Numerical Methods for Optimization-based Model Validation

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What Models We Are Looking For?
Why Do We Need These Models?
What Models We Are Looking For?

These? ... No!
What Models We Are Looking For?

Maybe this? ... Also no!

Barbara Meier, studied mathematics, the winner of the second cycle of Germany’s Next Topmodel

Photo by Manfred Werner-Tsui
What Models We Are Looking For?

... these also no!

Möbius band

Klein bottle
But The Models That Allow Simulation

From Merriam-Webster’s Dictionary

**Full Definition of simulation**

1. 1: the act or process of *simulating*
2. 2: a sham object: *counterfeit*

3. 3a: the imitative representation of the functioning of one system or process by means of the functioning of another *<a computer simulation of an industrial process>*
b: examination of a problem often not subject to direct experimentation by means of a simulating device

**Full Definition of simulator**

1. one that *simulates; especially*: a device that enables the operator to reproduce or represent under test conditions phenomena likely to occur in actual performance
Why Do We Need Simulation Models?

- E.g. the concept of “digital twins” (GE, Siemens, ...)
  - every new product or a physical economical process has a digital twin which includes a collection of models and algorithms;
  - which accompanies the process from the “origin” (modeling) through its life time, “growing” together with the process;
  - is used among others to analyze data, predict malfunctioning and perform optimal operation.
- Another example: development and admission of drugs
- Necessary precondition: validated models with reliable parameter estimates
Life Cycle of the Mathematical Model

- Experimental data
- Mathematical model
- Experimental design
- Parameter estimation
Outline

1. Parameter Estimation
2. Sensitivity Analysis of Parameter Estimates
3. Design of Optimal Experiments
4. Applications
First Step in Model Validation: Parameter Estimation
Constrained Parameter Estimation Problem

determine parameters $p$ and states $y$ to minimize deviation of the model response $\mathcal{M}[y; p]$ from measurements $\eta$ in a suitable norm (e.g. weighted $l_2$, $l_1$, hybrid)

$$\min_{y, p} \ ||\eta - \mathcal{M}[y; p]||,$$

such that model equations

$$\mathcal{F}[y; p] = 0$$

and additional “experimental constraints” are satisfied

$$C[y; p] \geq 0$$
Mathematical Model Classes for Dynamical Processes $\mathcal{F}[y; p] = 0$

- **Differential-Algebraic Equations (DAE)**

  $B(x, z, p)\dot{x} = f(x, z, p, q, u)$
  
  $0 = g(x, z, p, q, u)$

  - $x$: differential variables
  - $z$: algebraic variables, $y = (x, z)$
  - $p$: unknown parameters (to be estimated by PE)
  - $q$: design parameters (to be chosen in OED)
  - $u$: controls (to be chosen OED)

- **Partial-Differential Equations (PDE)**

  $u_t - \nabla(K \nabla u) = f(u, p)$

  → Semidiscretization in space or Rothe method

- **initial and boundary conditions!**
Observation Model and Data

\[ \eta_i = \mathcal{M}(t_i, y^{true}(t_i), p^{true}) + \varepsilon_i \]

at time points \( t_i, i = 1, \ldots, m_1 \)

- Data from multiple experiments under varying conditions
- \( \mathcal{M} \): nonlinear function of states (differential and algebraic)
- \( \varepsilon_i \): measurement errors
  - independent
  - in this talk: \( \varepsilon_i \sim \mathcal{N}(0, \sigma_i^2) \)
Numerical Methods for Parameter Estimation in ODE/DAE/PDE

- Direct “all-at-once” multiple shooting method
- Constrained Gauss Newton method
- Structure exploitation (multiple experiments, parameterization in time, spatial discretization of PDE)
- Efficient line search strategies
- Use of inexact Jacobians
- Robust parameter estimation based on $l_1$ or Huber
After (Multiple Shooting) Discretization: Large-Scale $l_2$ Parameter Estimation Problem

$$\min_x \frac{1}{2} \|F_1(x)\|_2^2, \quad \text{s.t.} \quad F_2(x) = 0$$

Optimization variables: $x^T := (p^T, s^T) \in \mathbb{R}^n$, with discretization variables $s$

Cost function: $F_1(x) := \Sigma^{-1} \begin{pmatrix} \eta_1 - \mathcal{M}(t_1, y(t_1; p, s), p) \\ \vdots \\ \eta_{m_1} - \mathcal{M}(t_{m_1}, y(t_{m_1}; p, s), p) \end{pmatrix} \in \mathbb{R}^{m_1}$

$$\Sigma^{-1} = \text{diag}\left( \frac{w_i}{\sigma_i}, \ i = 1, \ldots, m_1 \right), \ w_i \in \{0, 1\}$$

Constraints: $F_2(x) := \begin{pmatrix} C(p, s) \\ \text{Discretized BVP} \end{pmatrix} \in \mathbb{R}^{m_2}$

Jacobians: $J_1(x) := \frac{\partial F_1(x)}{\partial x}$ and $J_2(x) := \frac{\partial F_2(x)}{\partial x}$
Solution Approach: Generalized Gauss-Newton

Solve iteratively, given initial guess \( x^0 \)

\[
x^{k+1} = x^k + \left[ t^k \right] \Delta x^k
\]

\( \Delta x^k \) solves linearized problem

\[
\min_{\Delta x \in \Omega^k} \frac{1}{2} \| F_1(x^k) + J_1(x^k) \Delta x \|^2_2
\]
\[
\text{s.t.} \quad F_2(x^k) + J_2(x^k) \Delta x = 0
\]

\[
\Delta x^k = -J^+(x^k)F(x^k)
\]

\( J^+ \) is a generalized inverse: \( J^+J J^+ = J^+ \)

\[
J = \begin{pmatrix} J_1 \\ J_2 \end{pmatrix}, \quad F = \begin{pmatrix} F_1 \\ F_2 \end{pmatrix}
\]
Parameter Estimation and Sensitivity Analysis

Dynamical Process

Measurements with Errors

Mathematical Model

Parameter Estimation Problem

Estimates $x^*$

Qualitative Assessment of $x^*$

Quantitative Output

Qualitative Output?
Likelihood Ratio Confidence Regions

\[ \mathcal{D}_{lr}(\alpha) = \{ x \mid F_2(x) = 0, \| F_1(x) \|^2_2 - \| F_1(x^*) \|^2_2 \leq \gamma^2_{\bar{m}}(\alpha) \} \]

\( \gamma^2_{\bar{m}}(\alpha) \) is \((1 - \alpha)\)-quantile of \( \chi^2 \)-distribution with \( \bar{m} := n - m_2 \) degrees of freedom

Advantage

- High approximation quality

Disadvantage

- Very difficult to compute

Beale 60, Draper and Smith 81, Pazman 93
Linearized Confidence Regions

\[ \mathcal{D}_{\text{lin}}(\alpha) = \{ x \mid J_2(x^*)(x - x^*) = 0, \|J_1(x^*)(x - x^*)\|_2^2 \leq \gamma_m^2(\alpha) \} \]

Advantage

- Can be computed very efficiently
Another View: Parameter Sensitivity w.r.t. Measurement Errors

- Introduce an error weight \( \tau \in [0, 1] \):

\[
\begin{align*}
\min_x \| F_1(x) \|_2^2 & \quad \min_x \| F_1(x, \tau) \|_2^2 \\
\text{s.t. } F_2(x) = 0 & \quad \text{s.t. } F_2(x) = 0
\end{align*}
\]

where

\[
F_1(x, \tau) = \Sigma^{-1} \left( \begin{array}{c}
(M(t_1) + \tau \epsilon_1) - M(t_1, y(t_1; s), p) \\
\vdots \\
(M(t_m) + \tau \epsilon_m) - M(t_m, y(t_m; s), p)
\end{array} \right)
\]

- Measurements \( \overline{M} \) \( \Rightarrow \) estimates \( x(\overline{M}) \) resp. \( x(0) \)
- Measurements \( \overline{M} + \tau \epsilon \) \( \Rightarrow \) estimates \( x(\overline{M} + \tau \epsilon) \) resp. \( x(\tau) \)
- Question: what is the distribution of \( x(\tau) \)?

**Lemma**

*Taylor series for the solution of the modified problem*

- \( x(\tau) = \bar{x} + \tau J^+ \left( \begin{array}{c} \Sigma^{-1} \epsilon \\ 0 \end{array} \right) + \mathcal{O}(\tau^2) \)
Another View: Linearized Confidence Regions

\[ \bar{D}_{\text{lin}}(\alpha) = \{ x^* + \Delta x \mid \Delta x = -J^+(x^*) \begin{pmatrix} \eta \\ 0 \end{pmatrix}, \| \eta \|_2^2 \leq \gamma_m^2(\alpha) \} \]

- \[ \bar{D}_{\text{lin}}(\alpha) = \{ x \mid J_2(x^*)(x - x^*) = 0, \| J_1(x^*)(x - x^*) \|_2^2 \leq \gamma_m^2(\alpha) \} \]
- Linear approximation of the covariance matrix
  \[ C = \mathcal{E} \left( \Delta x \Delta x^T \right) \]
  \[ = J^+(x^*) \begin{pmatrix} \mathbb{I}_{m_1} & 0 \\ 0 & 0_{m_2} \end{pmatrix} J^T(x^*) \]
- \[ \bar{D}_{\text{lin}}(\alpha) \] is enclosed by a (minimal) box
  \[ \mathcal{G}_L(\alpha) \subset \bigtimes_{i=1}^n [x_i^* - \theta_i, x_i^* + \theta_i], \]
  where \( \theta_i = \sqrt{C_{ii}\gamma_m^2(\alpha)} \) and \( C_{ii} \) are the diagonal elements of the covariance matrix

Bock 1987
Next Step in Model Validation: Design of Optimal Experiments
Design of Optimal Experiments

Aim: choose optimal experimental conditions (design variables) to gain information about parameter estimates (to reduce parameter uncertainty)

Design variables

\[ \xi^T := (q^T, w^T) \in \Xi \]

- \( q \in \mathbb{R}^{n_q} \) (discretized) control functions and control parameters
- \( w \in \{0, 1\}^K \) sampling
Design of Optimal Experiments:
Problem Formulation

\[
\begin{align*}
\min_{\xi} & \quad \phi(\xi; x) \\
\text{s. t.} & \quad m_l \leq \psi(t, x, \xi) \leq m_u, t \in T \\
& \quad 0 = \chi(t, x, \xi), t \in T \\
& \quad w \in \{0, 1\}^M
\end{align*}
\]

- \(\xi^T = (q^T, w^T)\) are design variables
- \(x\) is an estimate of true parameter and (discretized) states values \(x^{true}\) satisfying the underlying parameter estimation problem
Design of Optimal Experiments: Cost Functionals

Typical cost functionals

$\phi$ is a functional of the covariance matrix $C$

\[
C = J^+(x) \begin{pmatrix} I_{m_1} & 0 \\ 0 & 0_{m_2} \end{pmatrix} J^T(x) = (I_{m_1} \ 0) \begin{pmatrix} J^T_1 J_1 & J^T_2 \\ J_2 & 0 \end{pmatrix}^{-1} (I_{m_1} \ 0)
\]

- A: $\phi_A(C) = \frac{1}{n} \text{Trace}(C)$
- D: $\phi_D(C) = \det(K^TCK)^{\frac{1}{n}} \text{ mit } K \in \mathbb{R}^{n \times n_k}$
- E: $\phi_E(C) = \max\{\lambda | \lambda \text{ is an eigenvalue of } C\}$

OED problem is a complex non-standard nonlinear mixed-integer optimal control problem

- Cost function already involves 1st order derivatives of PE problem and is implicitly defined by a generalized inverse
- Integer decisions: sampling design
Optimal Experimental Design is a Complex Non-Standard Nonlinear Mixed-Integer Optimal Control Problem

- Theory originally developed for linear models
  
  e.g. Kiefer, Wolfowitz 50’s, Box, Draper 1987, Pukelsheim 1993

- Algorithmic developments:
  

  Software VPLAN

- structure exploiting, direct, all-at-once optimization algorithms for DE models, based on multiple shooting

- efficient evaluation of higher order derivatives by structure exploiting “internal” and “algorithmic” differentiation

- optimal integer controls by exact lower bounds and intelligent approximation strategies

- robustification of optimization against uncertainties

- experimental design for model discrimination
What Improvements Can We Expect From Optimal Experimental Designs?
Application: Transport and Degradation of Xenobiotics in Soil
Transport and Degradation of Xenobiotics in Soil

- investigation of fate of pesticides in soil needs expensive lysimeter experiments for registration
- replacement by computer experiments requires validated models!
- here: optimal mini-lysimeter experiments
  - optimal irrigation
  - optimal solute application
Typical Column Outflow Experiment

Water transport: $\implies$ 3 unknown parameters $n$, $\alpha$, $K_s$

$$C(\psi) \frac{\partial \psi}{\partial t} = \frac{\partial}{\partial z} \left( K(\psi) \frac{\partial}{\partial z} (\psi - z) \right)$$

$$K(\psi) = K_s \left( 1 - (\alpha |\psi|)^{n-1} \right) \left( 1 + (\alpha |\psi|^{n})^{1/n-1} \right)^2$$

$$\left( 1 + (\alpha |\psi|)^{n} \right)^{1-1/n}$$

$$C(\psi) = \alpha (n - 1)(\theta_s - \theta_r) (\alpha |\psi|)^{n-1} \left( 1 + (\alpha |\psi|)^{n} \right)^{1/n-2}$$

- Initial condition: $\psi(0, z) = 670$, $z \geq 0$
- Upper boundary condition:

$$q(t, 0) = -K(\psi(t, 0)) \left( \frac{\partial \psi(t, 0)}{\partial z} - 1 \right) \quad \text{control: water flux}$$

- Lower boundary condition:

$$\frac{\partial \psi(t, L_e)}{\partial z} = 0, \quad t \geq 0$$
Typical Column Outflow Experiment

Solute transport: \( \implies 3 \text{ unknown parameters } k, b, D_m \)

\[
\frac{\partial (\theta c)}{\partial t} = \frac{\partial (\theta D_h(\theta) \frac{\partial c}{\partial z})}{\partial z} - \frac{\partial (qc)}{\partial z} - kc
\]

\[
D_h(\theta) = \frac{0.0046 e^{b\theta}}{\theta} + D_m
\]

- Initial condition: \( c(0, z) = 0, \ z \geq 0 \)
- Upper boundary condition:
  \[
  -D_h(\theta(t, 0)) \frac{\partial c(t, 0)}{\partial z} + \frac{q(t, 0)}{\theta(t, 0)} c(t, 0) = \frac{q(t, 0)}{\theta(t, 0)} c_0(t, 0) \quad \text{control: solute input}
  \]
- Lower boundary condition: \( \frac{\partial c(t, L_e)}{\partial z} = 0, \ t \geq 0 \)
Typical Column Outflow Experiment

Coupled water and solute transport: 6 unknown parameters
Optimization of Experimental Conditions

2 boundary controls - piecewise constant

- water flux $q(t, 0)$
  - changeable only every 24 h
  - $0 \leq q(t, 0) \leq 0.6$

- solute input $c_0(t, 0)$
  - changeable only every 24 h
  - $50 \leq c_0(t, 0) \leq 200$

sampling scheme: fixed measurement times

- 24 outflow measurements - 12 days, every 12h ($\sigma = 0.01$)
- 6 profile measurements ($\sigma = 0.1$)
  - only at end of experiment
  - evaluation of solute concentrations at 6 locations
Parameterized Expert Designs

Input water flux

\[ q(t, 0) \]

Substance input concentration

\[ c_0(t, 0) \]
Quality of Expert Designs: Criterion Values and Standard Deviations

Expert Design A

A-Criterion = 3.8859

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<tr>
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<th>scaled</th>
<th>standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>1.0</td>
<td>± 0.1604</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>1.0</td>
<td>± 1.5968</td>
</tr>
<tr>
<td>$K_s$</td>
<td>1.0</td>
<td>± 3.3752</td>
</tr>
<tr>
<td>$k$</td>
<td>1.0</td>
<td>± 0.0124</td>
</tr>
<tr>
<td>$b$</td>
<td>1.0</td>
<td>± 3.0460</td>
</tr>
<tr>
<td>$D_m$</td>
<td>1.0</td>
<td>± 0.2644</td>
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</table>

Expert Design B

A-Criterion = 0.75

<table>
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<td>± 0.8600</td>
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<td>$K_s$</td>
<td>1.0</td>
<td>± 1.6736</td>
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<td>$k$</td>
<td>1.0</td>
<td>± 0.0083</td>
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<tr>
<td>$b$</td>
<td>1.0</td>
<td>± 0.9712</td>
</tr>
<tr>
<td>$D_m$</td>
<td>1.0</td>
<td>± 0.1033</td>
</tr>
</tbody>
</table>
Optimal Experimental Conditions

Input water flux
\[ q(t, 0) \]

Substance input concentration
\[ c_0(t, 0) \]
### Comparison:
**Optimal Design vs Expert Designs A and B**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Optimal design</th>
<th>Expert design A</th>
<th>Expert design B</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-Criterion</td>
<td>0.0472</td>
<td>3.8859</td>
<td>0.750</td>
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<tr>
<td>$n$</td>
<td>1.0 ± 0.0191</td>
<td>± 0.1604</td>
<td>± 0.0800</td>
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<tr>
<td>$\alpha$</td>
<td>1.0 ± 0.2438</td>
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<td>± 0.8600</td>
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<tr>
<td>$K_s$</td>
<td>1.0 ± 0.4348</td>
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<tr>
<td>$k$</td>
<td>1.0 ± 0.0086</td>
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<td>± 0.0083</td>
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<td>$b$</td>
<td>1.0 ± 0.1852</td>
<td>± 3.0460</td>
<td>± 0.9712</td>
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<tr>
<td>$D_m$</td>
<td>1.0 ± 0.0108</td>
<td>± 0.2644</td>
<td>± 0.1032</td>
</tr>
</tbody>
</table>

All parameters can be simultaneously estimated!
Ongoing Developments

- Rich and well advanced theory of optimal experimental design for linear models
- Very high relevance in industrial applications
- BASF: “We save up to 80% costs with these methods and get much more precise results!”

“Bildzeitung”, 17.06.2008
Actual Developments

- Rich and well advanced theory of optimal experimental design for linear models
- Very high relevance in industrial applications
- BASF: “We save up to 80% costs with these methods and get much more precise results!”

- Efficient numerical methods for
  - robustification of OED against uncertainties in parameter estimates
  - parabolic PDE models
  - on-line design of optimal experiments
Robustification of OED Based on Second Order Sensitivity Analysis
Robustification of OED Based on Second Order Sensitivity Analysis

Consider again parametric PE problem depending on an error weight \( \tau \in [0, 1] \):

\[
\begin{align*}
\min_x & \quad \| F_1(x) \|_2^2 \\
\text{s.t.} & \quad F_2(x) = 0 \\
\end{align*}
\]

\[
\sim \quad \min_x \quad \| F_1(x, \tau) \|_2^2 \\
\text{s.t.} & \quad F_2(x) = 0
\]

where

\[
F_1(x, \tau) = \Sigma^{-1} \left( \begin{array}{c}
(\overline{M}(t_1) + \tau \epsilon_1) - M(t_1, y(t_1; s), p) \\
\vdots \\
(\overline{M}(t_m) + \tau \epsilon_m) - M(t_m, y(t_m; s), p)
\end{array} \right)
\]

**Lemma**

*Taylor series for the solution of the modified problem*

- \( x(\tau) = \bar{x} + \tau J^+ \left( \Sigma^{-1} \epsilon \right) + O(\tau^2) \)
- \( x(\tau) = \bar{x} + \tau J^+ \left( \Sigma^{-1} \epsilon \right) + \tau^2 \left( dJ^+ (I - JJ^+) - \frac{1}{2} J^+ (dJ) J^+ \right) \left( \Sigma^{-1} \epsilon \right) + O(\tau^3) \)
Properties of Taylor Series

Consider Taylor expansion at the parameter estimates $x = x^* + \Delta x + \frac{1}{2} \bar{\Delta} x$ with

$$\Delta x = -J^+ \begin{pmatrix} \eta \\ 0 \end{pmatrix}, \quad \bar{\Delta} x = -2 \left( dJ^+ (I - JJ^+) - \frac{1}{2} J^+ (dJ) J^+ \right) \begin{pmatrix} \eta \\ 0 \end{pmatrix}, \quad \| \eta \|_2^2 \leq \gamma^2_m(\alpha)$$

Then:

$$\| \Delta x \|_2 \leq \theta, \quad \| \Delta x + \frac{1}{2} \bar{\Delta} x \|_2 \leq \theta + \left( \tilde{\kappa}(x^*) + \frac{1}{2} \tilde{\omega}(x^*) \theta \right) \theta$$

where

$$\theta := \sqrt{\text{Trace}(C(x^*)) \gamma^2_m(\alpha)},$$

$$\tilde{\omega}(x^*) := \left\| J^+ (x^*) \frac{\partial J(x^*)}{\partial x} \right\|, \quad \tilde{\kappa}(x^*) := \left\| C \left( \frac{\partial J^T(x^*)}{\partial x} (I \otimes F_1(x^*)) \right) \right\|$$
Design of Optimal Experiments: “Q” Cost Functional

K., Nattermann 2015, 2016

New cost functional

\[ \phi_Q(\cdot) = \text{Trace}(C(\cdot)) \left( \tilde{\kappa}(\cdot) + \frac{\tilde{\omega}(\cdot)}{2} \text{Trace}(C(\cdot)) \right) \text{Trace}(C(\cdot)), \]

- \( \tilde{\omega} \) is a weighted Lipschitz constant of \( J \) (nonlinearity of the model functions)
- \( \tilde{\kappa} \) is a weighted Lipschitz constant of \( J^+ \) (compatibility of the data and the model, asymptotic convergence rate of Gauss-Newton)

Numerical experiments show that
- Q-optimal designs are significantly insensitive to uncertainties in parameter estimates,
- the condition of the corresponding PE problem is improved
OED for PDE Models
Choose design controls $\zeta$ as solution of the optimal control problem

$$\min_{\xi \in L^2(\Omega \times [0,T]), u \in W(0,T)} \quad tr(Cov[u, p, \xi]) + c\|\zeta\|_{L^2(\Omega \times [0,T])}^2$$

s.t. \quad \partial_t u + a(u, p, \xi) = 0,

\quad u(0) = u_0,

\quad Cov = (J_{red}^T J_{red})^{-1},

+ additional constraints on controls
Optimal Experimental Design for Parabolic PDE Models: Numerical Framework

- Parametrization of the underlying parameter estimation problem with multiple shooting approach
- Condensing technique in function space and efficient computation of the reduced covariance matrix for parameters
- Formulation of the OED problem as a multi-stage optimal control problem
- Efficient computation of reduced gradients by an adjoint approach which requires $n_p + 1$ PDE solves
- Efficient computation of Hesse operator by Lagrange function and adjoint equations
- Positive definite approximation of Hesse operator which requires solution of decoupled $n_p \times n_p$ adjoint equations
- Software on the basis of DEAL-II
Application: Catalytic Plug Flow Reactor

- A fluid flux through a packed bed of a porous catalyst, where an exothermic reaction takes place

- Aim: to calibrate the mathematical model for the reactor
Catalytic Plug Flow Reactor
Mathematical Model

Mass balance:

\[ \epsilon \frac{\partial c_i}{\partial t} = - \frac{\partial (u_f c_i)}{\partial z} + D_{eff,z} \frac{\partial^2 c_i}{\partial z^2} + D_{eff,r} \left( \frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} \right) + \frac{\rho_{s,bed}}{\rho_f} R_i \]

Energy balance:

\[ \left( \epsilon \rho_f c_{p,f} + (1 - \epsilon) \rho_{s,bed} c_{p,s} \right) \frac{\partial T}{\partial t} = -c_{p,f} \frac{\partial (u_f \rho_f T)}{\partial z} + \lambda_{eff,z} \frac{\partial^2 T}{\partial z^2} + \lambda_{eff,r} \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) \]

\[ + \rho_{s,bed} \sum_{i=1}^{N} \Delta H_{R,i} R_i \]

Catalyst activity:

\[ \frac{\partial a_{cat}}{\partial t} = c_A \left( k_{0,des} + A_{0,des} exp \left( -\frac{E_{a,des}}{R_g T} \right) \right) \]
The Optimal Experiment Design Problem

- 4 parameters to estimate: activation energies and frequency factors of the main and deactivation reaction
- 16 measurements of the temperature in the middle of the reactor at 5 different time points
- Boundary control: The temperature of the gas at the inlet of the reactor $T_{ent}$, and the concentration $c_{ent}$

$$\lambda_{eff,z} \frac{\partial T(t, 0, r)}{\partial z} = -u_f \rho_f c_{p,f}(T_{ent}(t, r) - T(t, 0, r)) \quad z = 0$$
$$c(t, 0, r) = c_{ent}(t, r) \quad z = 0$$
## Intuitive vs Optimal Design

<table>
<thead>
<tr>
<th>Parameter</th>
<th>True Values</th>
<th>Estimates</th>
<th>Uncertainty</th>
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<tbody>
<tr>
<td>$k_1$</td>
<td>$-1.76416$</td>
<td>$-1.79401 \pm 0.949$</td>
<td>52.9%</td>
</tr>
<tr>
<td>$k_2$</td>
<td>$-3.37131$</td>
<td>$-3.83068 \pm 0.232$</td>
<td>6.1%</td>
</tr>
<tr>
<td>$k_{1,deac}$</td>
<td>$-5.60809$</td>
<td>$-4.98277 \pm 8.117$</td>
<td>162.9%</td>
</tr>
<tr>
<td>$k_{2,deac}$</td>
<td>$-5.62849$</td>
<td>$-5.61164 \pm 1.160$</td>
<td>20.6%</td>
</tr>
<tr>
<td>trace</td>
<td>-</td>
<td>$7.18573$</td>
<td>-</td>
</tr>
</tbody>
</table>

Estimates Based on Intuitive Experimental Design

<table>
<thead>
<tr>
<th>Parameter</th>
<th>True Values</th>
<th>Estimates</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$-1.76416$</td>
<td>$-1.77712 \pm 0.628$</td>
<td>35.4%</td>
</tr>
<tr>
<td>$k_2$</td>
<td>$-3.37131$</td>
<td>$-3.84067 \pm 0.228$</td>
<td>5.9%</td>
</tr>
<tr>
<td>$k_{1,deac}$</td>
<td>$-5.60809$</td>
<td>$-5.57985 \pm 4.914$</td>
<td>88.1%</td>
</tr>
<tr>
<td>$k_{2,deac}$</td>
<td>$-5.62849$</td>
<td>$-5.61718 \pm 0.977$</td>
<td>17.4%</td>
</tr>
<tr>
<td>trace</td>
<td>-</td>
<td>$2.692312$</td>
<td>-</td>
</tr>
</tbody>
</table>

Estimates Based on the Optimal Experiment
Refinements: Online Optimal Experimental Design

Idea:

- new measurements gained in experiments can be used to improve the parameter estimates \( p^* \)
- re-optimize optimum experimental design over remaining experiment

\[
\min_{\xi \in \Omega \times [t, t_N]} \varphi(C(\xi, p^*))
\]

Challenges:

- real-time iteration and multi-level iteration for optimum experimental design
<table>
<thead>
<tr>
<th>Parameter</th>
<th>True Values</th>
<th>Estimates</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
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<td>35.4%</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>(-3.37131 )</td>
<td>(-3.84067 \pm 0.228 )</td>
<td>5.9%</td>
</tr>
<tr>
<td>( k_{1,\text{deac}} )</td>
<td>(-5.60809 )</td>
<td>(-5.57985 \pm 4.914 )</td>
<td>88.1%</td>
</tr>
<tr>
<td>( k_{2,\text{deac}} )</td>
<td>(-5.62849 )</td>
<td>(-5.61718 \pm 0.977 )</td>
<td>17.4%</td>
</tr>
<tr>
<td>trace</td>
<td>-</td>
<td>2.692312</td>
<td>-</td>
</tr>
</tbody>
</table>

Estimates Based on Offline Optimal Experimental Design

<table>
<thead>
<tr>
<th>Parameter</th>
<th>True Values</th>
<th>Estimates</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>(-1.76416 )</td>
<td>(-1.79392 \pm 0.492 )</td>
<td>27.4%</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>(-3.37131 )</td>
<td>(-3.8335 \pm 0.203 )</td>
<td>5.3%</td>
</tr>
<tr>
<td>( k_{1,\text{deac}} )</td>
<td>(-5.60809 )</td>
<td>(-5.42928 \pm 2.653 )</td>
<td>48.9%</td>
</tr>
<tr>
<td>( k_{2,\text{deac}} )</td>
<td>(-5.62849 )</td>
<td>(-5.59868 \pm 0.872 )</td>
<td>15.6%</td>
</tr>
<tr>
<td>trace</td>
<td>-</td>
<td>0.851882</td>
<td>-</td>
</tr>
</tbody>
</table>

Estimates Based on Online Optimal Experimental Design
One More Application:
Select Optimal Catalyst Geometry by Heat Transfer Coefficient – High Impact on the Value Chain
Estimation of Catalyst Properties

- silver catalyst on aluminum supports of different geometries
- ultimate aim: maximize selectivity of catalytic production process, e.g., ethene to ethene oxide

Important criterion: high heat transfer coefficient to avoid hot spots or explosion!
Experimental setup

- standard heat conduction test reactor

- special features:
  - non-stationary heating,
  - temperature range 20-350°C
  - temperature gradient over 200°C
Experimental setup

- 2D nonstationary PDE

\[ \tau \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left( \lambda_z \frac{\partial T}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \lambda_r \frac{\partial T}{\partial r} \right) - G c_p \frac{\partial T}{\partial z} \]

- \( \approx \) 1000 spatial grid points
- 2 controls: boundary temperature \( T_W \), mass current density \( G \)
- 4 parameters to estimate:
  - \( \lambda_z, \lambda_r \) (heat conductivity)
  - \( \tau, c_p \) (heat capacity)
- measurements: outlet temperature
Simulation of Heat Conduction

low heat conductivity $\lambda$

high heat conductivity $\lambda$

$T$

$r$

$z$

$G$

$CO_2$ gas inflow

Cooperation with

BASF

The Chemical Company
Optimal Experimental Design

Cooperation with

- intuitive expert design
  - experimental time 16h

- optimal design
  - experimental time 2.5h
  - uncertainty is halved

- four experiments
  - with constant $G = 0, 0.9, 1.8, 4 \text{ kg/m}^2\text{s}$
  - non-stationary heating with ramp $T_W = 20 - 350^\circ\text{C}$

- one experiment
  - with varying steps of $G = 0, 0.49, 4 \text{ kg/m}^2\text{s}$
  - stationary heating with $T_W = 350^\circ\text{C}$
Optimal Experimental Design

- Results: total heat transfer coefficients for 3 candidate shapes including error bars

![Graph showing heat transfer coefficients for 3 shapes with error bars]

- High accuracy decision basis for reactor design
- Market idea revised: shape 1 instead of shape 2 (original choice)

- Impact on value chain: catalyst investment over 1 M€!
Conclusions

- Numerical methods and software for parameter estimation and optimum experimental design
- Complex nonlinear problems modelled by ODE/DAE/PDE can be treated
- Optimal experimental design leads to acceleration of modeling process, allows to reduce e.g. development times for new products, prevents from making wrong decisions based on not calibrated models

- Challenges:
  - High potential, but practically no theory for nonlinear dynamical processes available
  - Also more efficient numerical methods needed
    - robustification of OED against uncertainties
    - more general problem classes, e.g., hybrid systems, PDE models
    - incorporation of OED in real time state and parameter estimation and feedback control
  - New application areas

THANK YOU!