

COST CM1404 Training School on the analysis, uncertainty quantification, validation, optimization and reduction of detailed combustion mechanisms for practical use of smart energy carriers

Lecture 1-2

Local sensitivity analysis



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Local sensitivity analysis

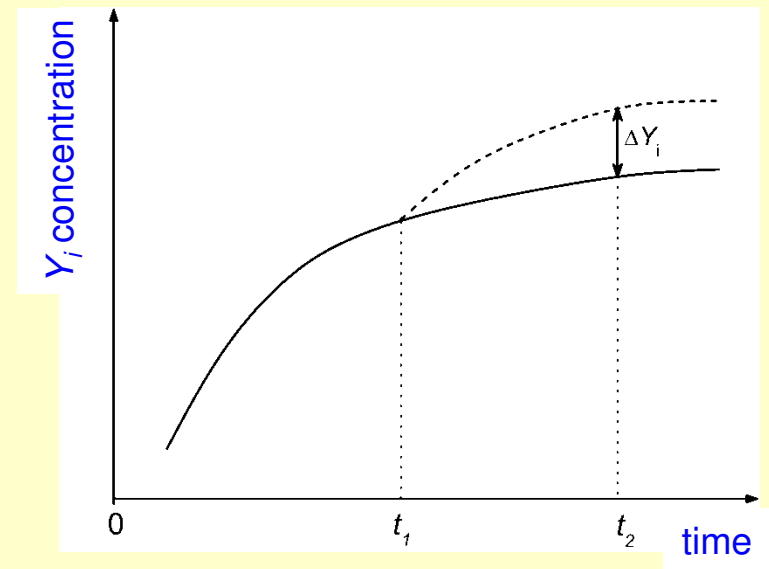
Sensitivity analysis is a family of mathematical methods. It investigates the dependence of the model results on the values of the parameters

Local sensitivity analysis: investigates the effect of the small change of parameters

Local sensitivity coefficients can be investigated by a finite difference approximation:

$$\frac{\partial Y_i}{\partial p_j}(t_1, t_2) \approx \frac{\Delta Y_i(t_2)}{\Delta p_j} = \frac{Y_i'(t_2) - Y_i(t_2)}{\Delta p_j}$$

parameter is changed at time t_1
the result is observed at time t_2



Local sensitivity analysis 2

Another approach: Taylor series expansion

$$Y_i(t, \mathbf{p} + \Delta \mathbf{p}) = Y_i(t, \mathbf{p}) + \sum_{j=1}^m \frac{\partial Y_i}{\partial p_j} \Delta p_j + \frac{1}{2} \sum_{k=1}^m \sum_{j=1}^m \frac{\partial^2 Y_i}{\partial p_k \partial p_j} \Delta p_k \Delta p_j + \dots$$

Local sensitivity coefficient: $s_{ik} = \frac{\partial Y_i}{\partial p_k}$

Local sensitivity matrix: $\mathbf{S} = \left\{ \frac{\partial Y_i}{\partial p_k} \right\}$

The effect of parameter changes can be estimated using local sensitivities:

Changing a single parameter: $Y_i'(t_2) = Y_i(t_2) + \frac{\partial Y_i}{\partial p_j} \Delta p_j$

Changing several parameters: $\mathbf{Y}'(t_2) = \mathbf{Y}(t_2) + \mathbf{S}(t_1, t_2) \Delta \mathbf{p}(t_1)$

Local sensitivity analysis 3

$$\frac{d\mathbf{Y}}{dt} = \mathbf{f}(\mathbf{Y}, \mathbf{p})$$

$$\mathbf{Y}(t_0) = \mathbf{Y}_0$$

Differentiation with respect p_j

$$\frac{d}{dt} \frac{\partial \mathbf{Y}}{\partial p_j} = \mathbf{J} \frac{\partial \mathbf{Y}}{\partial p_j} + \frac{\partial \mathbf{f}}{\partial p_j} \quad \frac{\partial \mathbf{Y}}{\partial p_j}(t_0) = 0 \quad j = 1, 2, \dots, m$$

The same equation with matrix-vector notation:

$$\dot{\mathbf{S}} = \mathbf{J}\mathbf{S} + \mathbf{F}, \quad \mathbf{S}(0) = \mathbf{0}$$

where $\mathbf{J} = \left\{ \frac{\partial f_i}{\partial Y_j} \right\}$ $\mathbf{F} = \left\{ \frac{\partial f_j}{\partial p_k} \right\}$

indirect effect

direct effect

Initial concentration sensitivities

initial concentration sensitivities: the consequence of changing the initial conc. can be calculated with finite differences:

$$\frac{\partial Y_i}{\partial Y_j(t_1)}(t_2) \approx \frac{\Delta Y_i(t_2)}{\Delta Y_j(t_1)} = \frac{Y_i'(t_2) - Y_i(t_2)}{\Delta Y_j(t_1)}$$

kinetic system of ODEs: $\frac{d\mathbf{Y}}{dt} = \mathbf{f}(\mathbf{Y}, \mathbf{p}) \quad \mathbf{Y}(t_0) = \mathbf{Y}_0$

Differentiating it with respect to $Y_j(t_1)$:

$$\frac{d}{dt} \frac{\partial \mathbf{g}}{\partial Y_j^0(t_1)} = \mathbf{J} \frac{\partial \mathbf{g}}{\partial Y_j^0(t_1)} \quad \frac{\partial \mathbf{Y}}{\partial Y_j^0(t_1)}(t_1) = \boldsymbol{\delta}_j \quad j = 1, 2, \dots, n$$

$$\frac{d}{dt} \mathbf{G}(t, t_1) = \frac{\partial \mathbf{f}}{\partial \mathbf{Y}}(t) \mathbf{G}(t, t_1) \quad \mathbf{G}(t_1, t_1) = \mathbf{I}$$

at time t_1 the initial value of variable j is changed and the effect is read at time t_2

$$g_{ij}(t, t_1) = \frac{\partial Y_i(t)}{\partial Y_j^0(t_1)} \quad \mathbf{g}_j(t, t_1) = \frac{\partial \mathbf{Y}(t)}{\partial Y_j^0(t_1)} \quad \text{Green function matrix } \mathbf{G}$$

Calculation of local sensitivity coefficients

1 Brute force method (finite difference approximation)

$$\frac{\partial Y_i}{\partial p_j}(t_2) \approx \frac{\Delta Y_i(t_2)}{\Delta p_j(t_1)} = \frac{Y_i(t_2) - Y_i(t_2)}{\Delta p_j(t_1)}$$

Δp_j small: large error caused by the limited number of digits handled by the computer

Δp_j large: large error due to nonlinearity

2 Direct method

2a. Coupled direct method:

coupled solution of the kinetic and sensitivity differential equations:

$$\frac{d\mathbf{Y}}{dt} = \mathbf{f}(\mathbf{Y}, \mathbf{p})$$

$$\mathbf{Y}(t_0) = \mathbf{Y}_0$$

$$\frac{d}{dt} \frac{\partial \mathbf{Y}}{\partial p_j} = \mathbf{J} \frac{\partial \mathbf{Y}}{\partial p_j} + \frac{\partial \mathbf{f}}{\partial p_j}$$

$$\frac{\partial \mathbf{Y}}{\partial p_j}(t_0) = 0$$

The coupled solution is repeated for each parameter:

$$j = 1, 2, \dots, m$$

Lots of unnecessary calculations.

Calculation of local sensitivity coefficients 2

2b. Decoupled Direct Method (DDM):

joint solution of the kinetic and sensitivity diff. equations in each step:

$$\frac{d\mathbf{Y}}{dt} = \mathbf{f}(\mathbf{Y}, \mathbf{p})$$

$$\mathbf{Y}(t_0) = \mathbf{Y}_0$$

$$\frac{d}{dt} \frac{\partial \mathbf{Y}}{\partial p_j} = \mathbf{J} \frac{\partial \mathbf{Y}}{\partial p_j} + \frac{\partial \mathbf{f}}{\partial p_j}$$

$$\frac{\partial \mathbf{Y}}{\partial p_j}(t_0) = 0$$

$$j = 1, 2, \dots, m$$

The Jacobian of these equations are identical, therefore in each step

⇒ transformation of the Jacobian to a triangle matrix

⇒ selection of stepsize Δt based on the Jacobian

⇒ solution of the stiff ODE: calculation of new \mathbf{Y}

⇒ calculation of the new sensitivity vector for parameter $j=1$
using the same triangle matrix

⇒ ⇒ ⇒ ⇒ ⇒ repeating for all parameters $j = 1, 2, \dots, m$

⇒ ⇒ repeating for new time steps from the transformation of \mathbf{J}

features:

- very fast method; the computer time only slightly increases with the number of parameters m (because the transformation of \mathbf{J} is the most time consuming)
- the accuracy of solution can be controlled

Automatic differentiation

The simulation result calculated on a computer is obtained by a sequence of simple operations such as additions, multiplications, and elementary functions such as sines and cosines.

By applying the chain rule over and over again to these simple operations it is possible to calculate the derivatives to machine precision in an automatic way.

ADIFOR: a Fortran simulation code is converted by a program to a modified code for the calculation of the local sensitivity coefficients

Bischof, C., Carle, A., Khademi, P., Mauer: The ADIFOR 2.0 system for the automatic differentiation of FORTRAN 77 programmes. *IEEE J. Comput. Sci. Eng.* **3**, 18-32. (1996)

ADIC: a C simulation code is converted by a program to a modified code for the calculation of the local sensitivity coefficients

Bischof, C.H., Roh, L., Mauer-Oats, A.J.: ADIC: an extensible automatic differentiation tool for ANSI-C. *Soft. Pract. Exper.* **27**, 1427-1456 (1997)

Interpretation of local sensitivity coefficients

$$s_{ik} = \frac{\partial Y_i}{\partial p_k}$$

(Original) local sensitivity coefficients:
the parameter is changed by one unit
inspected: the result is changed by how many units
[unit of result / unit of parameter]

Normalized local sensitivity coefficients:

$$\tilde{s}_{ik} = \frac{p_k}{Y_i} \frac{\partial Y_i}{\partial p_k} = \frac{\partial \ln Y_i}{\partial \ln p_k}$$

investigates relative changes
How much % change of the result
due to 1 % change of the parameter?
dimension free

So far: **single parameter** is changed
effect on a **single model result** is investigated

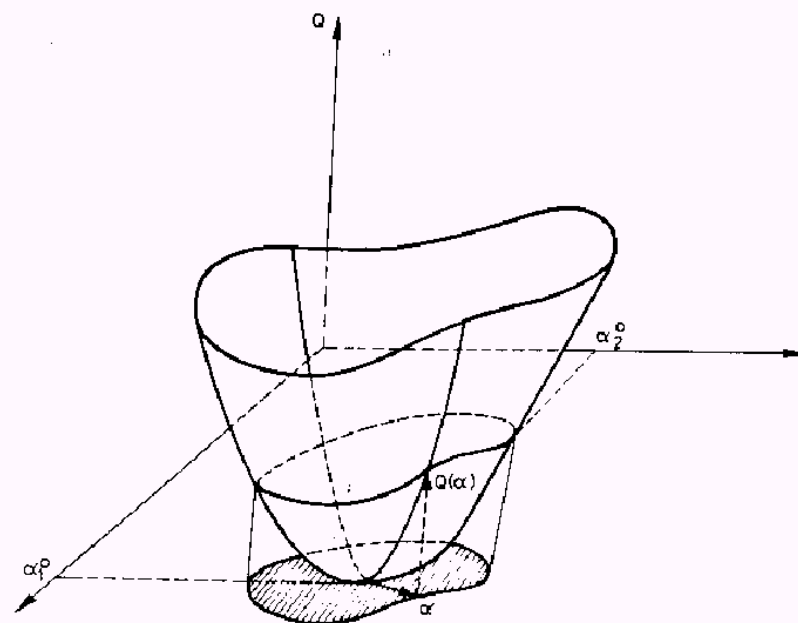
Further information can also be extracted from sensitivity matrix **S**
using principal component analysis, like the case when
several parameters are changed simultaneously, and
the effect on **multiple model results** is investigated.

PCAS: principal component analysis of the sensitivity matrix S

Several parameters are changed simultaneously and the effect on several model outputs is investigated.

The effect of changing parameters is measured by an objective function:

$$e(\mathbf{p}) = \int_{t_1}^{t_2} \sum_{i=1}^m \left(\frac{Y_i^*(t) - Y_i(t)}{Y_i(t)} \right)^2 dt$$



PCAS: principal component analysis of the sensitivity matrix S

The objective function can be approximated by:

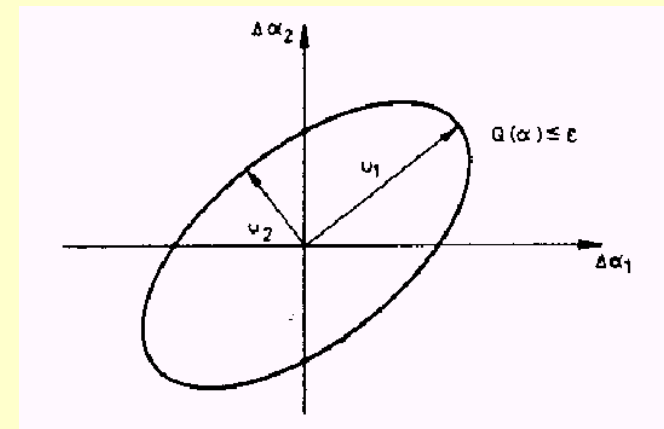
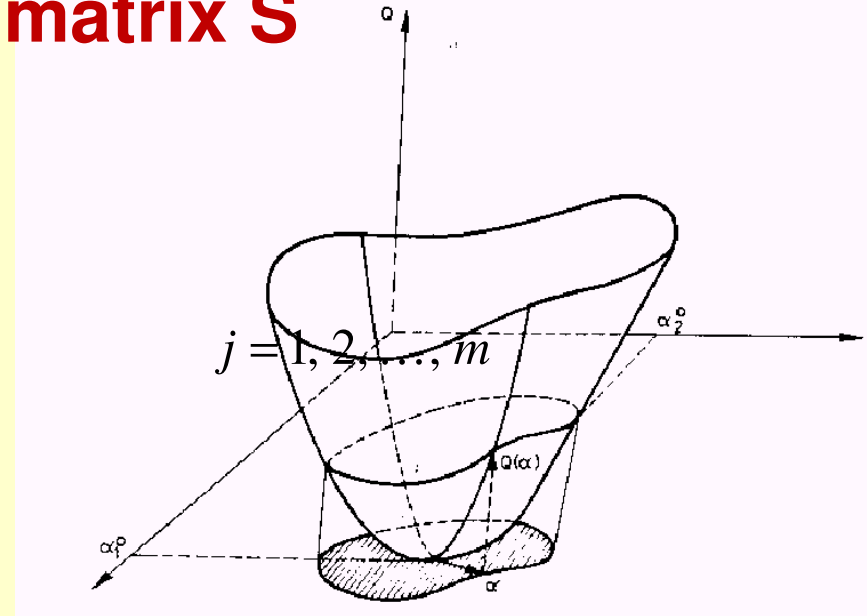
$$e(\boldsymbol{\alpha}) = (\Delta \boldsymbol{\alpha})^T \tilde{S}^T \tilde{S} (\Delta \boldsymbol{\alpha})$$

where

$$\Delta \boldsymbol{\alpha} = \Delta \ln \mathbf{p} \quad \tilde{S} = \begin{bmatrix} \tilde{S}_1 \\ \tilde{S}_2 \\ \vdots \\ \tilde{S}_n \end{bmatrix}$$

And the normed sensitivity matrix belonging to time t_r

$$\tilde{S}_r = \left\{ (p_k / Y_i) (\partial Y_i(t_r) / \partial p_k) \right\}$$



PCAS: principal component analysis of the sensitivity matrix S

$$e(\boldsymbol{\alpha}) = (\Delta\boldsymbol{\alpha})^T \tilde{S}^T \tilde{S} (\Delta\boldsymbol{\alpha})$$

This quadratic form determines a (hyper) ellipsoid:

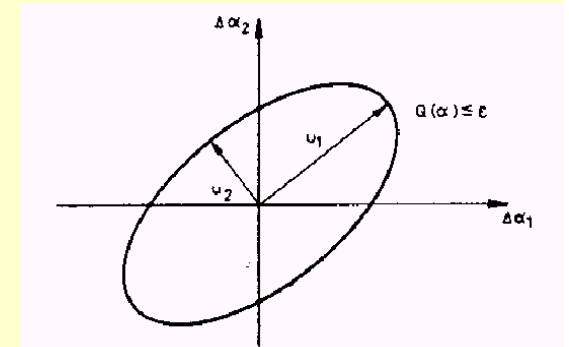
- 2D ellipse
- 3D ellipsoid (rugby ball shape)
- 4D hyper ellipsoid

Another characterization of the hyper ellipsoid:

- length of the axes
- direction of the axes

Eigenvalue-eigenvector decomposition of matrix $\tilde{S}^T \tilde{S}$

- λ_i eigenvalue i = length of axis i
if λ_i is small: the objective function increases rapidly to this direction
= parameter group i is highly influential
- \mathbf{u}_i eigenvector i = direction of axis i



PCAS: principal component analysis of the sensitivity matrix S

$$e(\boldsymbol{\alpha}) = (\Delta\boldsymbol{\alpha})^T \tilde{S}^T \tilde{S} (\Delta\boldsymbol{\alpha})$$

An alternative form of the objective function:

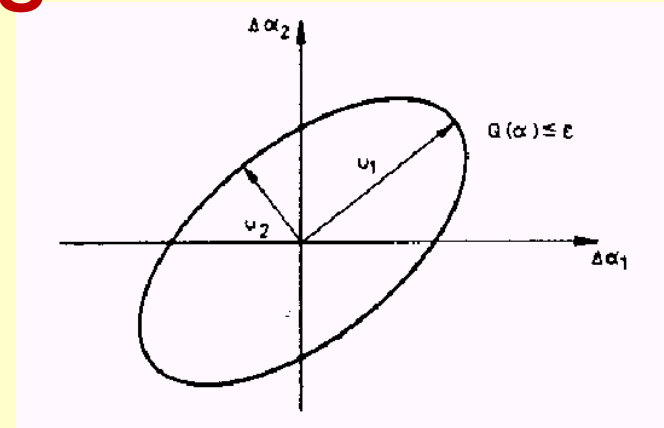
$$e(\boldsymbol{\alpha}) = \sum_{i=1}^r \lambda_i (\Delta\Psi_i)^2$$

where $\Delta\Psi_i = \mathbf{u}_i \boldsymbol{\alpha}$ transformed parameters called principal components

In the figure above:

λ_1 large; $\mathbf{u}_1 = (0,707, 0,707)$

λ_2 small; $\mathbf{u}_2 = (-0,707, 0,707)$



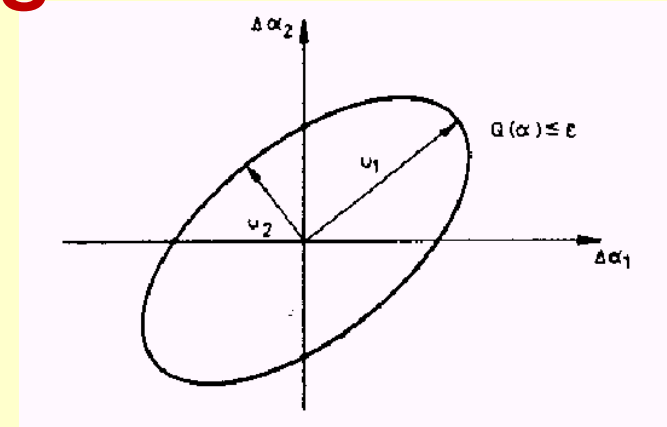
Note: the eigenvectors are unit vectors, therefore $0,707^2 + 0,707^2 = 1$

PCAS: principal component analysis of the sensitivity matrix S

Example:

λ_1 small \Rightarrow axis 1 is long; $\mathbf{u}_1 = (0.707, 0.707)$

λ_2 large \Rightarrow axis 2 is short; $\mathbf{u}_2 = (-0.707, 0.707)$



axis 1 is long \rightarrow changing the parameters to direction \mathbf{u}_1
the objective function changes little

\rightarrow if $\alpha_2 - \alpha_1 = \ln p_2 - \ln p_1 = \ln(p_2/p_1)$ constant, \Rightarrow little change of the objective function

\rightarrow if p_2/p_1 constant, \Rightarrow little change of the objective function

Thus, eigenvector $\mathbf{u} = (0.707, 0.707)$ means that keeping the ratio of the corresponding two parameters constant the inspected result(s) of simulation do not change.

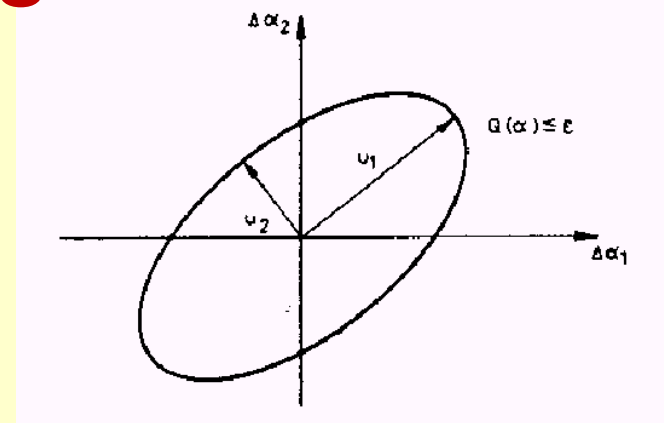
PCAS: principal component analysis of the sensitivity matrix S

Example 2:

$\mathbf{u}_1 = (0.707, 0.707, 0)$ large eigenvalue

$\mathbf{u}_2 = (-0.707, 0.707, 0)$ small eigenvalue

$\mathbf{u}_3 = (0, 0, 1)$ large eigenvalue



Interpretation of the eigenvectors:

p_1/p_2 and p_3 can be determined from the experimental data

p_3 can be determined independently

Only the ratio of p_1 and p_2 can be determined.

T. Perger, T. Kovács, T. Turányi, C. Treviño:

Determination of adsorption and desorption parameters from ignition temperature measurements in catalytic combustion systems, *J. Phys. Chem. B*, **107**, 2262-2274 (2003)

Local uncertainty analysis

If the parameters are correlated, then using the rule of spread of errors the uncertainty of model results can be calculated from the correlation matrix of parameters:

$$\sigma_Y = \mathbf{S}^T \Sigma_p \mathbf{S}$$

Here Σ_p is the covariance matrix of parameters, \mathbf{S} is the sensitivity matrix and σ_Y is the variance of simulation results.

If the parameters are uncorrelated, then variance $\sigma^2(y)$ of model result y can be calculated from the variance of parameters: $\sigma^2(p_k)$

$\sigma_k^2(y)$ is the contribution of parameter k to the variance of model result y

$$\sigma_k^2(y) = \sigma^2(p_k) \left(\frac{\partial y}{\partial p_k} \right)^2 \quad \sigma^2(y) = \sum_k \sigma_k^2(y)$$

T. Turányi, L. Zalotai, S. Dóbbé, T. Bérces: Effect of the uncertainty of kinetic and thermodynamic data on methane flame simulation results
Phys. Chem. Chem. Phys., **4**, 2568-2578 (2002)

Local uncertainty analysis 2

- Linear approximation of the variance of the model result
- Does not take into account the nonlinear effects
- The result belongs to the nominal set of model parameters
- Realistic results, if the model behaves qualitatively similarly in the whole domain of parameters
- Non-realistic results, if the model is qualitatively different in the various parts of the parameter domain
- Provides separately the contribution of parameters
- Can be calculated fast

Example: the uncertainty of methane flame simulation results

The investigated methane flames:

- one dimensional, adiabatic, freely propagating, laminar, premixed stationary flame investigated at equivalence ratios $\phi = 0.70$ (lean), 1.00 (stoichiometric), and 1.20 (rich)
- cold boundary conditions $p = 1.0$ atm and $T = 298.15$ K

Monitored outputs:

- laminar flame velocity
- maximum temperature
- maximum species concentration of H, O, OH, CH, CH₂

Uncertainty analysis of a laminar methane flame

Leeds Methane Oxidation Mechanism:
37 species and 175 reversible reactions
stationary, laminar 1D simulations

37 species: the recommended values of the enthalpies of formation and their variance was calculated from thermodynamic databases

175 reactions: uncertainty parameteres f were collected from Baulch *et al.*

The investigated simulation results:

maximal flame temperature, laminar flame velocity,
maximal concentrations of radicals H, O, OH, CH, CH₂

Uncertainty analysis methods:

local uncertainty analysis, Morris' method,
Monte Carlo with Latin Hypercube sampling, sensitivity indices

J. Zádor, I. Gy. Zsély, T. Turányi, M. Ratto, S. Tarantola, A. Saltelli: Local and global uncertainty analyses of a methane flame model, *J. Phys. Chem. A*, **109**, 9795-9807 (2005)

Local uncertainty analysis of chemical kinetic models

$f_j \rightarrow \sigma^2(\ln k_j)$ uncertainty parameter f_j is transformed to the variance of $\ln k_j$

$\partial Y_i / \partial \ln k_j$ seminormalized local sensitivity coefficients

$$\sigma_{Kj}^2(Y_i) = \left(\partial Y_i / \partial \ln k_j \right)^2 \sigma^2(\ln k_j)$$

contribution of the uncertainty of parameter k_j to the variance of result Y_i

$$\sigma_K^2(Y_i) = \sum_j \sigma_{Kj}^2(Y_i) \quad \text{variance of result } Y_i \text{ due to kinetic uncertainties}$$

$$\sigma_{Tj}^2(Y_i) = \left(\partial Y_i / \partial \Delta_f H_{298}^\circ(j) \right)^2 \sigma^2(\Delta_f H_{298}^\circ(j))$$

contribution of the uncertainty of the enthalpy of formation of species j to the variance of result Y_i

$$\sigma^2(Y_i) = \sigma_K^2(Y_i) + \sigma_T^2(Y_i) = \sum_j \sigma_{Kj}^2(Y_i) + \sum_j \sigma_{Tj}^2(Y_i)$$

estimated total variance of result Y_i from both kinetic and thermodynamic uncertainties

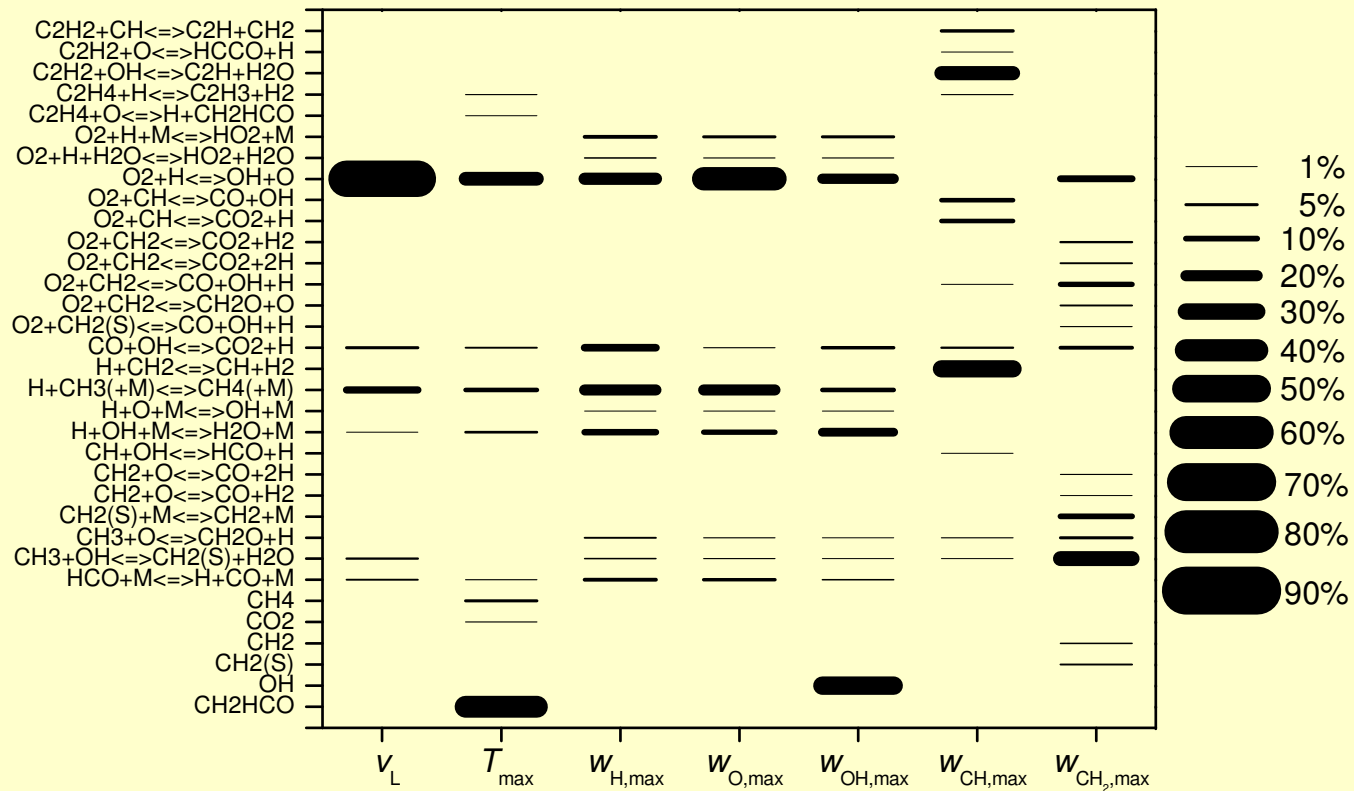
T. Turányi, L. Zalotai, S. Dóbbé, T. Bérces:

Effect of the uncertainty of kinetic and thermodynamic data on methane flame simulation results

Phys.Chem.Chem.Phys., **4**, 2568-2578 (2002)

Local uncertainty analysis results

% contribution of parameter uncertainties to the uncertainty of the simulated results



$$\phi = 1.0$$

Comparison of the results of local and global (Monte Carlo) uncertainty analyses for a stoichiometric, stationary, flat methane-air flame

	result	calculated variances from local Monte Carlo uncertainty analyses	
flame velocity	38.1 cm/s	4.6 cm/s	6.2 cm/s
max. T	2224.2 K	2.8 K	1.7 K
max. w_H	2.14×10^{-4}	14.7%	12.6%
max. w_O	1.74×10^{-3}	13.3%	10.4%
max. w_{OH}	5.27×10^{-3}	3.6%	4.0%
max. w_{CH}	8.07×10^{-7}	46.3%	49.2%
max. w_{CH_2}	2.54×10^{-5}	23.8%	24.0%

Largest and smallest results that can be achieved with any parameter combination, selected from the domain of uncertainty of the parameters

	nominal simulation result	minimal achievable result	maximal
flame velocity	38.1 cm/s	21.3 cm/s	61.6 cm/s
max. T	2224.2 K	2217.4 K	2228.6 K
max. w_H	2.14×10^{-4}	63.1%	144.4%
max. w_O	1.74×10^{-3}	66.9%	136.1%
max. w_{OH}	5.27×10^{-3}	86.4%	114.8%
max. w_{CH}	8.07×10^{-7}	15.5%	474.6%
max. w_{CH_2}	2.54×10^{-5}	37.9%	219.5%

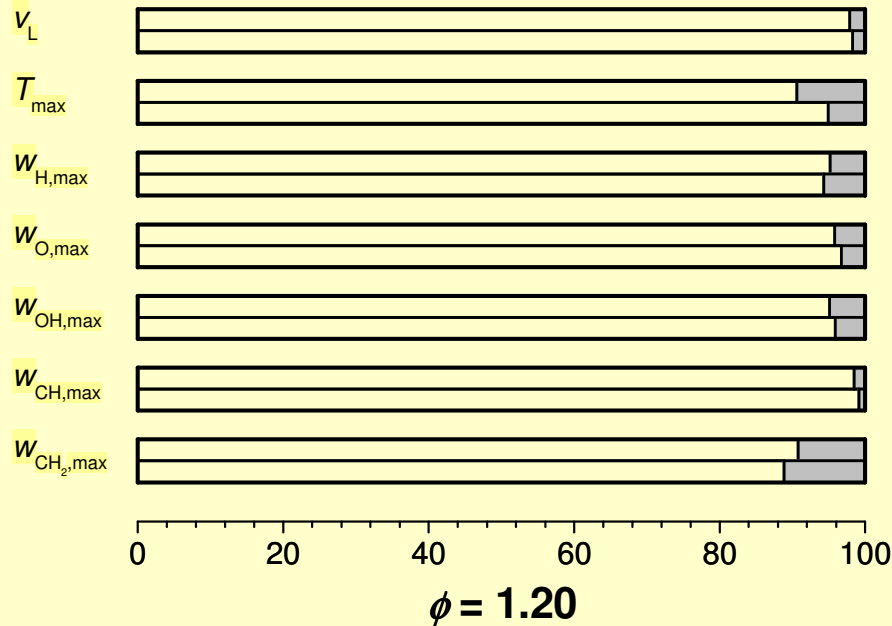
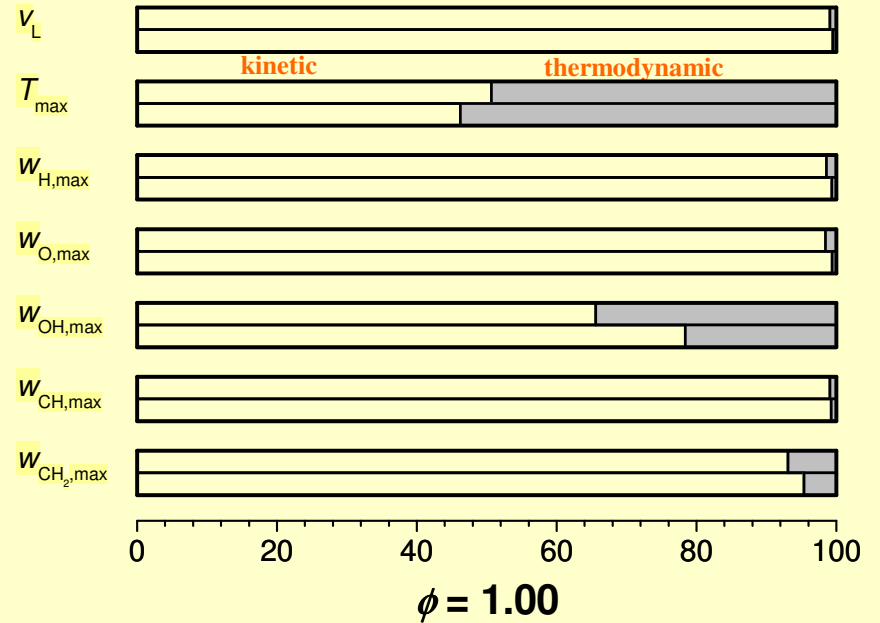
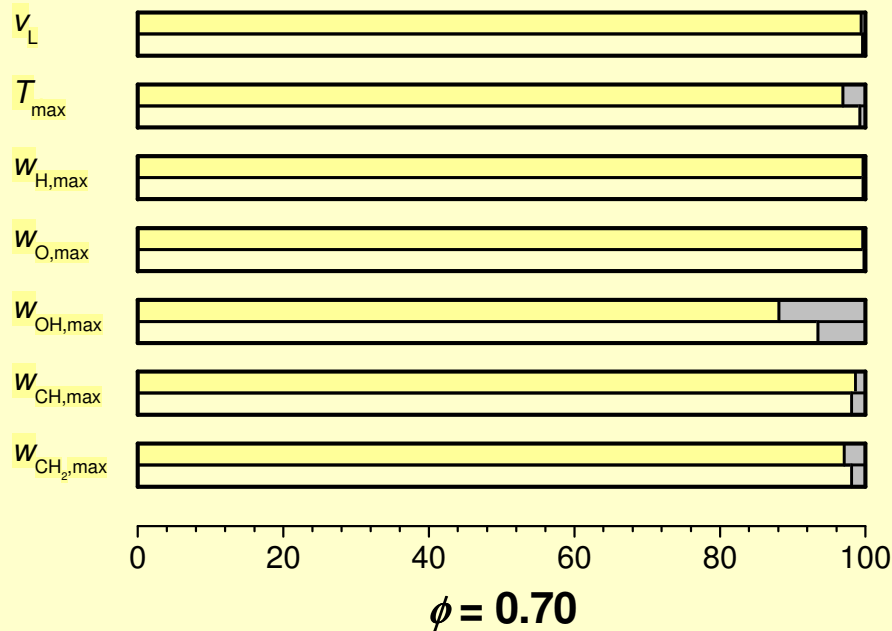
Conclusion:

Physically unrealistic results can be obtained, even if the parameters were randomly selected from the uncertainty ranges recommended by the gas kinetics databases.

Reasons: (1) these uncertainties are based on direct measurements;

(2) correlations of uncertainties are not taken into account.

Kinetic vs. thermodynamic contributions



upper bar: local results
lower bar: sensitivity index results

Share of thermodynamic uncertainty:
1%-12%. except for the
calculated temperature and w_{OH}
at stoichiometric conditions

Methane flame uncertainty analysis: general conclusions

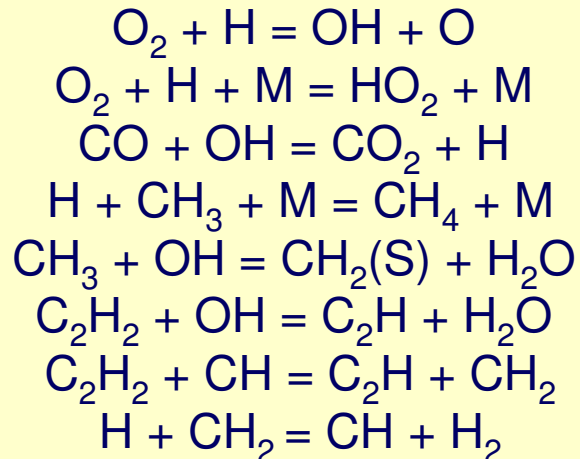
Good agreement between the calculated total variances by the local uncertainty analysis and the Monte Carlo method. (surprise)

Good agreement between the importance of parameters assessed by the local uncertainty analysis and the sensitivity indices. (surprise)

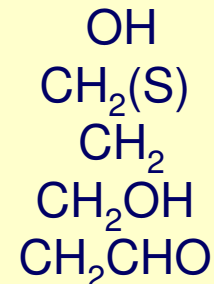
Better simulation results can be achieved, if the rate coefficients of a few reactions and the enthalpies of formation of a few species are known better (= with smaller variance)

These represent a small fraction of the total number of species/reactions.

Significant rate coefficients:



Significant enthalpies of formation:



The scatter of local sensitivity coefficients

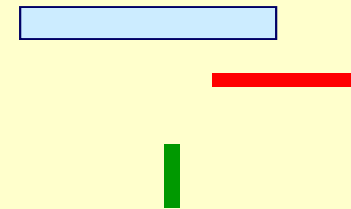
The calculated local sensitivity coefficients belong to a nominal parameter set
different parameter sets \Rightarrow different local sensitivity coefficients
(this is why these are called local ...)

local sensitivity coefficients of flame velocity
were calculated at 3000 randomly selected parameter sets

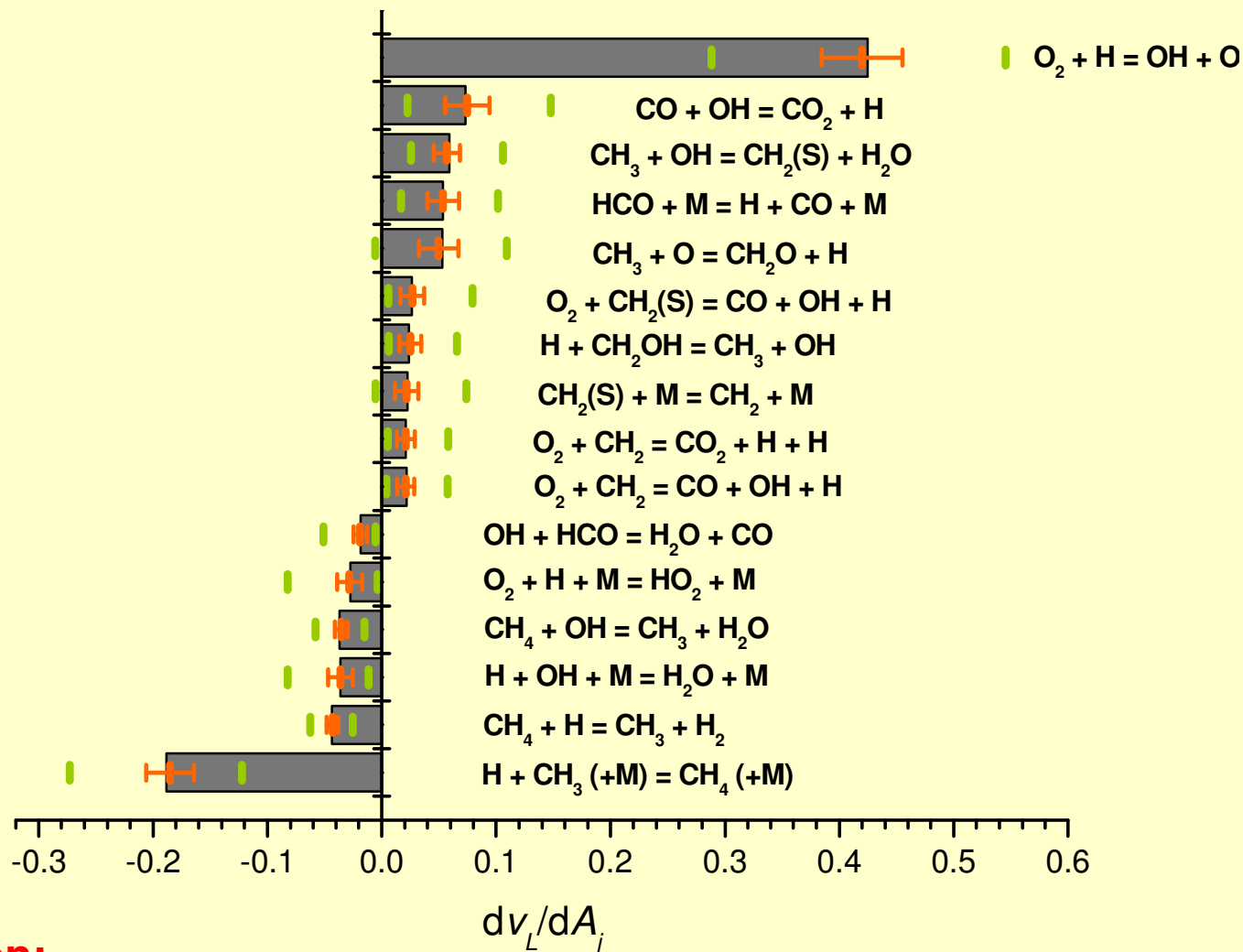
J. Zádor, I. Gy. Zsély, T. Turányi, M. Ratto, S. Tarantola, A. Saltelli: Local and global uncertainty analyses of a methane flame model, *J. Phys. Chem. A*, **109**, 9795-9807 (2005)

The plotted results:

- local sensitivity coefficients at the nominal set
- standard deviation of sensitivities
- the largest and the smallest calculated sensitivity coefficient



The scatter of local sensitivity coefficients 2



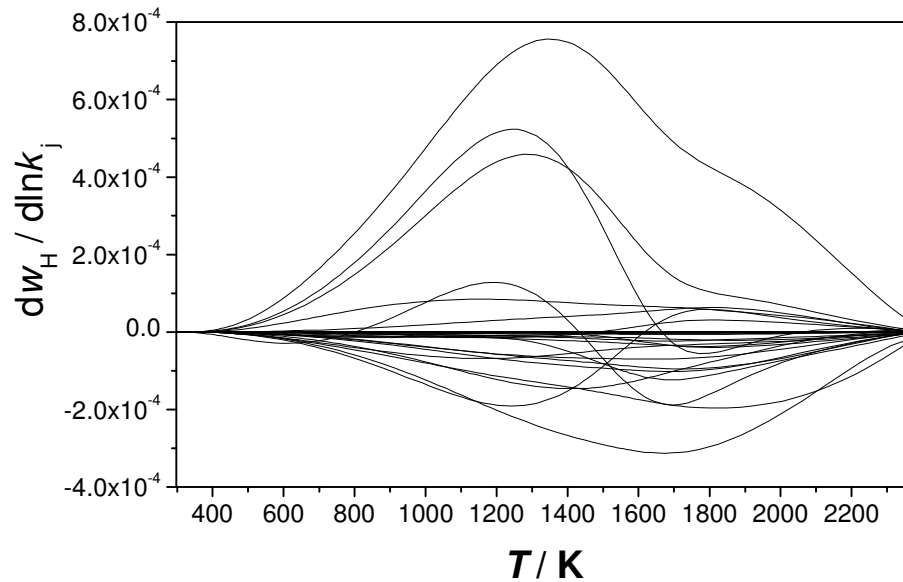
Conclusion:

There is a surprisingly little variation of the calculated local sensitivity coefficients with the changing parameters. The order of sensitivity coefficients is almost identical in the whole parameter space.

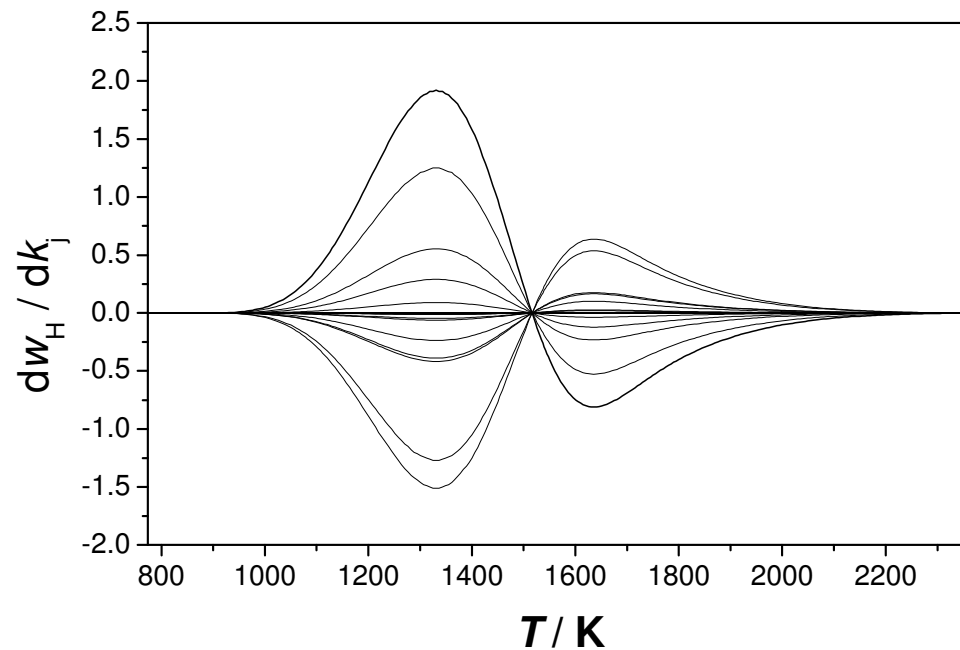
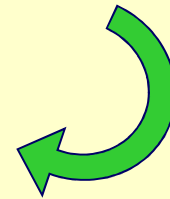
Similarity of sensitivity functions

local similarity and scaling relationships,
the origin of global similarity,
similarity of the sensitivity functions of biological models,
the importance of the similarity of sensitivity functions

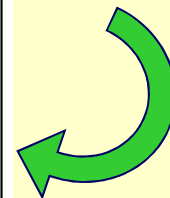
What is the similarity of sensitivity functions?



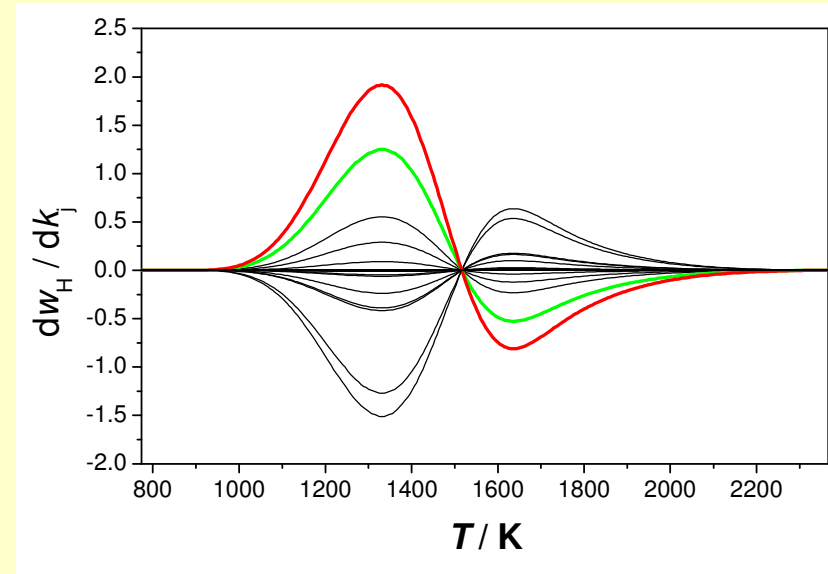
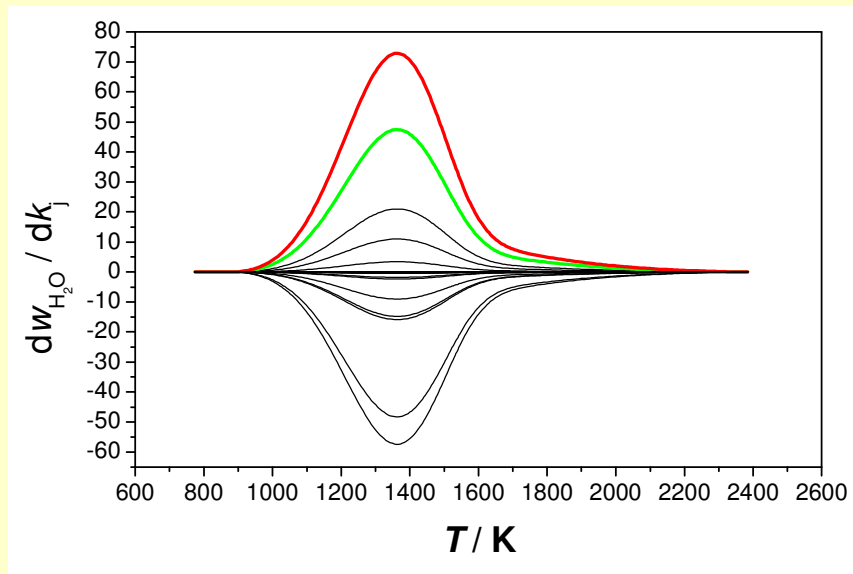
Generally, the sensitivity functions are not related, therefore they usually look scrabled.



Several researchers discovered that in some systems the sensitivity functions look very regularly.



Regularity 1: Local similarity of the sensitivity functions

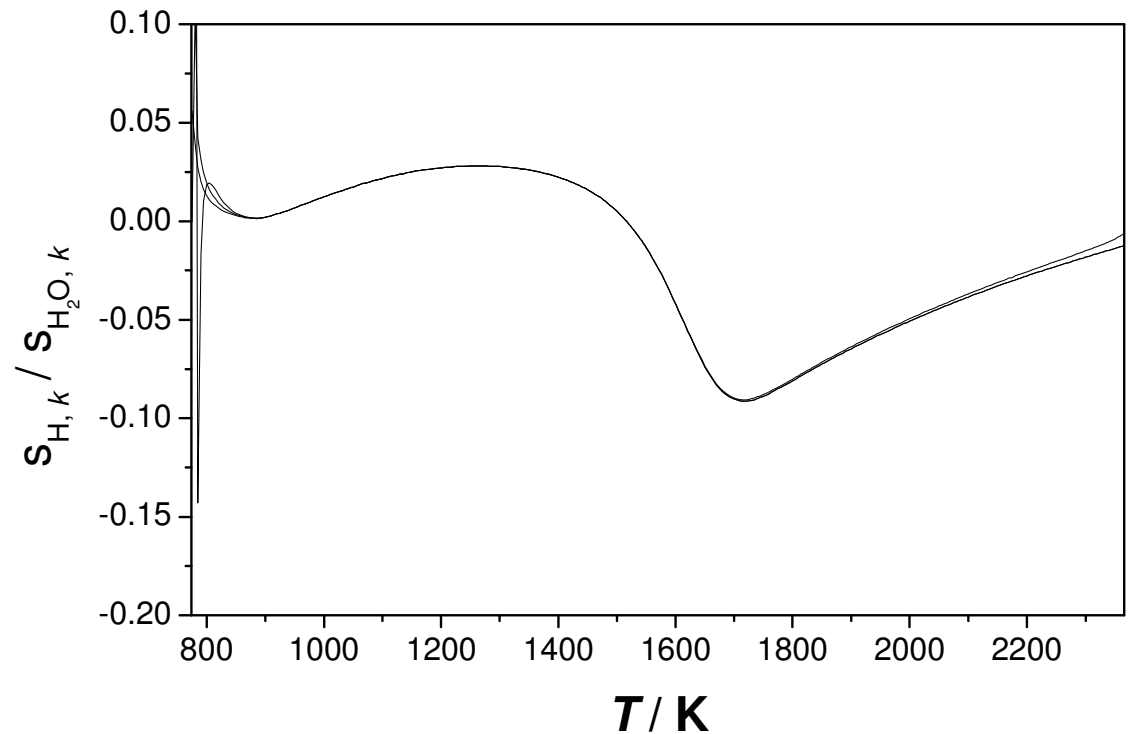


$$\lambda_{ij}(t) = \frac{s_{ik}(t)}{s_{jk}(t)}$$

[red is divided by red, green is divided by green]

Regularity 1: Local similarity of the sensitivity functions 2

$$\lambda_{ij}(t) = \frac{s_{ik}(t)}{s_{jk}(t)}$$



Reuven, Y., Smooke, M.D., Rabitz, H.: Sensitivity analysis of boundary value problems: Application to nonlinear reaction-diffusion systems. *J. Comput. Phys.* **64**, 27-55 (1986)

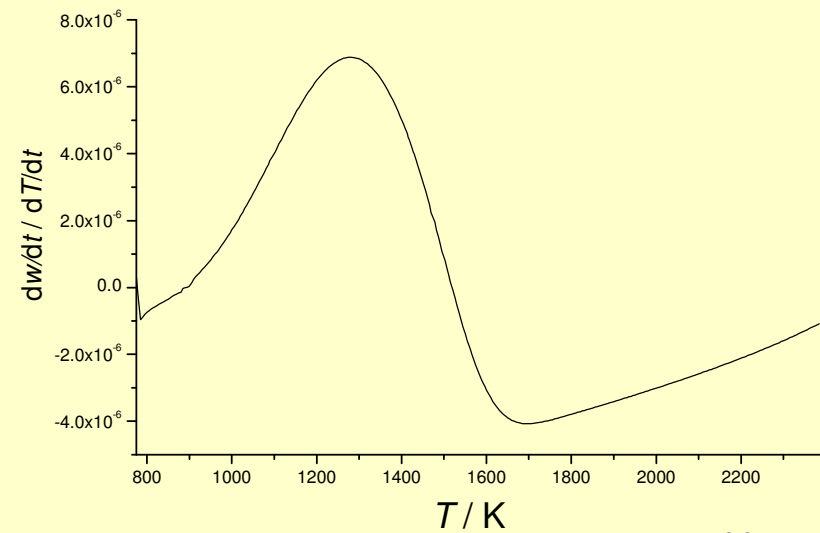
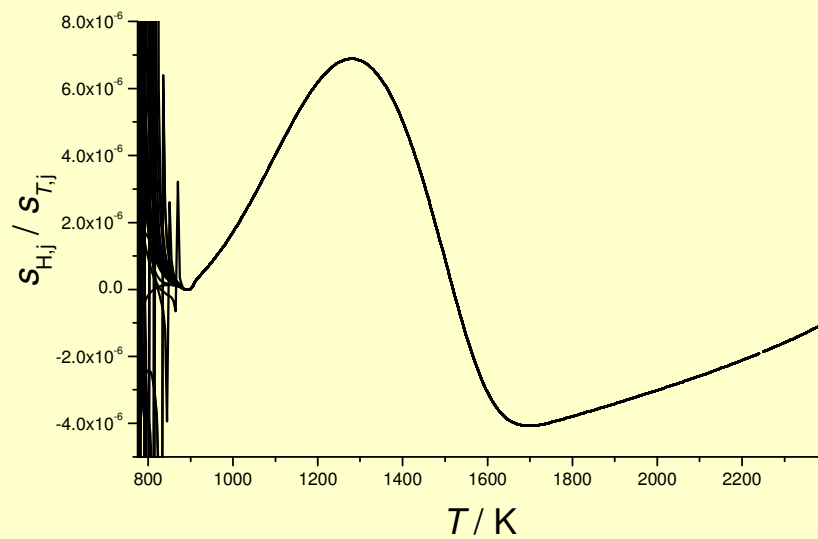
Smooke, M.D., Rabitz, H., Reuven, Y., Dryer, F.L.: Application of sensitivity analysis to premixed hydrogen-air flames. *Combust. Sci. Technol.* **59**, 295-319 (1988)

Regularity 2: Scaling relation

$$\lambda_{ij}(t) = \frac{s_{ik}(t)}{s_{jk}(t)}$$

$$\lambda'_{ij}(t) = \frac{\frac{dY_i}{dt}(t)}{\frac{dY_j}{dt}(t)}$$

$$\lambda_{ij}(t) = \lambda'_{ij}$$

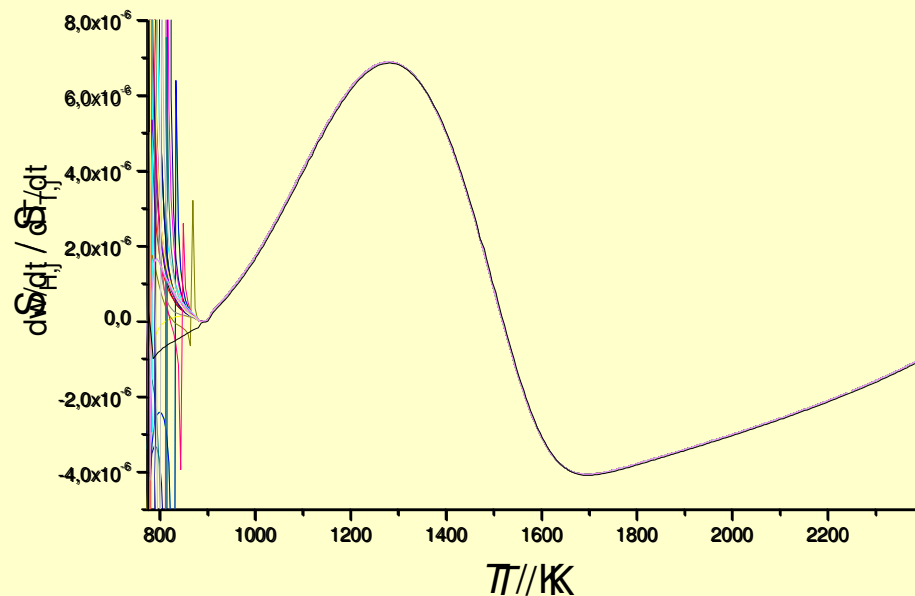


Regularity 2: Scaling relation 2

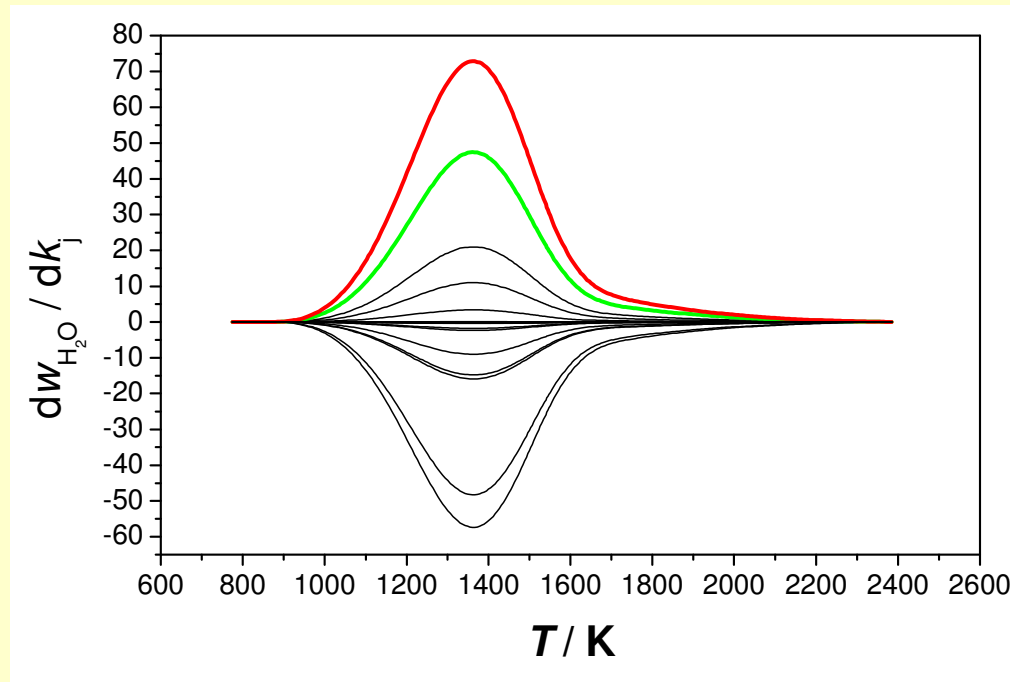
Rabitz, H., Smooke, M.D.: Scaling relations and self-similarity conditions in strongly coupled dynamical systems. *J. Phys. Chem.* **92**, 1110-1119 (1988)

$$\lambda_{i,j}(t) = \frac{s_{i,k}(t)}{s_{j,k}(t)}$$

$$\lambda'_{i,j}(t) = \frac{\frac{dY_i}{dt}(t)}{\frac{dY_j}{dt}(t)}$$



Regularity 3: Global similarity of the sensitivity functions



$$\mu_{ikm}(t) = \frac{s_{ik}(t)}{s_{im}(t)}$$

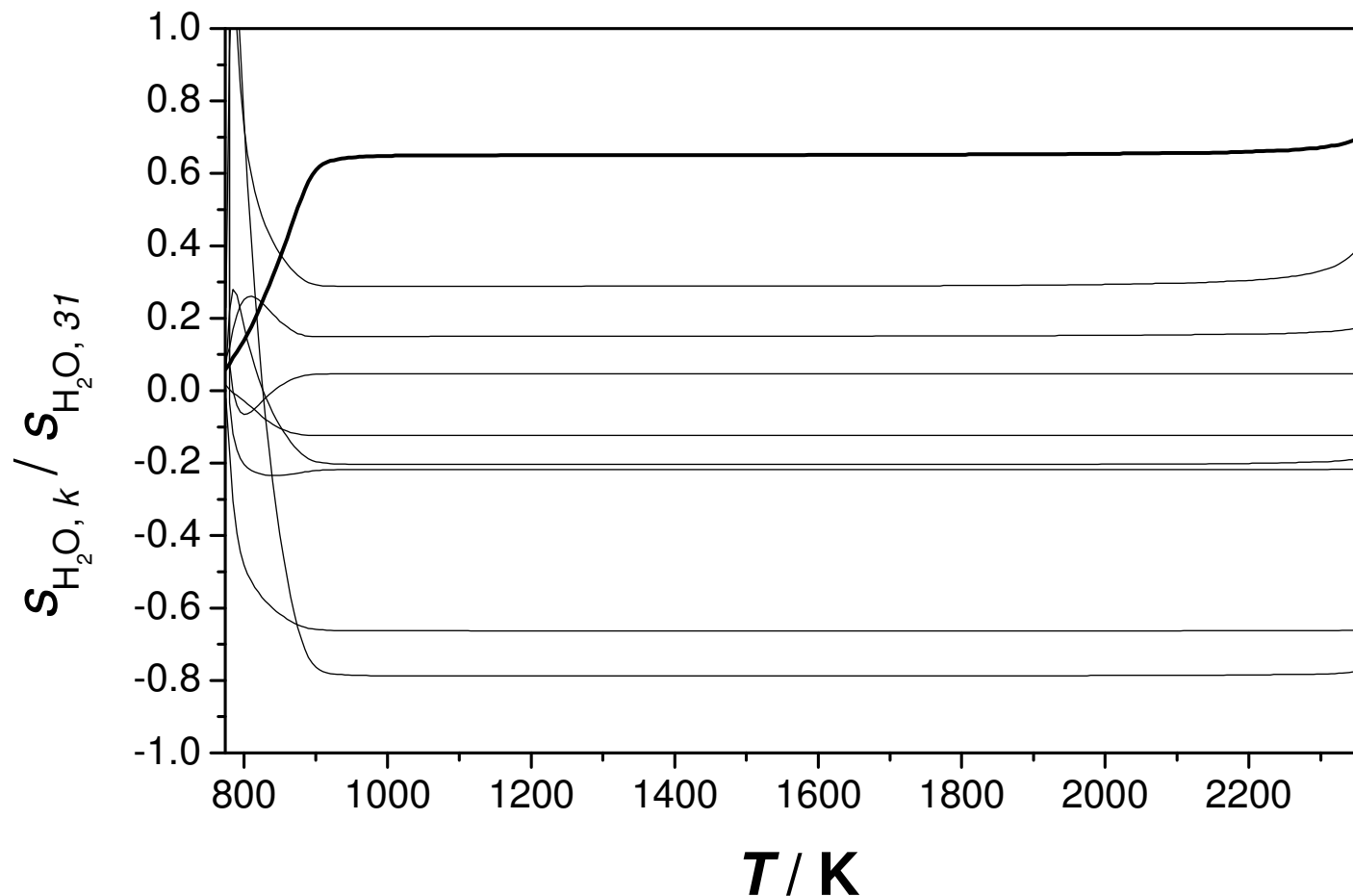
[red is divided by green]

Vajda, S., Rabitz, H.: Parametric sensitivity and self-similarity in thermal explosion theory.
Chem. Engng Sci. **47**, 1063-1078 (1992)

Regularity 3: Global similarity of the sensitivity functions 2

$$\mu_{km} = \frac{s_{ik}(t)}{s_{im}(t)}$$

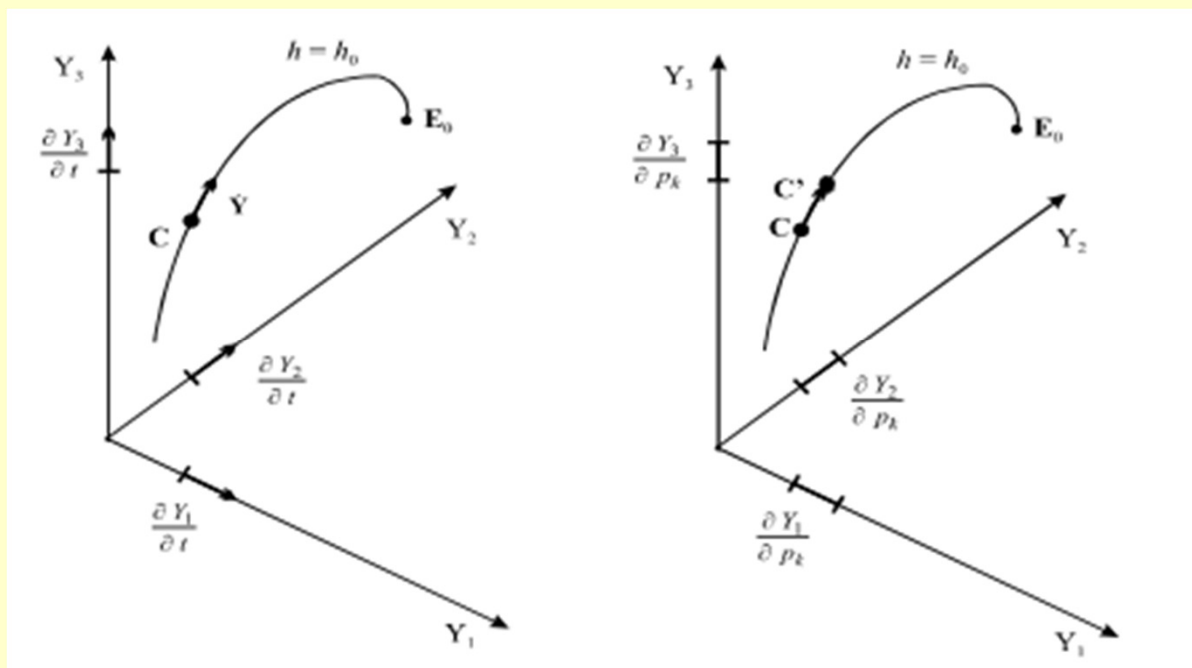
ratio is constant
in a wide range of the independent variable



Origin of local similarity and scaling relation on a 1D manifold – geometry based reasoning

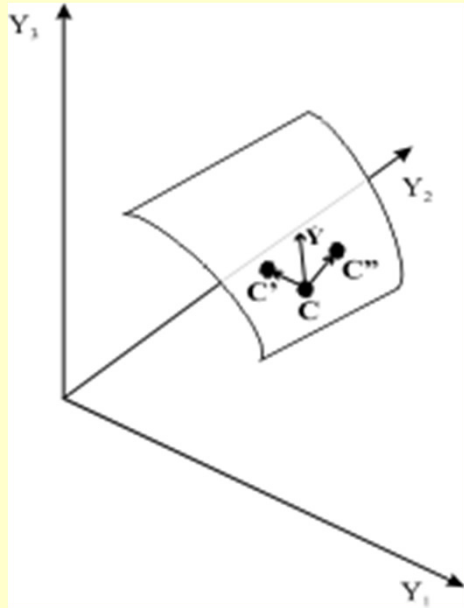
Necessary conditions:

1. The trajectory of the solution follows a 1D manifold
2. 1D manifold is not shifted due to parameter changes



Zsély, I.G., Zádor, J., Turányi, T.: Similarity of sensitivity functions of reaction kinetic models.
J. Phys. Chem. A **107**, 2216-2238 (2003)

Movement on a non-1D manifold



dimension of the manifold is larger than one ($n > 1$)

⇒ the sensitivity vectors are usually not parallel to the vector of production rates

⇒ local similarity and scaling relation will not emerge, but all these vectors are within an n -dimensional subspace

consequence:

dimension of the manifold \geq rank of the sensitivity matrix

Zsély, I.G., Zádor, J., Turányi, T.: On the similarity of the sensitivity functions of methane combustion models. *Combust. Theory Modell.* 9, 721-738 (2005)

Zádor, J., Zsély, I.G., Turányi, T.: Investigation of the correlation of sensitivity vectors of hydrogen combustion models. *Int. J. Chem. Kinet.* 36, 238-252 (2004)

Origin of local similarity and scaling relation on a 1D manifold – calculus based reasoning

equation of 1D manifold:

Y_1 parameterising variable

F_i value of variable i

z independent variable (e.g. time)

$$Y_i(z, \mathbf{p}) = F_i(Y_1(z, \mathbf{p}))$$

Derivation with respect z

$$\frac{\partial Y_i(z, \mathbf{p})}{\partial z} = \frac{\partial F_i}{\partial Y_1} \frac{\partial Y_1(z, \mathbf{p})}{\partial z}$$

Derivation with respect p_j

$$\frac{\partial Y_i(z, \mathbf{p})}{\partial p_j} = \frac{\partial F_i}{\partial Y_1} \frac{\partial Y_1(z, \mathbf{p})}{\partial p_j}$$

Joining the two equations above:
(this is a general equation,
since the selection of y_1 is arbitrary)

$$\frac{\frac{\partial Y_i(z)}{\partial p_j}}{\frac{\partial Y_1(z)}{\partial p_j}} = \frac{\frac{\partial Y_i}{\partial z}}{\frac{\partial Y_1}{\partial z}}$$

Dimension of the manifold \geq rank of matrix **S** (calculus based reasoning)

equation on *n-dimensional manifold*

Y_1, Y_2, \dots, Y_n are the parameterizing variables

F_i value of variable i

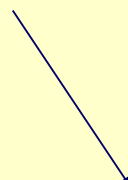
z independent variable (e.g. time)

$$Y_i(z, \mathbf{p}) = F_i(Y_1(z, \mathbf{p}), Y_2(z, \mathbf{p}), \dots, Y_n(z, \mathbf{p}))$$

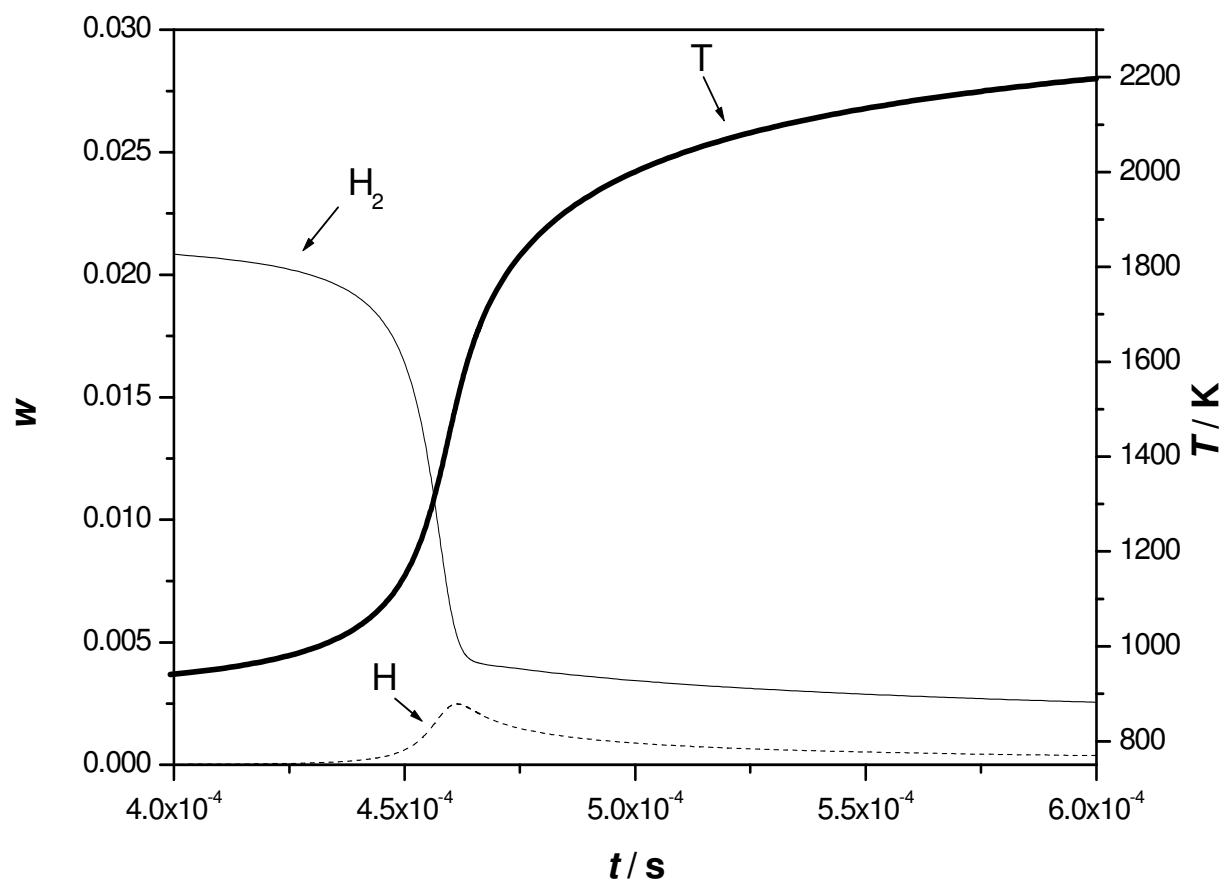
Derivative with respect p_j

$$\frac{\partial Y_i}{\partial p_j} = \left(\frac{\partial F_i}{\partial Y_1} \right) \left(\frac{\partial Y_1}{\partial p_j} \right) + \left(\frac{\partial F_i}{\partial Y_2} \right) \left(\frac{\partial Y_2}{\partial p_j} \right) + \dots + \left(\frac{\partial F_i}{\partial Y_n} \right) \left(\frac{\partial Y_n}{\partial p_j} \right)$$

rank of matrix **S**
is at most n


$$\mathbf{s}_i^T = \lambda_{i1} \mathbf{s}_1^T + \lambda_{i2} \mathbf{s}_2^T + \dots + \lambda_{in} \mathbf{s}_n^T$$

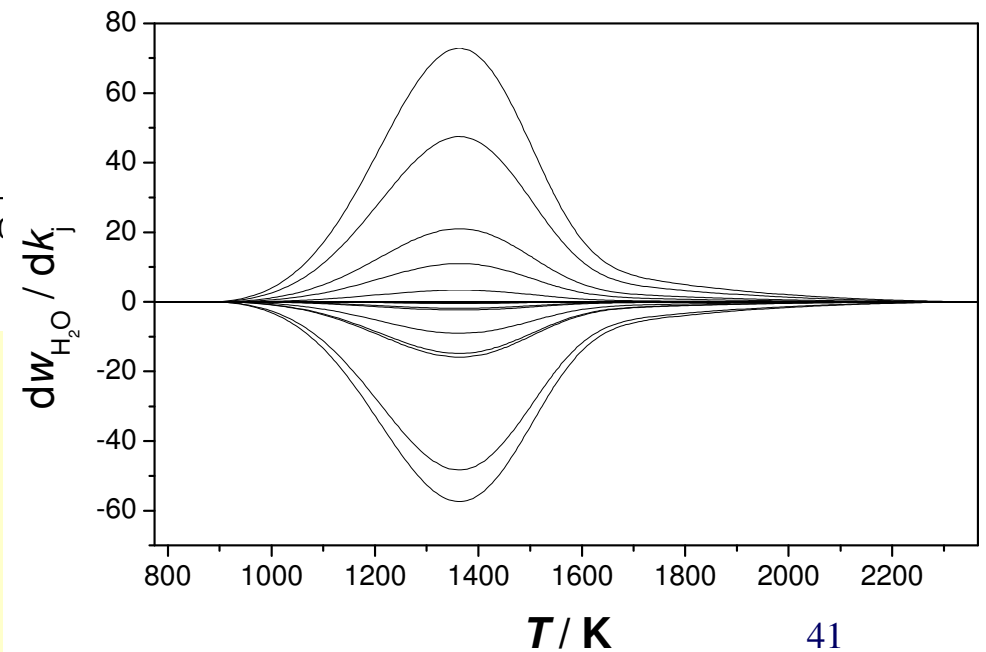
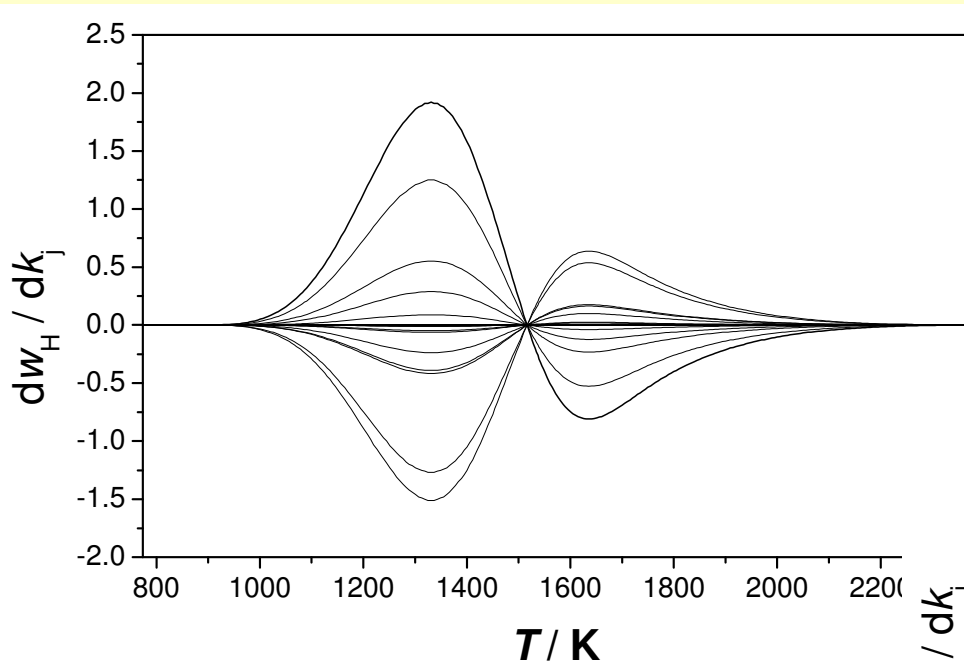
Adiabatic explosion of H₂–air mixtures



Zsély, I.G., Turányi, T.: The influence of thermal coupling and diffusion on the importance of reactions: The case study of hydrogen-air combustion. *Phys.Chem.Chem.Phys.* **5**, 3622-3631 (2003)

The sensitivity functions related to the adiabatic explosion of H₂-air mixtures...

... are very nice looking!



Adiabatic hydrogen/air explosion

Just after the explosion, the concentrations are moving on a 1D manifold.

Local similarity:

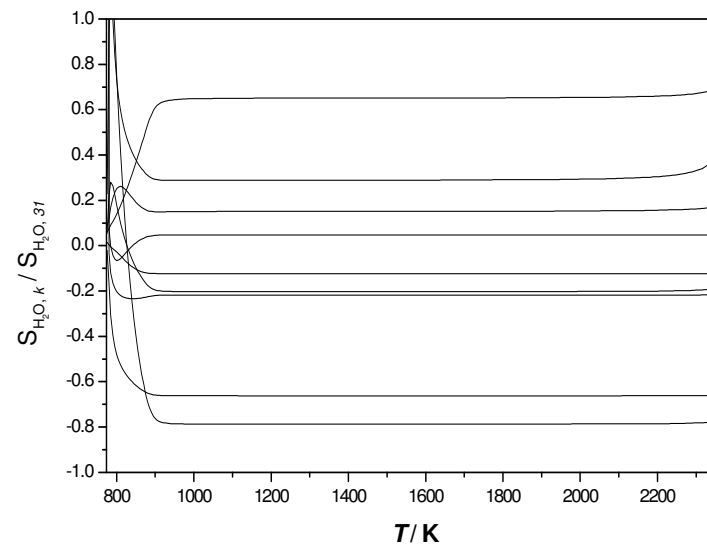
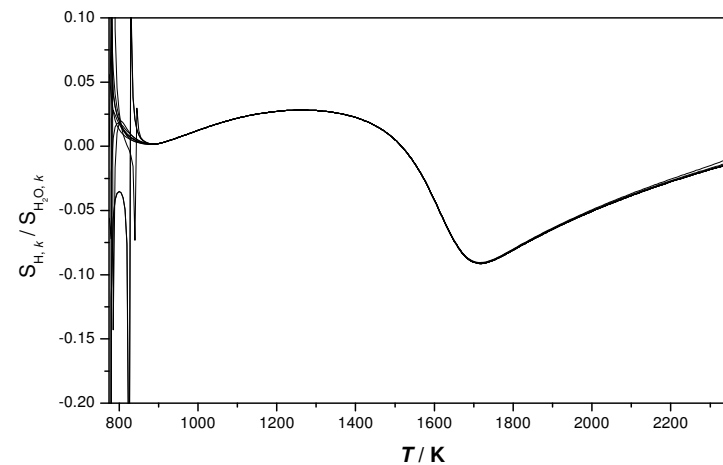
YES

Scaling relation:

YES

Global similarity:

YES



Why is global similarity important?

a very simple mechanism:



analytical solution:

$$x = \frac{k_1}{k_2} (1 - e^{-k_2 t})$$

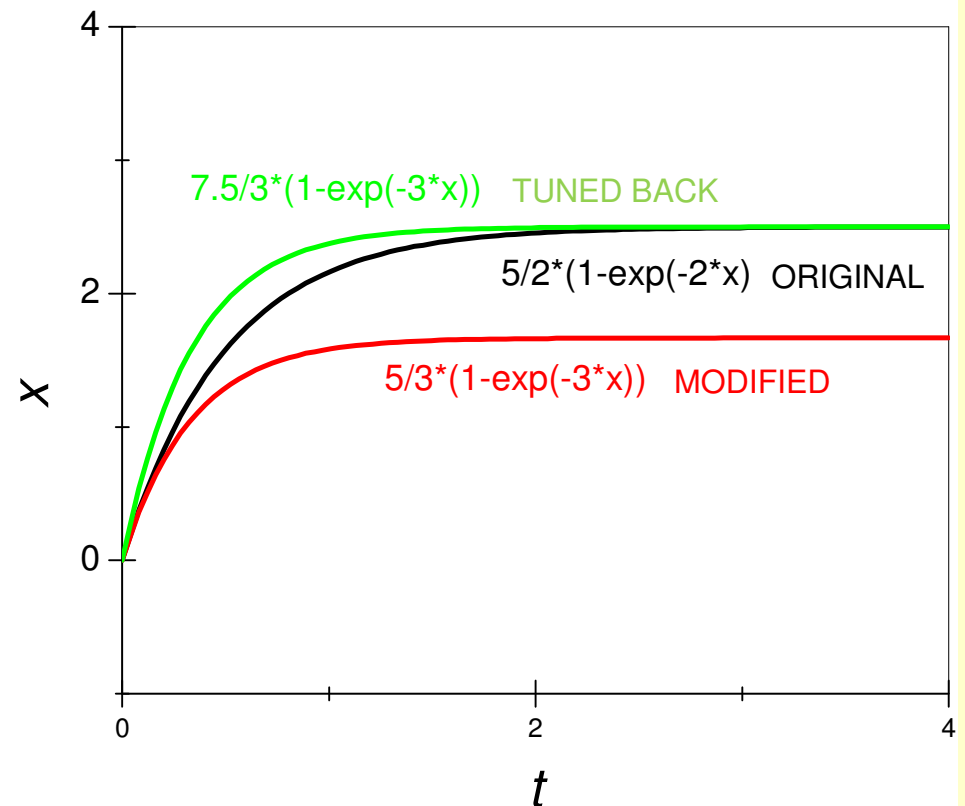
In this model the sensitivity functions do not show global similarity.

If k_2 is changed, it cannot be compensated by changing k_1 . The concentration curve of X is not reproduced.

(Proper tuning of k_1 reproduces X at later times, but not at early times.)

the corresponding ODE:

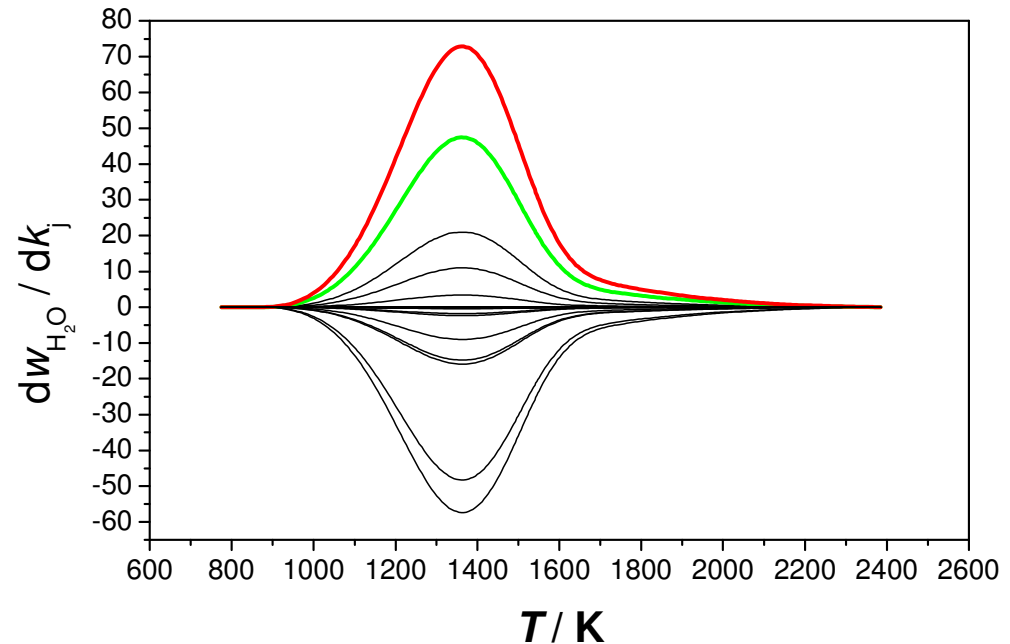
$$\dot{x} = k_1 - k_2 x$$



Regularity 3: Global similarity of the sensitivity functions

$$\mu_{ikm}(t) = \frac{s_{ik}(t)}{s_{im}(t)}$$

[red is divided by green]

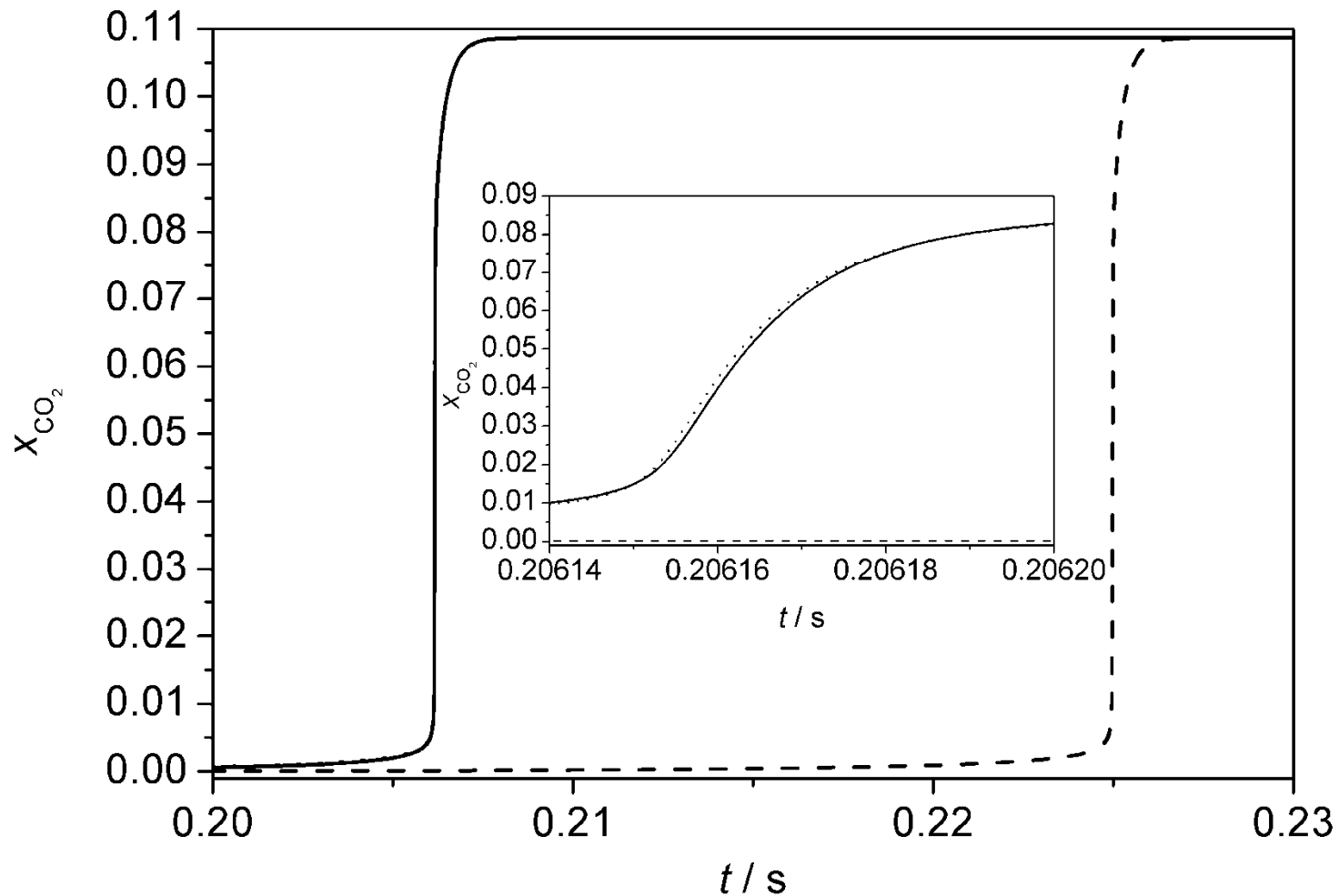


- 1 Global similarity means that a larger change of the **green** parameter may have **identical effect** to a smaller change of the **red** parameter at all times.
- 2 Global similarity means that a larger change of the **green** parameter can be **fully compensated** by a smaller **negative** change of the **red** parameter at all times.

Why is global similarity important?

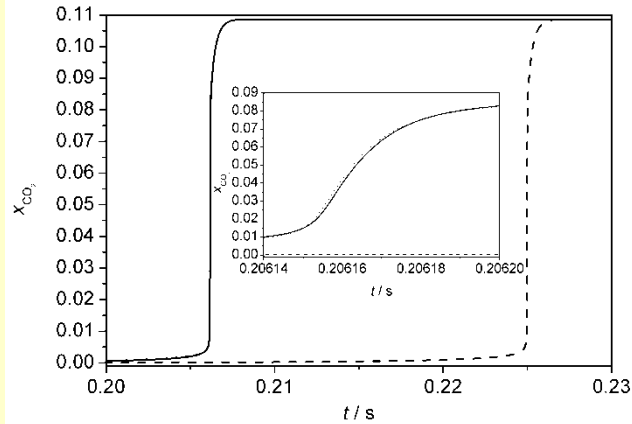
calculated
mole fraction of CO_2

- methane explosion (calculated by the original mechanism)
- - - - 4 important parameters are changed by 50%
- 5th parameters is **also** changed by 9.875%

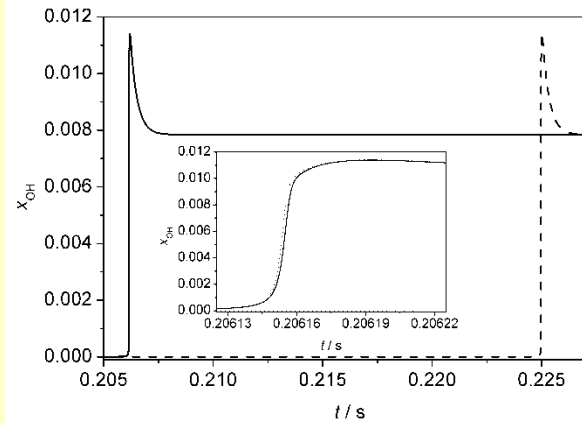


Why is global similarity important 2

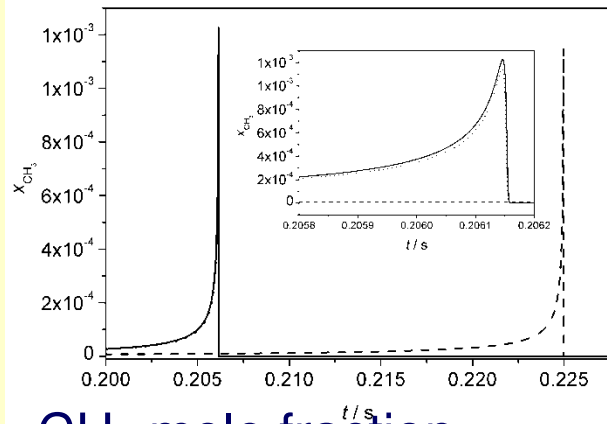
- methane explosion (calculated by the original mechanism)
- - - 4 important parameters are changed by 50%
- 5th parameters is **also** changed by 9.875%



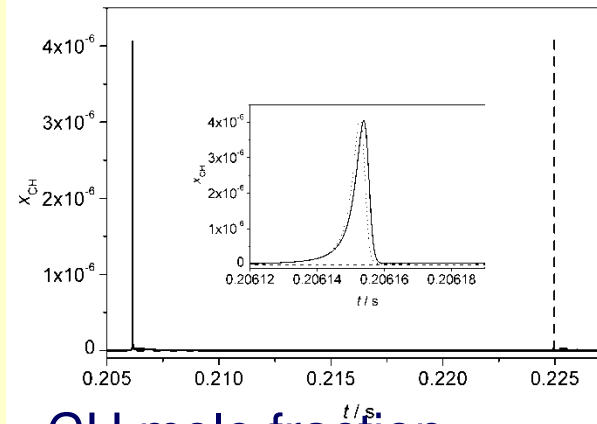
CO₂ mole fraction



OH mole fraction



CH₃ mole fraction



CH mole fraction

the original concentration curves are obtained back
for all variables and in the whole time interval

In the case of global similarity ...

Empirical models

These can be tuned with a single arbitrary but effective parameter

Physical models

The simulation results can be „validated” by indirect simulations,
BUT the fitted parameter values in general has no physical meaning.
(*e.g.* wrong k values can be obtained from flame measurements)

Self-regulation of biological systems

changing a single parameter may restore the optimal time profile
of all species.

Is global similarity a general feature of dynamic models?

Most physical and chemical models describe interconnected fast and slow processes

⇒ existence of very different time scales

⇒ existence of attracting slow manifolds ⇒ **local similarity**

Dynamical systems close to the stationary (or equilibrium) point follow an attracting 1D manifold

⇒ 1D slow manifold ⇒ **scaling relation**

autocatalytic processes are widespread in chemical kinetics
(e.g. explosions, runaways, molecular biology switches)

autocatalytic processes \Leftrightarrow pseudo homogeneity

local similarity & pseudo homogeneity of the ODE

⇒ **global similarity**

Applications of local sensitivities

1. Analysis of models
 - Estimation of the effect of parameter perturbation
 - Identification of cooperating parameters
2. Reduction of models
 - Identification of ineffective parameters;
production of a simpler model with less parameters, but almost identical results
3. Local uncertainty analysis
 - May replace global uncertainty analysis:
less accurate, much faster
4. Parameter estimation
 - All gradient methods are based on the (hidden) application of local sensitivity coefficients
 - Identification of effective parameters
 - Experimental design



*Thank you for
your attention!*