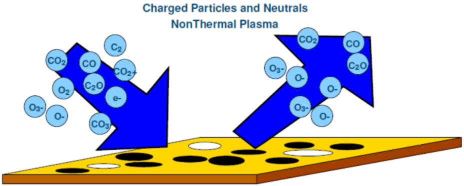


MODEL REGRESSION METHODS TO COMPLEMENT REACTION KINETICS IN HETEROGENEOUS CATALYSIS

1 July 2020 | D. Reiser | Institute for Energy and Climate Research - Plasma Physics, Research Center Jülich GmbH, Association FZJ-Euratom, D-52425 Jülich, Germany

Introduction

Model Regression = empirical determination of physical processes

Extraction of parameters for mathematical models based on

Reaction Kinetics

(Systems of Ordinary Differential Equations)

Machine Learning Methods might automate this approach

Background Dirk Reiser

Forschungszentrum Jülich GmbH, IEK-4 Plasma Physics

Theory and Simulation of Plasmas in Nuclear Fusion Devices

Plasma Transport, Turbulence, Plasma-Wall Interaction

Numerical Simulations

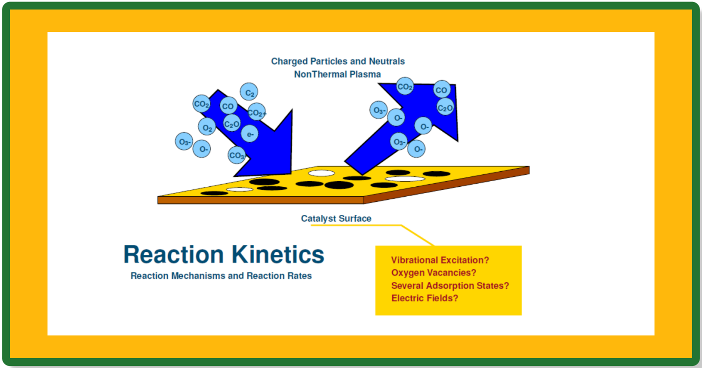
Current Focus: Transfer of Models and Methods to

Plasma Assisted CO_2 Dissociation with Catalysts

Strong Interaction with RUB

Model Discovery for Catalytic Reaction Kinetics

Plasma Chemistry coupled to Catalyst Surface Reactions



Highly non-linear Reaction Kinetics

Extension of Reaction Kinetics by Surface Species

Example: Eley-Rideal mechanism (surface species labeled by $*$)

Elementary Reactions

$$\mathrm{CO_2} \underset{k_0^-}{\overset{k_0^+}{\rightleftharpoons}} \mathrm{CO} + \mathrm{O}$$

$$2\,\mathrm{O} \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} \mathrm{O_2}$$

$$\mathrm{CO_2} + * \underset{k_2^-}{\overset{k_2^+}{\rightleftharpoons}} \mathrm{CO_2}^*$$

$$\mathrm{CO_2}^* \underset{k_3^-}{\overset{k_3^+}{\rightleftharpoons}} \mathrm{CO} + \mathrm{O}^*$$

$$2\ \mathrm{O}^* \underset{k_4^-}{\overset{k_4^+}{\rightleftharpoons}} \mathrm{O_2} + 2\ *$$

$$\Theta_* = 1 - \Theta_\mathrm{O} - \Theta_\mathrm{CO_2}$$

Rate Laws

$$\frac{\partial[\mathrm{CO_2}]}{\partial t} = -k_0^+\,[\mathrm{CO_2}] + k_0^-\,[\mathrm{CO}][\mathrm{O}] - \frac{N}{V}\,k_2^+\,\Theta_*\,[\mathrm{CO_2}] + \frac{N}{V}\,k_2^-\,\Theta_\mathrm{CO_2}$$

$$\frac{\partial[\mathrm{CO}]}{\partial t} = k_0^+\,[\mathrm{CO_2}] - k_0^-\,[\mathrm{CO}][\mathrm{O}] + \frac{N}{V}\,k_3^+\,\Theta_\mathrm{CO_2} - \frac{N}{V}\,k_3^-\,\Theta_\mathrm{O}\,[\mathrm{CO}]$$

$$\frac{\partial[\mathrm{O}]}{\partial t} = k_0^+\,[\mathrm{CO_2}] - k_0^-\,[\mathrm{CO}][\mathrm{O}] - 2\,k_1^+\,[\mathrm{O}]^2 + 2\,k_1^-\,[\mathrm{O_2}]$$

$$\frac{\partial[\mathrm{O_2}]}{\partial t} = k_1^+\,[\mathrm{O}]^2 - k_1^-\,[\mathrm{O_2}] + \frac{N}{V}\,k_4^+\,\Theta_\mathrm{O}^2 - \frac{N}{V}\,k_4^-\,\Theta_*^2\,[\mathrm{O_2}]$$

$$\frac{\partial\Theta_\mathrm{CO_2}}{\partial t} = k_2^+\,\Theta_*\,[\mathrm{CO_2}] - k_2^-\,\Theta_\mathrm{CO_2} - k_3^+\,\Theta_\mathrm{CO_2} + k_3^-\,\Theta_\mathrm{O}\,[\mathrm{CO}]$$

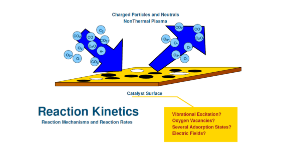
$$\frac{\partial\Theta_\mathrm{O}}{\partial t} = k_3^+\,\Theta_\mathrm{CO_2} - k_3^-\,\Theta_\mathrm{O}\,[\mathrm{CO}] - 2\,k_4^+\,\Theta_\mathrm{O}^2 + 2\,k_4^-\,\Theta_*^2\,[\mathrm{O_2}]$$

Coverages, free sites etc.

determined by rate laws.

Model Discovery for Catalytic Reaction Kinetics

How to connect the unknown macroscopic parameters
in Rate Laws with atomistic processes?



$$\frac{\partial n_s}{\partial t} = \sum_{r=1}^{N_R} \nu_{s,r}\, k_r \prod_{s=1}^{N_S} n_s^{\nu'_{s,r}}$$

The rate coefficients k_r represent possible reaction channels in plasma-catalyst chemistry.

JÜLICH Forschungszentrum

Problem with Rate Equations

Rate Coefficients k_i^+ and k_i^- are often not known

and difficult to measure!

Proposals for determination are numerous!

A few standard methods, but no universal approach!

Forward Modelling might benefit from Regression Methods!

Least-Squares-Problem

Least Squares problem of reaction kinetics!

The discretized system of ODE's

$$\frac{\partial n_s}{\partial t} = \sum_{r=1}^{N_R} \nu_{s,r}\, k_r \prod_{s=1}^{N_S} n_s^{\nu'_{s,r}}$$

can be transferred to a Least Squares Problem

$$\min_{\alpha} \; \|\mathbf{T} - \mathbf{H} \cdot \mathbf{k}\|_2^2$$

Numerical Details

General model

$$\frac{\partial n_s}{\partial t} = \sum_{r=1}^{N_R} P_{s,r}\, k_r$$

Discretized model equations for N_t time points and N_s species

$$\frac{\partial n_{s,t}}{\partial t} = \sum_{r=1}^{N_R} P_{s,t,r}\, k_r \quad , \quad s = 1, \ldots, N_s \quad , \quad t = 1, \ldots, N_t$$

Matrix form

$$\mathbf{H} \cdot \mathbf{k} = \mathbf{T} \quad , \quad T_i = \frac{\partial n_{s,t}}{\partial t} \quad , \quad H_{ir} = P_{s,t,r}$$

with multi-index $\mathbf{i} = (s, t)$

Numerical Details

Cost functional $\mathcal{C}$

$$\mathcal{C} = (\mathbf{T} - \mathbf{H} \cdot \mathbf{k})^{\mathrm{T}} \cdot (\mathbf{T} - \mathbf{H} \cdot \mathbf{k})$$

Optimal solution $\mathbf{k}^*$ minimizes $\mathcal{C}$

$$\mathbf{k}^* = \mathbf{H}^+ \cdot \mathbf{T}$$

Pseudoinverse $\mathbf{H}^+$ obtained via Singular Value Decomposition

$$\mathbf{H} = \mathbf{U} \cdot \mathbf{S} \cdot \mathbf{V}^{\mathrm{T}} \qquad , \qquad \mathbf{H}^+ = \mathbf{V} \cdot \mathbf{S}^+ \cdot \mathbf{U}^{\mathrm{T}}$$

Ordinary Least Squares

The discretized PDE

$$\frac{\partial n_s}{\partial t} = \sum_{r=1}^{N_R} \nu_{s,r}\, k_r \prod_{s=1}^{N_S} n_s^{\nu'_{s,r}}$$

can be transferred to a Least Squares Problem

$$\min_k \; \|\mathbf{T} - \mathbf{H} \cdot \mathbf{k}\|_2^2$$

Ridge Regression

The discretized PDE

$$\frac{\partial n_s}{\partial t} = \sum_{r=1}^{N_R} \nu_{s,r}\, k_r \prod_{s=1}^{N_S} n_s^{\nu'_{s,r}}$$

can be transferred to a Least Squares Problem

$$\min_{k} \; \|\mathbf{T} - \mathbf{H} \cdot \mathbf{k}\|_2^2 + \eta \; \|\mathbf{k}\|_2^2$$

Ridge Regression: `https://en.wikipedia.org/wiki/Tikhonov_regularization`

LASSO Regression

The discretized PDE

$$\frac{\partial n_s}{\partial t} = \sum_{r=1}^{N_R} \nu_{s,r}\, k_r \prod_{s=1}^{N_S} n_s^{\nu'_{s,r}}$$

can be transferred to a Least Squares Problem

$$\min_{k} \; \|\mathbf{T} - \mathbf{H} \cdot \mathbf{k}\|_2^2 + \eta \; \|\mathbf{k}\|_1^2$$

LASSO: `https://en.wikipedia.org/wiki/Lasso_(statistics)`

Example: CO-oxidization on Pt-Catalyst

Elementary Reactions

$$\mathrm{O_2} + 2\,* \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} 2\,\mathrm{O}^*$$

$$\mathrm{CO_2} + * \underset{k_2^-}{\overset{k_2^+}{\rightleftharpoons}} \mathrm{CO_2}^*$$

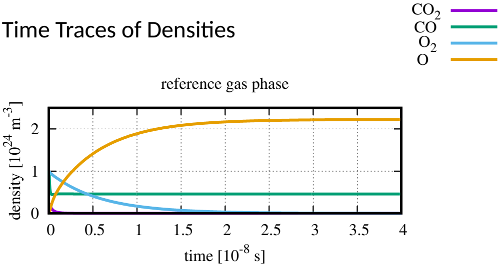
$$\mathrm{CO} + * \underset{k_3^-}{\overset{k_3^+}{\rightleftharpoons}} \mathrm{CO}^*$$

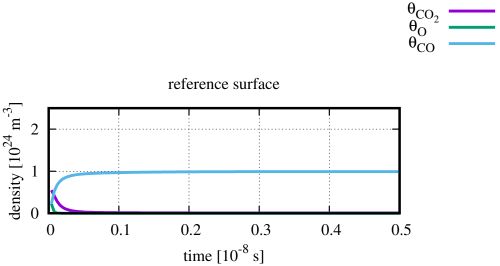
$$\mathrm{CO}^* + \mathrm{O}^* \underset{k_4^-}{\overset{k_4^+}{\rightleftharpoons}} \mathrm{CO_2}^* + *$$

$$\mathrm{CO_2} \underset{c_1^-}{\overset{c_1^+}{\rightleftharpoons}} \mathrm{CO} + \mathrm{O}$$

$$\mathrm{O_2} \underset{c_2^-}{\overset{c_2^+}{\rightleftharpoons}} 2\,\mathrm{O}$$

Time Traces of Densities





Model Discovery for Catalytic Reaction Kinetics

The case of full data allows accurate reconstruction using SVD!

Problem: not all species can be observed experimentally (especially surface species)

The missing time traces have to be replaced by
additional model assumptions and constraints.

First step: steady state for surface species (reduced data)!

But: then the problem becomes nonlinear!

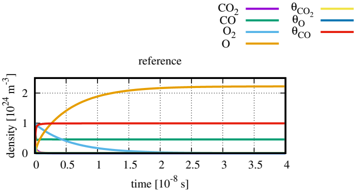
SVD must be replaced by nonlinear minimization methods!

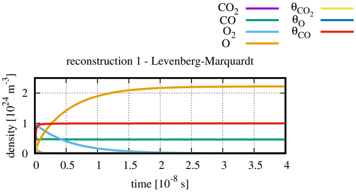
Here: Levenberg-Marquardt, Hanson-Krogh, Genetic Algorithm

JÜLICH Forschungszentrum

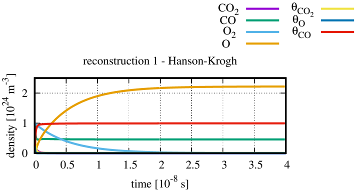
Model Discovery for CO-oxidization on Pt-Catalyst

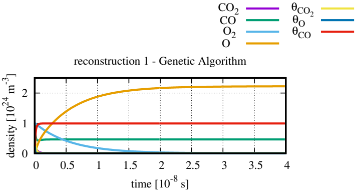
Time Traces of Densities





Time Traces of Densities





Full Data : Perfect match for perfect guess for all methods applied!

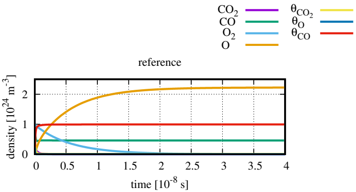
Hanson-Krogh: `https://doi.org/10.1145/146847.146857`

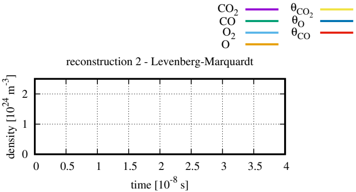
Levenberg-Marquardt: `https://en.wikipedia.org/wiki/Levenberg-Marquardt_algorithm`

JÜLICH Forschungszentrum

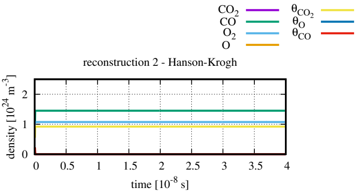
Model Discovery for CO-oxidization on Pt-Catalyst

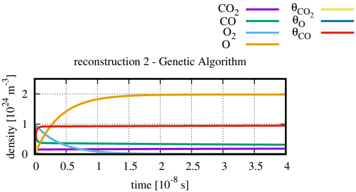
Time Traces of Densities





Time Traces of Densities

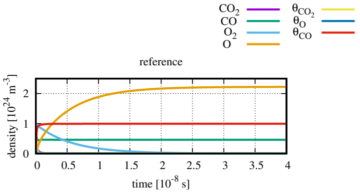


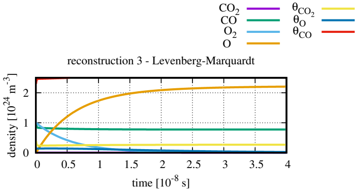


Full Data : For bad guess Genetic Algorithm is superior!

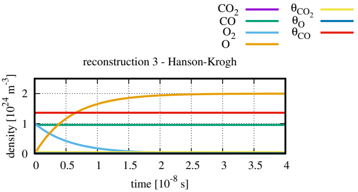
Model Discovery for CO-oxidization on Pt-Catalyst

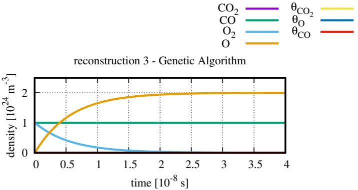
Time Traces of Densities





Time Traces of Densities

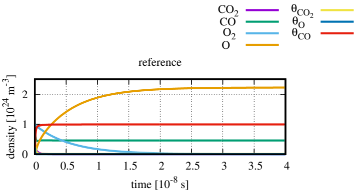


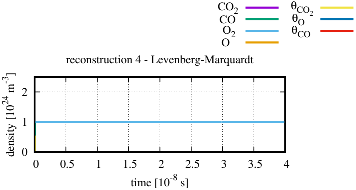


Reduced Data : For perfect guess all methods give reasonable results!

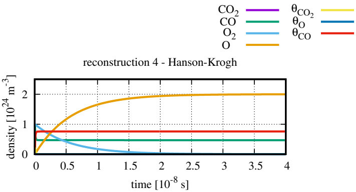
Model Discovery for CO-oxidization on Pt-Catalyst

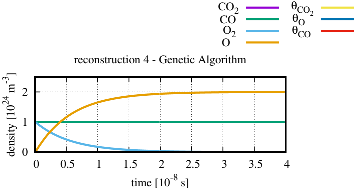
Time Traces of Densities





Time Traces of Densities





Reduced Data : For bad guess the results are of very different quality!

JÜLICH Forschungszentrum

Improvements

The steady state approximation in the Pt-example above:

$$\frac{\partial \Theta_{\mathrm{CO_2}}}{\partial t} = \frac{\partial \Theta_{\mathrm{CO}}}{\partial t} = \frac{\partial \Theta_{\mathrm{O}}}{\partial t} = \frac{\partial \Theta_{*}}{\partial t} = 0$$

Not entirely needed, because:

$$[*] + [\mathrm{CO_2}^*] + [\mathrm{CO}^*] + [\mathrm{O}^*] = \text{const.}$$

$$[\mathrm{CO_2}] + [\mathrm{CO}] + [\mathrm{CO_2}^*] + [\mathrm{CO}^*] = \text{const.}$$

$$[\mathrm{CO_2}] + 2[\mathrm{O_2}] + [\mathrm{O}] + [\mathrm{CO_2}^*] + [\mathrm{O}^*] = \text{const.}$$

Conservation laws can be taken into account automatically!

JÜLICH Forschungszentrum

General Remark

The steady state approximation is a possible idea
to define cost functions

But, several variants are possible!

The proposed approach consists of a
flexible tool box to analyze arbitrary model variants!

An Example from Gas Chemistry

Elementary Reactions

$$CH_4 + O + O \xrightarrow{k_1} H_2O + H_2O + C$$

$$O + C \xrightarrow{k_2} CO$$

$$O + CO \xrightarrow{k_3} CO_2$$

$$O_2 + e^- \xrightarrow{k_4} O + O + e^-$$

$$O + O \xrightarrow{k_5} O_2$$

$$O_2 + C \xrightarrow{k_6} CO_2$$

$$CO_2 + e^- \xrightarrow{k_7} O + CO + e^-$$

$$H_2O + e^- \xrightarrow{k_8} O + H_2 + e^-$$

$$CH_4 + e^- \xrightarrow{k_9} C + H_2 + H_2 + e^-$$

Rate Laws

$$\frac{\partial[CH_4]}{\partial t} = -k_1\,[CH_4][O]^2 - k_9\,[CH_4][e^-]$$

$$\frac{\partial[O_2]}{\partial t} = -k_4\,[O_2][e^-] + k_5\,[O]^2 - k_6\,[O_2][C]$$

$$\frac{\partial[O]}{\partial t} = -2\,k_1\,[CH_4][O]^2 - k_2\,[O][C] - k_3\,[O][CO] + 2\,k_4\,[O_2][e^-] -2\,k_5\,[O]^2 + k_7\,[CO_2][e^-] + k_8\,[H_2O][e^-]$$

$$\frac{\partial[CO_2]}{\partial t} = k_3\,[O][CO] + k_6\,[O_2][C] - k_7\,[CO_2][e^-]$$

$$\frac{\partial[CO]}{\partial t} = k_2\,[O][C] - k_3\,[O][CO] + k_7\,[CO_2][e^-]$$

$$\frac{\partial[H_2O]}{\partial t} = 2\,k_1\,[CH_4][O]^2 - k_8\,[H_2O][e^-]$$

$$\frac{\partial[C]}{\partial t} = k_1\,[CH_4][O]^2 - k_2\,[O][C] - k_6\,[O_2][C] + k_9\,[CH_4][e^-]$$

$$\frac{\partial[H_2]}{\partial t} = k_8\,[H_2O][e^-] + 2\,k_9\,[CH_4][e^-]$$

CH_4, CO_2, CO and H_2O measured

O_2, O, C and H_2 not known

JÜLICH Forschungszentrum

An Example from Gas Chemistry

$$2\,[\mathrm{CH_4}] - 2\,[\mathrm{O_2}] - [\mathrm{O}] - 2\,[\mathrm{CO_2}] - [\mathrm{CO}] + [\mathrm{H_2}] = c_1$$
$$[\mathrm{CH_4}] + [\mathrm{CO_2}] + [\mathrm{CO}] + [\mathrm{C}] = c_2$$
$$2\,[\mathrm{O_2}] + [\mathrm{O}] + 2\,[\mathrm{CO_2}] + [\mathrm{CO}] + [\mathrm{H_2O}] = c_3$$

Conservation laws provide information on three invisible species.

$$[\mathrm{O}] = -2\,[\mathrm{O_2}] - 2\,[\mathrm{CO_2}] - [\mathrm{CO}] - [\mathrm{H_2O}] + c_3$$
$$[\mathrm{C}] = -[\mathrm{CH_4}] - [\mathrm{CO_2}] - [\mathrm{CO}] + c_2$$
$$[\mathrm{H_2}] = -2\,[\mathrm{CH_4}] - [\mathrm{H_2O}] + c_3 + c_1$$

The constants c_1, c_2 and c_3 are known from initial conditions.

An Example from Gas Chemistry

$$\frac{\partial[\mathrm{C}]}{\partial t} = k_1\,[\mathrm{CH_4}][\mathrm{O}]^2 - k_2\,[\mathrm{O}][\mathrm{C}] - k_6\,[\mathrm{O_2}][\mathrm{C}] + k_9\,[\mathrm{CH_4}][\mathrm{e^-}] = 0$$

Steady state assumption for a single species

$$[\mathrm{O_2}] = \frac{k_1\,[\mathrm{CH_4}][\mathrm{O}]^2 - k_2\,[\mathrm{O}][\mathrm{C}] + k_9\,[\mathrm{CH_4}][\mathrm{e^-}]}{k_6\,[\mathrm{C}]}$$

The final equation introduces non-linearities in model parameters!

Conclusion

Extracted rate coefficients reflect quite well the order of magnitude.

Further improvement by constraints due to stoichiometric conservation laws!

This will be implemented now and can be automated easily.

Results are promising, but quality assessment is urgently needed for practical situations.

Summary and Outlook

Summary:

Model discovery methods based on Least-Squares-methods work fine.

Several variants are known from the literature.

New interest in the context of Machine Learning (automatic decisions)

Open Questions:

Is the steady state approach useful for catalyst reaction kinetic modelling?

What kind of constraints might be taken into account?

What might be a good test for errors and quality of results?

Contribution to SFB 1316

- Modelling of surface reactions via reaction kinetics
- Data driven model discovery of plasma-gas-surface interactions
- Coupling of gas phase simulation with catalyst model
- Two-way approach using statistical methods and TST

Thank you very much for your attention!