



ÉCOLE POLYTECHNIQUE  
FÉDÉRALE DE LAUSANNE



# Incremental Model Identification of Distributed Two-phase Reaction Systems

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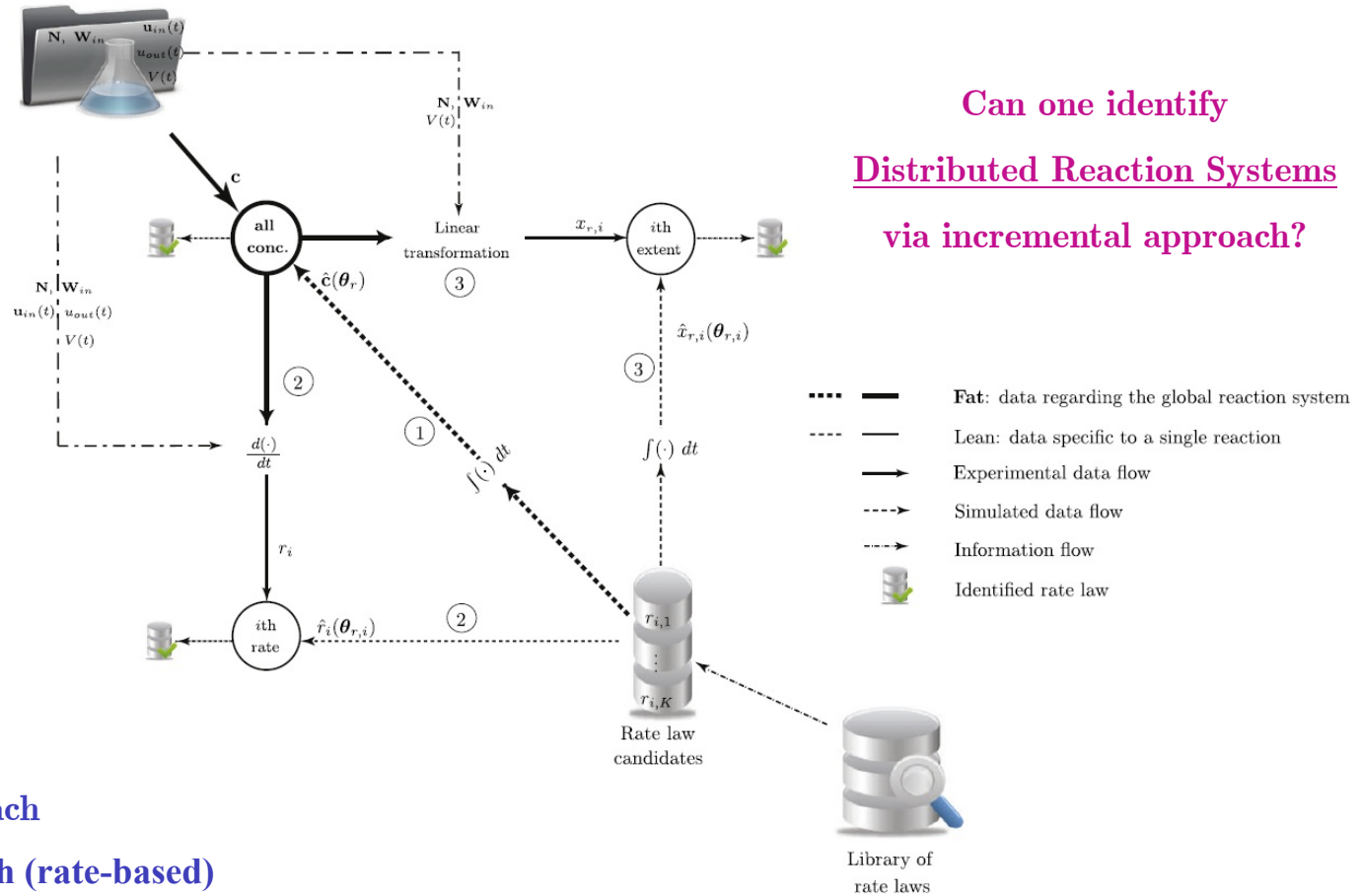
# Outline

- Kinetic Identification Methods
- Incremental Model Identification (using PDE)  
with Material Balance Equations in  $(z,t)$  domain
- Simplified Incremental Identification (using ODE)  
with Material Balance Equations in  $\tau$  domain
- Simulated Example
- Conclusion and Perspectives

# Kinetic Identification Methods

## From data to rates/extents

Experiments, measurements



- ① Simultaneous approach
- ② Incremental approach (rate-based)
- ③ Incremental approach (extent-based)

# Incremental Model Identification (PDE)

## Material balance equations in $(z,t)$ domain

- **Two-phase plug-flow reactor** (1 dimension, without diffusion) with
  - $s_f$  species
  - $r_f$  reactions
  - $m$  mass transfers

described by a set of  $s_f$  **P**artial **D**ifferential **E**quations (PDE)

$$\underbrace{\frac{\partial}{\partial t} (\boldsymbol{\varepsilon}_f \mathbf{c}_f(z, t))}_{\text{Accumulation}} + \underbrace{\frac{\partial}{\partial z} (\boldsymbol{\varepsilon}_f v_f \mathbf{c}_f(z, t))}_{\text{Transport by advection}} = \underbrace{\mathbf{N}_f^T \boldsymbol{\varepsilon}_f \mathbf{r}_f(z, t)}_{\text{Reaction}} \pm \underbrace{\mathbf{E}_{m,f} \boldsymbol{\varepsilon}_f \boldsymbol{\phi}_{m,f}(z, t)}_{\text{Mass Transfer}}$$

$$\mathbf{c}_f(z, 0) = \mathbf{c}_{f,0}(z) \text{ (IC)}, \quad \mathbf{c}_f(0, t) = \mathbf{c}_{f,in}(t) \text{ (BC)}, \quad F = \{L, G\}, \quad f = \{l, g\}$$

**State variables:**  $\mathbf{c}_f(z, t)$  ( $s_f \times 1$ ) concentrations,  $\boldsymbol{\varepsilon}_f := \boldsymbol{\varepsilon}_f(z, t)$  volumetric fraction,  $v_f := v_f(z, t)$  velocity of phase F

**Structural information:**  $\mathbf{N}_f$  ( $r_f \times s_f$ ) stoichiometry,  $\mathbf{E}_{m,f}$  ( $s_f \times m$ ) mass-transfer matrix (+ for L, – for G)

**Time-variant signals:**  $\mathbf{r}_f(z, t)$  ( $r_f \times 1$ ) reaction rates,  $\boldsymbol{\phi}_{m,f}(z, t)$  ( $m \times 1$ ) mass-transfer rates

# Incremental Model Identification (PDE)

## Step 1: Transformation to extents (1/2)

- The effect of **advection on IC and BC** in absence of other dynamic effects is computed using  $\mathbf{c}_{ibc,f}$  ( $s_f \times 1$ ) and the velocity profile  $v_f(z, t)$

$$\frac{\partial}{\partial t} (\boldsymbol{\varepsilon}_f \mathbf{c}_{ibc,f}(z, t)) + \frac{\partial}{\partial z} (\boldsymbol{\varepsilon}_f v_f \mathbf{c}_{ibc,f}(z, t)) = \mathbf{0}_{s_f}$$

$$\mathbf{c}_{ibc,f}(z, 0) = \mathbf{c}_{f,0}(z) \text{ (IC)}, \quad \mathbf{c}_{ibc,f}(0, t) = \mathbf{c}_{f,in}(t) \text{ (BC)}$$

- Removing the effect of advection on IC and BC via  $\delta \mathbf{c}_f := \mathbf{c}_f - \mathbf{c}_{ibc,f}$  yields

$$\frac{\partial}{\partial t} (\boldsymbol{\varepsilon}_f \delta \mathbf{c}_f(z, t)) + \frac{\partial}{\partial z} (\boldsymbol{\varepsilon}_f v_f \delta \mathbf{c}_f(z, t)) = \underbrace{\mathbf{N}_f^T \boldsymbol{\varepsilon}_f \mathbf{r}_f(z, t)}_{\text{Reaction}} \pm \underbrace{\mathbf{E}_{m,f} \boldsymbol{\varepsilon}_f \boldsymbol{\phi}_{m,f}(z, t)}_{\text{Mass Transfer}}$$

$$\delta \mathbf{c}_f(z, 0) = \delta \mathbf{c}_f(0, t) = \mathbf{0}_{s_f}$$

# Incremental Model Identification (PDE)

## Step 1: Transformation to extents (2/2)

- If  $\text{rank}([\mathbf{N}_f^T \ \pm \mathbf{E}_{m,f}]) = r_f + m$ , then  $\mathbf{T}_f := [\mathbf{N}_f^T \ \pm \mathbf{E}_{m,f} \ \mathbf{P}_f]^{-1}$  transforms  $\delta \mathbf{c}_f$  in

$$\begin{bmatrix} \mathbf{x}_{r,f}(z,t) \\ \mathbf{x}_{m,f}(z,t) \\ \mathbf{x}_{iv,f}(z,t) \end{bmatrix} = \mathbf{T}_f \delta \mathbf{c}_f(z,t) \quad \mathbf{c}_f(z,t) = \mathbf{N}_f^T \mathbf{x}_{r,f}(z,t) \pm \mathbf{E}_m \mathbf{x}_{m,f}(z,t) + \mathbf{c}_{ibc,f}(z,t)$$

- $\mathbf{T}_f$  splits the material balance in **3 sets of PDE**:

$$\frac{\partial}{\partial t} (\mathcal{E}_f \mathbf{x}_{r,f}(z,t)) + \underbrace{\frac{\partial}{\partial z} (\mathcal{E}_f v_f \mathbf{x}_{r,f}(z,t))}_{\text{Advection of material produced by the reactions}} = \mathcal{E}_f \mathbf{r}_f(z,t), \quad \mathbf{x}_{r,f}(z,0) = \mathbf{x}_{r,f}(0,t) = \mathbf{0}_{r_f} \quad \text{Reaction variants}$$

$$\frac{\partial}{\partial t} (\mathcal{E}_f \mathbf{x}_{m,f}(z,t)) + \underbrace{\frac{\partial}{\partial z} (\mathcal{E}_f v_f \mathbf{x}_{m,f}(z,t))}_{\text{Advection of material exchanged between phases}} = \mathcal{E}_f \phi_{m,f}(z,t), \quad \mathbf{x}_{m,f}(z,0) = \mathbf{x}_{m,f}(0,t) = \mathbf{0}_m \quad \text{Mass-transfer variants}$$

$$\mathbf{x}_{iv,f}(z,t) = \mathbf{0}_{s_f - (r_f + m)} \quad \text{Invariants}$$

# Incremental Model Identification (PDE)

## Step 2: Model identification

- Incremental identification of the **reaction rates**  $\mathbf{r}_f$

$$\begin{aligned} \min_{\boldsymbol{\theta}_{r,f,i}} \quad & \sum_{p=1}^P \sum_{h=1}^H \left( \tilde{x}_{r,f,i}(z_p, t_h) - \mathbf{x}_{r,f,i}(z_p, t_h, \boldsymbol{\theta}_{r,f,i}) \right)^2 & \forall i = 1, \dots, r_f \\ \text{s.t.} \quad & \frac{\partial}{\partial t} (\boldsymbol{\varepsilon}_f \mathbf{x}_{r,f,i}(z, t, \boldsymbol{\theta}_{r,f,i})) + \frac{\partial}{\partial z} (\boldsymbol{\varepsilon}_f \nu_f \mathbf{x}_{r,f,i}(z, t, \boldsymbol{\theta}_{r,f,i})) = \boldsymbol{\varepsilon}_f \mathbf{r}_{f,i}(\tilde{\mathbf{c}}_f(z, t), \boldsymbol{\theta}_{r,f,i}) \\ & x_{r,f,i}(z, 0, \boldsymbol{\theta}_{r,f,i}) = x_{r,f,i}(0, t, \boldsymbol{\theta}_{r,f,i}) = \mathbf{0} \end{aligned}$$

- Incremental identification of the **mass-transfer rates**  $\boldsymbol{\phi}_{m,f}$

$$\begin{aligned} \min_{\boldsymbol{\theta}_{m,f,j}} \quad & \sum_{p=1}^P \sum_{h=1}^H \left( \tilde{x}_{m,f,j}(z_p, t_h) - \mathbf{x}_{m,f,j}(z_p, t_h, \boldsymbol{\theta}_{m,f,j}) \right)^2 & \forall j = 1, \dots, m \\ \text{s.t.} \quad & \frac{\partial}{\partial t} (\boldsymbol{\varepsilon}_f \mathbf{x}_{m,f,j}(z, t, \boldsymbol{\theta}_{m,f,j})) + \frac{\partial}{\partial z} (\boldsymbol{\varepsilon}_f \nu_f \mathbf{x}_{m,f,j}(z, t, \boldsymbol{\theta}_{m,f,j})) = \boldsymbol{\varepsilon}_f \boldsymbol{\phi}_{m,f,j}(\tilde{\mathbf{c}}_l(z, t), \tilde{\mathbf{c}}_g(z, t), \boldsymbol{\theta}_{m,f,j}) \\ & x_{m,f,j}(z, 0, \boldsymbol{\theta}_{m,f,j}) = x_{m,f,j}(0, t, \boldsymbol{\theta}_{m,f,j}) = \mathbf{0} \end{aligned}$$

- This method requires **measurements along the  $z$  direction** of the reactor!

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( $\tilde{\cdot}$ ) denote measured quantities or variables computed from measured quantities

# Simplified Incremental Identification (ODE)

## Material balance equations in $\tau$ domain

- Typically: **measurements are only available at the reactor exit!**
- **Simplifications**
  - Steady-state mass transfers,
  - Constant volumetric fractions,
  - Constant and identical velocity in the two phases,
  - Constant boundary conditions.
- *To an observer sitting on a particle of velocity  $v$ , the state vector  $\mathbf{c}(z,t)$  is viewed as  $\mathbf{c}_p(\tau)$ , with  $z = v \tau$  and  $t = \tau$  (**time spent in the reactor up to position  $z$** ), described by a set of  $(s_l + s_g)$  **Ordinary Differential Equations (ODE)***

$$\frac{d}{d\tau} \mathbf{c}_p(\tau) = \mathbf{N}^T \mathbf{r}(\tau) + \mathbf{E}_m \phi_m(\tau), \quad \mathbf{c}_p(0) = \mathbf{c}_{in} = \begin{bmatrix} \mathbf{c}_{l,in} \\ \mathbf{c}_{g,in} \end{bmatrix}$$

$$\mathbf{c}_p = \begin{bmatrix} \mathbf{c}_{p,l} \\ \mathbf{c}_{p,g} \end{bmatrix}, \quad \mathbf{N}^T = \begin{bmatrix} \mathbf{N}_l^T \\ \mathbf{0}_{s_g \times r} \end{bmatrix} \text{ and } \mathbf{E}_m = \begin{bmatrix} +\mathbf{E}_{m,l} \\ -\mathbf{E}_{m,g} \end{bmatrix}$$



# Simplified Incremental Identification (ODE)

## Step 1: Transformation to extents

- If  $\text{rank}([\mathbf{N}^T \ \mathbf{E}_m]) = r + m$ ,  $\mathbf{T} := [\mathbf{N}^T \ \mathbf{E}_m \ \mathbf{P}]^{-1}$  is applied to  $\delta\mathbf{c}_p := \mathbf{c}_p - \mathbf{c}_{in}$

$$\begin{bmatrix} \mathbf{x}_{p,r}(\tau) \\ \mathbf{x}_{p,m}(\tau) \\ \mathbf{x}_{p,iv}(\tau) \end{bmatrix} = \mathbf{T} \delta\mathbf{c}_p(\tau) \quad \mathbf{c}_p(\tau) = \mathbf{N}^T \mathbf{x}_{p,r}(\tau) + \mathbf{E}_m \mathbf{x}_{p,m}(\tau) + \mathbf{c}_{in}$$

- $\mathbf{T}$  splits the material balance in **3 sets of ODE**:

$$\begin{aligned} \frac{\partial}{\partial \tau} \mathbf{x}_{p,r}(\tau) &= \mathbf{r}(\tau), & \mathbf{x}_{p,r}(\tau) &= \mathbf{0}_r & \text{Reaction variants} \\ \frac{\partial}{\partial \tau} \mathbf{x}_{p,m}(\tau) &= \boldsymbol{\phi}_m(\tau), & \mathbf{x}_{p,m}(\tau) &= \mathbf{0}_m & \text{Mass-transfer variants} \\ \mathbf{x}_{p,iv}(\tau) &= \mathbf{0}_{(s_i+s_g)-(r+m)} & & & \text{Invariants} \end{aligned}$$

# Simplified Incremental Identification (ODE)

## Step 2: Model identification

- Model identification requires measurements  $\mathbf{c}_p(\tau_k)$  for various values of  $\tau_k$

$K$  measurements can be obtained by measuring the **concentrations**  $\mathbf{c}_p(\tau_k)$  at the reactor exit  $z = z_e$  for  $K$  different values of the **velocity**  $v_k = \frac{z_e}{\tau_k}$

- Incremental identification of the **reaction rates**  $\mathbf{r}$

$$\begin{aligned} \min_{\boldsymbol{\theta}_{r,i}} \quad & \sum_{k=1}^K \left( \tilde{x}_{p,r,i}(\tau_k) - x_{p,r,i}(\tau_k, \boldsymbol{\theta}_{r,i}) \right)^2 & \forall i = 1, \dots, r \\ \text{s.t.} \quad & \frac{d}{d\tau} x_{p,r,i}(\tau, \boldsymbol{\theta}_{r,i}) = r_i(\tilde{\mathbf{c}}_{p,l}(\tau), \boldsymbol{\theta}_{r,i}), & x_{p,r,i}(0, \boldsymbol{\theta}_{r,i}) = \mathbf{0} \end{aligned}$$

- Incremental identification of the **mass-transfer rates**  $\phi_m$

$$\begin{aligned} \min_{\boldsymbol{\theta}_{m,j}} \quad & \sum_{k=1}^K \left( \tilde{x}_{p,m,j}(\tau_k) - x_{p,m,j}(\tau_k, \boldsymbol{\theta}_{m,j}) \right)^2 & \forall j = 1, \dots, m \\ \text{s.t.} \quad & \frac{d}{d\tau} x_{p,m,j}(\tau, \boldsymbol{\theta}_{m,j}) = \phi_{m,j}(\tilde{\mathbf{c}}_{p,l}(\tau), \tilde{\mathbf{c}}_{p,g}(\tau), \boldsymbol{\theta}_{m,j}), & x_{p,m,j}(0, \boldsymbol{\theta}_{m,j}) = \mathbf{0} \end{aligned}$$

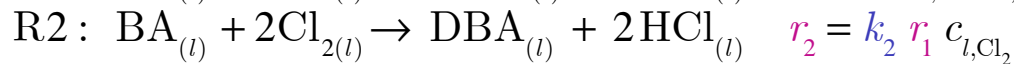
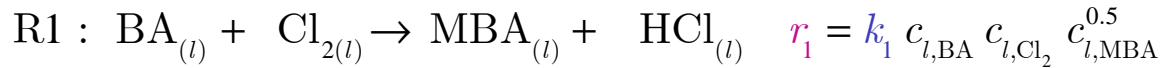
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( $\tilde{\cdot}$ ) denote measured quantities or variables computed from measured quantities

# Simulated Example

## Chlorination of butanoic acid

- System composed of  $s_g = 2$  species in phase G and  $s_l = 5$  species in phase L
- $r = 2$  reactions in the phase L



- $m = 2$  steady-state mass transfers obeying the rates

$$\phi_{m,\text{Cl}_2} = k_{\text{Cl}_2} a (c_{\text{Cl}_2}^{\star} - c_{l,\text{Cl}_2}), \quad c_{\text{Cl}_2}^{\star} = \frac{p_{\text{Cl}_2}}{H_{\text{Cl}_2}}$$

$$\phi_{m,\text{HCl}} = k_{\text{HCl}} a (c_{\text{HCl}}^{\star} - c_{l,\text{HCl}}), \quad c_{\text{HCl}}^{\star} = \frac{p_{\text{HCl}}}{H_{\text{HCl}}}$$

- Known structural information

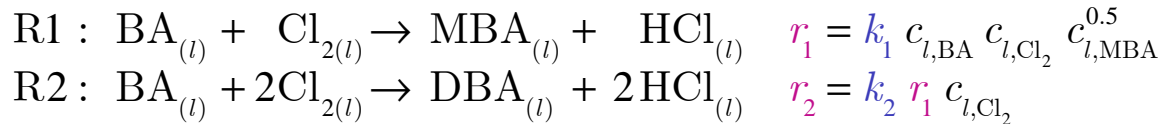
$$(z, t): \quad \mathbf{N}_l^T = \begin{bmatrix} -1 & -2 \\ -1 & -1 \\ 1 & 0 \\ 1 & 2 \\ 0 & 1 \end{bmatrix}, \quad \mathbf{E}_{m,l} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 1 \\ 0 & 0 \end{bmatrix}, \quad \mathbf{N}_g^T = \mathbf{0}_{2 \times 2}, \quad \mathbf{E}_{m,g} = \mathbf{I}_2 \quad \tau: \quad \mathbf{N}^T = \begin{bmatrix} \mathbf{N}_l^T \\ \mathbf{0}_{2 \times 2} \end{bmatrix}, \quad \mathbf{E}_m = \begin{bmatrix} +\mathbf{E}_{m,l} \\ -\mathbf{E}_{m,g} \end{bmatrix}$$

# Simulated Example

## Chlorination of butanoic acid

- System composed of  $s_g = 2$  species in phase G and  $s_l = 5$  species in phase L

- $r = 2$  reactions in the phase L

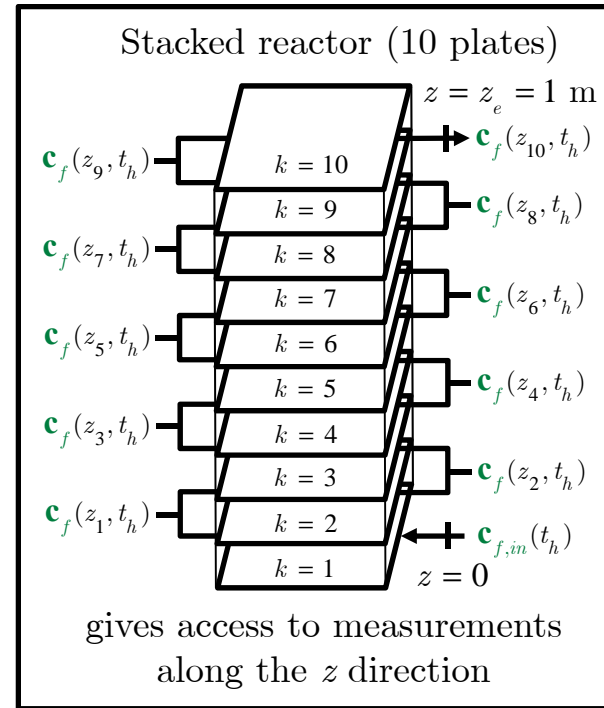


- $m = 2$  steady-state mass transfers obeying the rates

$$\begin{aligned} \phi_{m,\text{Cl}_2} &= k_{\text{Cl}_2} a (c_{\text{Cl}_2}^{\star} - c_{l,\text{Cl}_2}), & c_{\text{Cl}_2}^{\star} &= \frac{p_{\text{Cl}_2}}{H_{\text{Cl}_2}} \\ \phi_{m,\text{HCl}} &= k_{\text{HCl}} a (c_{\text{HCl}}^{\star} - c_{l,\text{HCl}}), & c_{\text{HCl}}^{\star} &= \frac{p_{\text{HCl}}}{H_{\text{HCl}}} \end{aligned}$$

- Known structural information

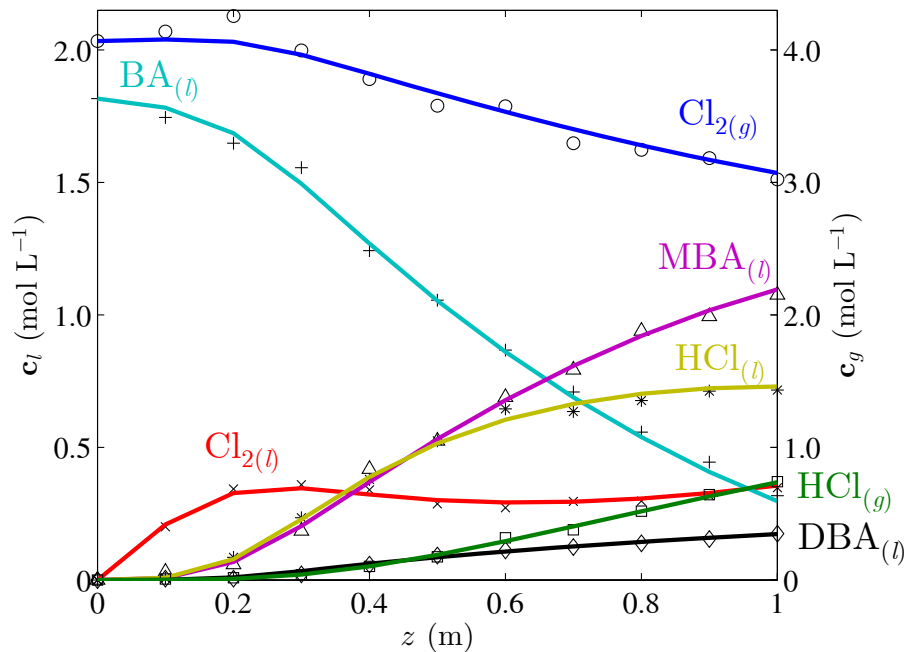
$$(z, t): \mathbf{N}_l^T = \begin{bmatrix} -1 & -2 \\ -1 & -1 \\ 1 & 0 \\ 1 & 2 \\ 0 & 1 \end{bmatrix}, \mathbf{E}_{m,l} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 1 \\ 0 & 0 \end{bmatrix}, \mathbf{N}_g^T = \mathbf{0}_{2 \times 2}, \mathbf{E}_{m,g} = \mathbf{I}_2$$



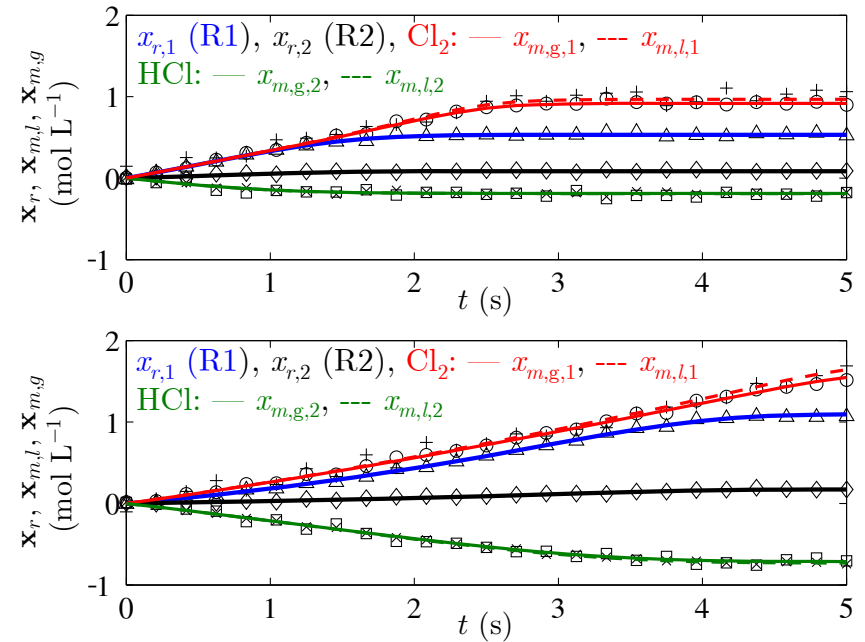
$$\tau: \mathbf{N}^T = \begin{bmatrix} \mathbf{N}_l^T \\ \mathbf{0}_{2 \times 2} \end{bmatrix}, \mathbf{E}_m = \begin{bmatrix} +\mathbf{E}_{m,l} \\ -\mathbf{E}_{m,g} \end{bmatrix}$$

# Simulated Example

## Dynamic experiments in $(z,t)$ domain (PDE)



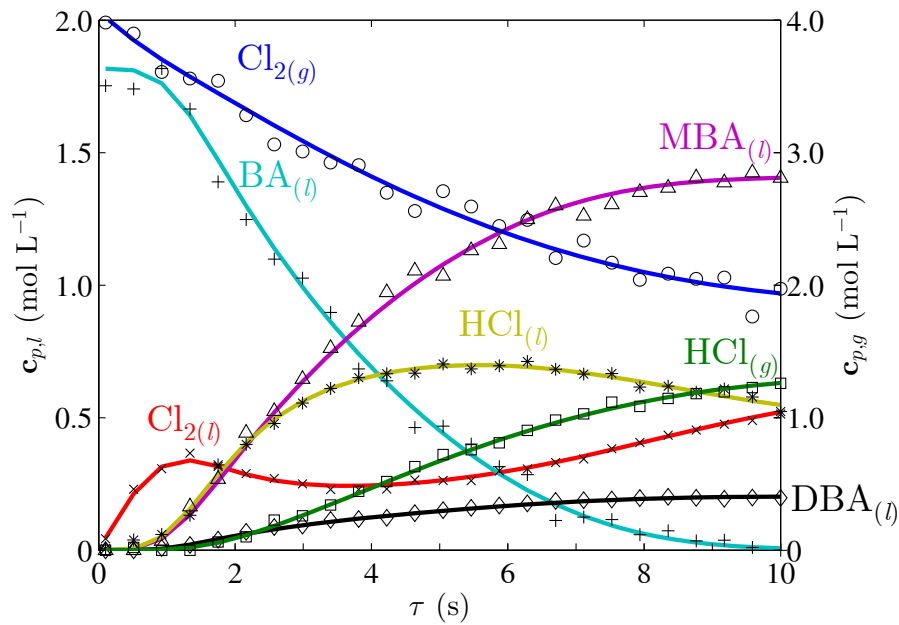
Simulated (noise-free, —) and experimental (2% noise) concentrations at  $t = 5$  s



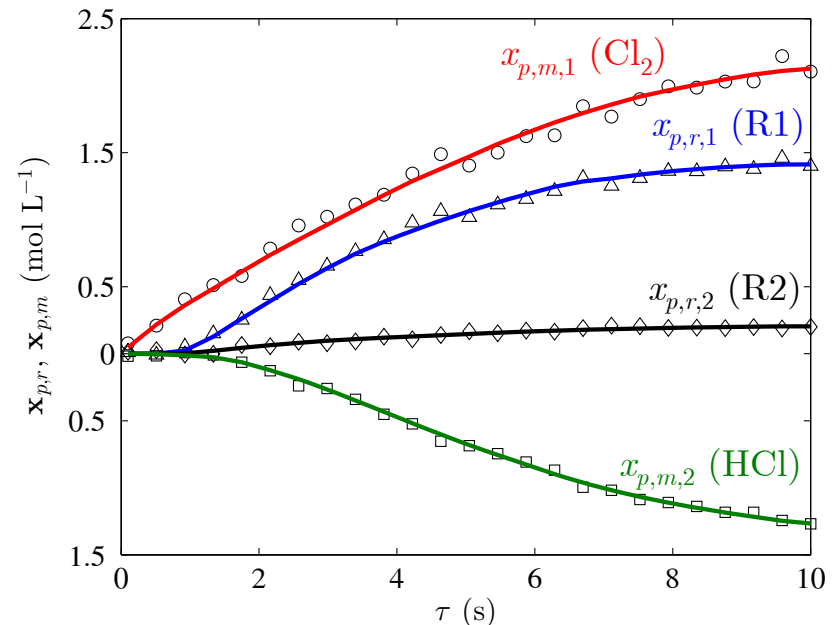
Modeled (with identified models, —) and experimental (2% noise) extents at  $z = 0.5$  m (above) and  $z = z_e = 1$  m (below)

# Simulated Example

## Steady-state experiments in $\tau$ domain (ODE)



Simulated (noise-free, —)  
and experimental (2% noise) concentrations



Modeled (with identified models, —)  
and experimental (2% noise) extents

$$\tau \in [0.1, 10] \text{ s} \Leftrightarrow v \in [10, 0.1] \frac{\text{m}}{\text{s}}$$

# Simulated Example

## Incremental identification of reaction rates

Incremental model identification of reactions R1 and R2  
 based on their respective extents of reaction,  
 with corresponding sum of squared errors (SSE)

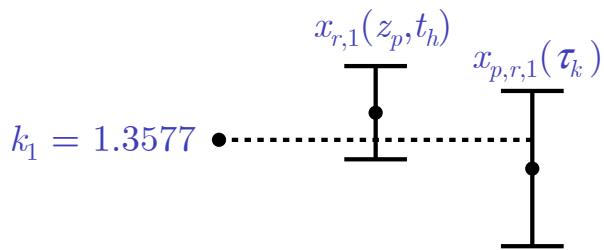
R1	Rate expression	SSE		R2	Rate expression	SSE	
		$x_{r,1}(z_p, t_h)$	$x_{p,r,1}(\tau_k)$			$x_{r,2}(z_p, t_h)$	$x_{p,r,2}(\tau_k)$
$\hat{r}_1^{(1)}$	$k_1 c_{l,Cl_2}$	0.923	1.270	$\hat{r}_2^{(1)}$	$k_2 k_1 c_{l,BA} c_{l,Cl_2}^2$	0.153	0.018
$\hat{r}_1^{(2)}$	$k_1 c_{l,BA} c_{l,Cl_2}$	5.120	0.563	$\hat{r}_2^{(2)}$	$k_2 k_1 c_{l,BA} c_{l,Cl_2}^2$	0.131	0.017
$\hat{r}_1^{(3)}$	$k_1 c_{l,BA} c_{l,Cl_2} c_{l,MBA}$	2.013	0.320	$\hat{r}_2^{(3)}$	$k_2 k_1 c_{l,BA} c_{l,Cl_2}^2 c_{l,MBA}$	0.107	0.010
$\hat{r}_1^{(4)}$	$k_1 c_{l,BA} c_{l,Cl_2} c_{l,MBA}^{0.5}$	<b>0.089</b>	<b>0.026</b>	$\hat{r}_2^{(4)}$	$k_2 k_1 c_{l,BA} c_{l,Cl_2}^2 c_{l,MBA}^{0.5}$	<b>0.049</b>	<b>0.005</b>

# Simulated Example

## Parameter estimation

Estimated rate constants for reactions R1 and R2, and mass-transfer coefficients for  $\text{Cl}_2$  and  $\text{HCl}$ , with corresponding 99% confidence intervals

Reaction R1 ( $r_1$ )



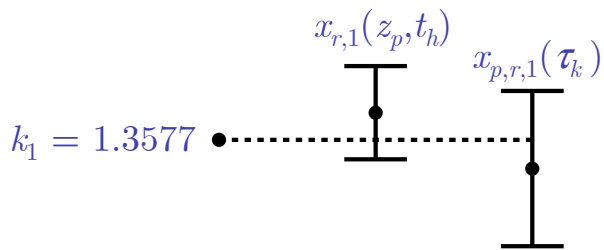


# Simulated Example

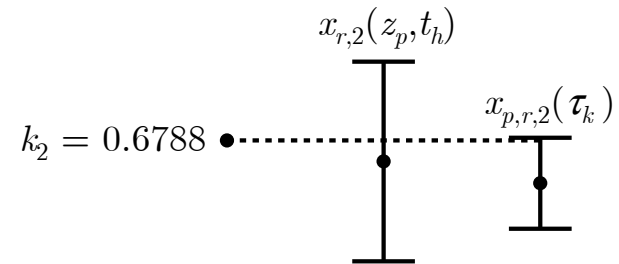
## Parameter estimation

Estimated rate constants for reactions R1 and R2, and mass-transfer coefficients for  $\text{Cl}_2$  and  $\text{HCl}$ , with corresponding 99% confidence intervals

Reaction R1 ( $r_1$ )



Reaction R2 ( $r_2$ )

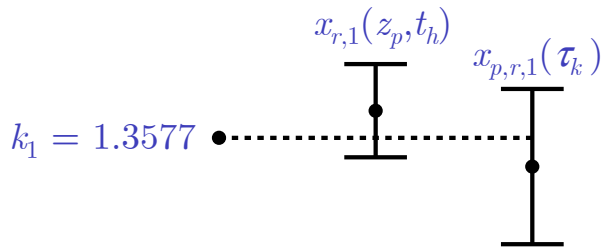


# Simulated Example

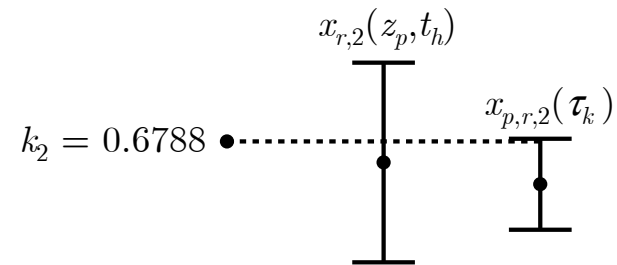
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Estimated rate constants for reactions R1 and R2, and mass-transfer coefficients for  $\text{Cl}_2$  and  $\text{HCl}$ , with corresponding 99% confidence intervals

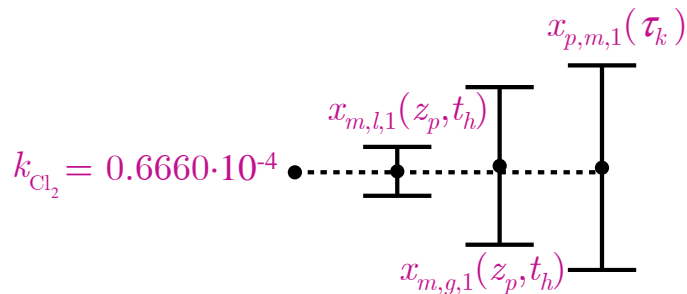
Reaction R1 ( $r_1$ )



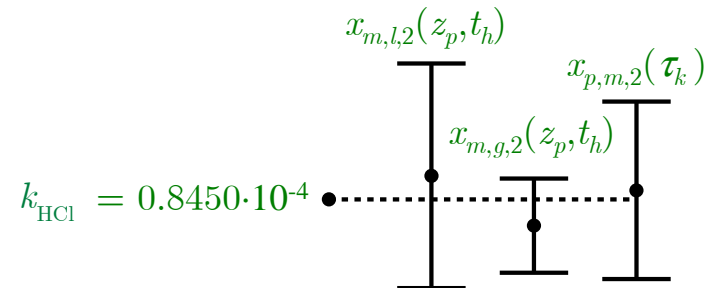
Reaction R2 ( $r_2$ )



Mass transfer  $\text{Cl}_2$  ( $\phi_{m,\text{Cl}_2}$ )



Mass transfer  $\text{HCl}$  ( $\phi_{m,\text{HCl}}$ )



# Conclusion and Perspectives

- **Extend-based model identification** for **2-phase distributed reaction systems**
  - via dynamic experiments collected at several  $(z,t)$  points  $\rightarrow (z,t)$  domain  $\rightarrow$  PDE
  - via steady-state experiments collected under various velocities  $\rightarrow \tau$  domain  $\rightarrow$  ODE
- **Extension** to **distributed systems with diffusion**
  - to identify kinetics independently from the effects of diffusion
  - to extract extents of diffusion
- **Applications** of **industrial relevance**
  - to distributed reaction-separation systems (reactive absorption, reactive distillation)
  - to 3D distributed reaction systems (tubular reactors, micro-reactors)

# Final word

Thank you for your attention

## References

- Brendel M., Bonvin D., Marquardt W., Incremental identification of kinetic models for homogeneous reaction systems, *Chem. Eng. Sci.* 61 (**2006**) 5404
- Bhatt N., Amrhein M., Bonvin D., Incremental identification of reaction and mass-transfer kinetics using the concept of extents, *Ind. Eng. Chem. Res.* 50 (**2011**) 12960
- Rodrigues D., Srinivasan S., Billeter J., Bonvin D., Variant and invariant states for chemical reaction systems, *Comp. Chem. Eng.* 73 (**2015**) 23