Model-Based Experimental Analysis of Multi-Phase Reaction Systems

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Managing Complexity of Kinetic Phenomena

product & process systems

kinetic phenomena

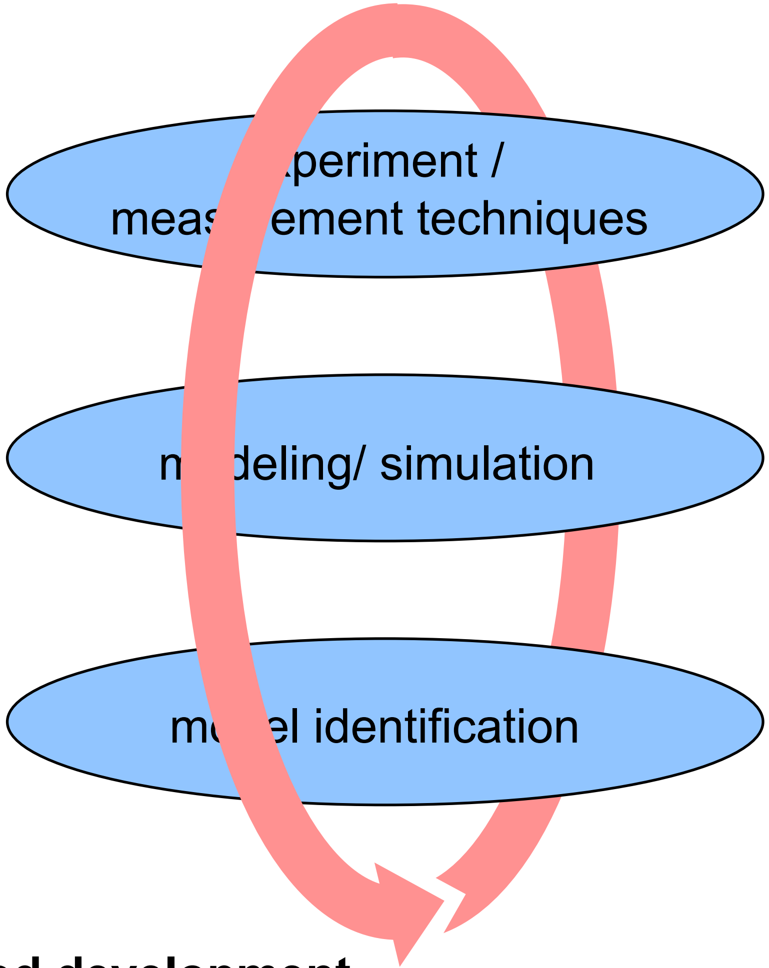
- diffusion
- heat and mass transfer
- interface phenomena
- multiphase transport
- (bio-)chemical reaction
- nucleation ...

multi-phase reaction and separation **processes**

fluid, structured & functional **products**

biological systems

experimental and theoretical methods & tools



integrated method development towards a work process of model-based experimental analysis

Model-based Experimental Analysis of Kinetic Phenomena in Fluid Multi-phase Reactive Systems

13 research groups with cross-disciplinary expertise

- biotechnolgy (Ansorge-Schuhmacher)
- biochemical engineering (Büchs)
- reaction engineering (Greiner, Leitner)
- thermal separations (Pfennig)
- transport phenomena (Kneer)
- multiphase fluid dynamics (Modigell)
- computational engineering science (Behr)
- process systems engineering (Bardow, Marquardt)
- numerical mathematics (Reusken)
- scientific computing (Bischof, Bücker)
- NMR imaging (Blümich, Stapf)
- optical spectroscopy (Koß, Lucas, Poprawe)

Funded by DFG (Deutsche Forschungs-gemeinschaft) since 1999
Director: W. Marquardt

Research Agenda of CRC 540

development of a work process
Model-based Experimental Analysis (MEXA)
for systematic mechanistic modeling by means of multi-method integration
and
its application to **modeling of multi-phase fluid reaction processes**

reaction and multi-component diffusion in liquids

transport and (bio-)reaction in heterogeneous systems

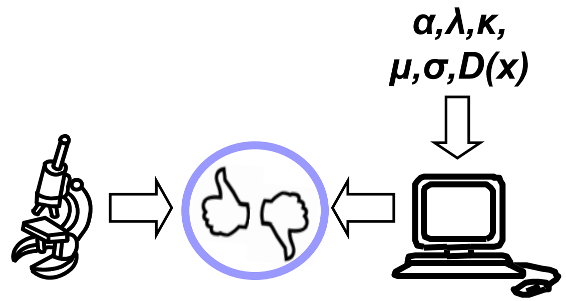
transport and reaction in single dispersed liquid droplets

transport and reaction in liquid falling films

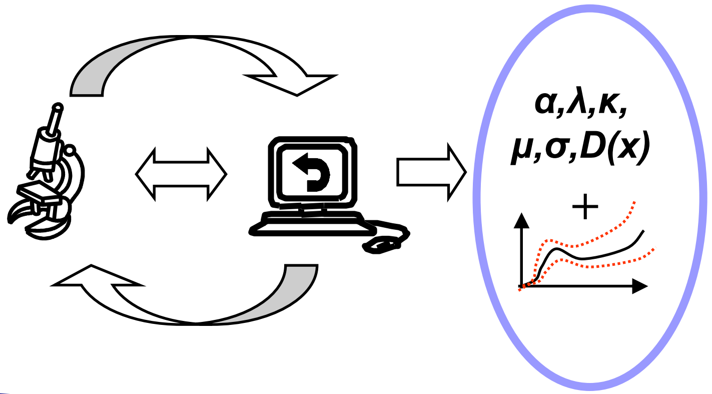
Integration of Modeling and Experimentation

cf. J.V. Beck, *Meas. Sci. Techn.* 9 (1998)

- **common approach in research and industrial practice**
  - coupled phenomena
  - detailed models, numerical case studies
  - comparison of simulation and experimental results
  - **evaluation of the model, but no model identification !**

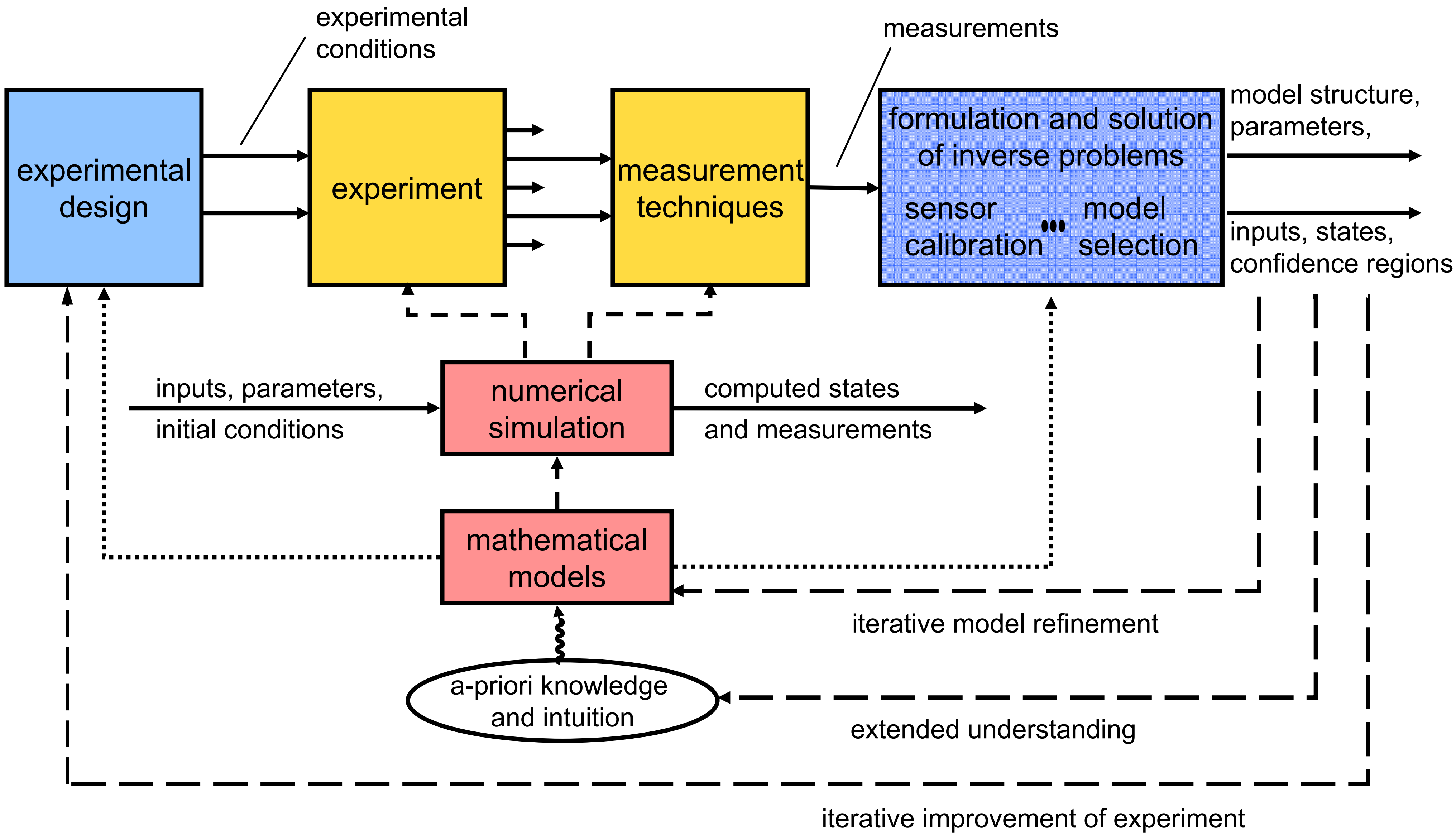


- **suggested approach**
  - coordinated design of model and experiment
  - model refinement based on experimental evidence
  - accounting for inevitable measurement errors
  - **identification of a valid (mechanistic) model (structure & parameters) !**

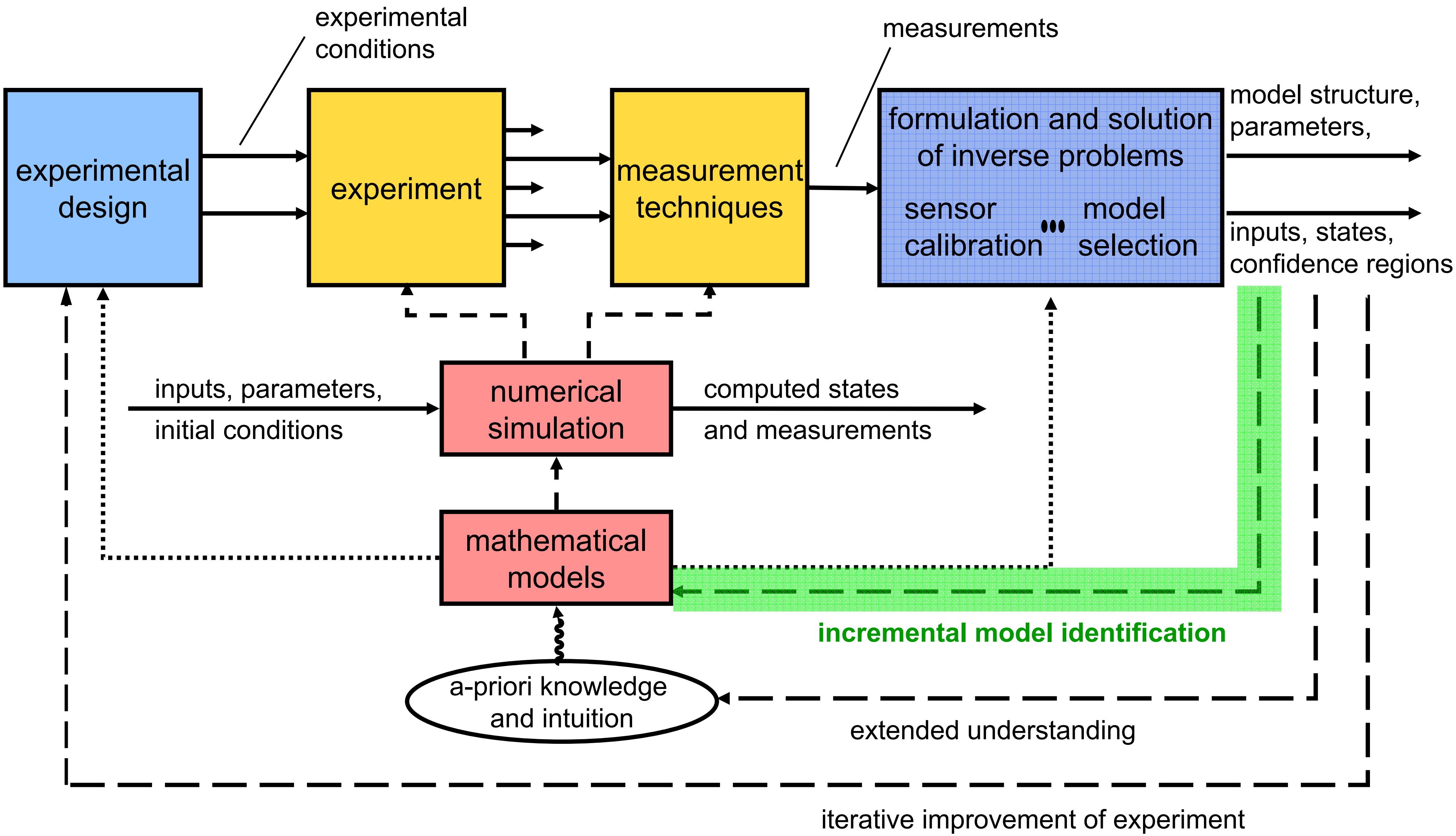


model-based experimental analysis – MEXA:
valid models at minimal effort

MEXA Methodology



MEXA Methodology



Simultaneous Model Identification

measurements y

model of observations $y(x,\theta,t)$

- mass/heat balances
- thermodynamics
- reaction kinetics
- ...

model parameters θ

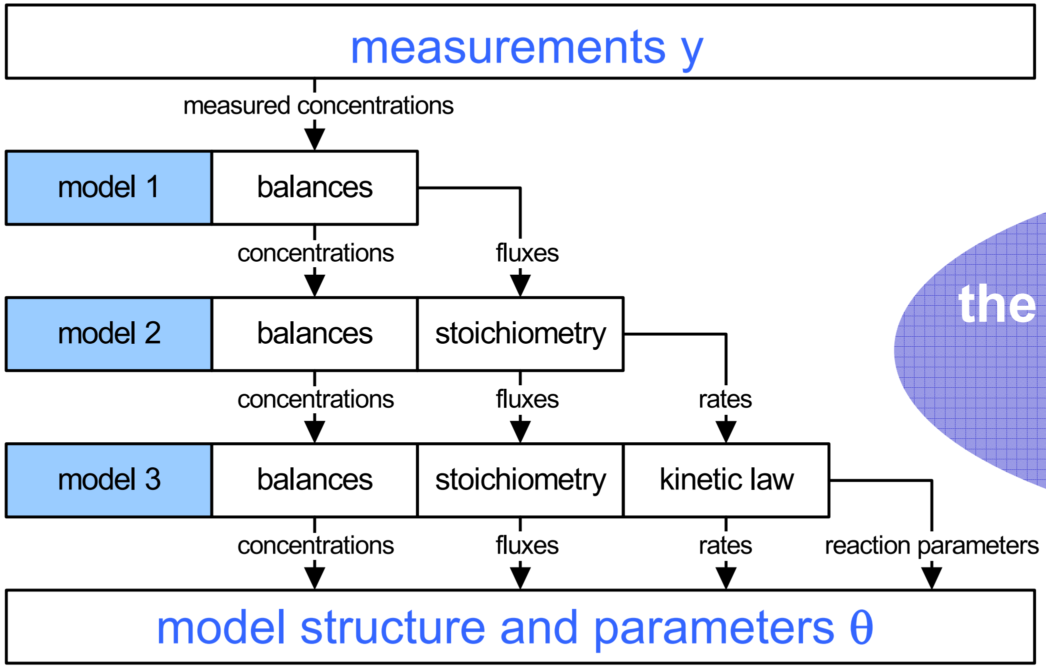
Overall process model $y(x,\theta,t)$ is fitted to experimental data:

$$\min_{\boldsymbol{\theta}} \frac{1}{2}\sum_{i=1}^{n} w_i \sum_{j=1}^{m}\left(y(\mathbf{x},\boldsymbol{\theta},t_j)-\tilde{y}(t_j)\right)^2$$

s.t. dynamic model & constraints

- **What if we do not know any candidate model structure ?**
- **How to select a suitable model structure ?**
- **Is bias due to model structure defects or a lack of information content in data ?**
- **How to deal with very few or very many observations ?**
- **How to deal with convergence & robustness problems of estimation algorithm?**

Incremental Model Identification

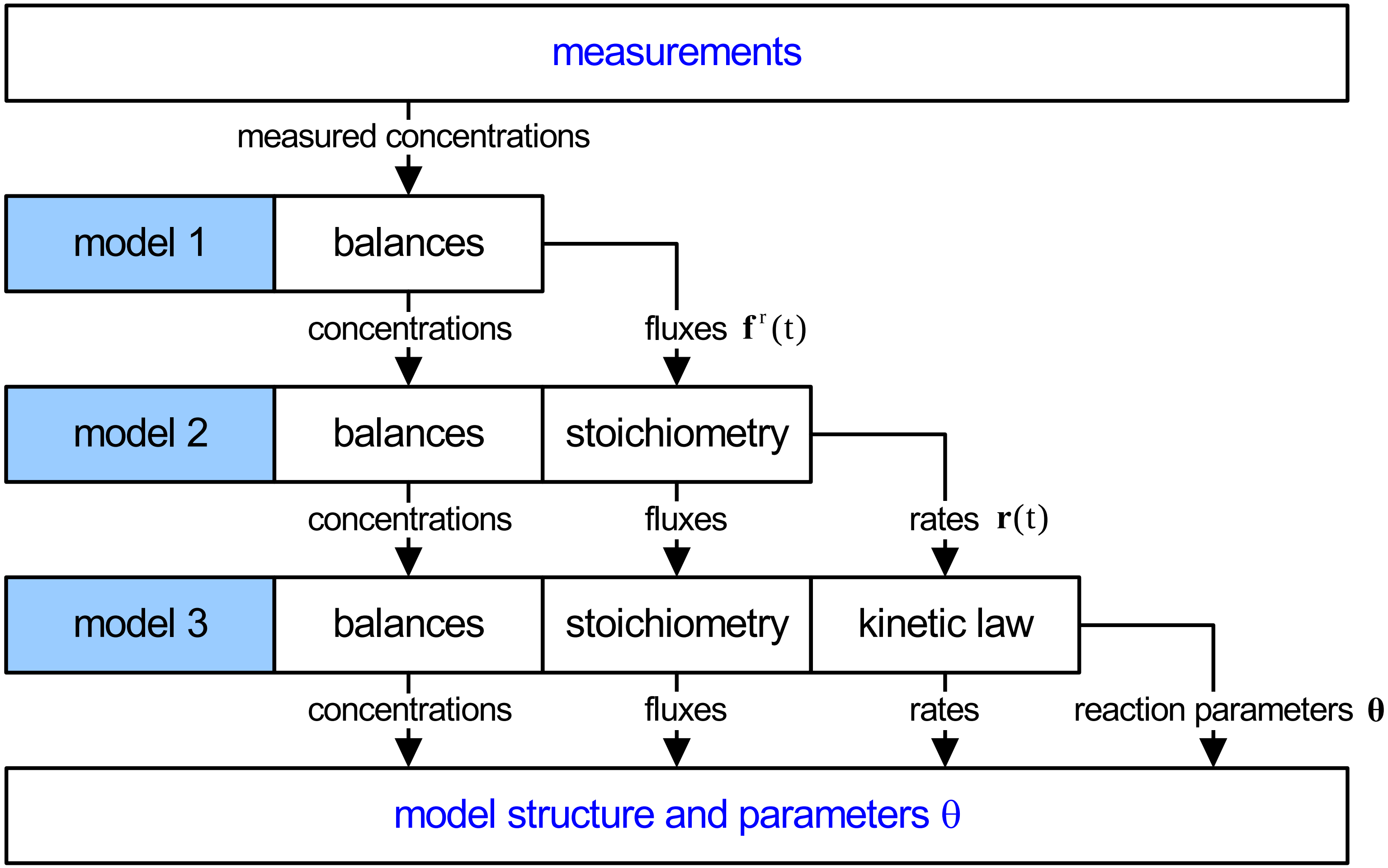


Decompose the model identification and selection task into fully transparent steps !

- **computationally efficient (minutes rather than days)**
- **numerically robust and fully transparent**
- **a-priori knowledge can be integrated into the identification process**
- **complex and interacting kinetic phenomena can be identified**

Incremental Model Development

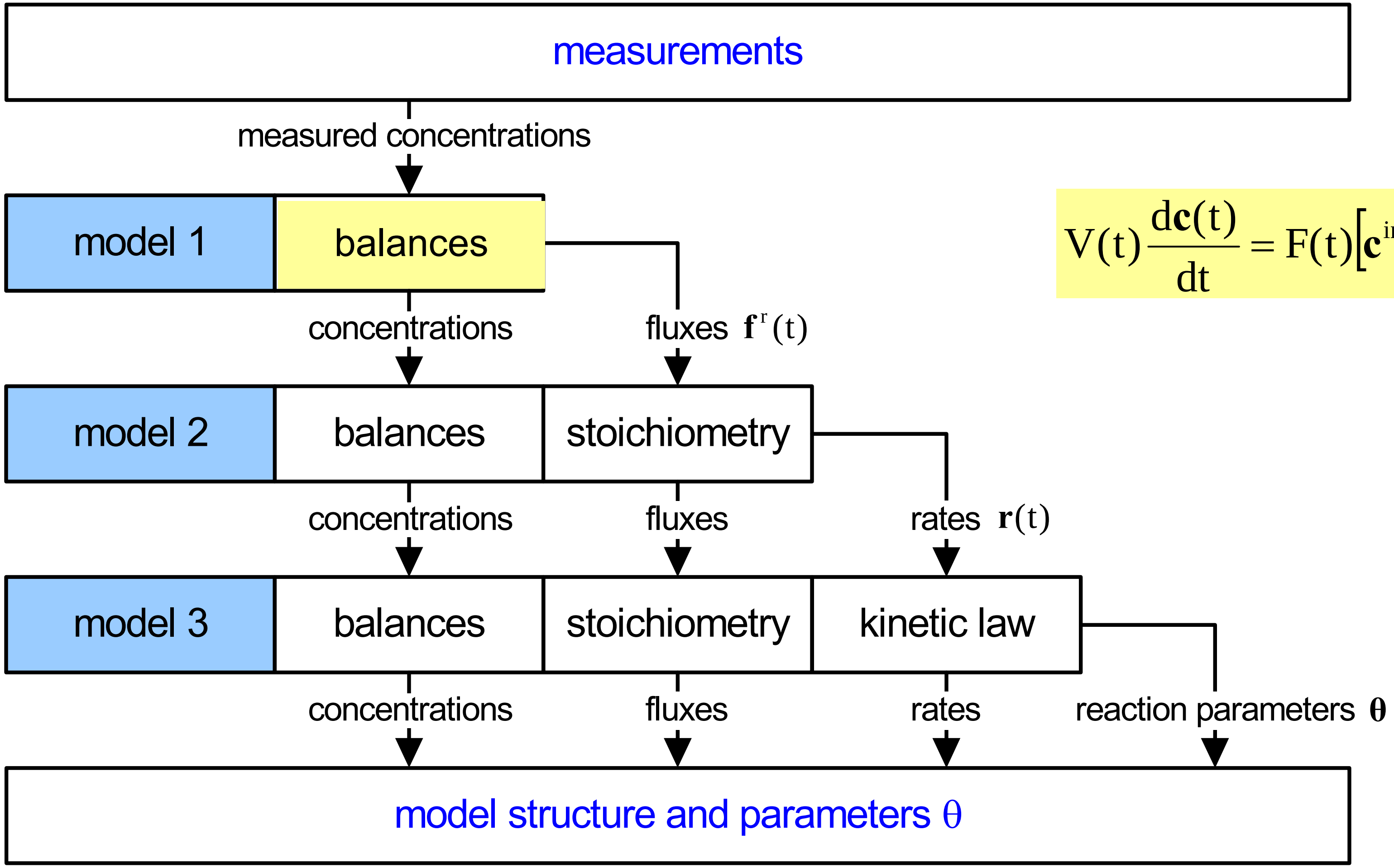
Illustratrion with a CSTR



(Marquardt, 1996)

Incremental Model Development

Illustratrion with a CSTR

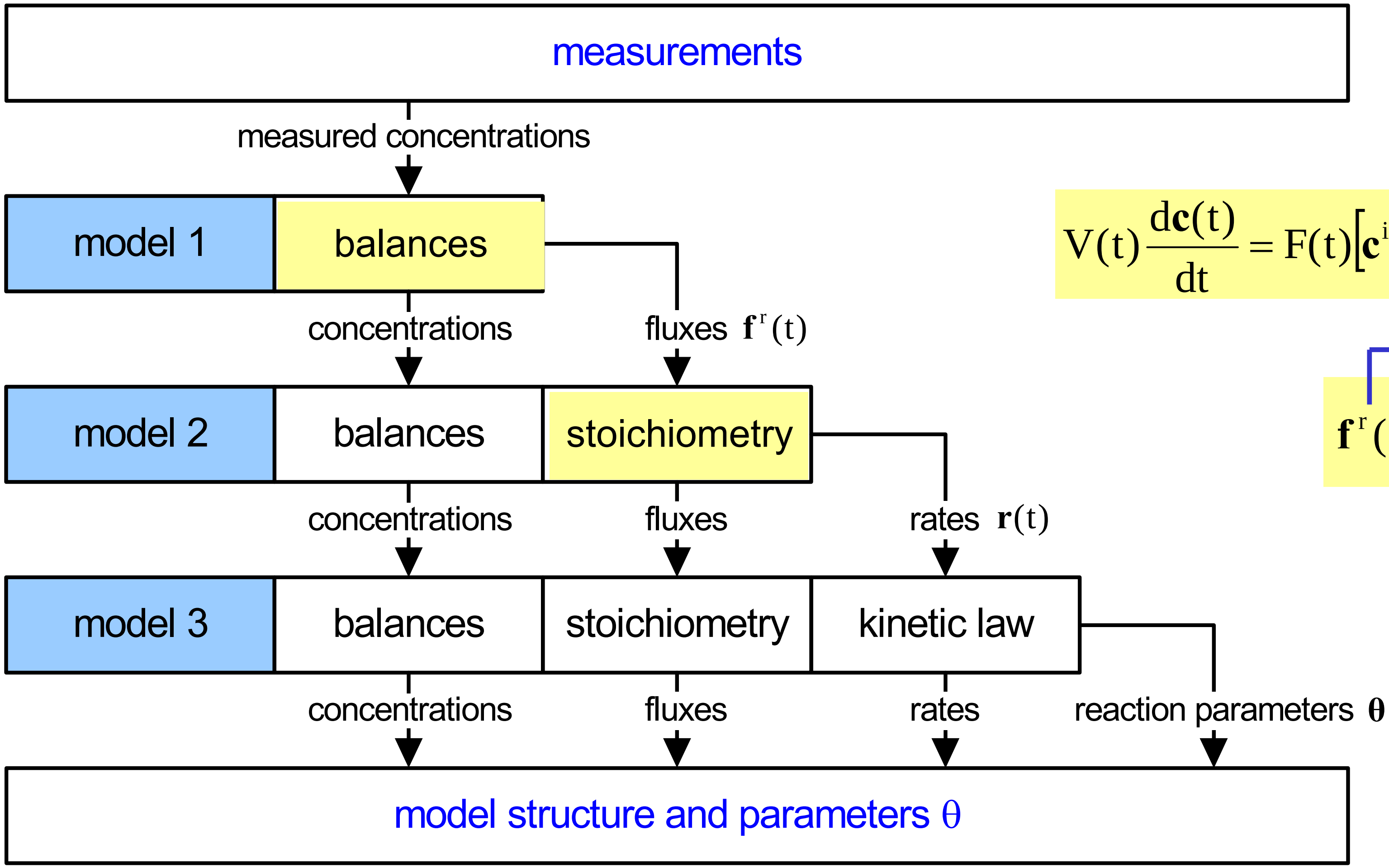


$$V(t)\frac{d\mathbf{c}(t)}{dt} = F(t)\left[\mathbf{c}^{in} - \mathbf{c}(t)\right] + \mathbf{f}^r(t)$$

(Marquardt, 1998)

Incremental Model Development

Illustratrion with a CSTR



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$$\mathbf{f}^r(t) = V(t)\mathbf{r}(t)\mathbf{N}$$

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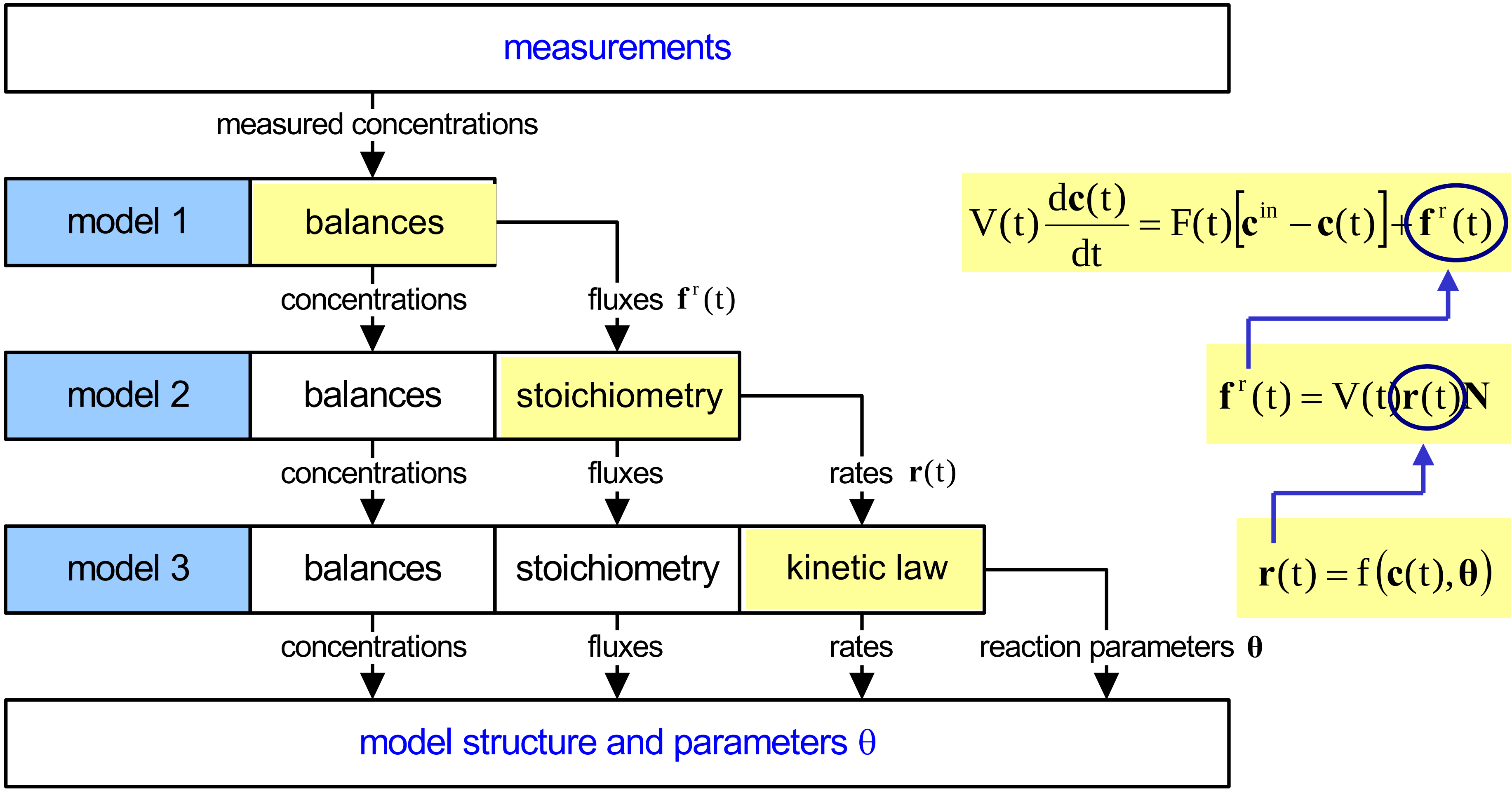
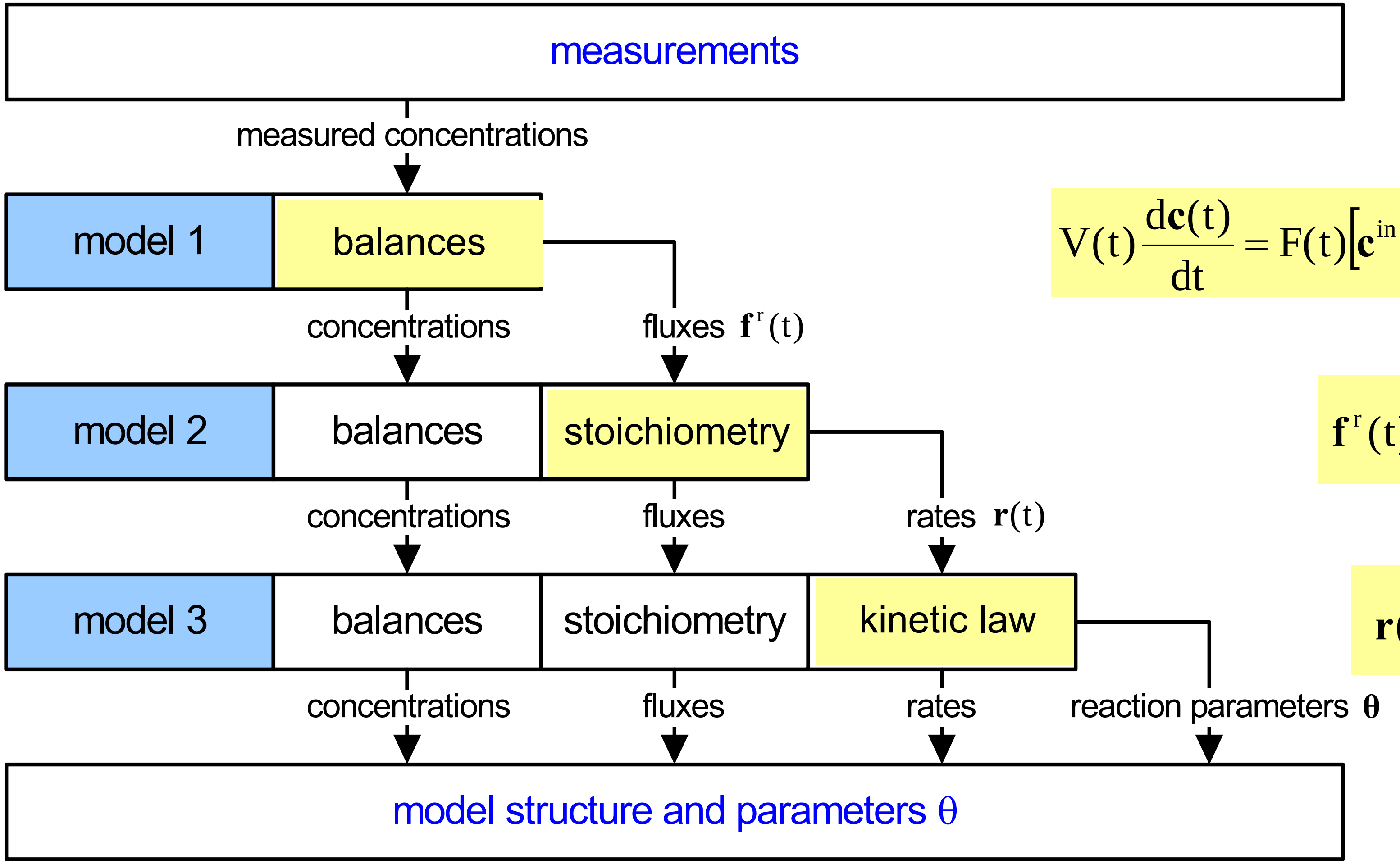
Illustratrion with a CSTR



(Marquardt, 1998)

Incremental Model Identification

Illustratrion with reaction kinetcis idenfication in a CSTR



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$$\mathbf{f}^r(t) = V(t)\mathbf{r}(t)\mathbf{N}$$

$$\mathbf{r}(t) = f\left(\mathbf{c}(t), \boldsymbol{\theta}\right)$$

(Marquardt, 1998)

Incremental Model Identification

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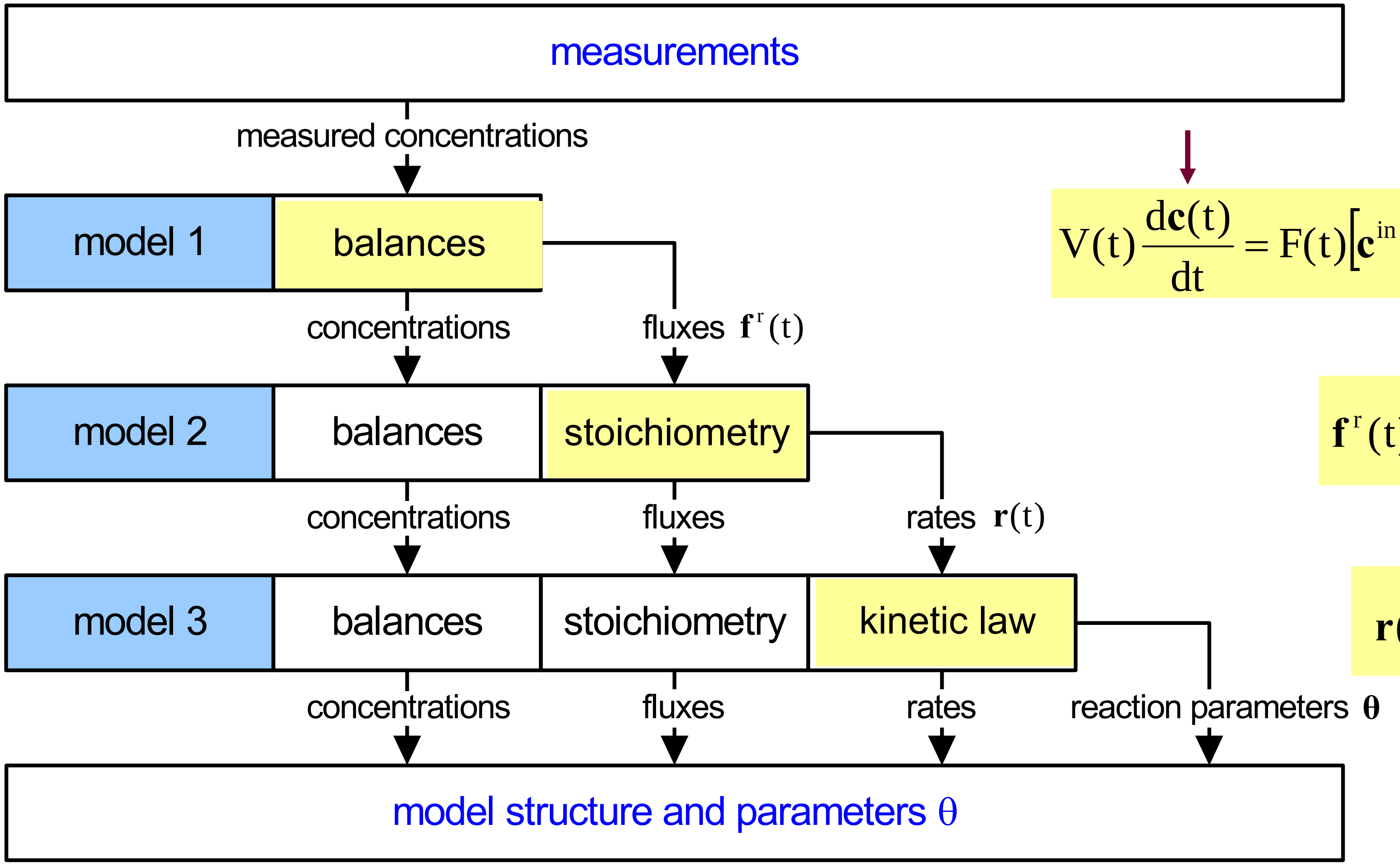

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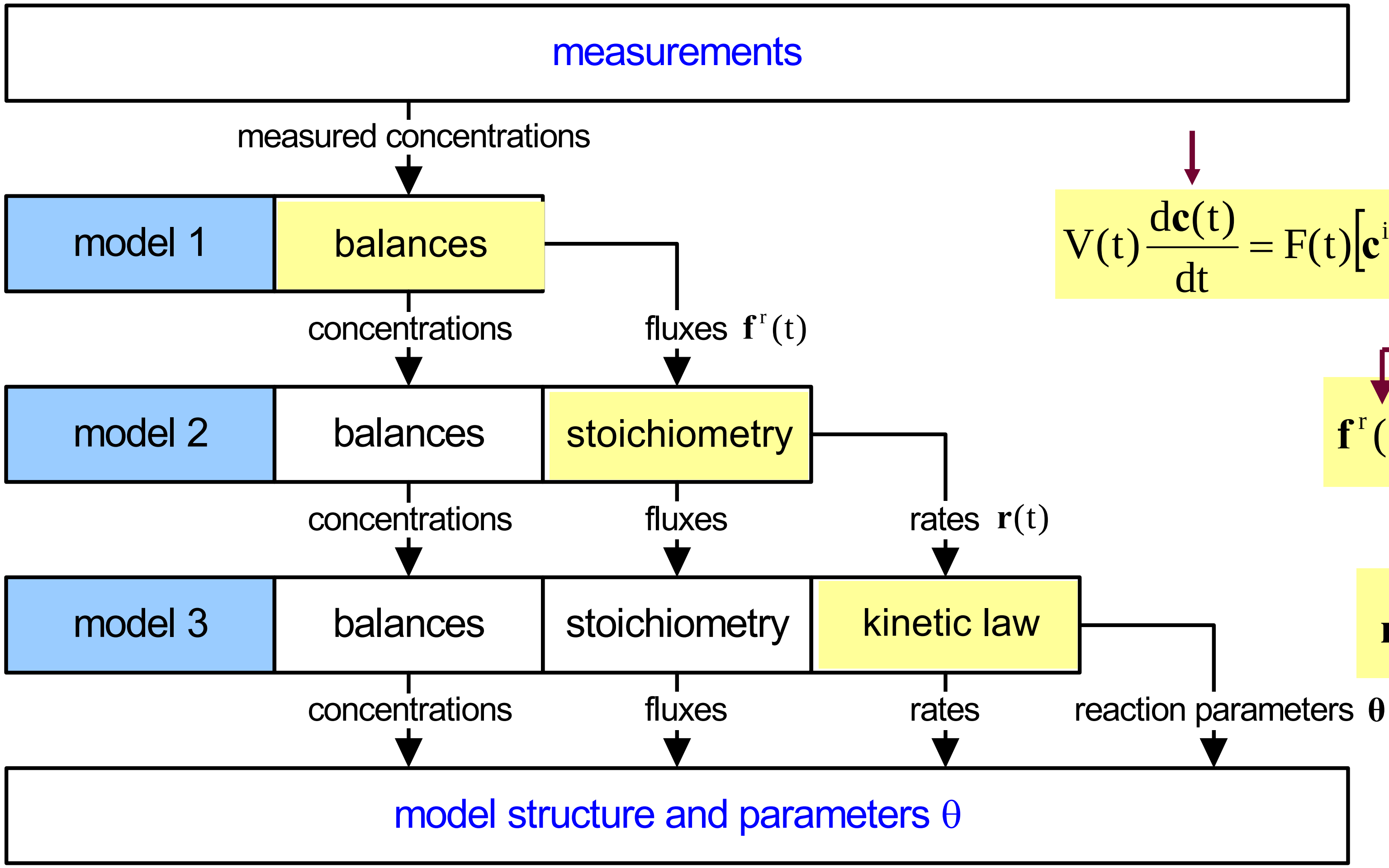

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Incremental Model Identification

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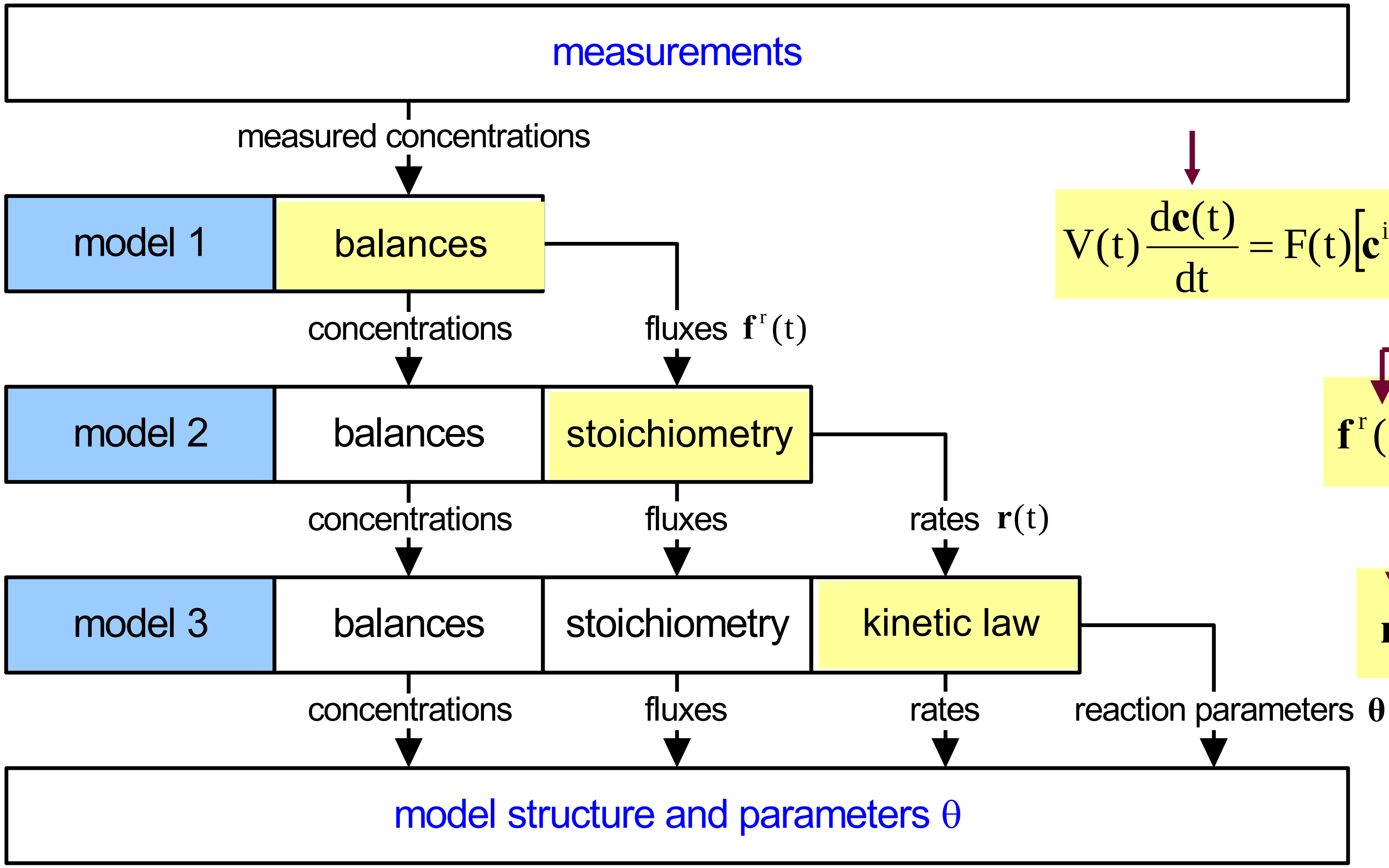

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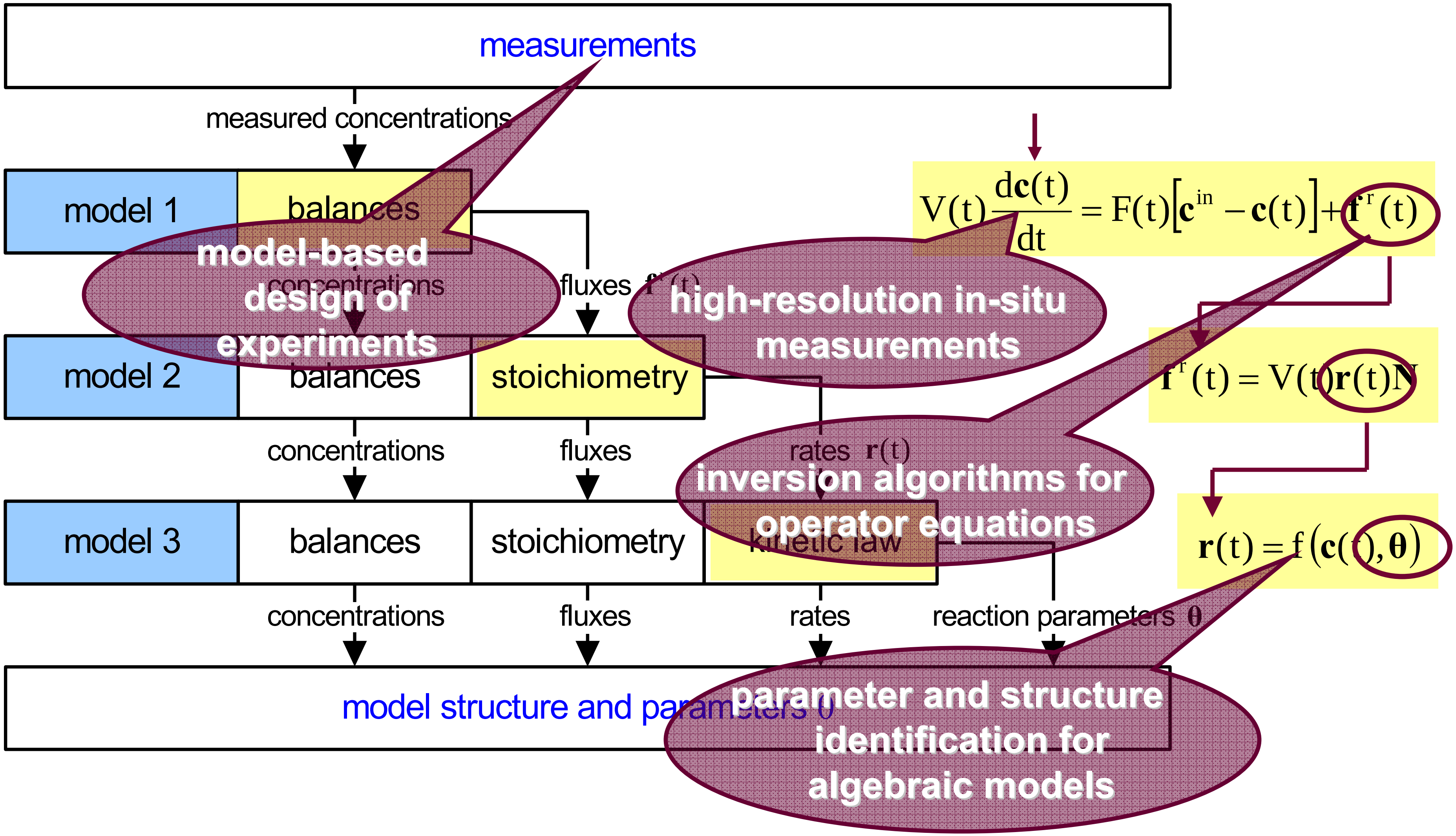
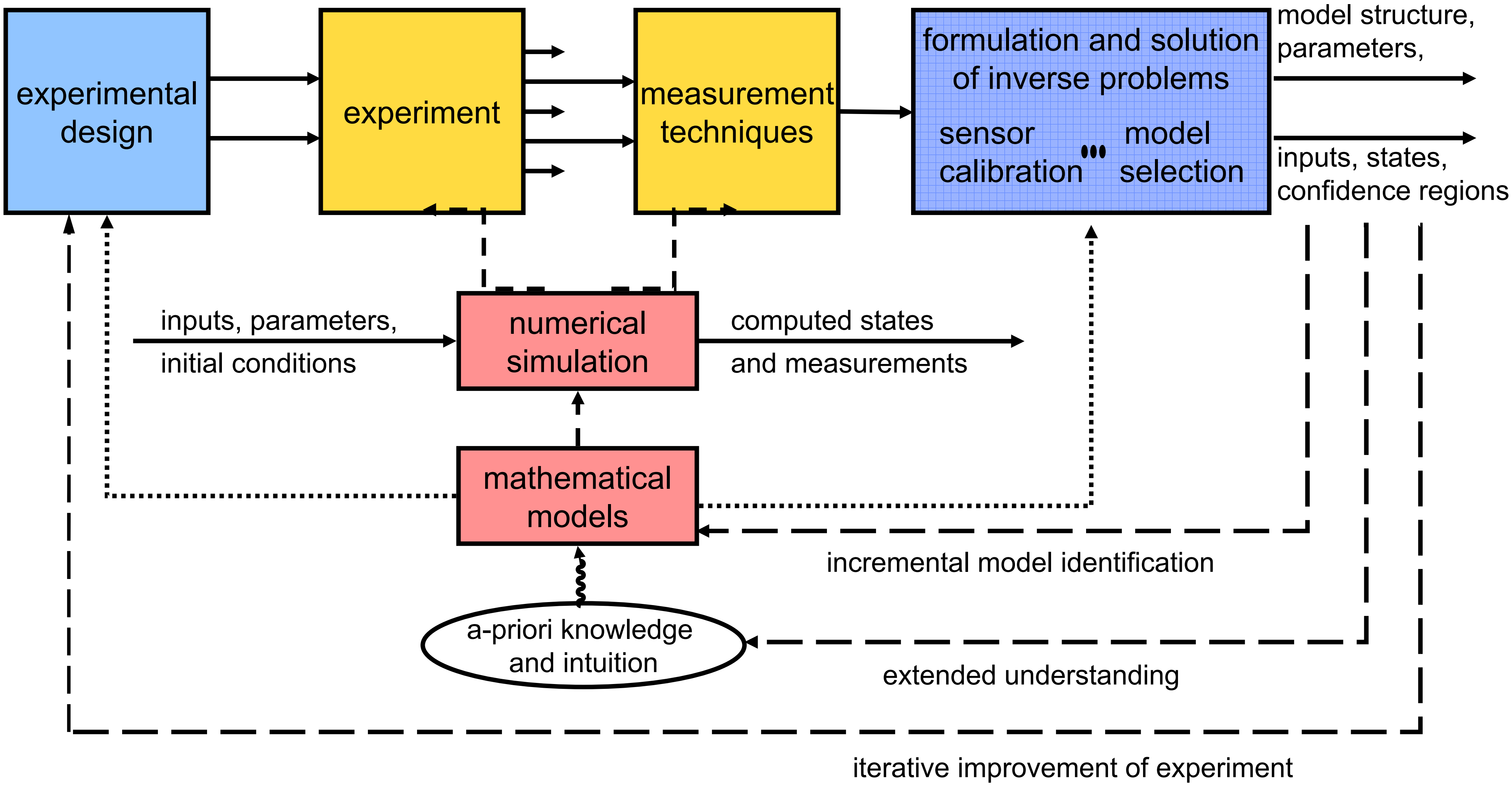
(Marquardt, 1998)

What are the ingredients for implementation ?



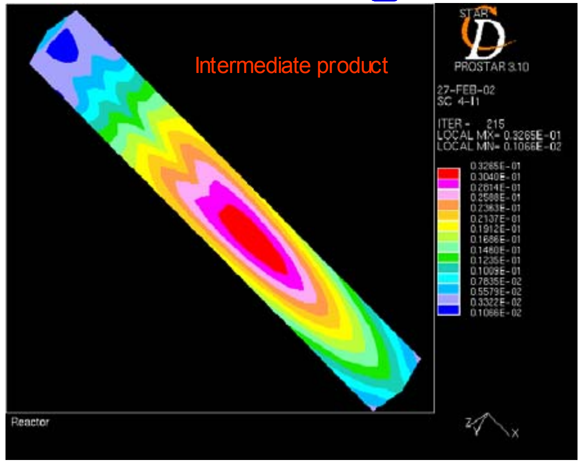
Benchmarking with all kinds of modelling problems in progress !



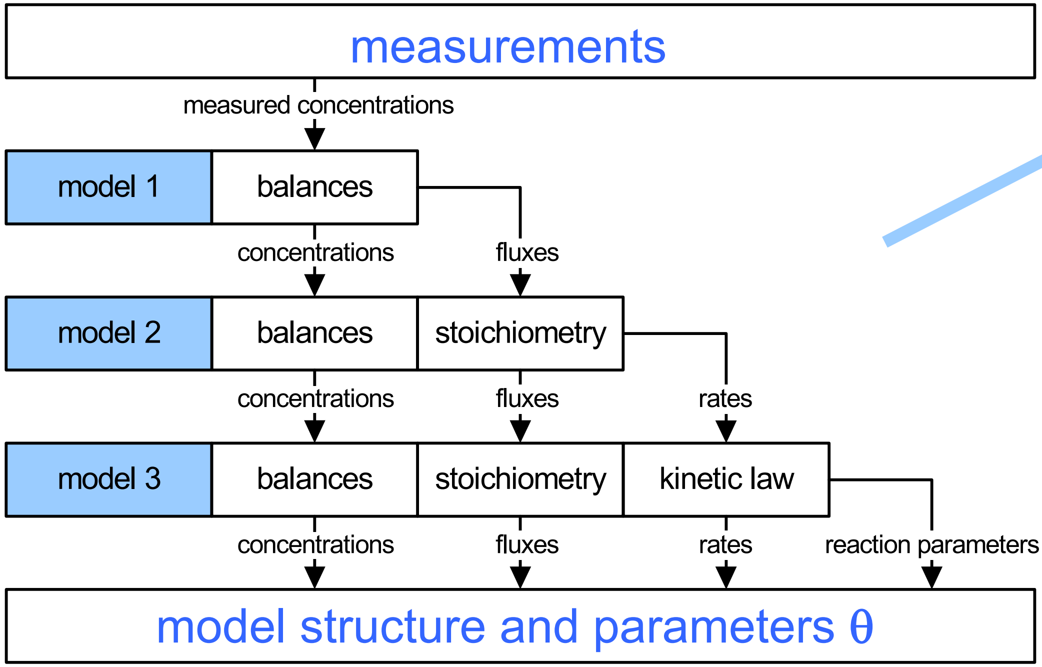
MEXA for Multi-Component Diffusion Modeling

Why studying diffusion ?

- detrimental for product and process design
- very high experimental effort
- very few multi-component diffusion data available
- validity of diffusion models still a matter of debate



selectivity of heterogeneously catalyzed reactions (Pantelides & Urban, 2004)



- a good model problem for the development of MEXA methodology

Incremental Model Identification

measurements y

binary diffusion

structure of system

$$\frac{\partial c}{\partial t} = -\frac{\partial J^V}{\partial z}$$

model for fluxes

$$J^V = -D^V \frac{\partial c}{\partial z}$$

model for coefficient

$$D^V = f(c, \theta)$$

model B	balances		
model BF	balances	flux models	
model BFD	balances	flux models	diffusion coefficient

parameters θ

Incremental Model Identification

binary diffusion

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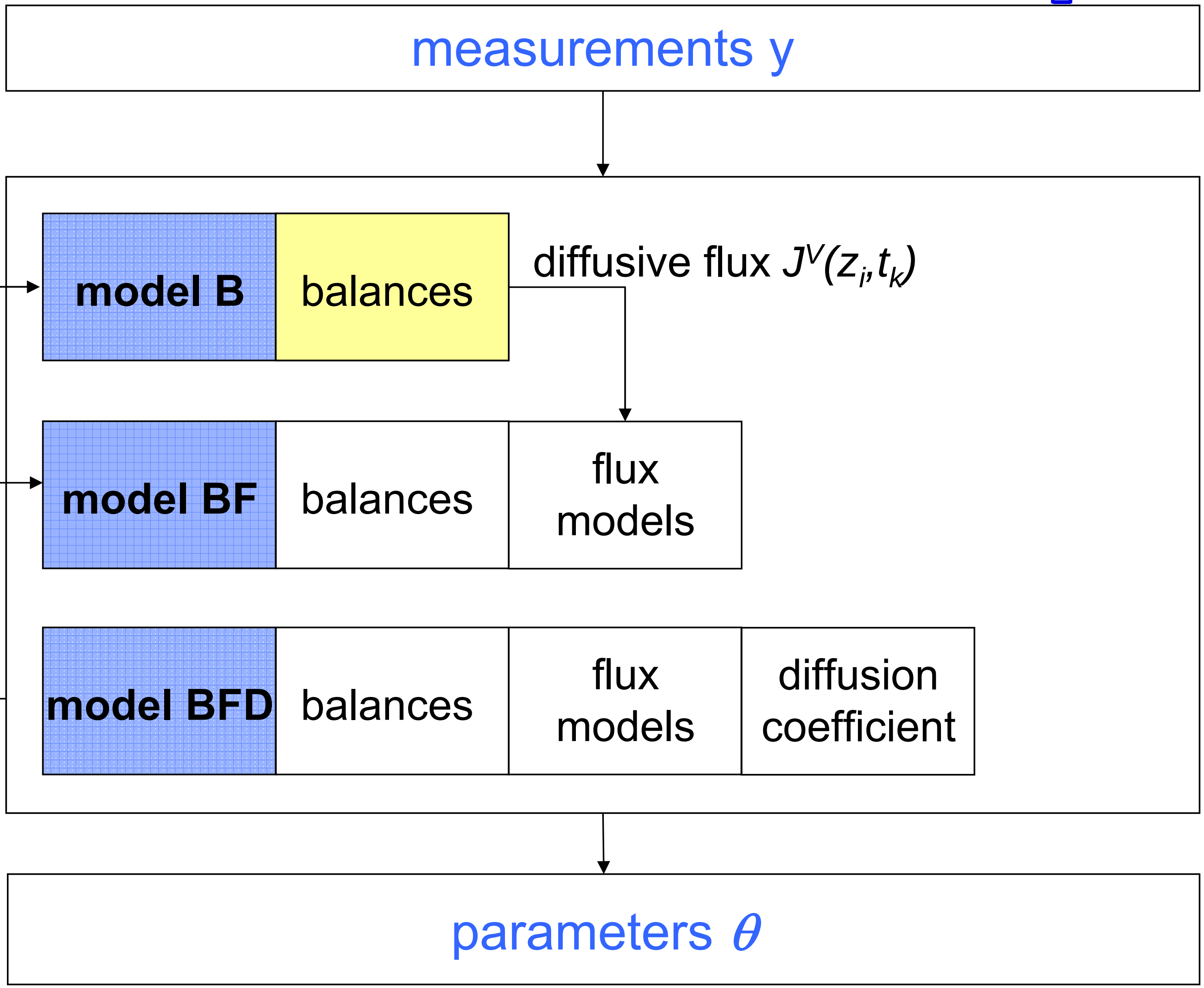

Incremental Model Identification

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model B | balances

diffusive flux $J^V(z_i,t_k)$

model BF | balances | flux models

coefficient $D^V(z_i,t_k)$

model BFD | balances | flux models | diffusion coefficient

parameters θ

Incremental Model Identification

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binary diffusion

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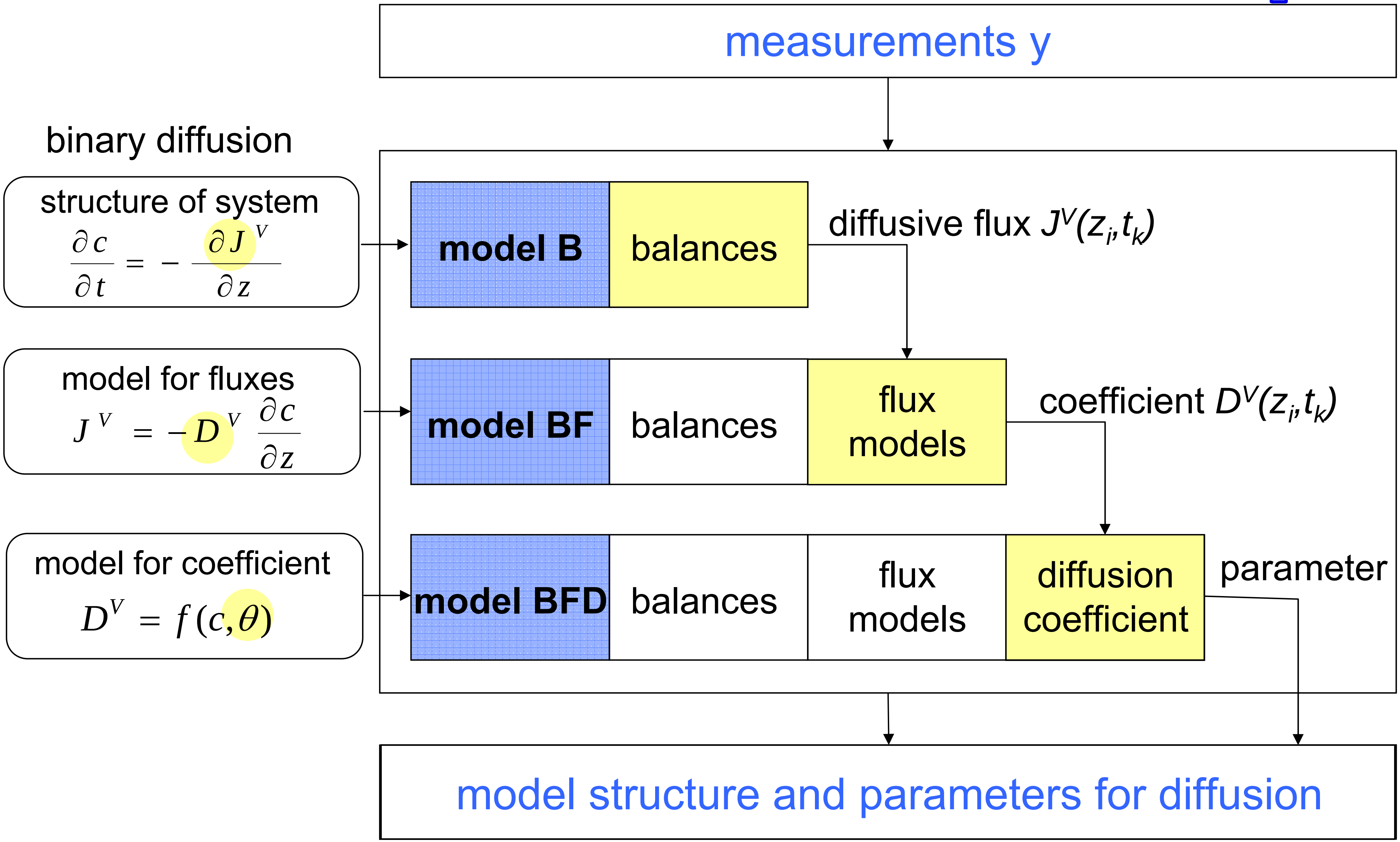
diffusive flux $J^V(z_i, t_k)$

coefficient $D^V(z_i, t_k)$

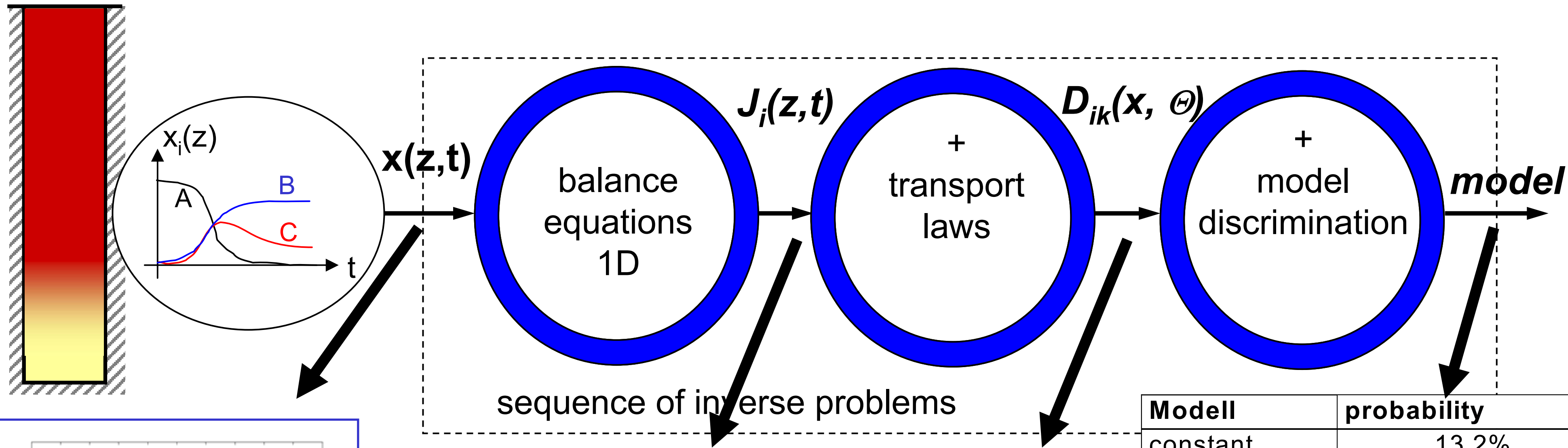
parameter

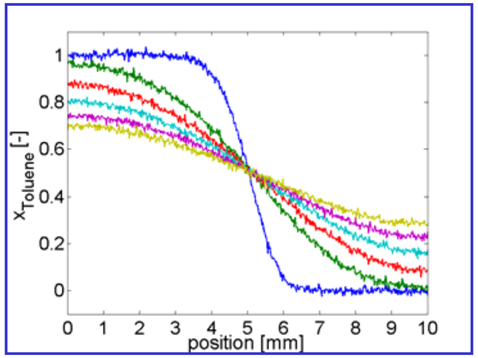
parameters θ

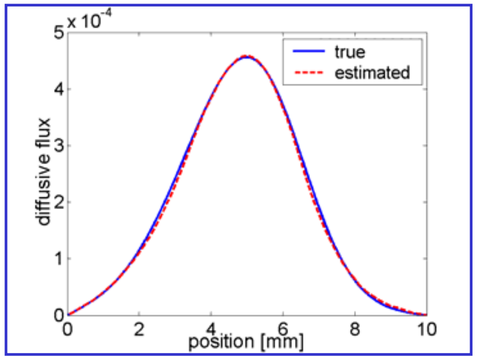
Incremental Model Identification

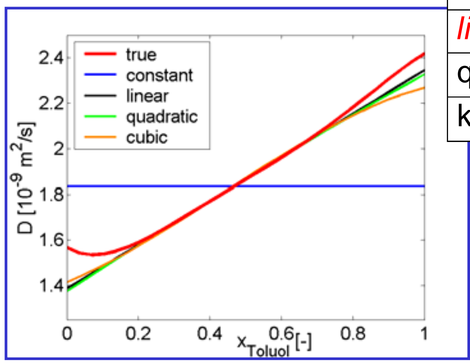


Incremental Model Identification







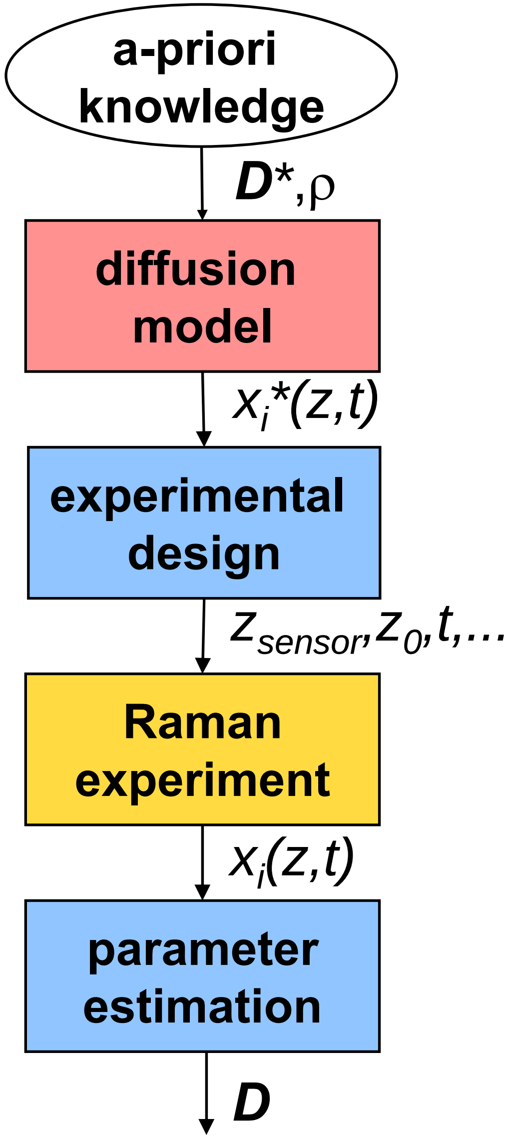


Modell	probability
constant	13,2%
linear	*39,3%*
quadratic	27,8%
kubic	19,7%

robust and efficient identification of models

experimental results for binary and ternary diffusion

Bardow, Göke, Koß & Marquardt (2003, 2006)


a-priori knowledge
D*,ρ
diffusion model
x_i*(z,t)
experimental design
z_sensor,z_0,t,...
Raman experiment
x_i(z,t)
parameter estimation
D

a-priori knowledge

D^*, ρ

diffusion model

$x_i^*(z,t)$

experimental design

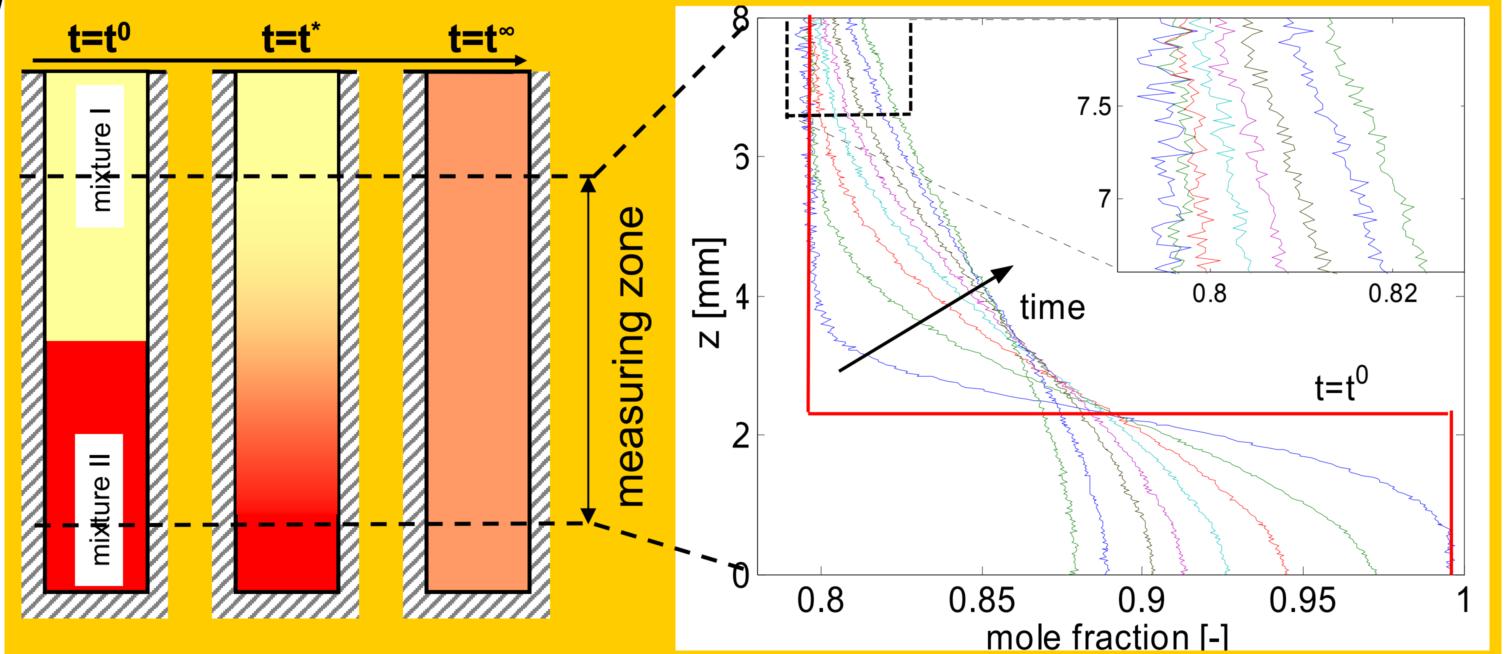
$z_{sensor}, z_0, t, \ldots$

Raman experiment

$x_i(z,t)$

parameter estimation

D



- analysis of one-dimensional diffusion
- nonlinear calibration approach (Alsmeyer et al., 2003,2004)
- simultaneous measurement of all mole fractions
- high resolution (Δt = 10 s, Δz = 20 μm)
- measurement error:

  statistical ≤ 0.2 mol-%, systematic ≤ 0.5 mol-%,

Experimental Setup

a-priori knowledge

↓ D^*, ρ

diffusion model

↓ $x_i^*(z,t)$

experimental design

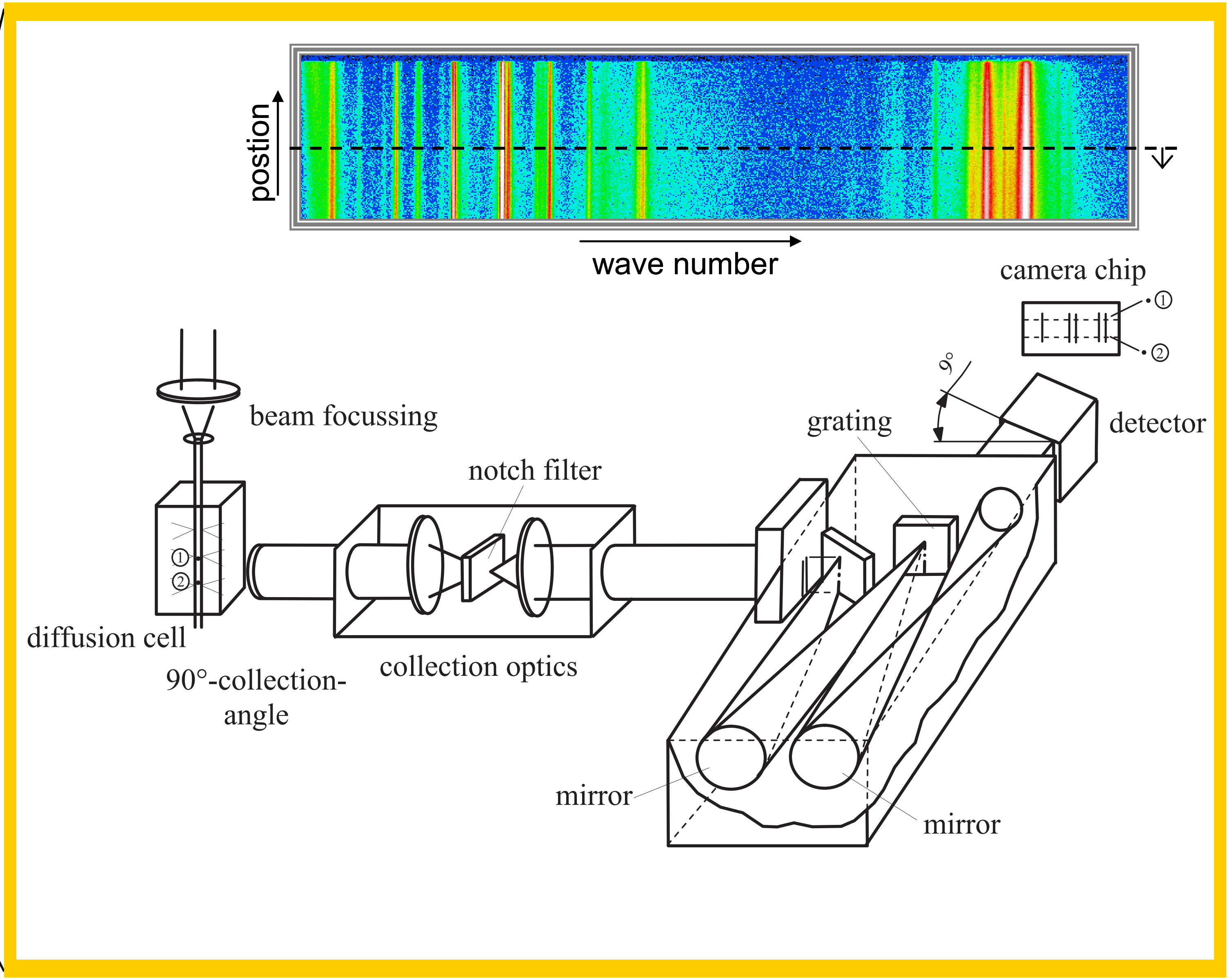
↓ $z_{sensor}, z_0, t, \ldots$

Raman experiment

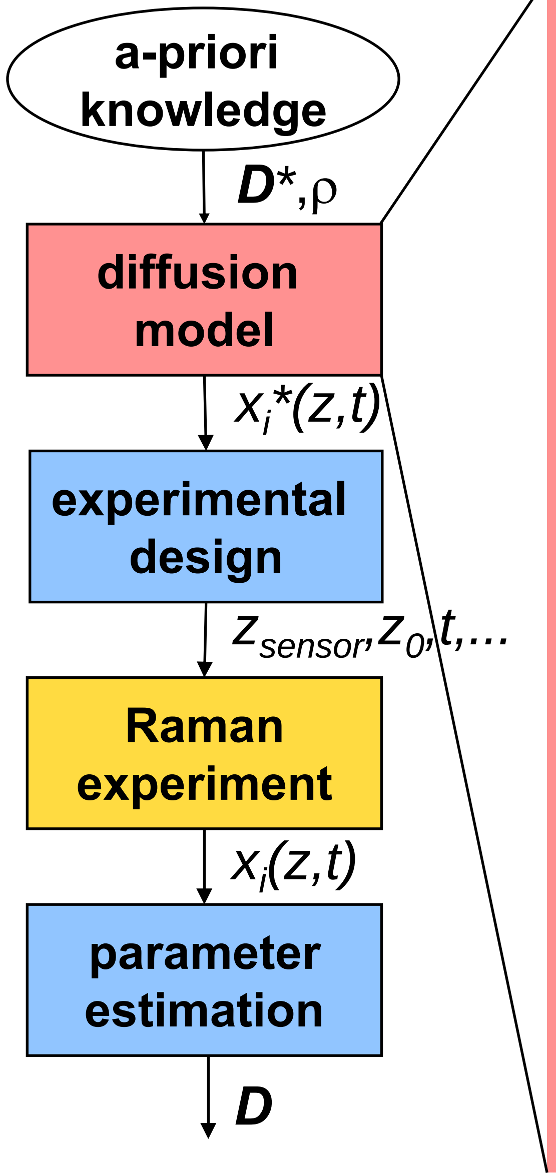
↓ $x_i(z,t)$

parameter estimation

↓ D



Diffusion Model



Ternary experiments:

- Δc small $\Rightarrow$ $\mathbf{D}, V_i = const.$
- Process:

$$\frac{\partial c_i(z,t)}{\partial t} = \sum_{j=1}^{n-1} D_{ij}^V \frac{\partial^2 c_j(z,t)}{\partial z^2}$$

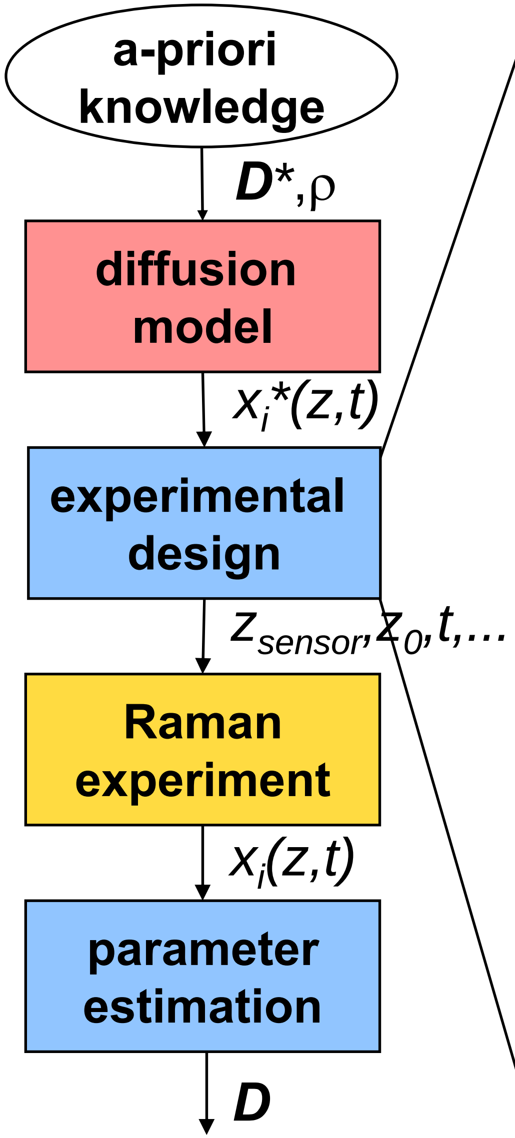
- Measurements:

$$x_i(z,t) = c_i(z,t)/c_t(z,t)$$

- Measurement error:

$$\sigma^2 = const.$$

Optimal Experimental Design



1. Qualitative Design: Identifiability

$\rightarrow$ ternary diffusion matrix from one short experiment

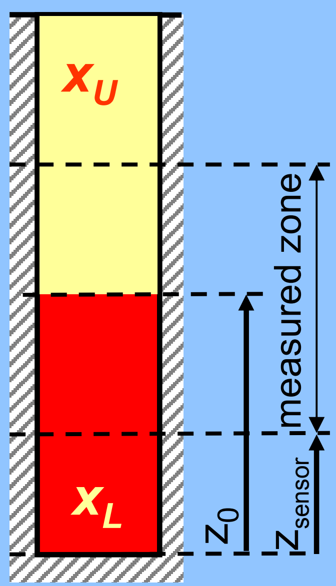
2. Quantitative Design: $\rightarrow$ what mixture volume ratio?

$\rightarrow$ where to measure?

$\rightarrow$ how long to measure?

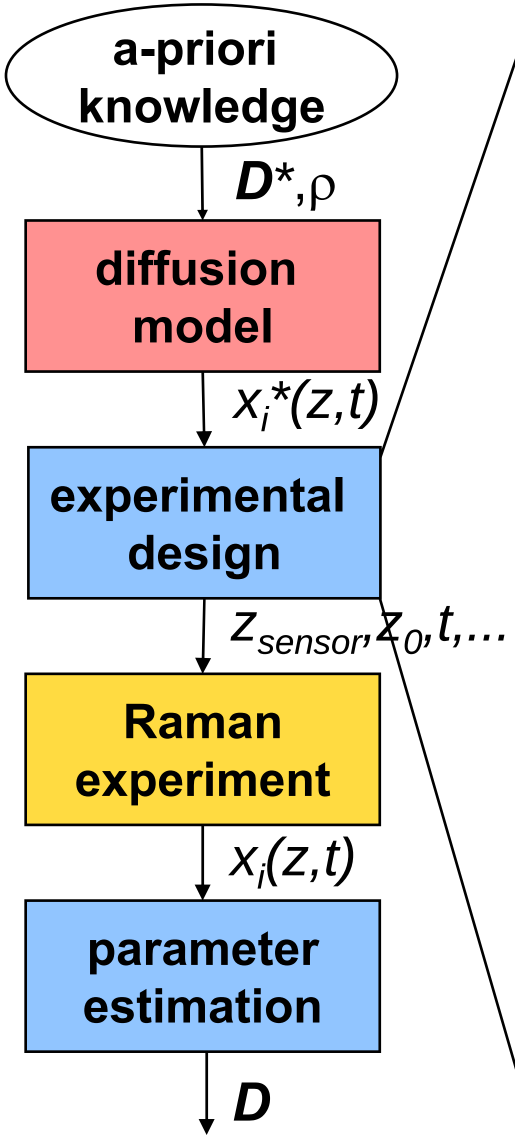
$\rightarrow$ which mixture compositions?

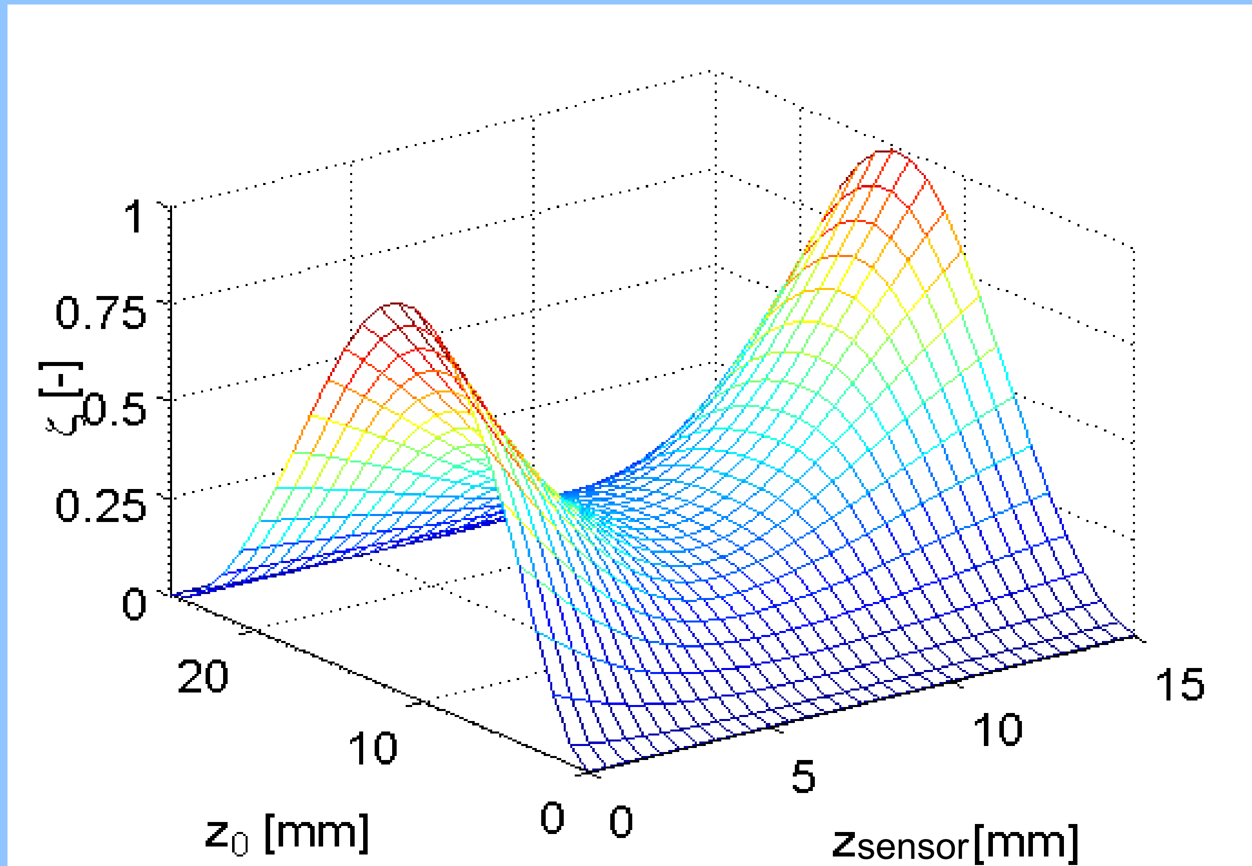
$\rightarrow$ when is the run stable?



Model-based design:
choose free settings such that information on diffusion coefficients is maximized

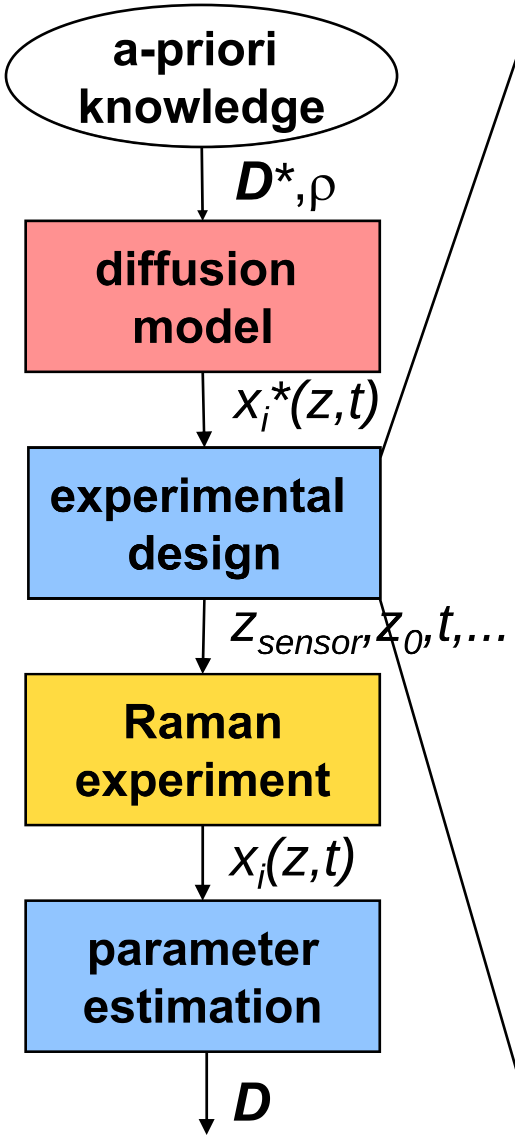
Experimental Design Study Results (1)





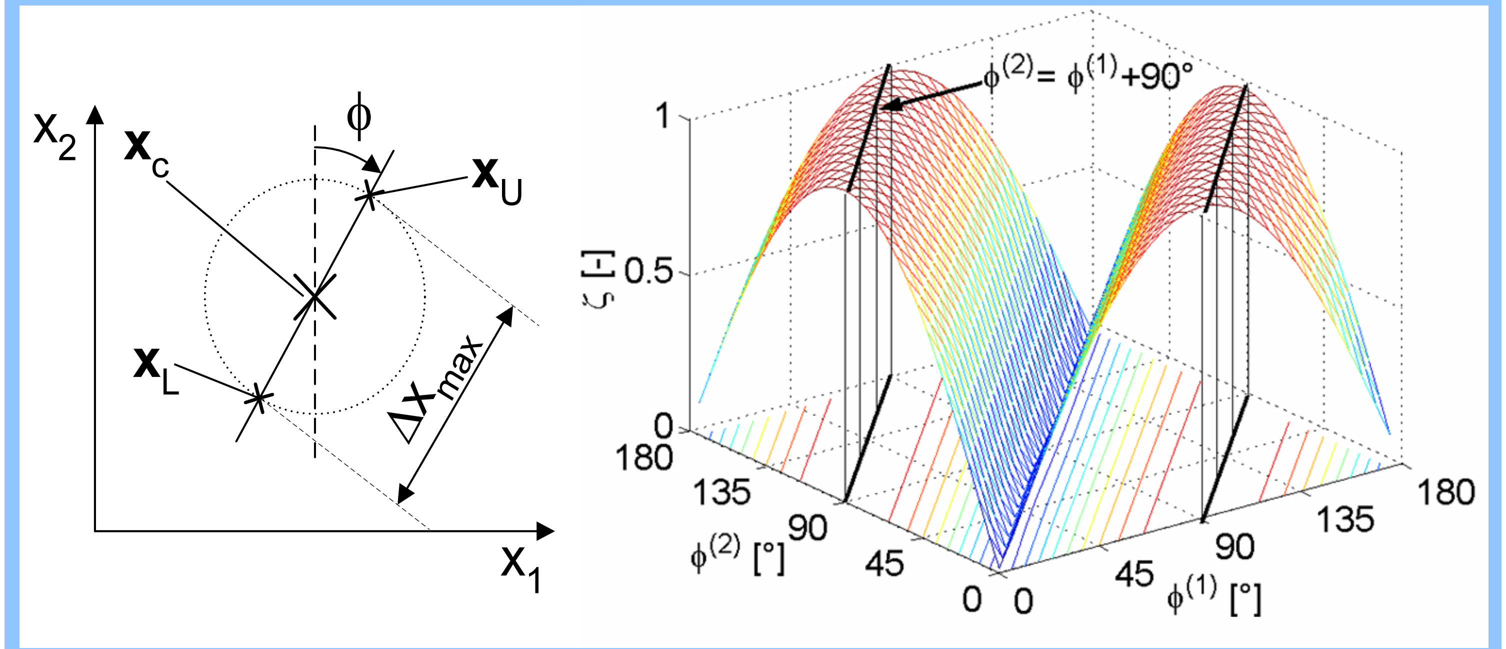
- scaled objective ζ-efficiency measures information per parameter
- measurements at the wall, i.e. restricted diffusion experiments
- slightly unequal volume of both phases
- experiment duration characterized by optimal Fourier time

Experimental Design Study Results (2)



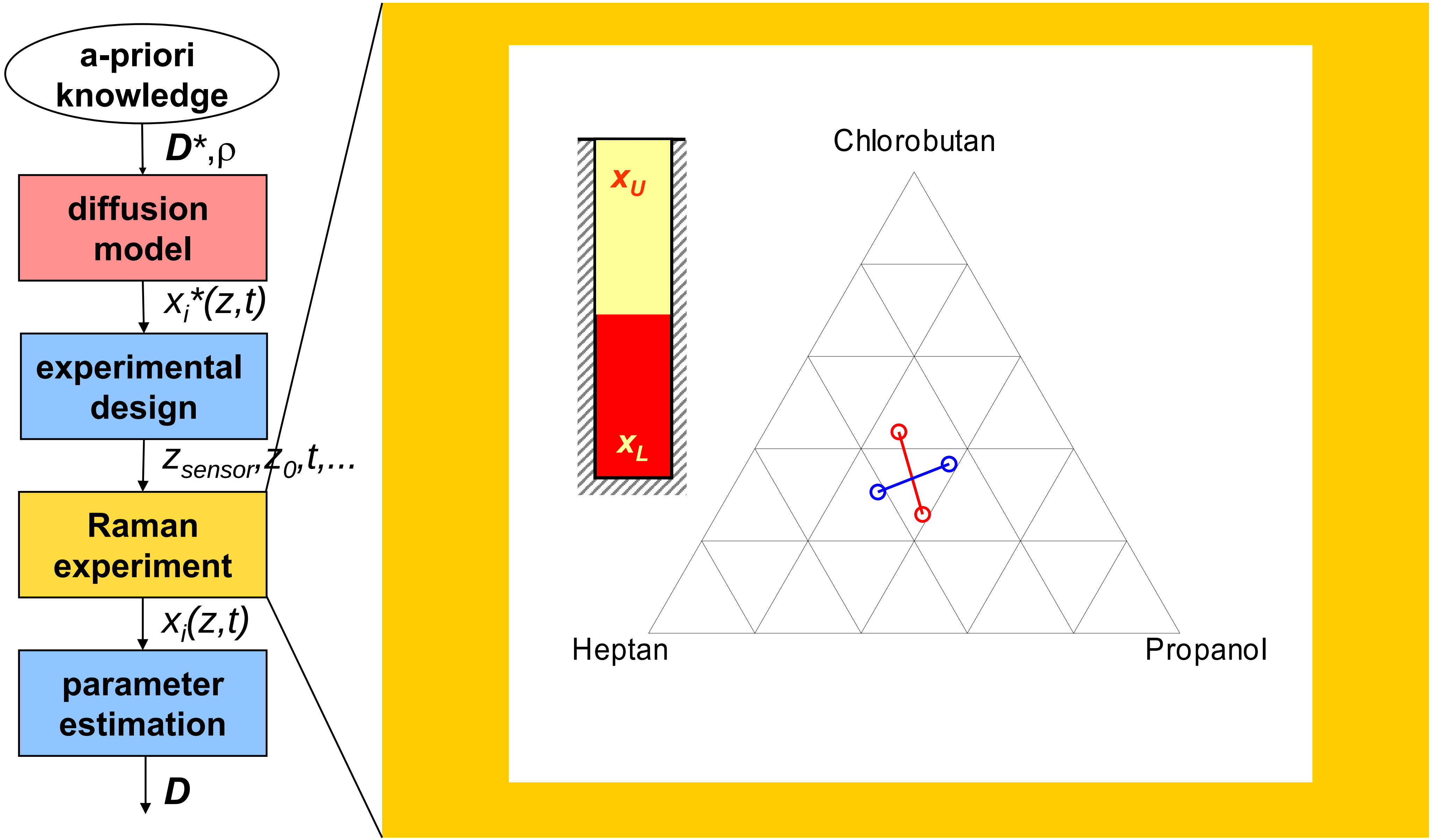
- one experiment sufficient
- but 10-fold increase in precision if two runs are used

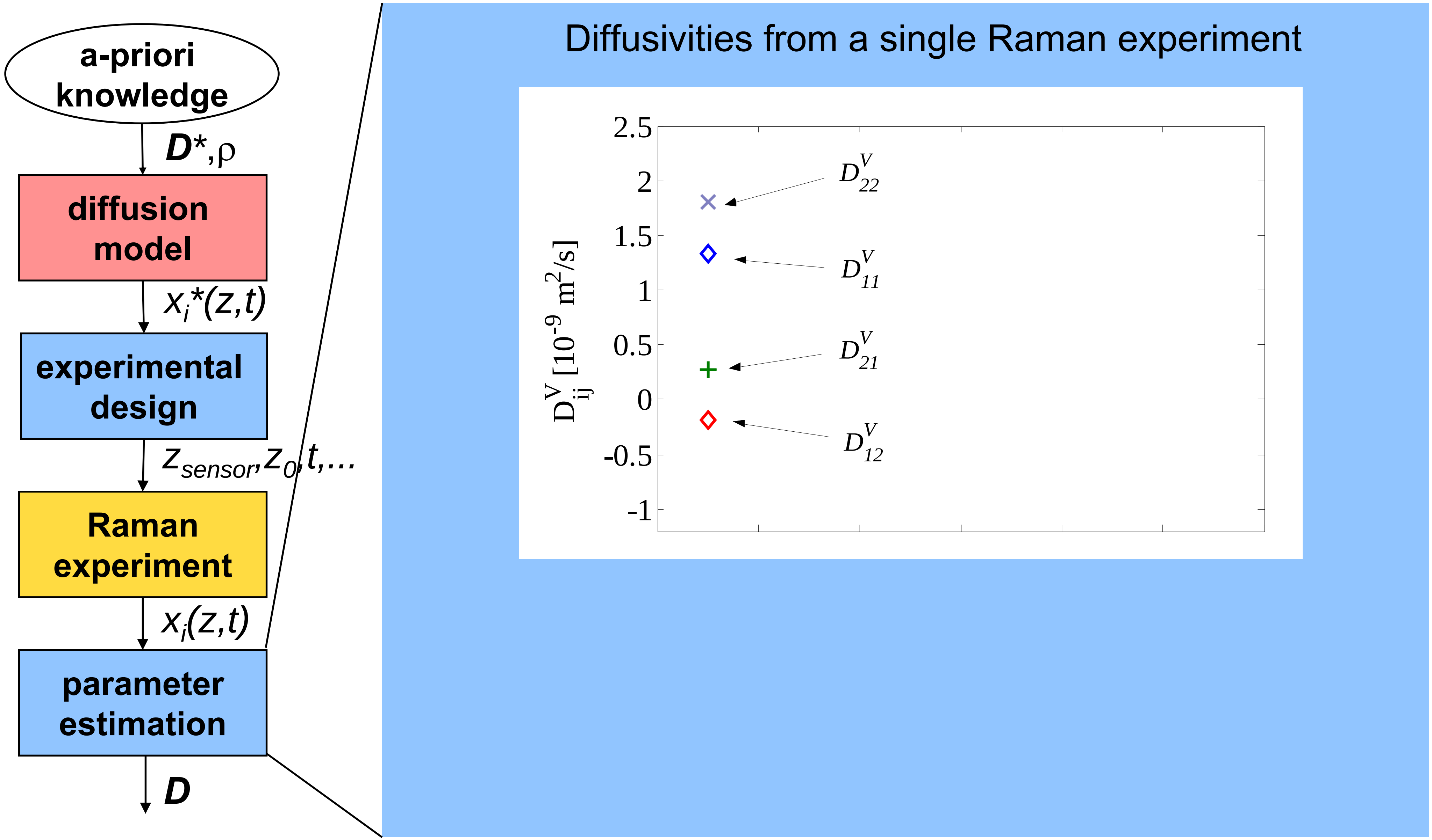
$\rightarrow$ optimize initial composition



- experiments should be as distinct as possible ($\phi^{(2)}=\phi^{(1)}+90°$)
- additional conditions to ensure hydrodynamic stability

Raman Experiment

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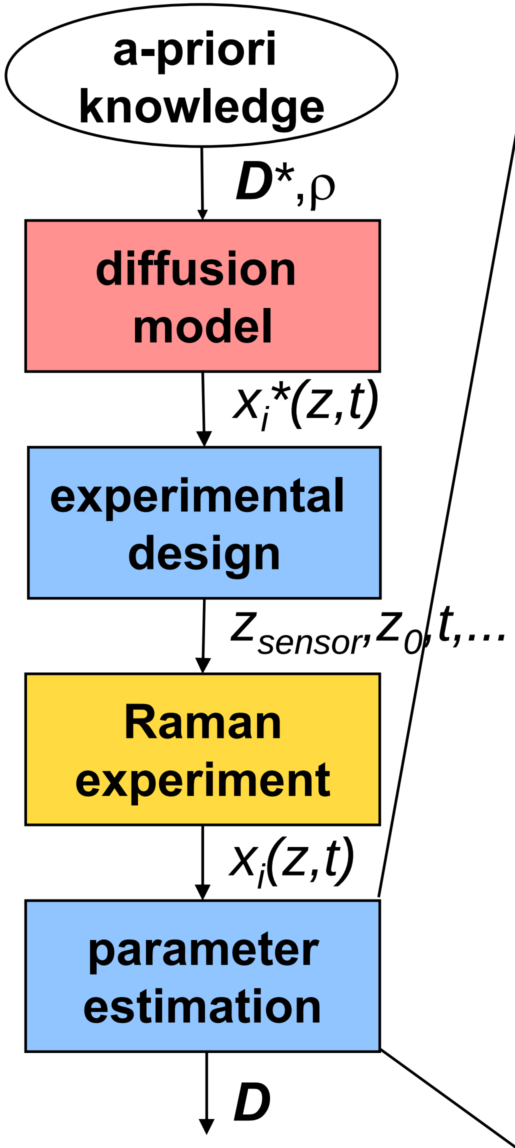
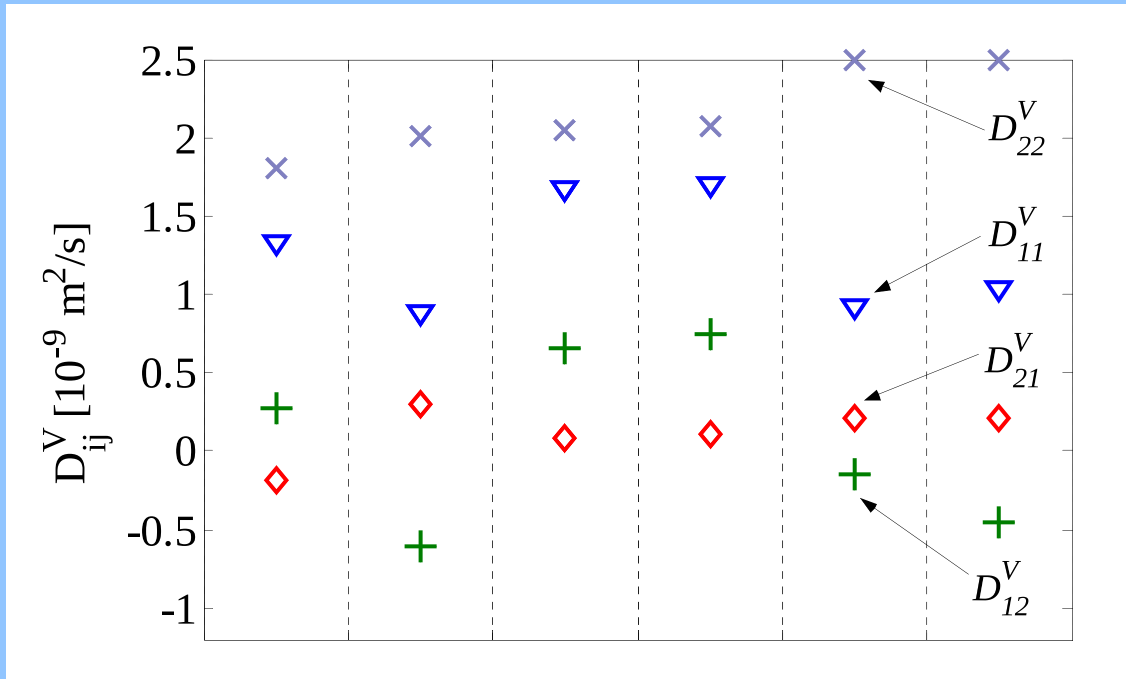
Raman experiment
x_i(z,t)
parameter estimation
D
Diffusivities from a single Raman experiment
D^V_ij [10^-9 m^2/s]
2.5
2
1.5
1
0.5
0
-0.5
-1
D^V_22
D^V_11
D^V_21
D^V_12

Ternary Results

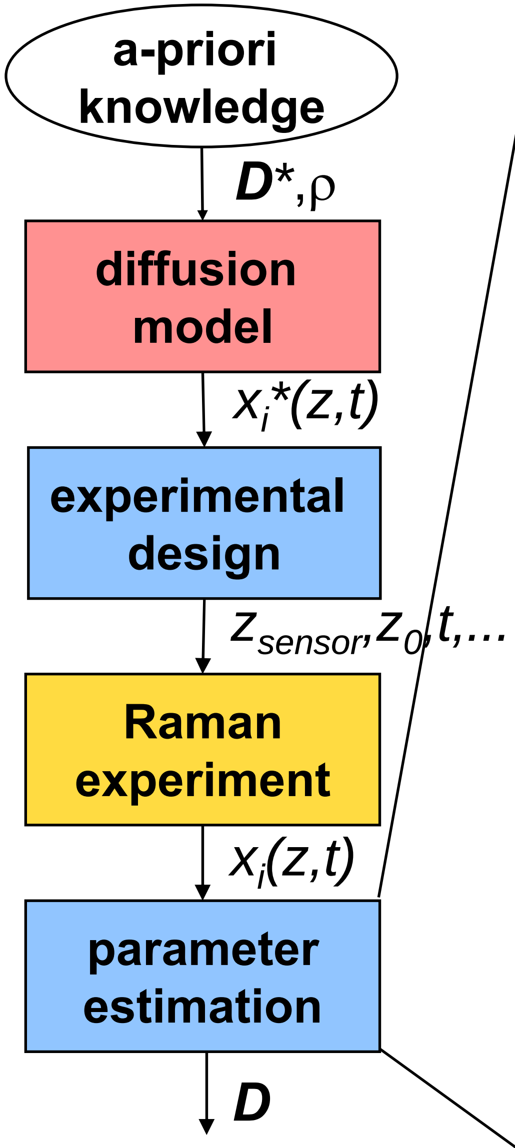


Diffusivities from a single Raman experiment

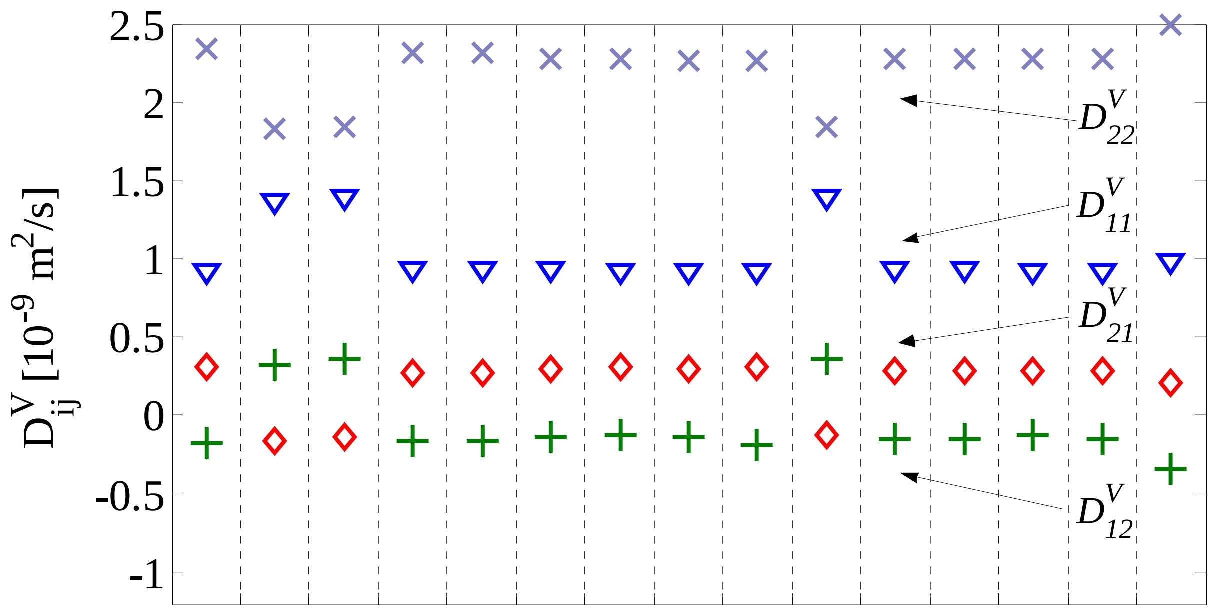


→ one Raman experiment gives full diffusion matrix
→ currently scatter in data is still significant

Ternary Results



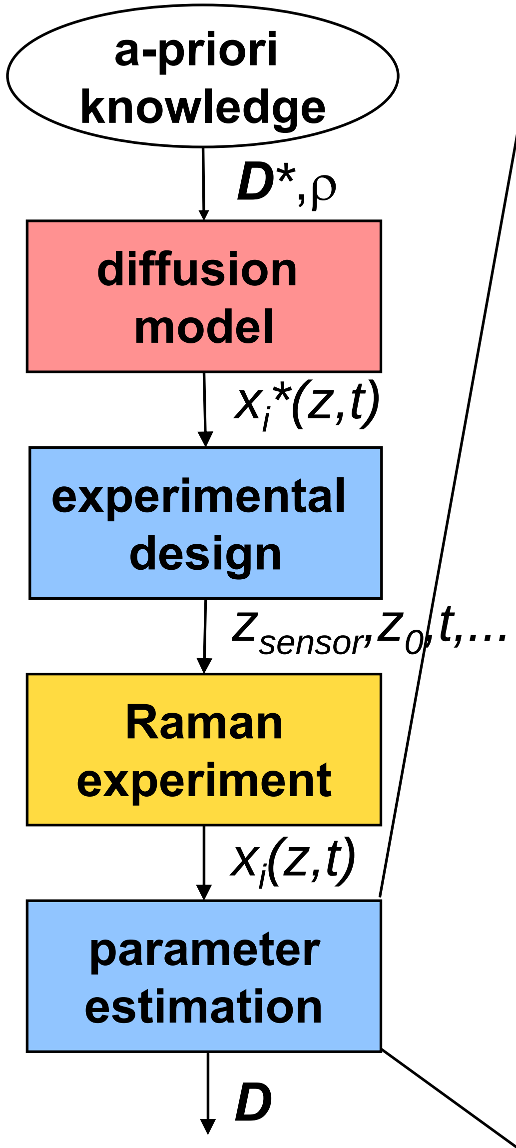
Diffusivities from two Raman experiments



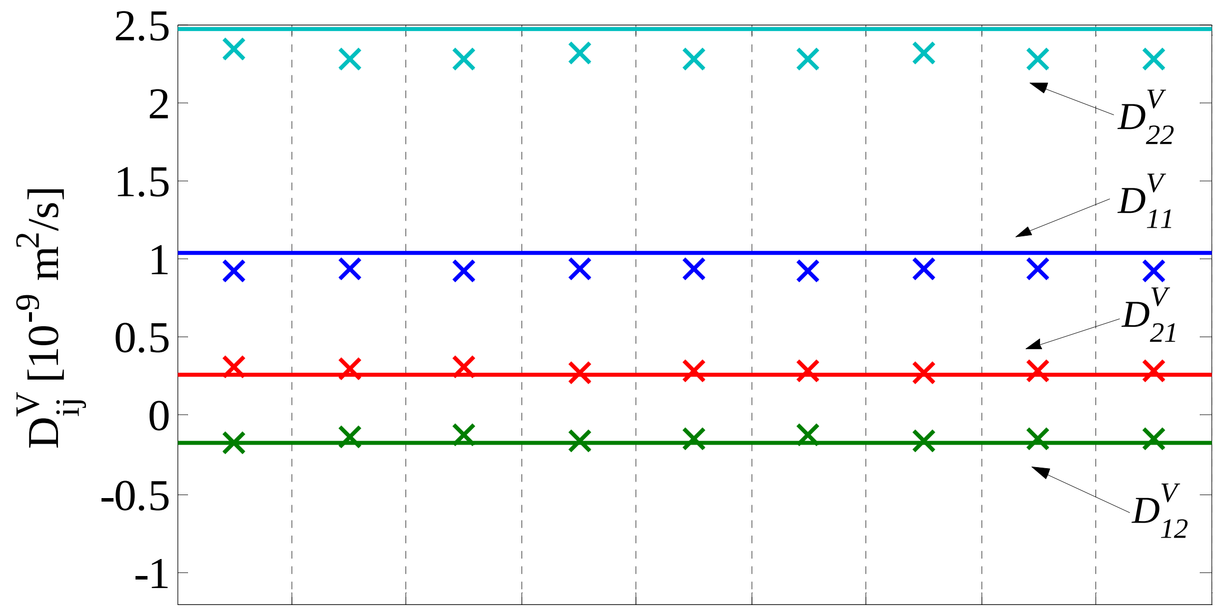
with reference data from Weingärtner et al. (1994)

→ one Raman experiment gives full diffusion matrix
→ good precision from 2 optimized runs
→ robust & efficient measurement
→ quantitative validation of design predictions

Ternary Results



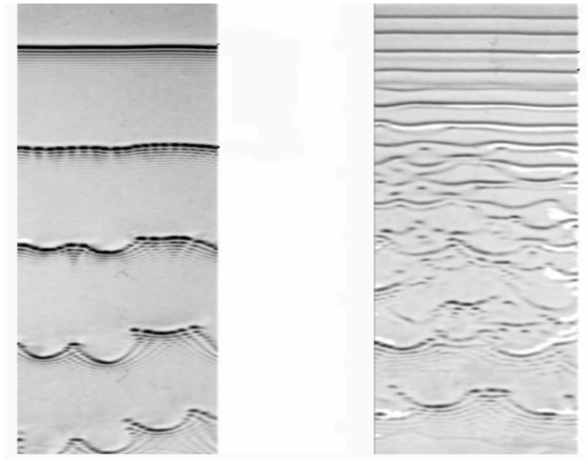
Diffusivities from two ***optimal*** Raman experiments

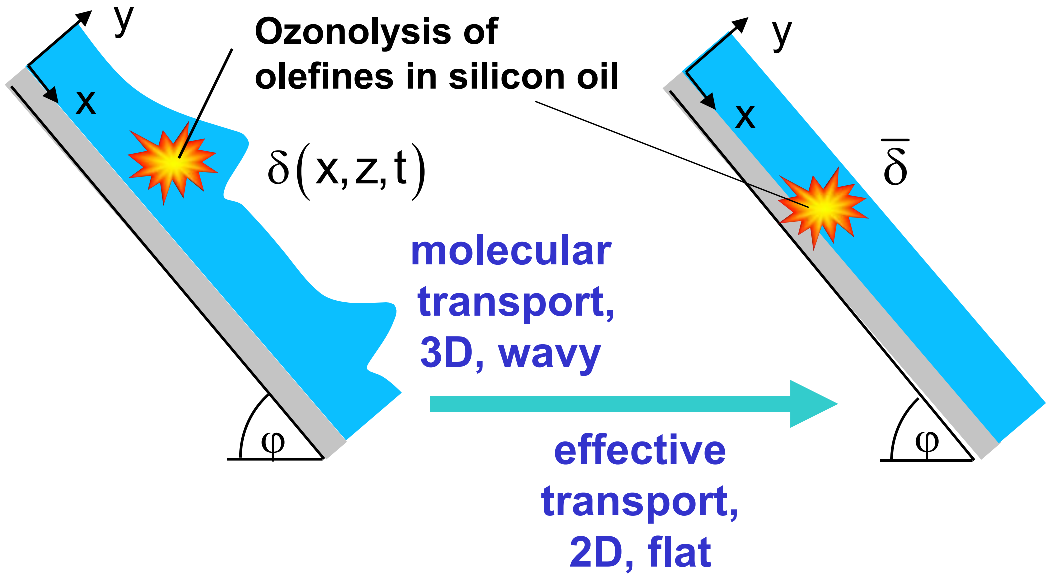


with reference data from Weingärtner et al. (1994)

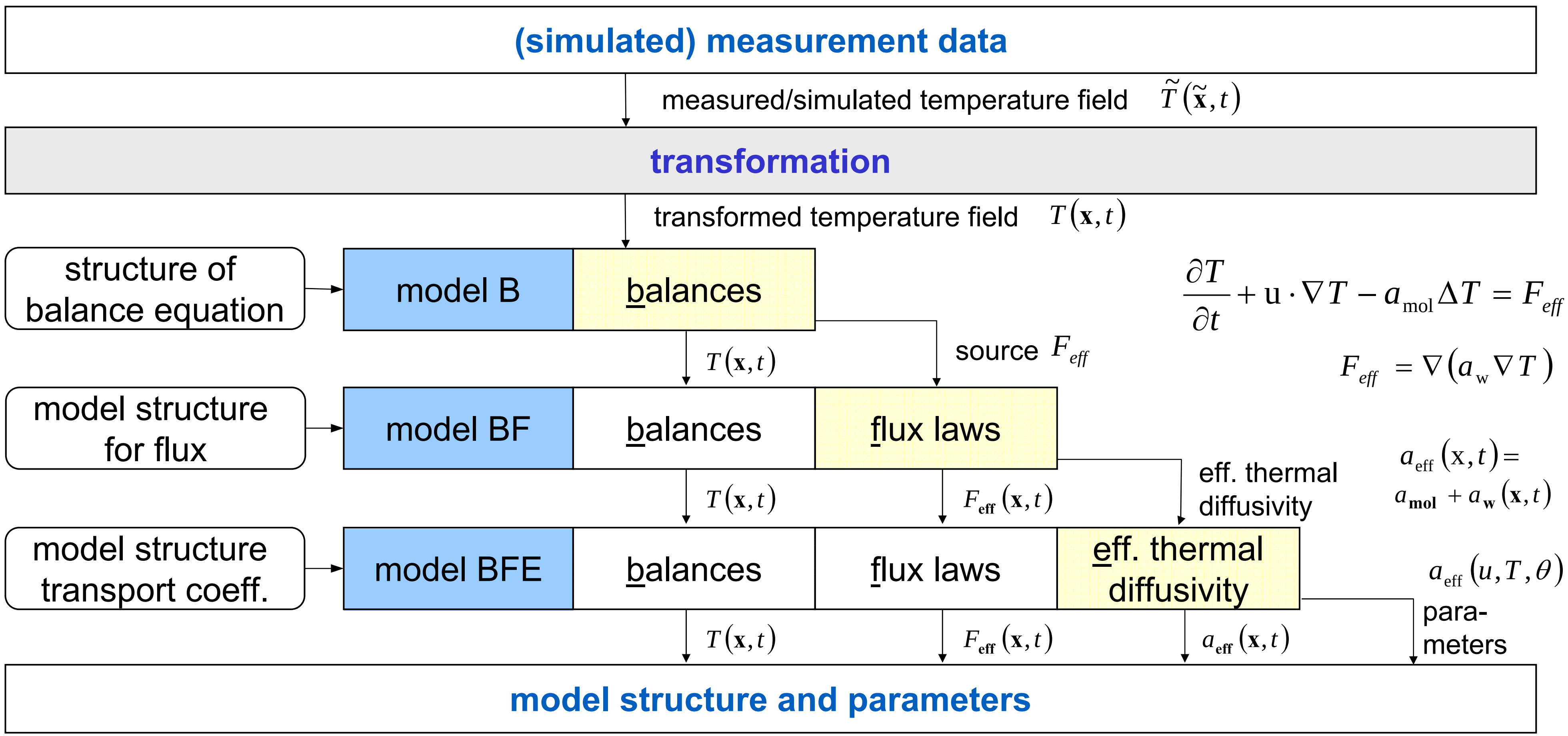
→ one Raman experiment gives full diffusion matrix
→ good precision from 2 optimized runs
→ robust & efficient measurement
→ quantitative validation of design predictions

- falling films are all around:
  - falling film cooler
  - falling film evaporator
  - falling film absorber
  - falling film reactors
- transport phenomena are hardly understood, interaction between
  - fluid dynamics with free surface
  - heat and mass transfer
  - chemical reaction
- first step: modelling of heat transfer with effective transport coefficients





… incremental identification adapted to multi-dimensional PDE problem



… a generic concept applicable to all kinds of kinetic problems (Marquardt, 2005)

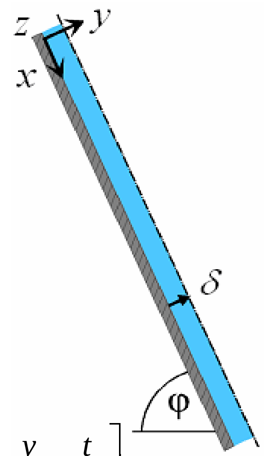
Test Problem – No Measurement Error

Domain:

$$\Omega:[0,0.18]\times[0,0.3\cdot 10^{-3}]\times[0,0.3\cdot 10^{-3}][m^3];\ t\in[0,0.5s]$$

Discretisation:

$$|\Omega_h|:150\times 9\times 3;\ \Delta t = 0.01s$$



Material: Polydimethylsiloxane DMS-T05

$$\rho = 912[\mathbf{kg/m^3}],\ c = 1540[\mathbf{J/kgK}],\ \nu = 4.7\cdot 10^{-6}[\mathbf{m^2/s}]$$

$(\,\mathrm{Pr} = 56\,)$

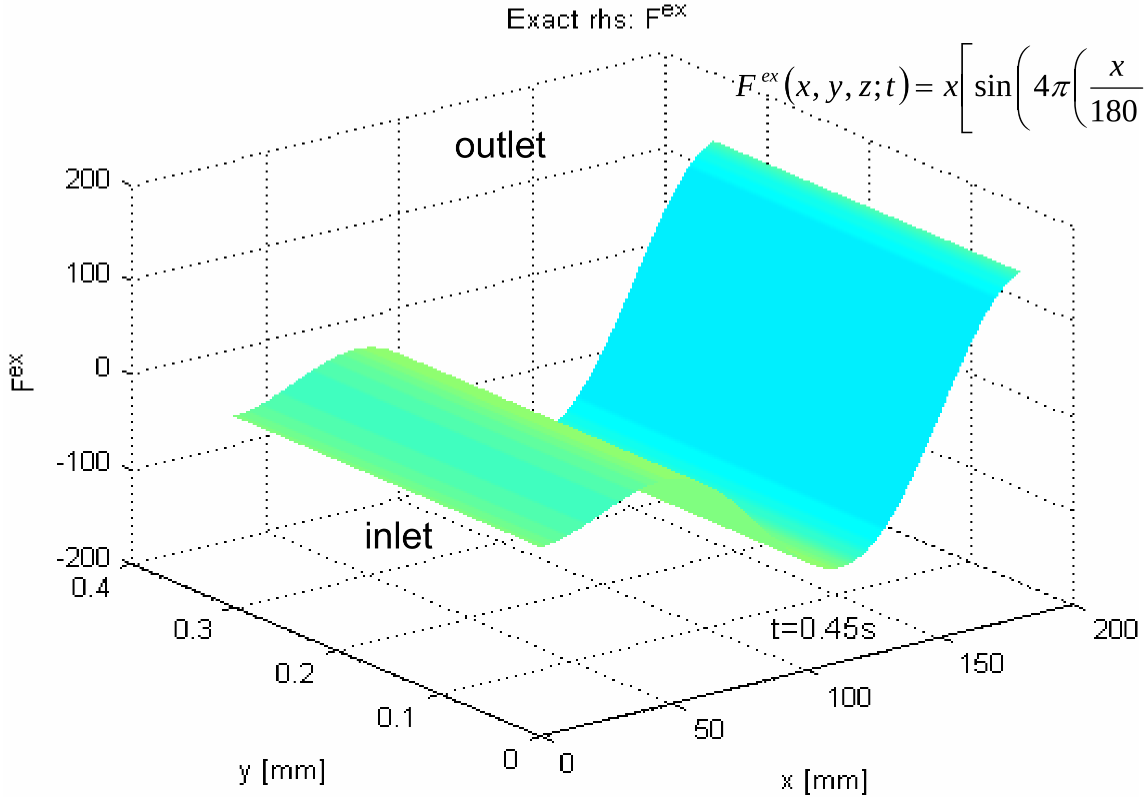
$$a_{\mathbf{mol}} = 8.4\cdot 10^{-8}\left[\mathbf{m^2/s}\right]$$

IC & BC:

$T_0 = \mathbf{20\ [C]}$ $\quad T_{in} = \mathbf{20\ [C]}$

$q_h = \mathbf{5960[kW/m^2]}$

$$F^{ex}(x,y,z;t) = x\left[\sin\left(4\pi\left(\frac{x}{180}+\frac{t}{50}\right)\right)+\frac{y}{0.3}\cdot\frac{t}{50}\right]$$



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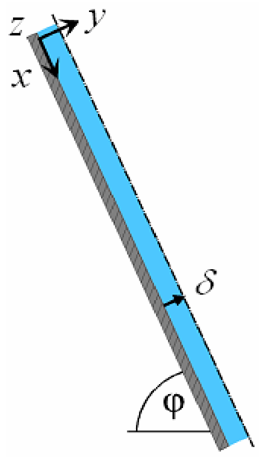

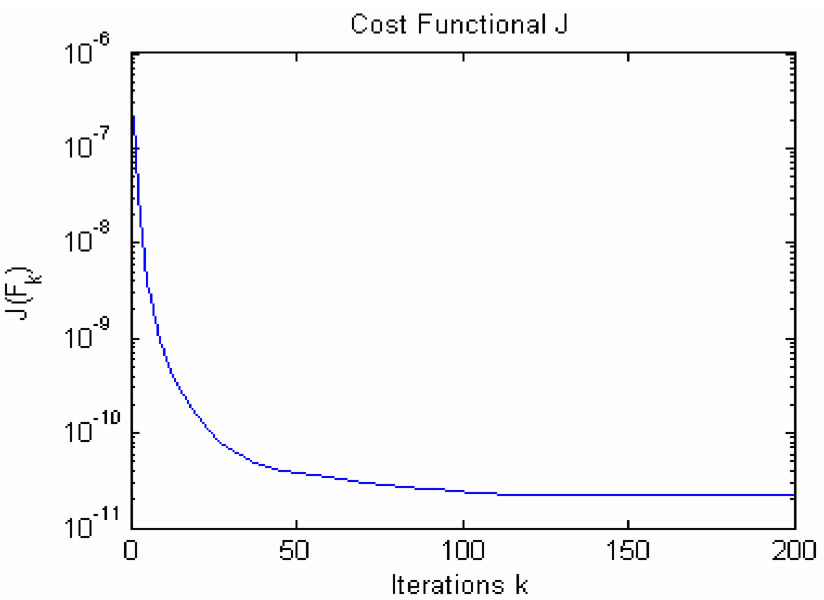

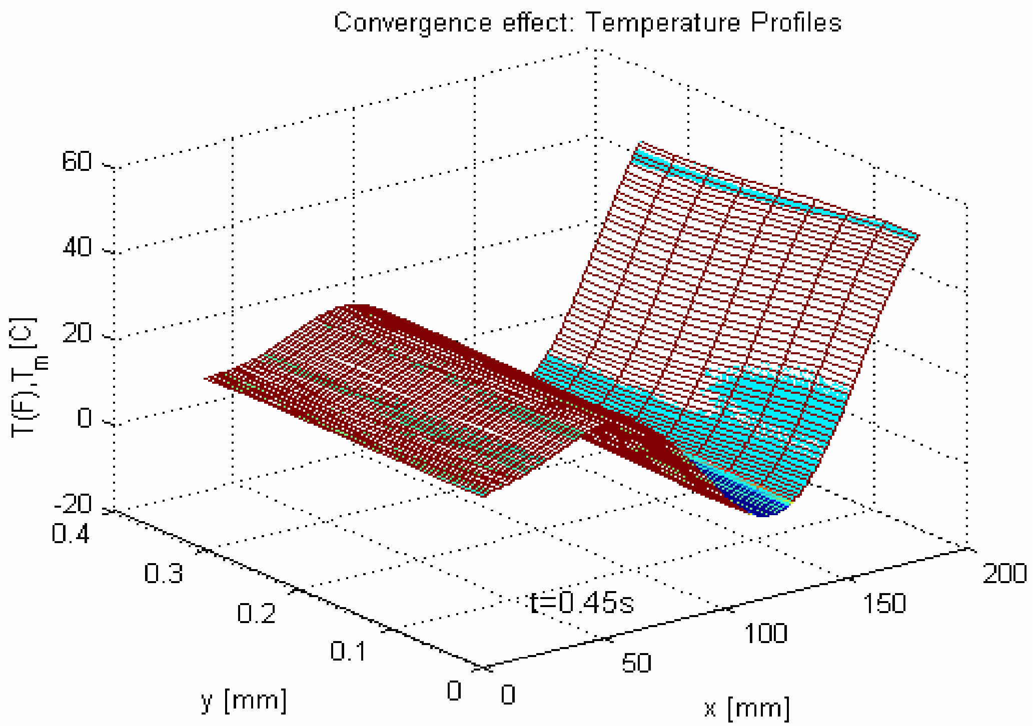

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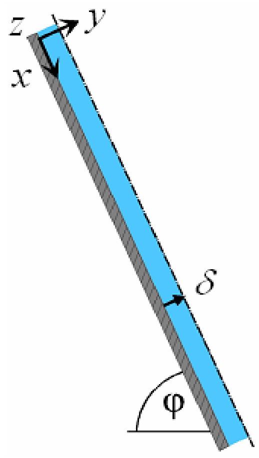

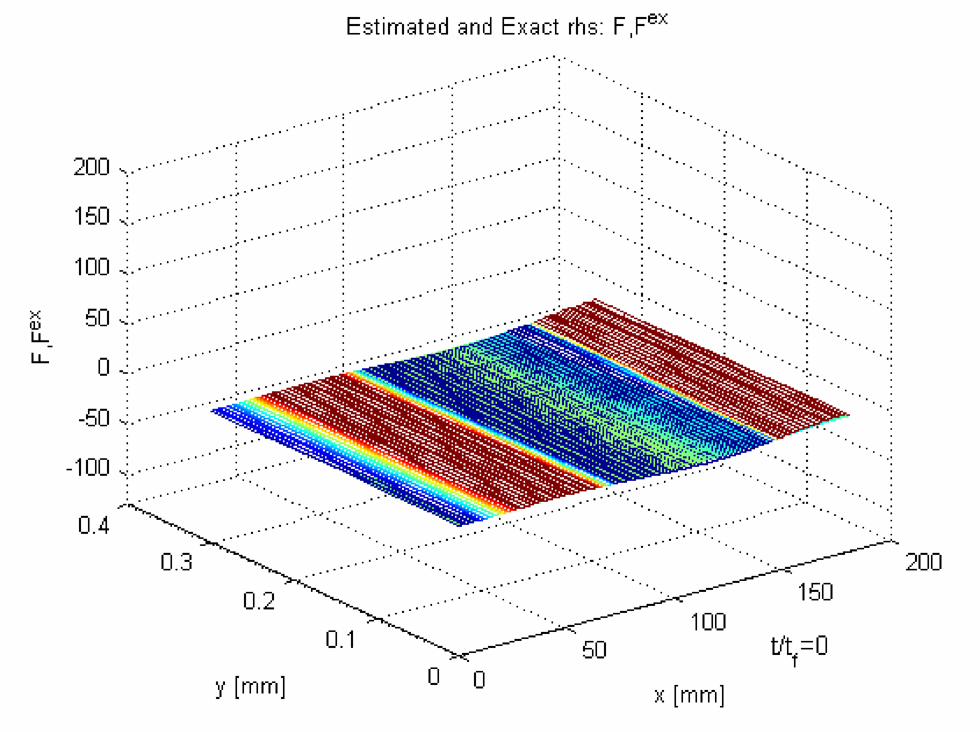

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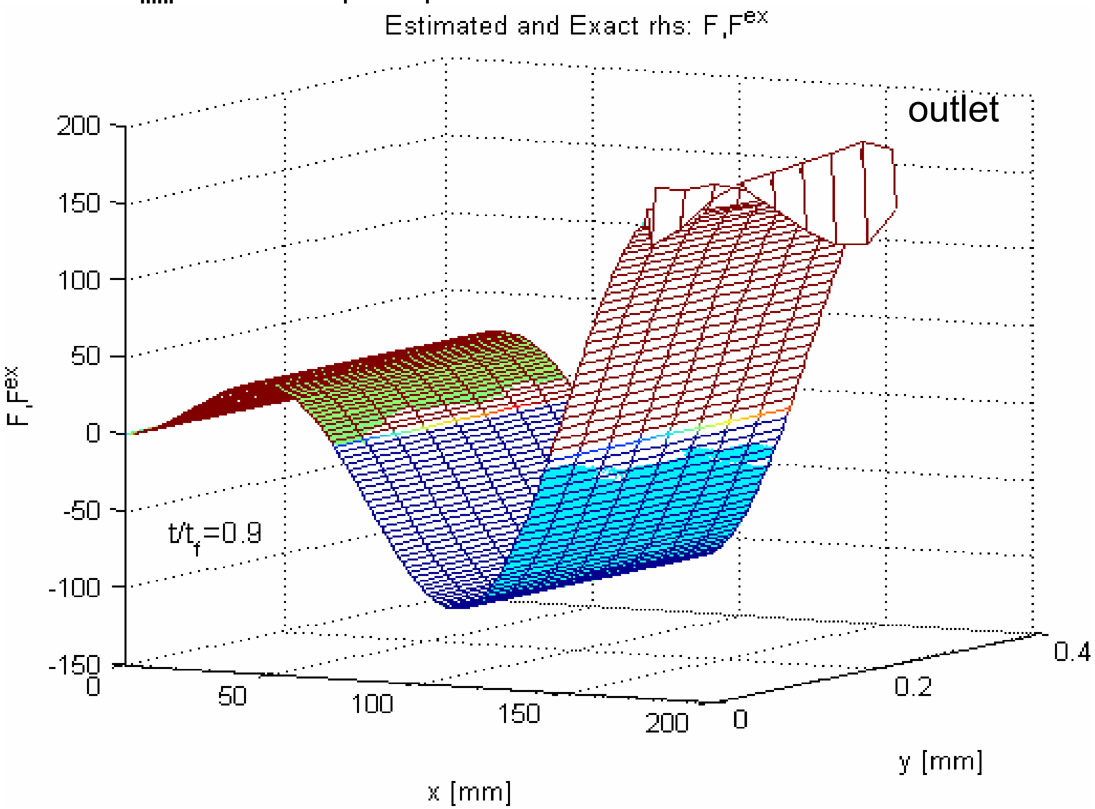

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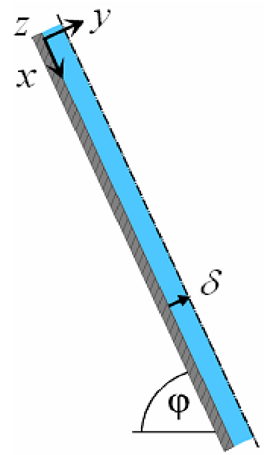

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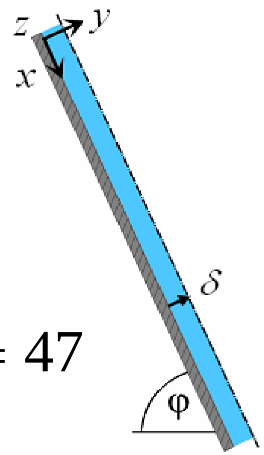
$\nabla J(F_k(\mathbf{x},t))|_{\Gamma_{in}} = 0 \Rightarrow F_k(\mathbf{x},t)|_{\Gamma_{in}}$ will *not* change

F *deviates* from $F^{\mathbf{ex}}$

- lack of information at the outlet due to the convection
- as $t/t_f \to 1$:
  $\nabla J(F_k(\mathbf{x},t_f)) = 0 \Rightarrow F_k(\mathbf{x},t_f)$ will *not* change



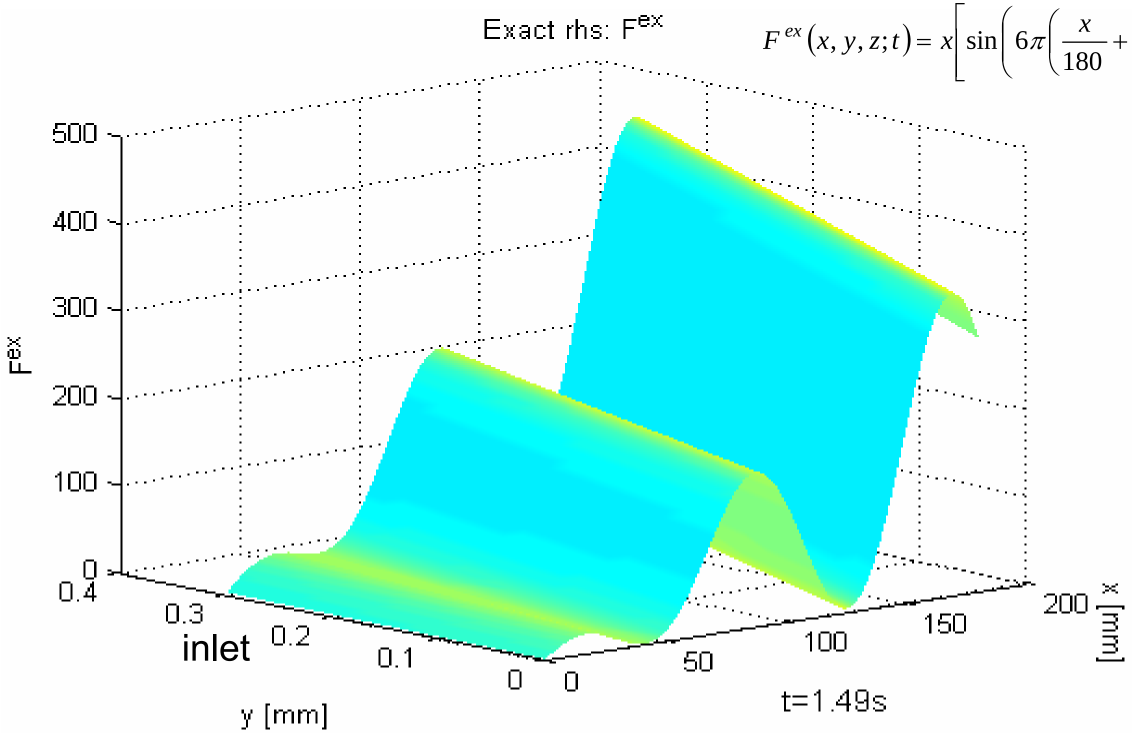
Measurement error $T_m = T_m^{ex} + \sigma\varpi$

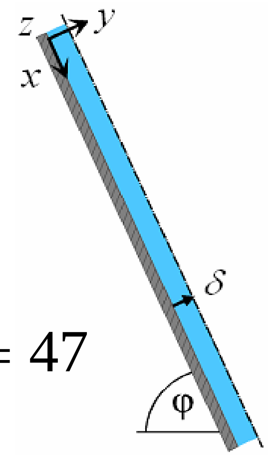
standard deviation of the measurement error: σ
zero mean normal distribution with variance one: ϖ

Regularisation via discretization and suitable stopping criteria:

discrepancy principle: $J(x,t;F_w^{n_{opt}}) < \kappa\sigma,\ \kappa > 1 \quad i.e.\ \kappa = 1.02,\ k = 47$

$$F^{ex}(x,y,z;t) = x\left[\sin\left(6\pi\left(\frac{x}{180}+\frac{t}{200}\right)\right)+\frac{y}{0.3}\cdot\frac{t}{200}+\frac{z}{0.3}\right]$$





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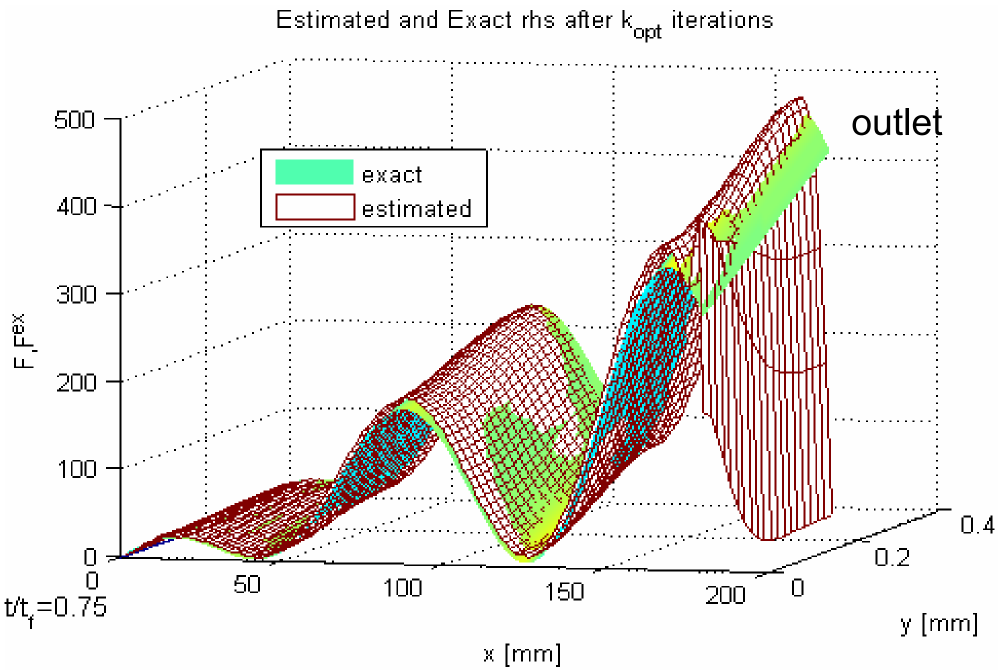
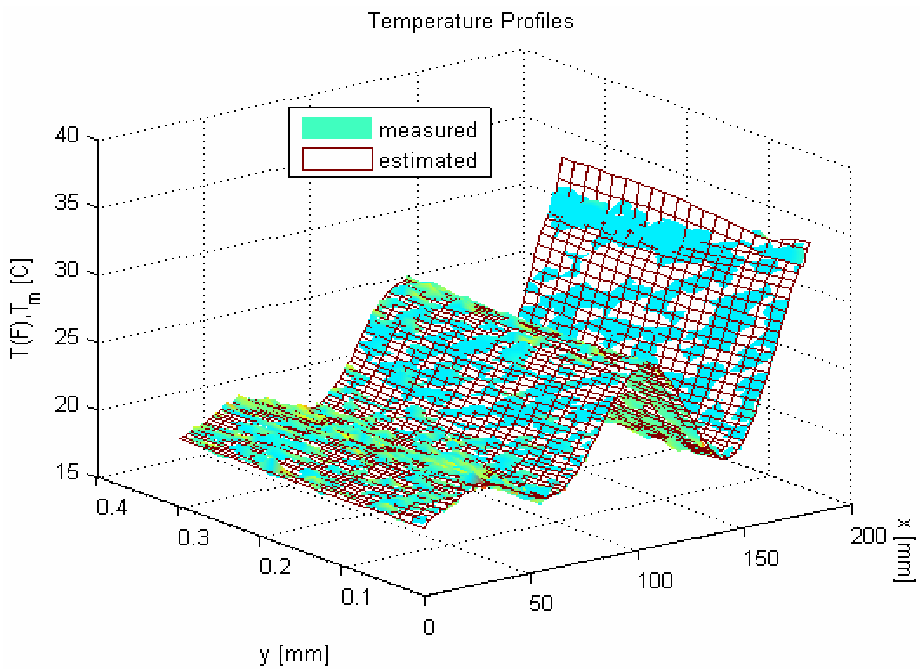
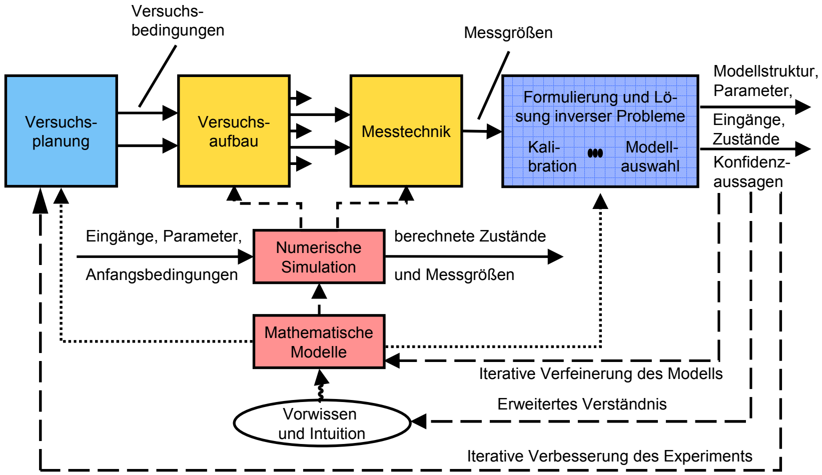






method integration has high potential !

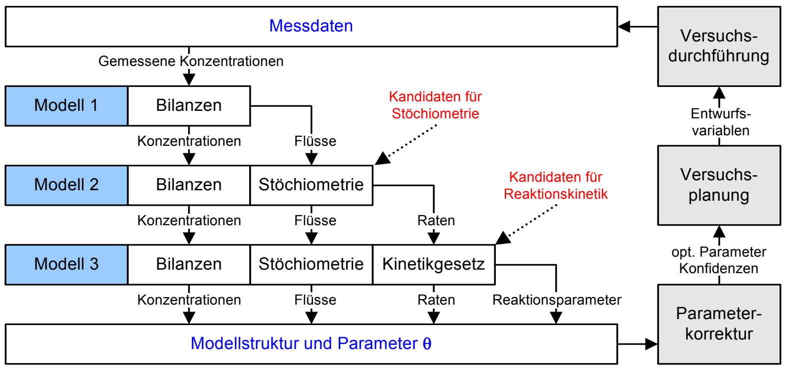
- optimal experimental design reduces effort
- structure identification leads to mechanisms

- improvement of method integration in particular for distributed problems

incremental refinement has high potential !

- homogenous reactions, multi-component diffusion, diffusion & bioreaction in gels
- drastic reduction of experimental and engg. effort
- significantly improved transparency

- further development for CFD problems



Lessons Learned

- **accept interactions** between kinetic phenomena **in experiments**,
  but
  isolate them **during identification** by a suitable decomposition strategy

- **high precision calibration** of high-resolution measurements
  (PIV, LIC, LCSM, NMR imaging, Raman / IR spectroscopy etc.)
  often is a difficult modeling problem in itself

- **statistics of measurement errors** need to be included in the analysis

- **flux estimation** is the key to reliable identification

- **tremendous improvements** are possible by systematic
  cross-disciplinary linking of **process systems** and **experimental skills**

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R. Kneer	S. Stapf

and others