Synchronization of a Hierarchical Ensemble of Coupled Excitable Oscillators

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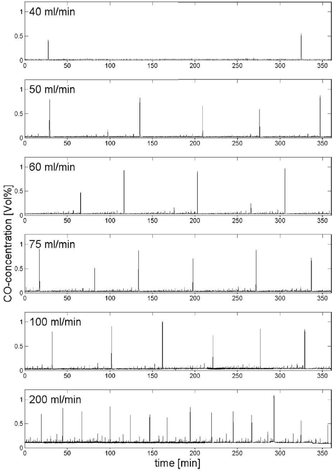
The exothermic CO-Oxidation on Palladium-supported catalyst

Langmuir-Hinschelwood-mechanism:

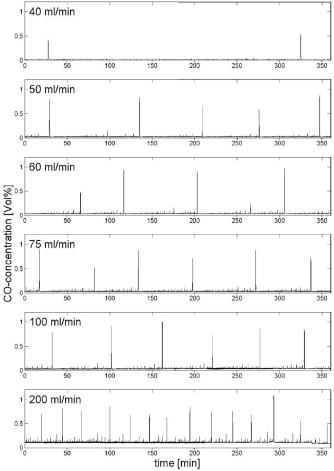
$$\mathrm{CO} + * \leftrightarrow \mathrm{CO}* \quad (1)$$
$$\mathrm{O}_2 + 2* \rightarrow 2\,\mathrm{O}* \quad (2)$$
$$\mathrm{CO}* + \mathrm{O}* \rightarrow 2\,\mathrm{CO}_2 + 2* \quad (3)$$

*: place of adsorption on Pd

The exothermic CO-Oxidation on Palladium-supported catalyst



The exothermic CO-Oxidation on Palladium-supported catalyst



- The frequency of big excursions increases.
- The amplitudes of small excursions increase.
- The complexity of the structure of small excursions increases.
- The maximum conversion rate of CO decreases.

The basic model

The basic ingredient:

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  - corresponding to a single Palladium particle.

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- palladium
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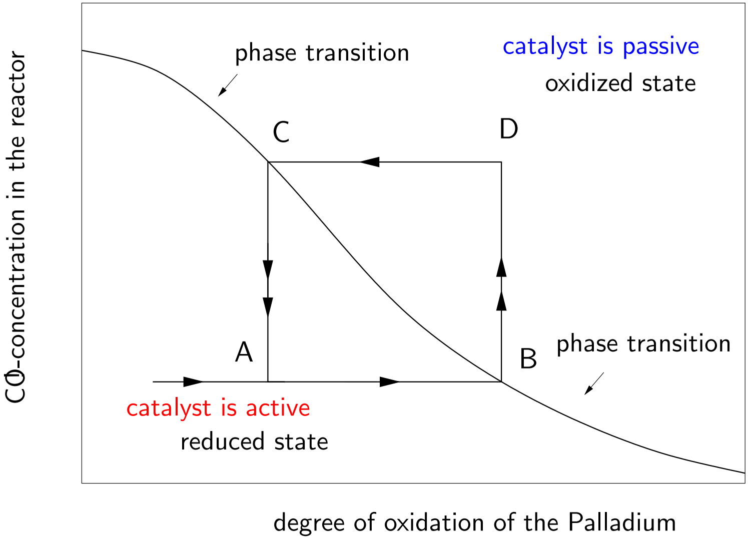
- palladium $\Longrightarrow$ **active** = reduced
- palladium oxide $\Longrightarrow$ **inactive** = oxidized


phase transition
catalyst is passive
oxidized state
C
D
A
B
phase transition
catalyst is active
reduced state
CO-concentration in the reactor
degree of oxidation of the Palladium

Phase space consists of two regions with different dynamical behaviour:

- active region
- passive region

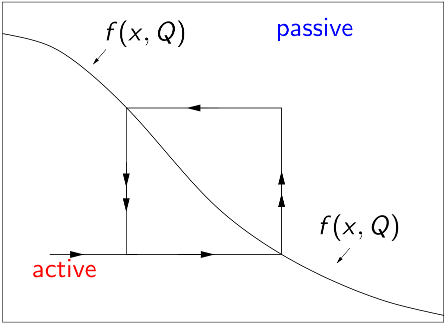
These regions are separated by a line which is given by a function

$$y = f(x, Q) \tag{4}$$

x : degree of oxidation
y : CO-concentration in the reactor
Q : determines the shape of f

We choose the function f as

$$f(x,Q) = \exp\left(\frac{-x^2}{Q}\right). \quad (5)$$



Dynamical behaviour

- active region:

$$\dot{x} = \bar{\beta}(1-x) \quad (6)$$

$$\dot{y} = -y + \alpha y_0 \quad (7)$$

y_0 : CO inlet concentration, $y_0 \leq 1$
α : exchange factor,
representing the flow rate F through the reactor:
$0 \leq \alpha \leq 1, \qquad \lim_{F\to\infty} \alpha = 1.$

Dynamical behaviour II

- passive region:

$$\dot{x} = -\beta_0 x \quad (8)$$

$$\dot{y} = \alpha\left(y_0 - y\right) \quad (9)$$

Dynamical behaviour III

Introducing the function

$$\Theta(x, y, Q) := \Theta_0 \left(\exp\left(\frac{-x^2}{Q} \right) - y \right) = \begin{cases} 1 & \text{active region} \\ 0 & \text{passive region} \end{cases} \quad (10)$$

with Θ_0 denoting the usual Heaviside step function, all the equations above can be summarized in:

Dynamical behaviour III

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with Θ_0 denoting the usual Heaviside step function, all the equations above can be summarized in:

$$\dot{x} = [\Theta(x,y,Q) - x] \cdot \beta \qquad (11)$$

$$\dot{y} = \underbrace{-\Theta(x,y,Q)y}_{\text{reaction}} + \underbrace{\alpha y_0}_{\text{gas inlet}} \underbrace{-\alpha[1-\Theta(x,y,Q)] \cdot y}_{\text{gas outlet}} \qquad (12)$$

Dynamical behaviour IV

The frequency β is defined by

$$\beta = \Theta(x, y, Q) \cdot \bar{\beta} + (1 - \Theta(x, y, Q)) \cdot \beta_0. \tag{13}$$

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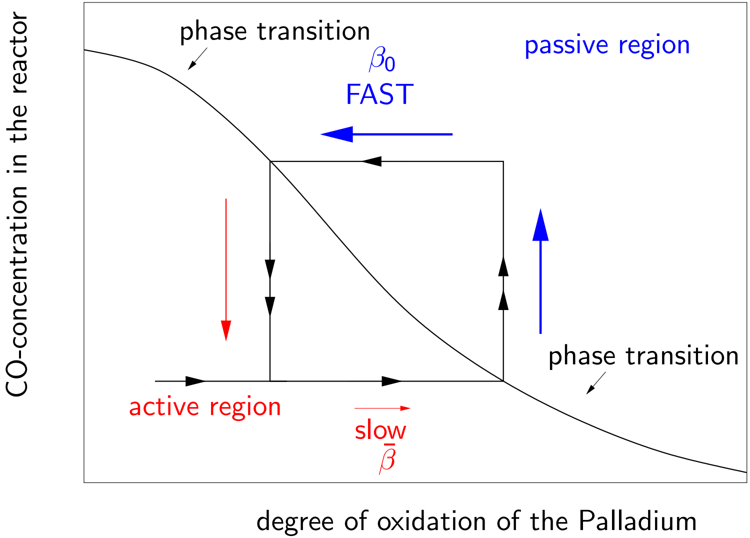
with

$$\beta_0 \gg \bar{\beta} \tag{14}$$

$$\Longrightarrow \text{two different time scales} \tag{15}$$

$$\Longrightarrow \text{relaxation oscillator} \tag{16}$$


CO-concentration in the reactor
phase transition
β_0
FAST
passive region
phase transition
active region
slow
$\bar{\beta}$
degree of oxidation of the Palladium

The frequency $\bar{\beta}$ is a monotonically increasing function of the flow rate α:

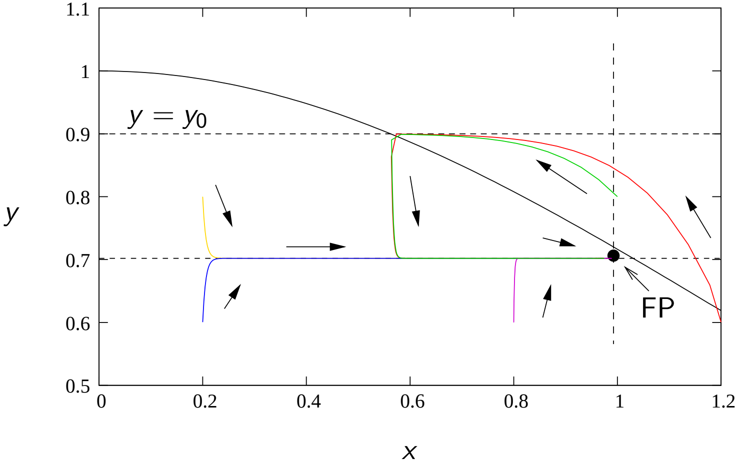
$$\bar{\beta} = \bar{\beta}(\alpha) \tag{17}$$

Long time behaviour

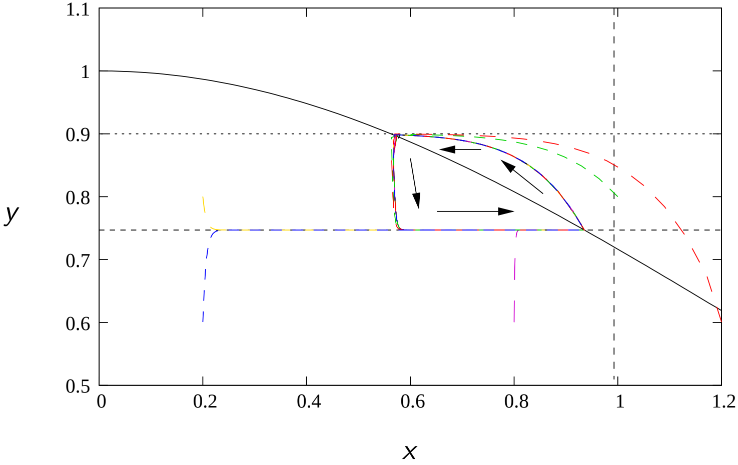
There exists a critical flow rate α_c:

$$\begin{aligned} \alpha < \alpha_c &\implies \text{fixed point} \\ \alpha > \alpha_c &\implies \text{limit cycle} \end{aligned} \tag{18}$$

$$\alpha < \alpha_c$$

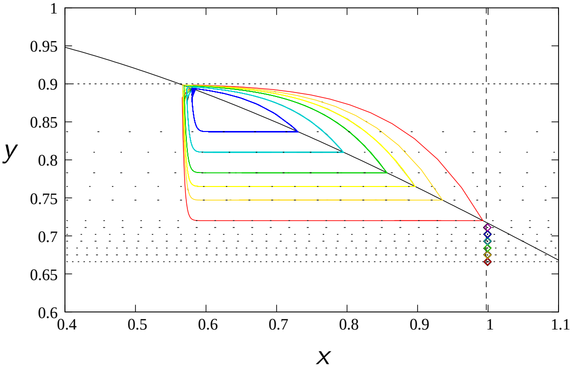


$$\alpha > \alpha_c$$



Long time behaviour for different flow rates

Fixed points for $\alpha = 0.74, 0.75, ...0.79$, limit cycles for $\alpha = 0.80, 0.83, 0.85, 0.87, 0.90, 0.93$.



The extended model

The extended model contains N coupled relaxation oscillators. Thereby, there are several assumptions which are based on experimental observations:

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The extended model contains N coupled relaxation oscillators. Thereby, there are several assumptions which are based on experimental observations:

- The gases' concentrations are the same everywhere in the reactor (instantaneous changes).
- There are large distances between the Pd particles due to the low concentration of Pd in the catalyst.
- The particles do not have exactly the same size, there is a distribution of the Pd particle sizes.

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- The oscillators have different frequencies which are hierarchically ordered, representing the hierarchically ordered sizes of the palladium particles.

The dynamical sytem now reads:

$$\dot{x}_i = [\Theta(x_i, y, Q) - x_i] \cdot \beta_i, \quad i = 1, \ldots N \tag{19}$$

$$\dot{y} = \underbrace{-\overline{N}y}_{\text{reaction}} + \underbrace{\alpha y_0}_{\text{gas inlet}} \underbrace{-\alpha[1 - \overline{N}] \cdot y}_{\text{gas outlet}} \tag{20}$$

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Thereby, the average conversion rate $\overline{N}$ and the frequencies β_i are given by

$$\overline{N} = \frac{1}{N} \sum_{i=1}^{N} \Theta(x_i, y, Q) \tag{23}$$

$$\beta_i = [1 - \Theta(x_i, y, Q)]\beta_0 + \Theta(x_i, y, Q)\overline{\beta_i} \tag{24}$$

Frequencies of the active particles

The frequencies $\overline{\beta_i}$ are chosen to show a linear decay, dependent on

- the particle size,
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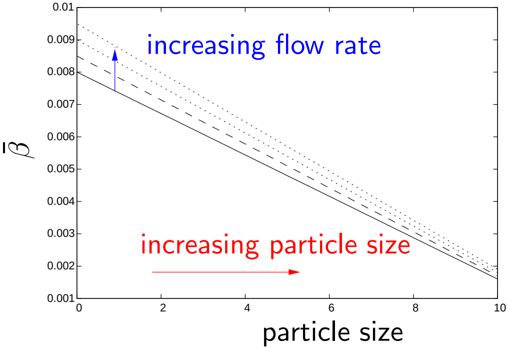
- the particle size,
  - smaller particles have higher frequencies than bigger ones
- and the flow rate,
  - for small flow rates all the particles have more similar frequencies.


increasing flow rate
increasing particle size
particle size
$\bar{\beta}$
0.01
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
2
4
6
8
10

$$\beta_i = \beta_i(\alpha) = H(i, \alpha) \tag{25}$$

$H(i, \alpha)$:	mon. decreasing with growing i
$H(i, \alpha)$ and $\frac{\partial H}{\partial i}(i, \alpha)$:	mon. increasing with growing α

Numerical Simulations - a single oscillator

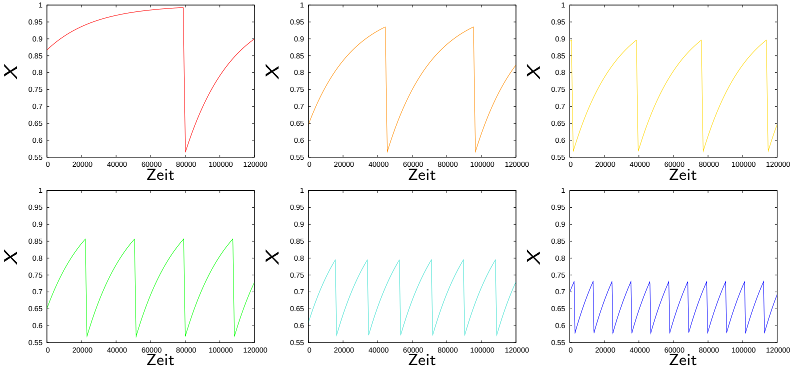
Runge-Kutta method of order 4, step-size 0.005.

$$
\begin{aligned}
Q &= 3 \\
y_0 &= 0.9 \\
\bar{\beta} &= 0.0098 \cdot \alpha, \qquad \beta_0 = 0.09
\end{aligned}
$$

$$\alpha_c = \exp\left(-\frac{1}{Q}\right)\frac{1}{y_0} \approx 0.796. \tag{26}$$

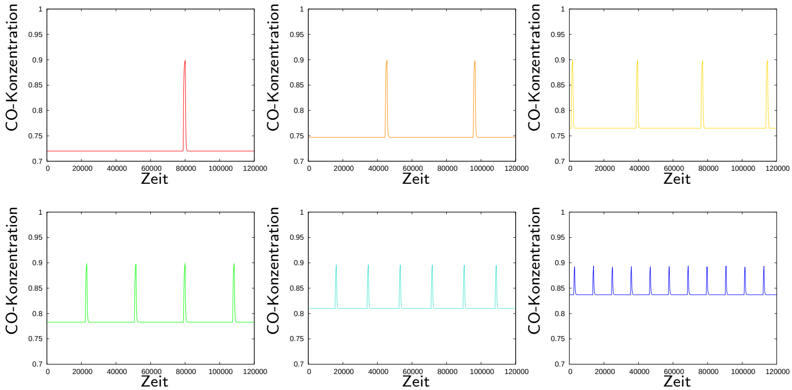
Time-series of the degree of oxidation

$$\alpha = 0.80, 0.83, 0.85, 0.87, 0.90, 0.93$$



Time-series of the CO-concentration

$$\alpha = 0.80, 0.83, 0.85, 0.87, 0.90, 0.93$$



Numerical simulations - $N = 10$ coupled oscillators

$$Q = 3$$

$$y_0 = 0.9$$

$$\bar{\beta}_i = 0.01 \left[1 - \frac{(N-2)}{N^2} \cdot i \right] \cdot \alpha, \qquad \beta_0 = 0.09$$

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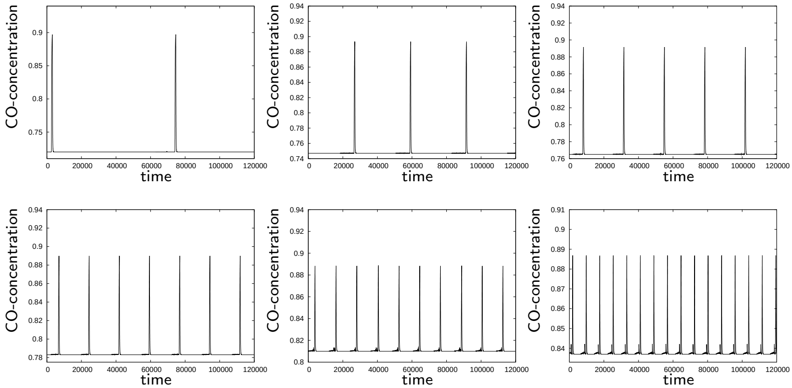

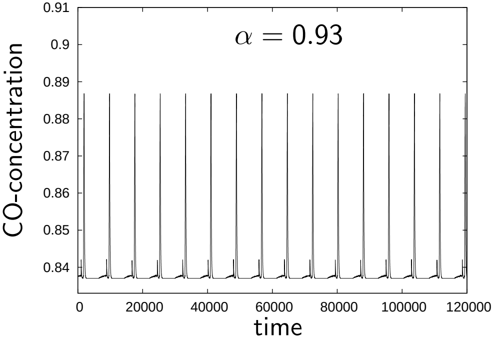

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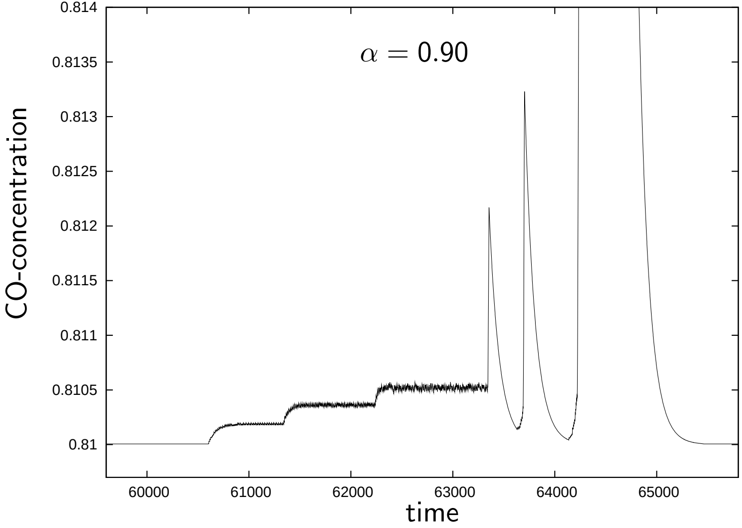
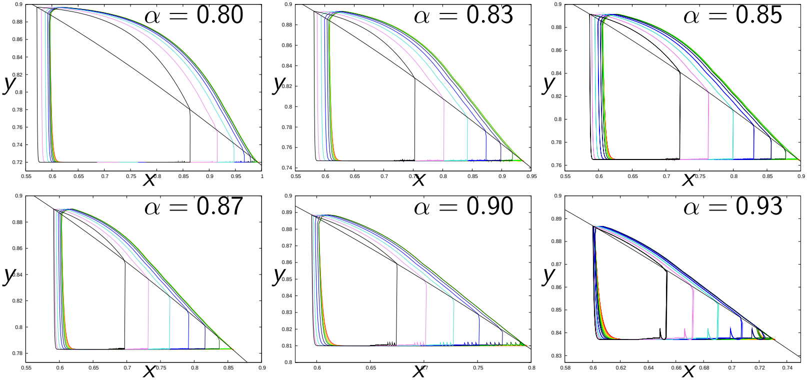
N coupled oscillators



- Where do the additional excursions come from?
- Why does their amplitude grow with increasing flow rate?
- What does actually happen when one couples the oscillators?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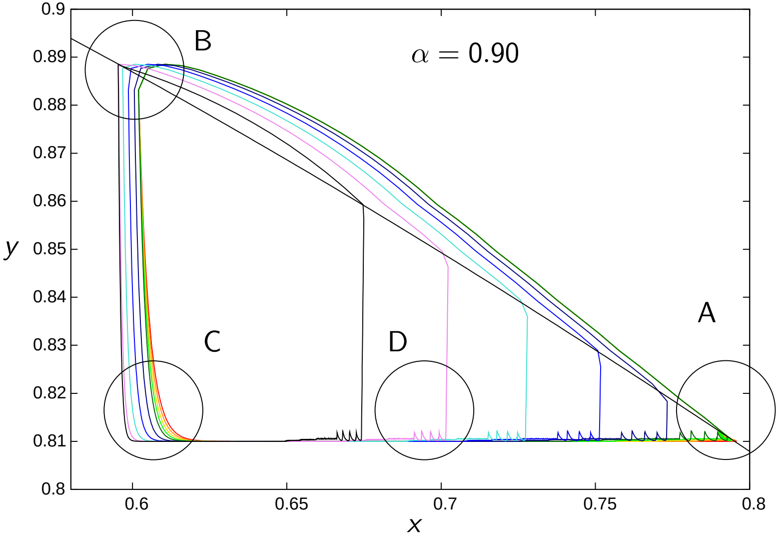
$\alpha = 0.90$
$\alpha = 0.93$
x
y

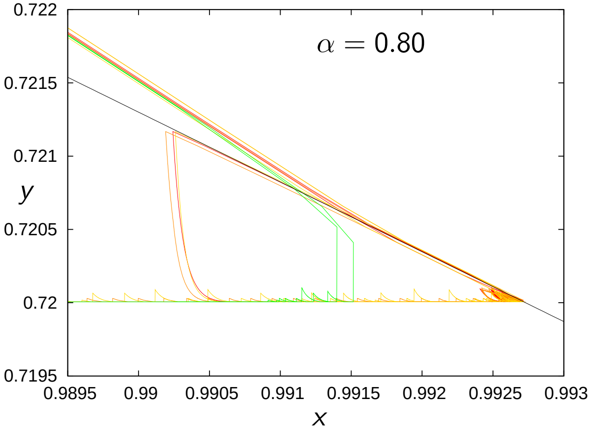
N coupled oscillators



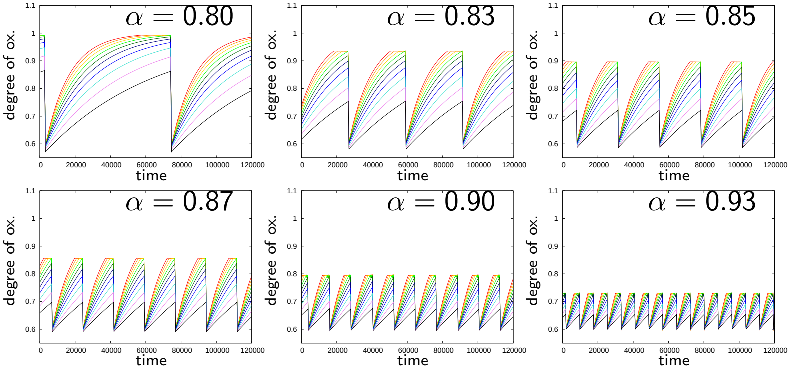
- **region A**: The fast oscillators move to the passive state, apparently uninfluenced..
- **region B**: All oscillators move to the active state - prematurly compared to the uncoupled scenario.
- **region C**: According to the different frequencies $\bar{\beta}_i$ the limit cycles spread.
- **region D**: The slow oscillators move prematurely to the passive state.

region A

$\alpha = 0.80$



Time-series of the degree of oxidation



Several observations:

- There is a basic frequency which characterizes the big breakdowns. $\Longrightarrow$ synchronization of the oszillators.

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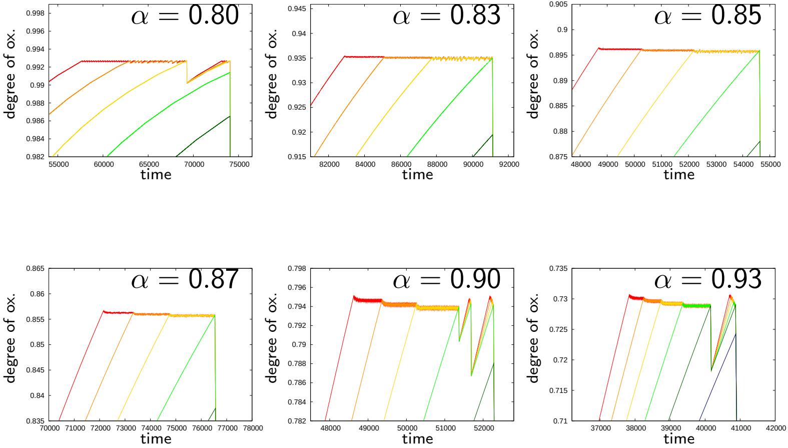
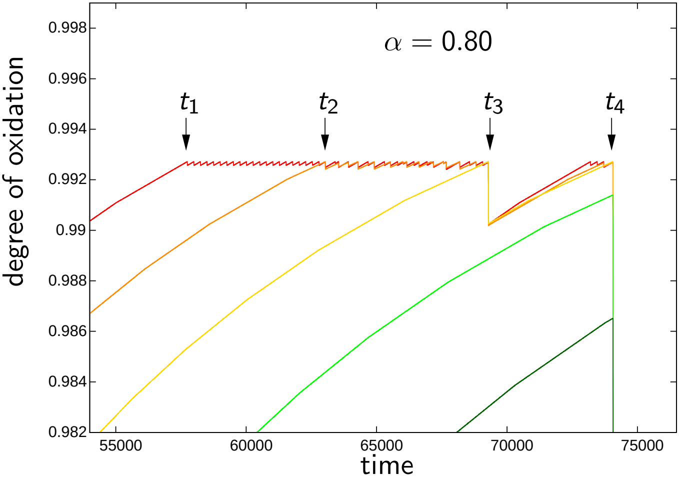
- This basic frequency is **not** the natural frequency of the fastest oscillator. $\Longrightarrow$ existence of plateaus.

Time-series of the degree of oxidation II



Cascade of breakdowns



Cascade of breakdowns II

Observation: With growing flow rate α more and more particles are needed to start the final cascade of breakdowns.

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There are two concurring mechanisms:

Cascade of breakdowns III

- If a particle moves to the passive region, y grows up to some value $\tilde{y}$ which is dependent on
  - α (flow rate)
  - I (part of particles which are in the active region)

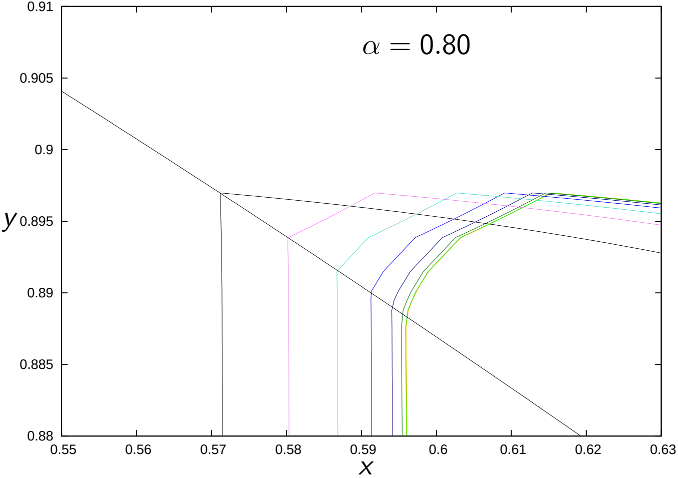
For given α and I and for growing α $\tilde{y}$ increases. $\Rightarrow$ **Less** particles need to move to the passive region.

Cascade of breakdowns III

- If a particle moves to the passive region, y grows up to some value $\tilde{y}$ which is dependent on
  - α (flow rate)
  - I (part of particles which are in the active region)

  For given α and I and for growing α $\tilde{y}$ increases. $\Rightarrow$ **Less** particles need to move to the passive region.
- With growing α the relative differences between the frequencies grow, too: compared to the fast oscillators the slow osillators get slower....... $\Longrightarrow$ **More** particles need to move to the passive region to be able to make the others go with them.

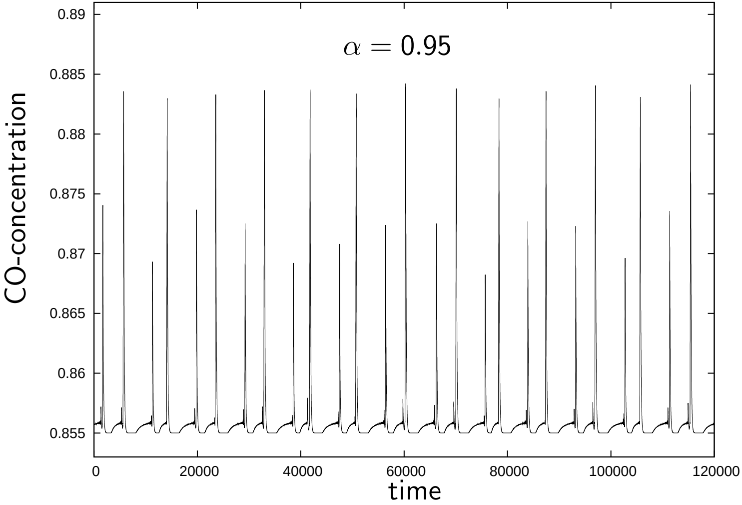
region B


$\alpha = 0.80$
0.91
0.905
0.9
0.895
0.89
0.885
0.88
y
0.55
0.56
0.57
0.58
0.59
0.6
0.61
0.62
0.63
x

Numerical simulations - $N = 100$ coupled oscillators

$$Q = 3$$
$$y_0 = 0.9$$
$$\bar{\beta}_i = 0.01 \left[1 - \frac{(N-2)}{N^2} \cdot i \right] \cdot \alpha, \qquad \beta_0 = 0.09$$

N coupled oscillators



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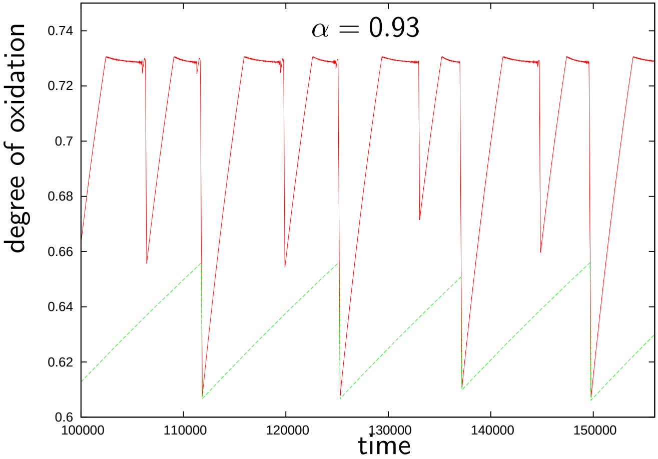
Explaination:

- $\approx 70 - 80$ particles move to the passive region.
- There are oscillators which are so slow that they can join only every second breakdown.

Time-series of the degree of oxidation of particles No. 1 and No. 91.



Conclusions

- We made a model for an ensemble of coupled relaxation oscillators and examined its properties regarding the appearance of synchronization.
- Motivation: experimental observations of the exothermic CO-oxidation on Palladium-supported catalyst.
- The oscillators are coupled globally; their frequencies obey a hierarchical distribution.
- Most important according to the dynamics of the system is some kind of cascade of breakdowns which is the the result of several mechanisms.
- These mechanism and thus frequency and form of the breakdowns can be controlled by the choice of the distribution of frequencies.

Thank you for your attention!