt} = F_{n_s}(\psi) = R_{15} + R_{16} - \dots$$

- The choice of the species $\{j_1, \dots, j_{n-m}\}$ is very crucial

# Solution II: standard approaches – PEA

- The decomposition can be represented by using elementary reaction rates

$$\frac{d\psi}{dt} = F(\psi) = \begin{pmatrix} s_{1,1} & s_{1,2} & \dots & s_{1,n_r} \\ \dots & \dots & \dots & \dots \\ s_{n_s,1} & s_{n_s,2} & \dots & s_{n_s,n_r} \end{pmatrix} \cdot \begin{pmatrix} R_1(\psi) \\ R_2(\psi) \\ \dots \\ R_{n_r}(\psi) \end{pmatrix} = \begin{pmatrix} F_1(\psi) \\ F_2(\psi) \\ \dots \\ F_n(\psi) \end{pmatrix}$$

- Some elementary reactions are assumed to be at partial equilibrium

$$M^0_{PEA} = \left\{ R_{i_1}(\psi) = 0, \dots, R_{i_{n_f}}(\psi) = 0 \right\} \quad m = n - n_f$$

$$\frac{d[H_2]}{dt} = F_1(\psi) = -R_2 - R_3 + R_5 + \dots$$

$$\dots$$

$$\frac{d[H_2O_2]}{dt} = F_{n_s}(\psi) = R_{15} + R_{16} - \dots$$

- The choice of the elementary reactions $\{i_1,\dots,i_{n-m}\}$ becomes crucial

# Solutions I+II: standard approaches – Problems

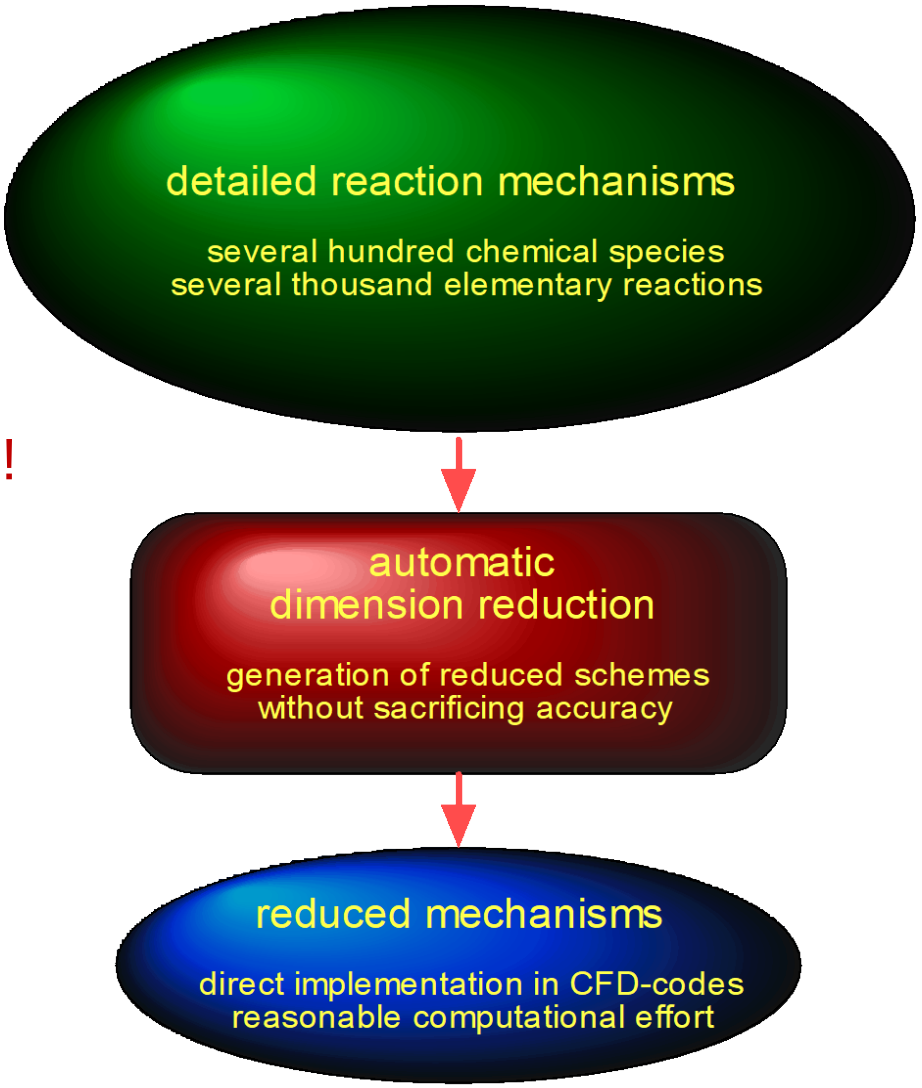
- Original coordinates of the system might not be suitable for the decomposition in terms of the species or elementary reactions

- Approximation of the system solution by either QSSA or PEA might be valid in a narrow range of the system parameters

- Empirical choice of such reactions and/or species is very demanding!

# Concept: dimension reduction

- Problems of detailed chemical kinetics:
  - several hundreds chemical species
  - several thousands elementary reactions
  - stiffness of the governing equations system
- But: only few reactions are rate limiting!
- Fundamental concepts:
  - Multiple time scales
  - Decomposition of motions
  - Existence of manifolds of fast and slow motions



# Solution III: Multiple time scales – ILDM, GQL

- Reactions and combination of species are identified corresponding to relevant characteristic time scales $\tau_i = 1/|\lambda_i|$

$$\frac{d\psi}{dt} = F(\psi) = \begin{pmatrix} s_{1,1} & s_{1,2} & \dots & s_{1,n_r} \\ \dots & \dots & \dots & \dots \\ s_{n_s,1} & s_{n_s,2} & \dots & s_{n_s,n_r} \end{pmatrix} \cdot \begin{pmatrix} R_1(\psi) \\ R_2(\psi) \\ \dots \\ R_{n_r}(\psi) \end{pmatrix} = \begin{pmatrix} F_1(\psi) \\ F_2(\psi) \\ \dots \\ F_n(\psi) \end{pmatrix} \Rightarrow J(\psi) = \left( \frac{\partial F_i}{\partial \psi_j} \right) = [Z_1 Z_2 \dots Z_n] \begin{bmatrix} \lambda_1 & 0 & \dots & 0 \\ 0 & \lambda_2 & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \lambda_n \end{bmatrix} \begin{bmatrix} \tilde{Z}_1 \\ \tilde{Z}_2 \\ \dots \\ \tilde{Z}_n \end{bmatrix}$$

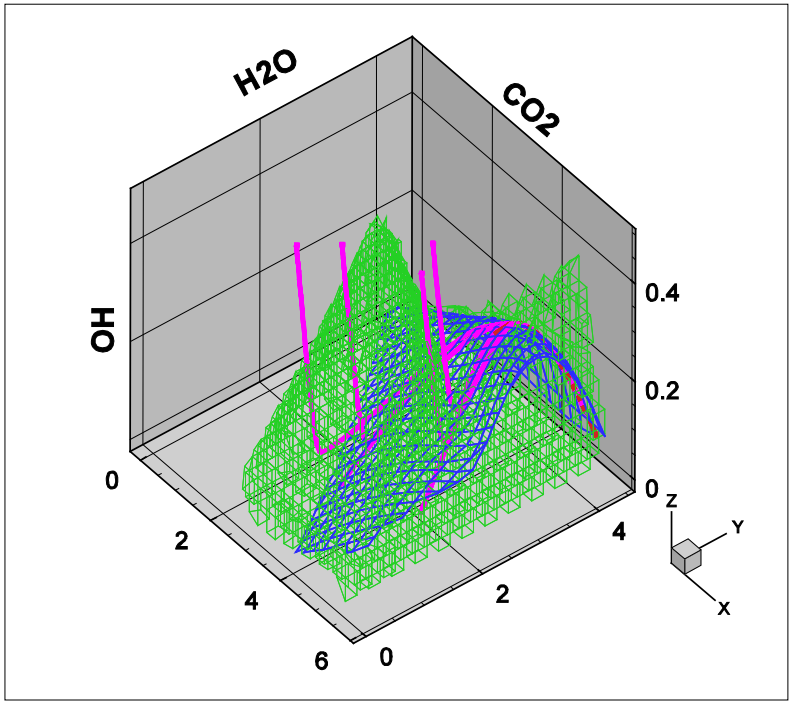
- Thus, manifold (states) accounting for partially equilibrating processes described by invariant eigenspaces becomes available:

$$M_{ILDM} = \left\{ \tilde{Z}^{f}_{1}(\psi) \cdot F(\psi) = 0, \dots, \tilde{Z}^{f}_{n-m}(\psi) \cdot F(\psi) = 0 \right\}$$

- The problem of the empirical choice is overcome!
  - Ref.: Maas, Pope, Comb. Flame (1992)

# Solution III: ILDM application – Syngas

- Syngas mechanism $n_r$ =38, $n_s$=13 is considered
- 2D, 3D manifolds of relatively slow motion are calculated and tabulated
- A number of detailed system solution trajectories are shown
- Tabulation concept permits efficient application

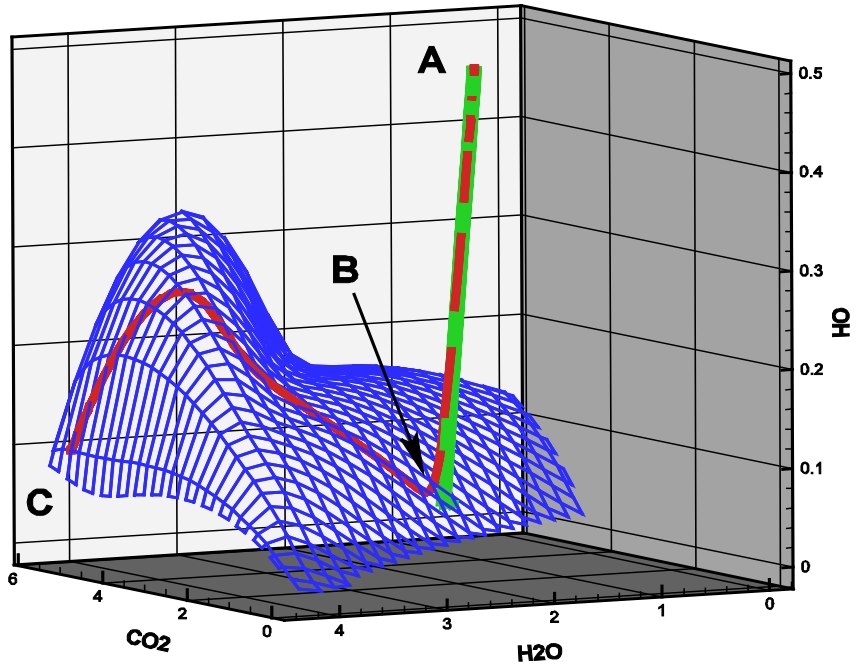



$CO-H_2-O_2$ homogeneous system, magenta – system trajectories, blue is 2D ILDM, green represents 3D ILDM

# Solution III: Overview

- Rigorous time scale analysis allows us
  - Check the system hierarchy!
  - Estimate the reduced dimension!
  - Approximate manifolds representing reduced model!
  - Decompose the system!

- Ref.: Bykov, Gol'dshtein, Maas, CTM, 12(2), 389 – 405 (2008)




$CO$-$H_2$-$O_2$ homogeneous system, red line – system trajectory, blue mesh is 2D ILDM mesh, green line represents (n-m)-dim. fast relaxation part of the trajectory

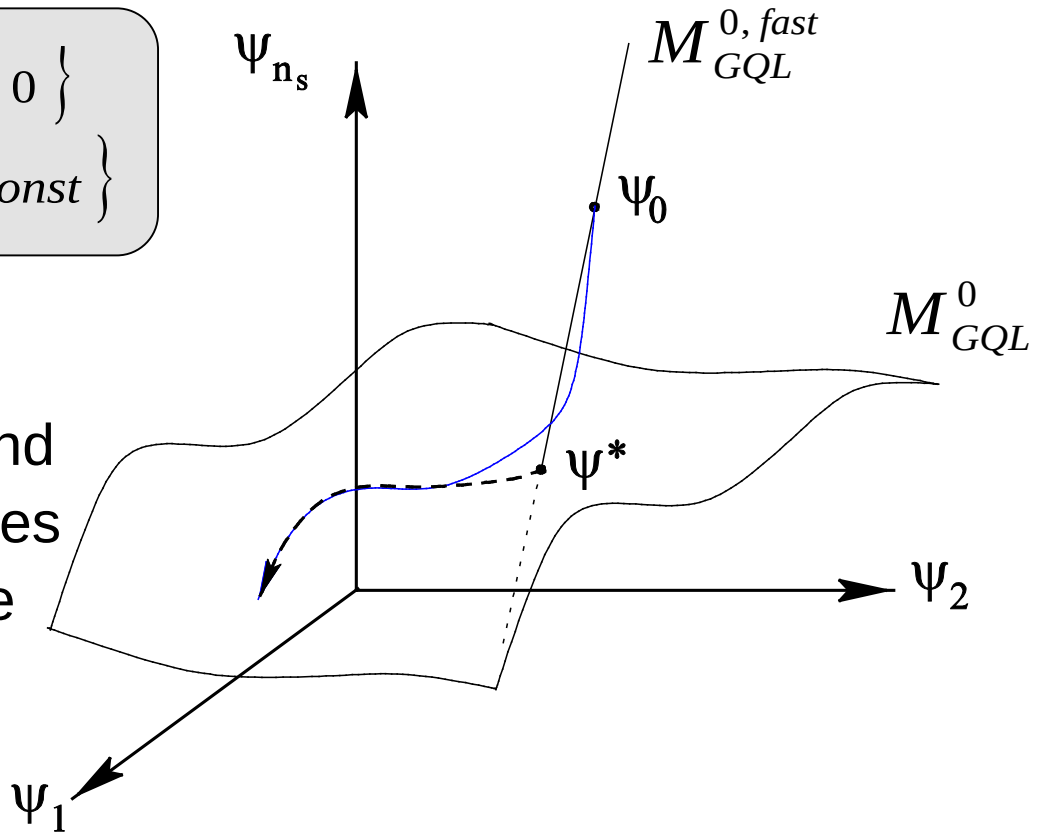
# ILDM versus GQL

- The system dynamics can be decomposed explicitly

$$M^{0}_{GQL} = \left\{ \tilde{Z}^{f}_{j_1} \cdot F(\psi) = 0, \ldots, \tilde{Z}^{f}_{j_{n_f}} \cdot F(\psi) = 0 \right\}$$

$$M^{0,\,fast}_{GQL} = \left\{ \tilde{Z}^{s}_{j_1} \cdot \psi = const, \ldots, \tilde{Z}^{s}_{j_{n_s}} \cdot \psi = const \right\}$$

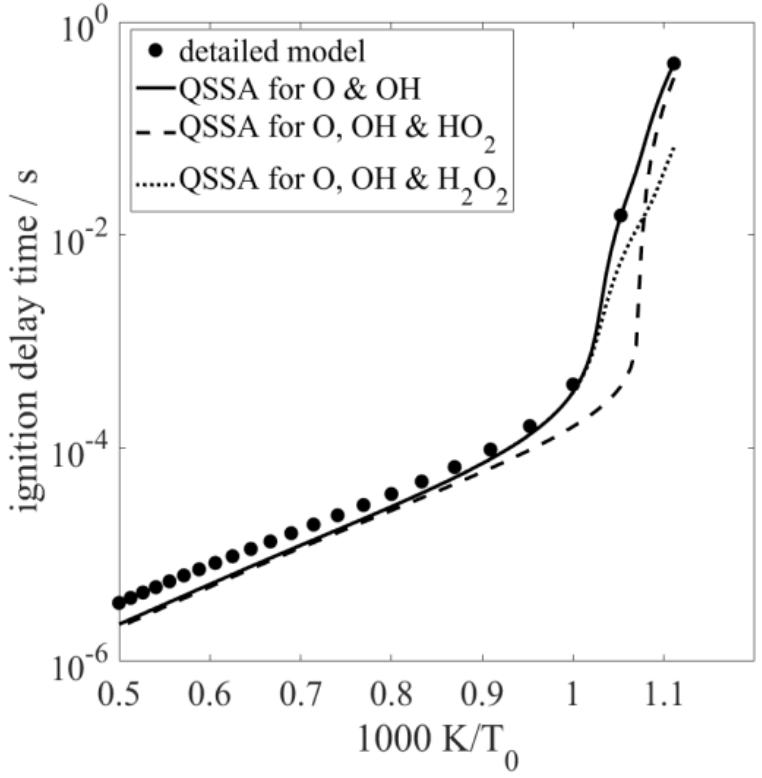
- The equations are simplified and solved for independent variables and reduced mode is therefore defined!

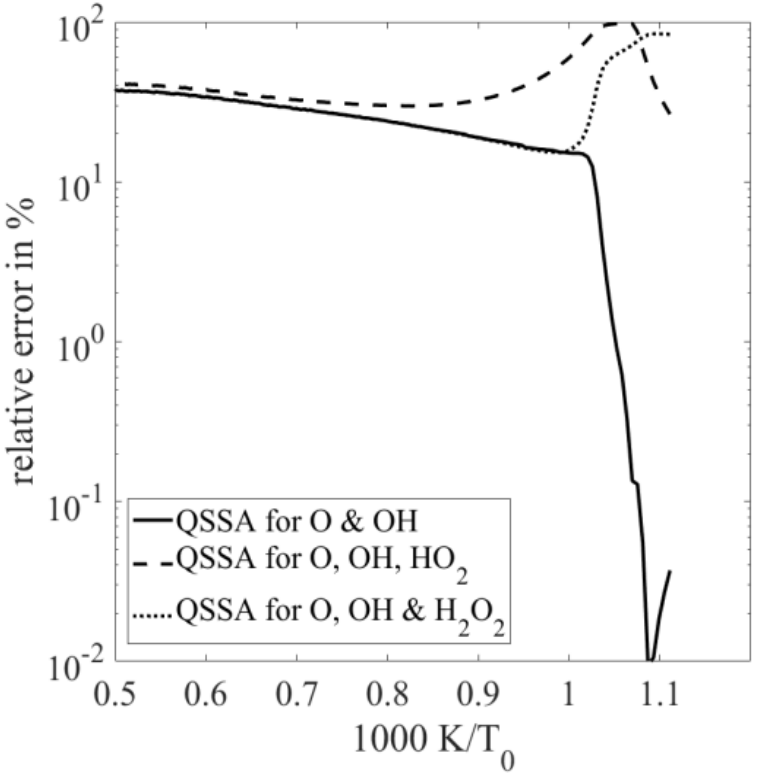



- Ref.: Bykov, Gol'dshtein, Maas, CTM, 12(2), 389 – 405 (2008)

# Application: Auto-ignition problem

- Application of the standard method - QSSA



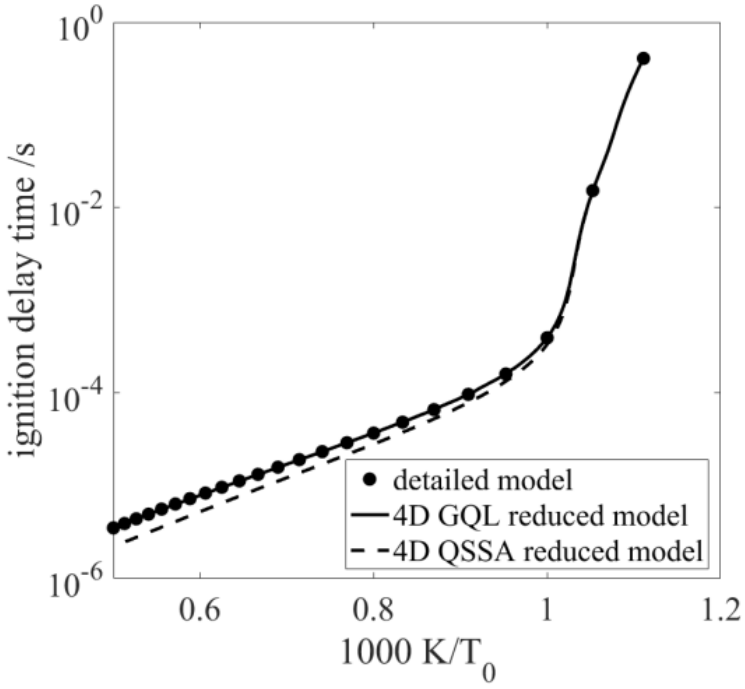



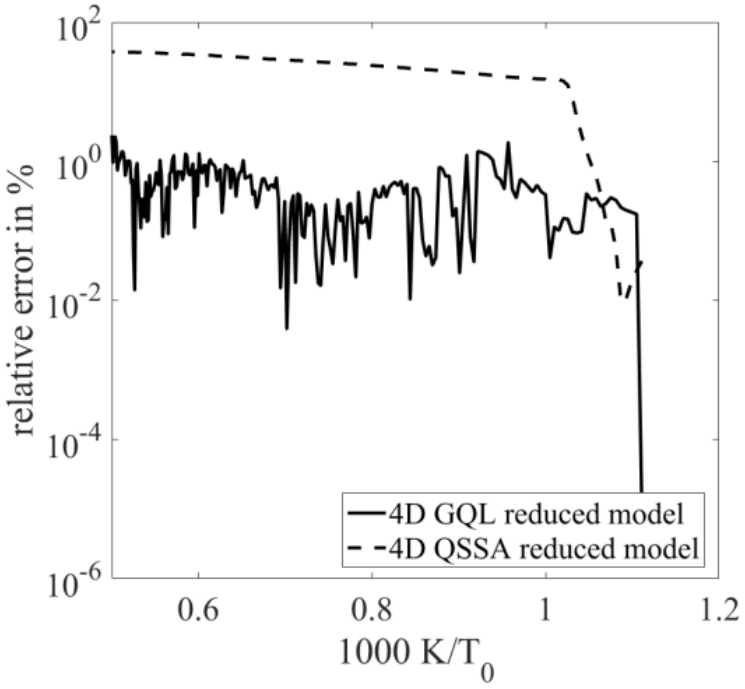

- QSSA for different species under

$$p_0 = 1\ bar \text{ and } \Phi = 1.0 \text{ for } 900\ K \leq T_0 \leq 2000\ K.$$

# Application: Auto-ignition problem

- Comparison of the GQL and the best performing QSSA

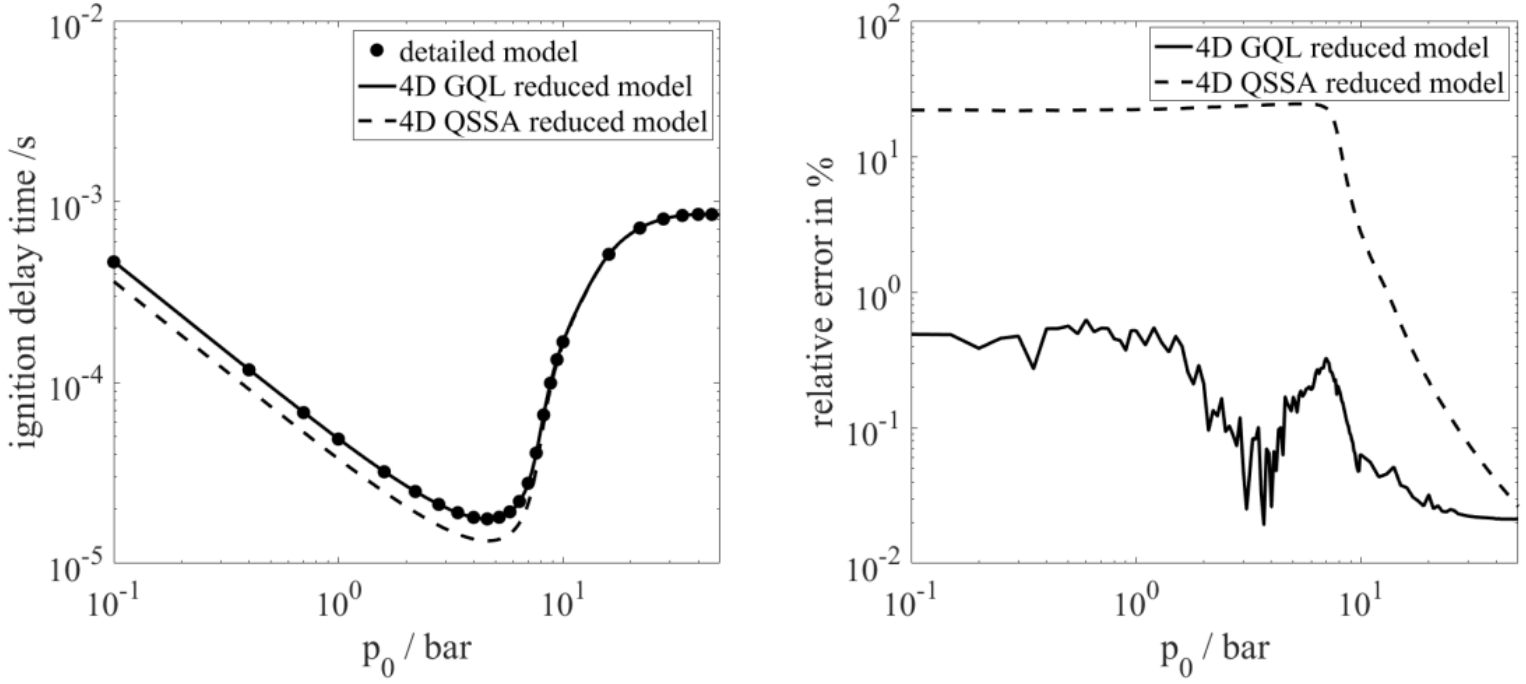



- The ignition delay time at $p_0 = 1\ bar$ and $\Phi = 1.0$. On the left: delay time prediction, right figure: relative errors in % versus initial temperature $T_0$.

# Application: Auto-ignition problem

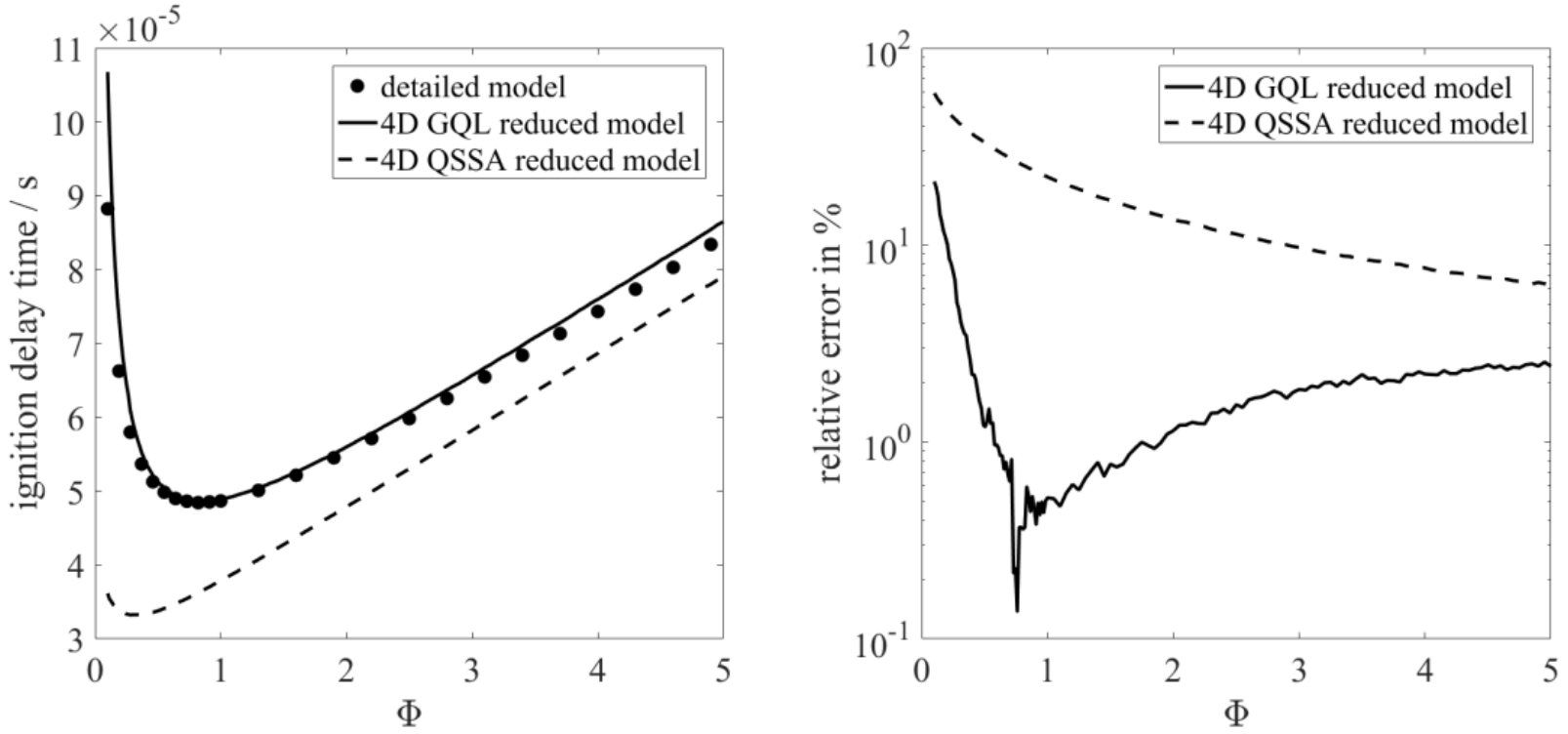
- Comparison of the GQL and the best performing QSSA




- The ignition delay time at $T_0 = 1200\ K$ and $\Phi = 1.0$. Left figure: delay times; right figure: relative errors in % versus initial pressure $p_0$.

# Application: Auto-ignition problem

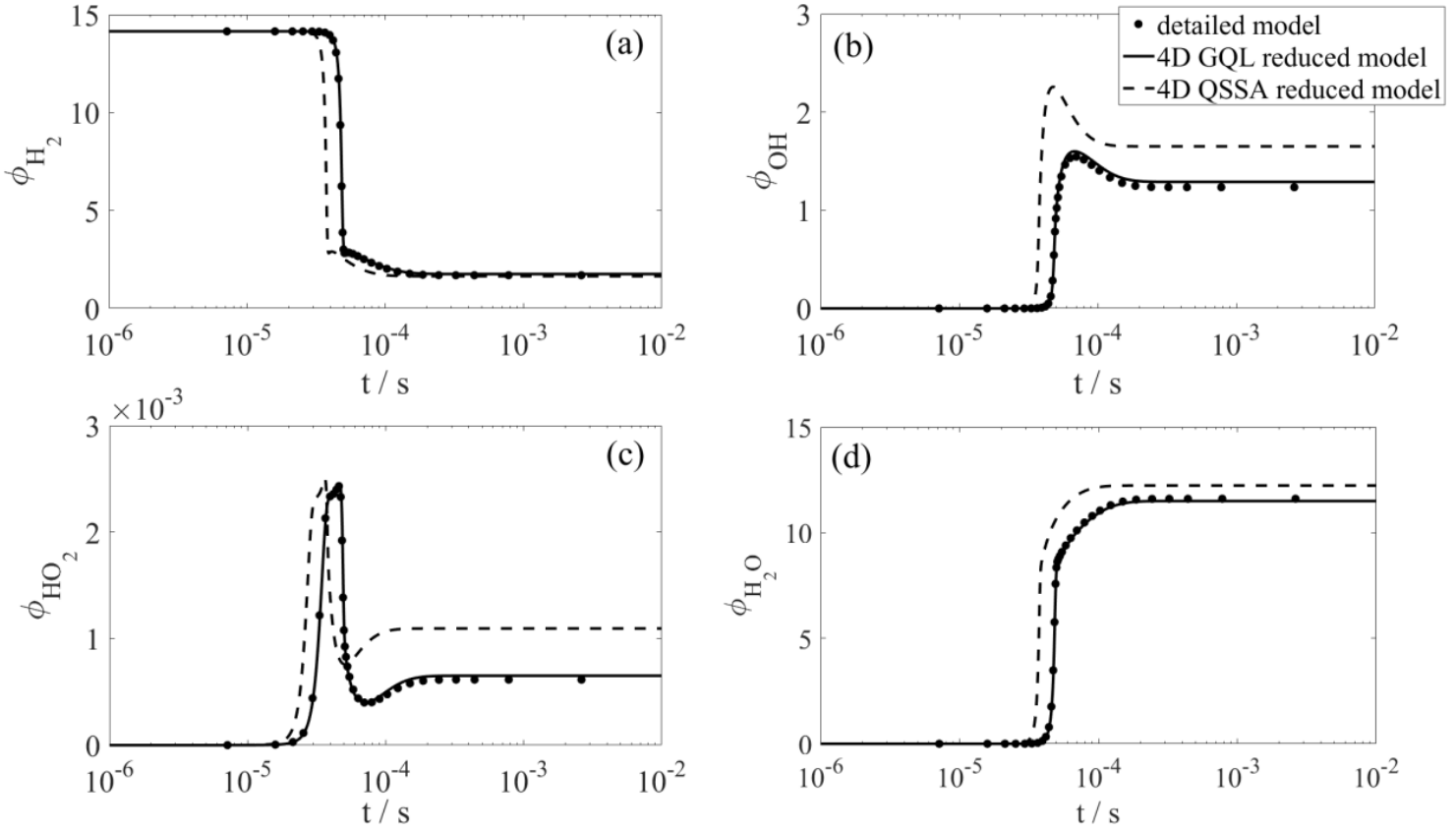
- Comparison of the GQL and the best performing QSSA




- The ignition delay time at $T_0 = 1200\ K$ and $p_0 = 1\ bar$. Left figure: delay times; right figure: relative errors in % versus initial fuel/air equivalence ratio $\Phi$.

# Application: Auto-ignition problem

- Comparison of the GQL and the best performing QSSA, time history




- Time history of species $H_2$ (a), OH (b), $HO_2$ (c) and $H_2O$ (d)

  Specific mole number is given in $\phi_i = [w_i/M_i] = mol/g$

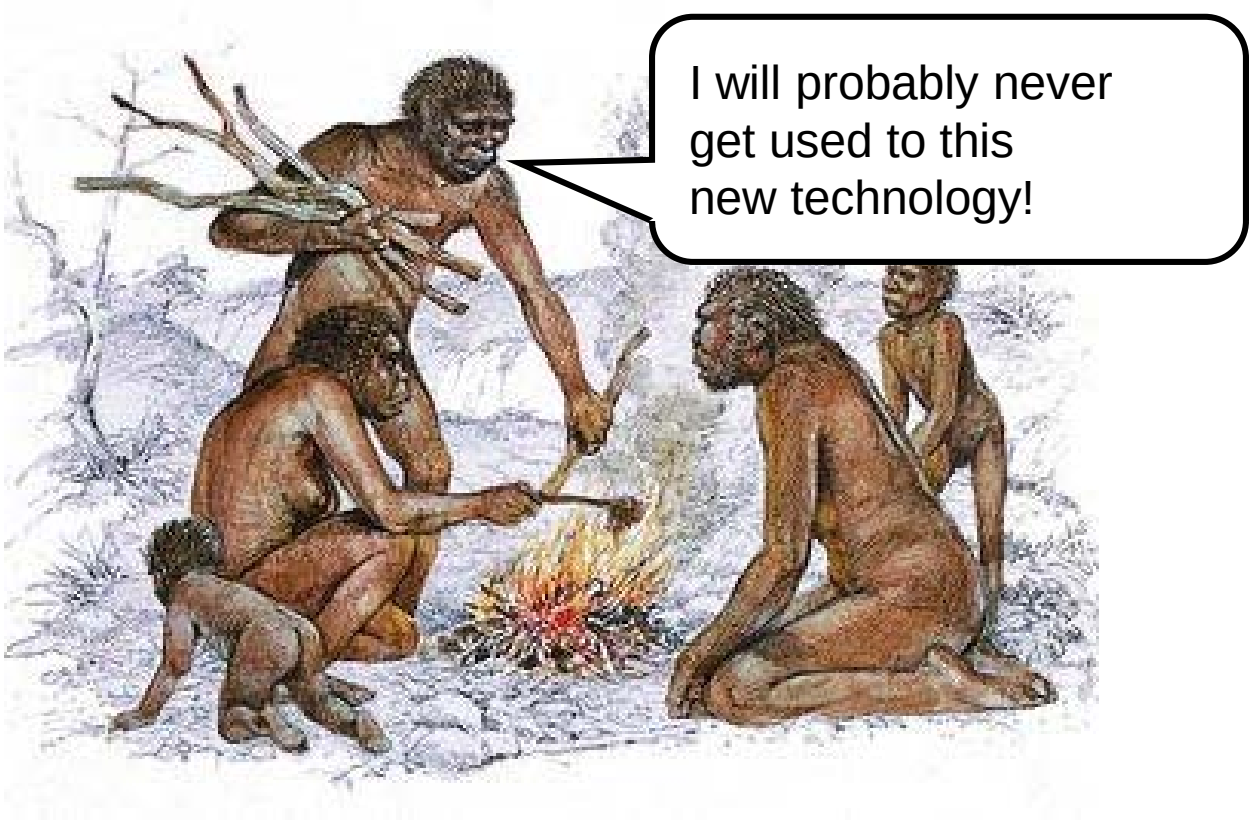
# Summary

- The problem of detailed modelling of combustion kinetics was discussed
- Methods to treat and implement model reduction of combustion systems were outlined
- Key concepts of multiple time scales, decomposition of motions as well as a transparent application example was presented

- Acknowledgments: Ulrich, Vladimir, Chunkan Yu…

# Future work, questions

- One has to use the multiple-time scale separation explicitly!




- Thank you very much for your attention!

# Mechanisms of detailed chemical kinetics - Modelling

- Model example - Lindemann mechanism: $A \rightarrow P$

  - Network of chemical (elementary) reactions:

$$k_1 : A + M \quad \leftrightarrow \quad A^* + M$$
$$k_2 : A^* \rightarrow P$$

  - Elementary reaction rates:

$$M = \alpha_A A + \alpha_B A^* + \alpha_P P$$

$$R_1(\psi) = k_1^+(T)[A][M] - k_1^+(T)[A][A^*]$$
$$R_2(\psi) = k_2^+(T)[A^*], \qquad \psi = ([A], [A^*], [P])$$

  - Dynamical system as a system of ODEs:

$$\frac{d[A]}{dt} = -R_1 = -k_1^+(T)[A][M] + k_1^+(T)[A][A^*]$$
$$\frac{d[A^*]}{dt} = R_1 - R_2 \Rightarrow \quad \psi = (A, A^*)$$
$$\frac{d[P]}{dt} = R_2 \Rightarrow [A] + [A^*] + [P] = [A]_0$$

# Mechanisms of detailed chemical kinetics – Dynamical system

- Plane system

$$\psi = \left( [A]/[A]_0, [A^*]/[A]_0 \right)$$

$$\frac{d\psi_1}{dt} = -R_1(\psi_1, \psi_2), \quad \psi_1(t=0) = 1$$

$$\frac{d\psi_2}{dt} = R_1(\psi_1, \psi_2) - R_2(\psi_1, \psi_2), \quad \psi_2(t=0) = 0$$

$$R_1(\psi) = \psi_1^2 - K_1 \psi_1 \psi_2$$

$$R_2(\psi) = K_2 \psi_2$$

$$d\tau = k_1^+ [A]_0 \, dt$$

- Dimensionless form of the system with stoichiometric matrix and reaction rate vector

$$\frac{d}{d\tau}\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} R_1(\psi_1, \psi_2) \\ R_2(\psi_1, \psi_2) \end{pmatrix} \Rightarrow \frac{d\psi}{d\tau} = F(\psi)$$

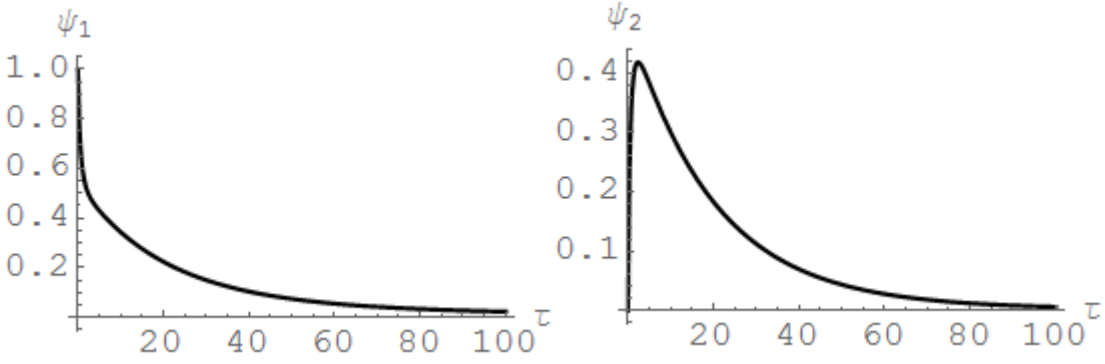
- Two model parameters controlling elementary reaction rates

$$K_1 = \frac{k_1^-}{k_1^+}, \quad K_2 = \frac{k_2^+}{k_1^+ [A]_0}$$

# Mechanisms of detailed chemical kinetics - Properties

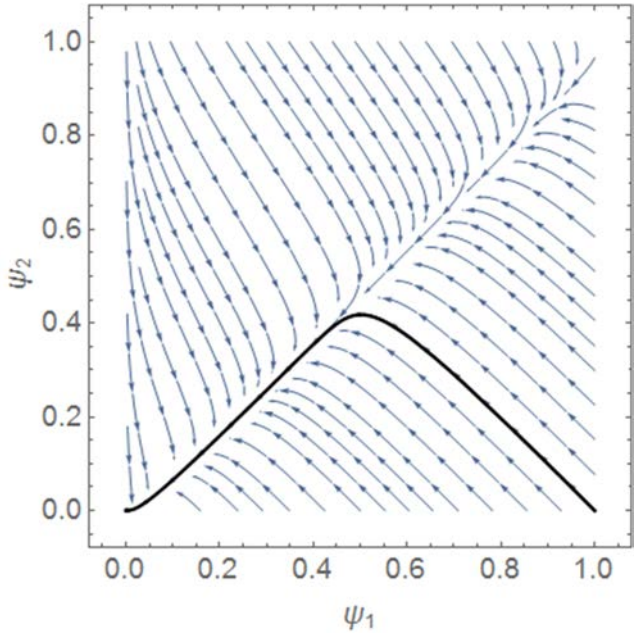
- Smooth dependence on system parameters (rate constants)

$$\frac{d}{dt}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}=\begin{pmatrix}-1 & 0\\ 1 & -1\end{pmatrix}\begin{pmatrix}R_1(\psi_1,\psi_2)\\ R_2(\psi_1,\psi_2)\end{pmatrix}$$



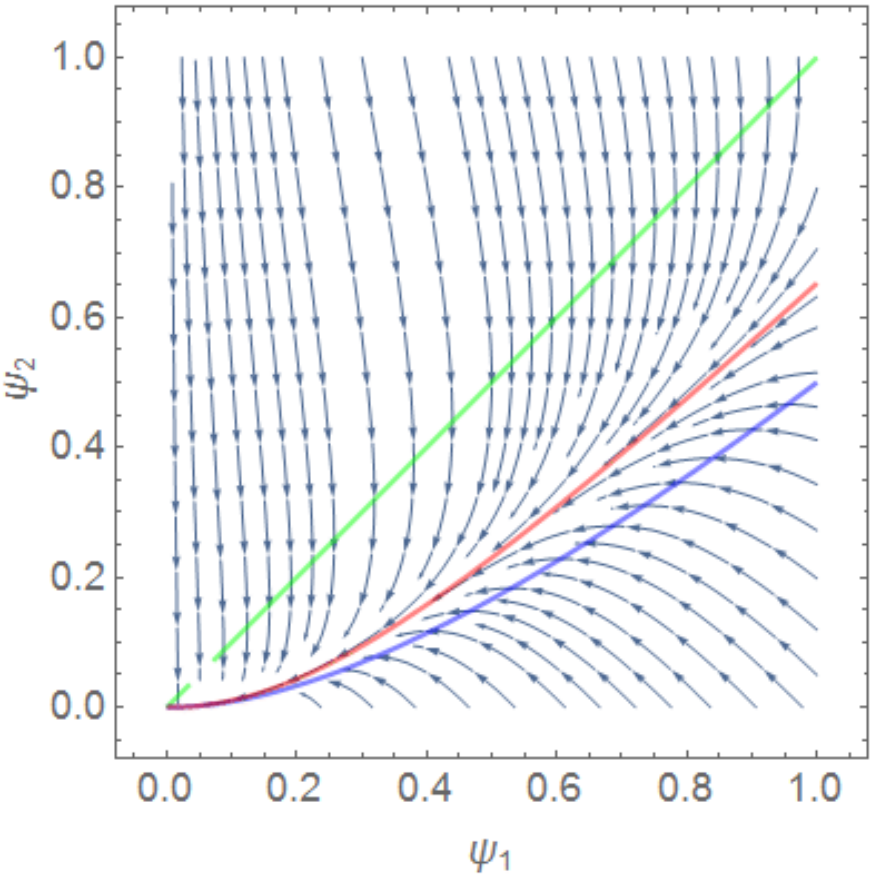

- Typically system solution has particular properties: relatively fast transient following smooth evolution towards global equilibrium

$$K_1 = 1, \quad K_2 = 0.1$$



# Solution III: ILDM application – Lindemann mechanism

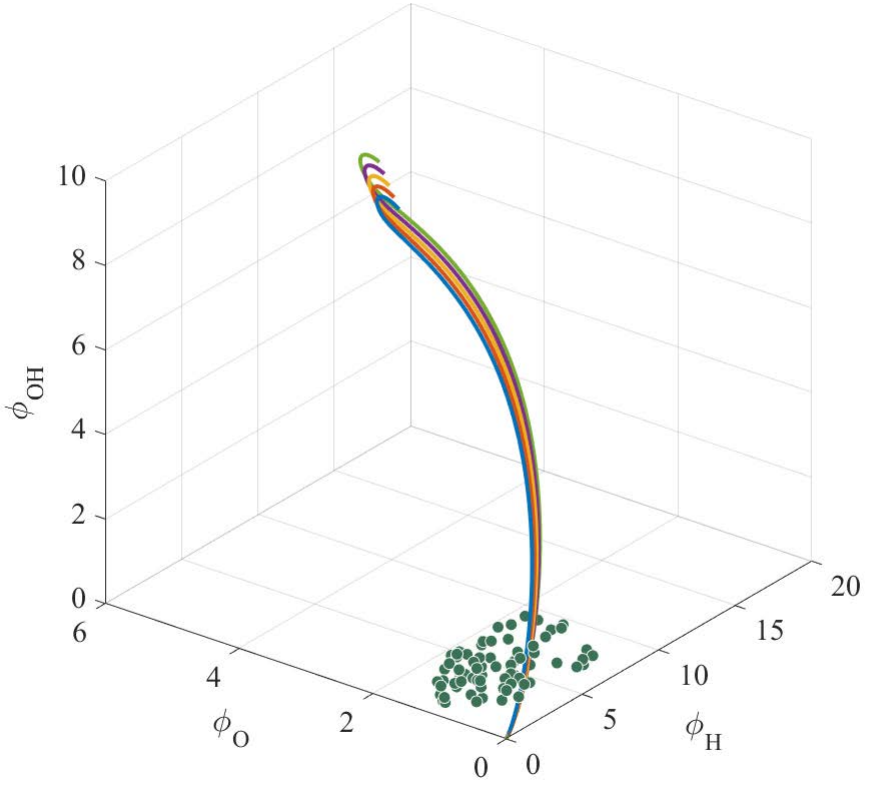
- ILDM, PEA and QSSA are compared
- Decomposition is identified automatically and independently on particular choice
- Thus, the main problem of the empirical choice is overcome!




Green line is PEA curve, red line represents QSSA, while red line represents ILDM curve

# Application: Auto-ignition problem

- Rigorous time scale analysis allows us




- State space projection into O-H-OH space with trajectories calculated based on detailed kinetics model (coloured lines). Green points are the candidate selected points.