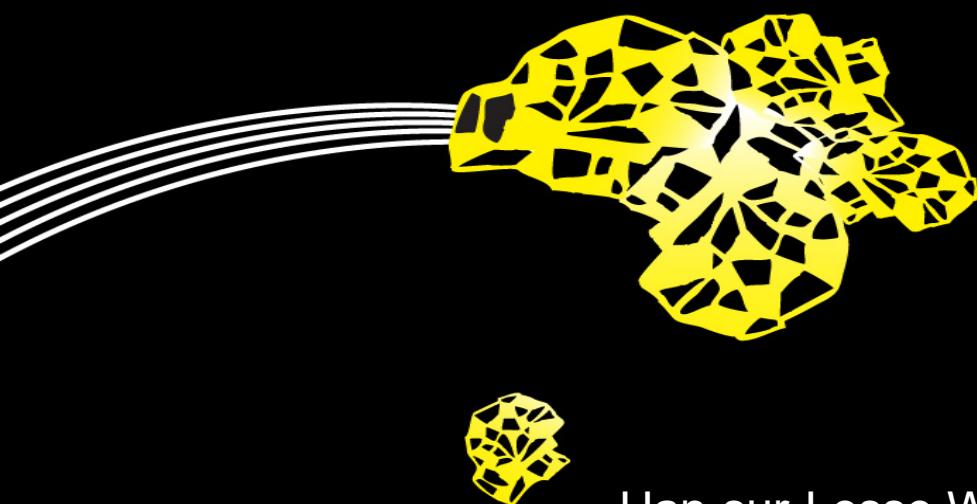


# UNIVERSITY OF TWENTE.

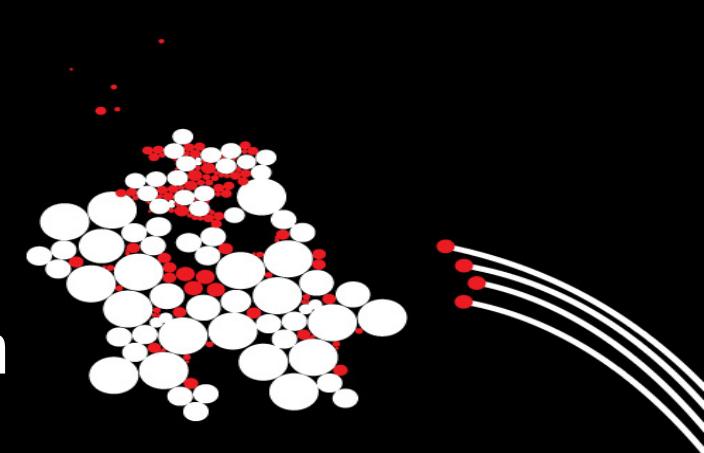
From benchtop experiments to industrial systems: an introduction  
to transport phenomena, reaction engineering and multi-scale  
modelling

Aayan Banerjee

Catalytic Processes and Materials, Faculty of Science and Technology



Han-sur-Lesse Winterschool, November 2021



# Content

---

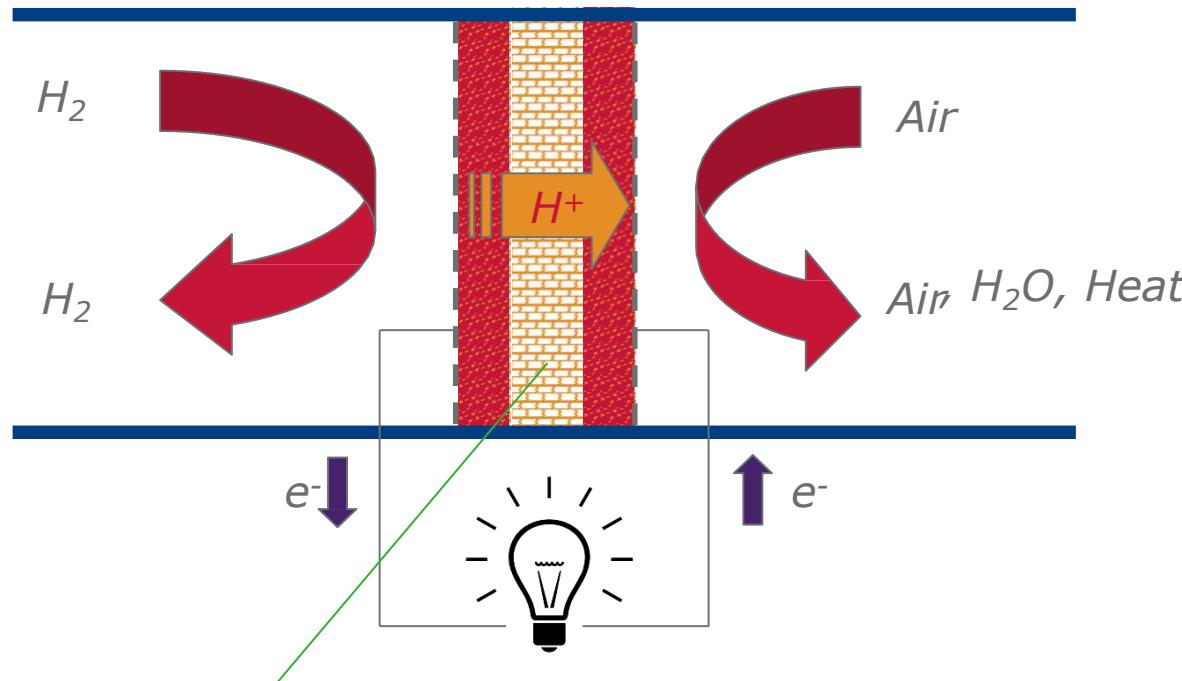
- Multi-scale modelling: Why? and How?
- The continuum approach
- Engineering descriptions of reaction kinetics
- Common types of chemical reactors
- Binary diffusion: A common pitfall in reaction engineering
- Brief Introduction to Systems Modelling

# Content

---

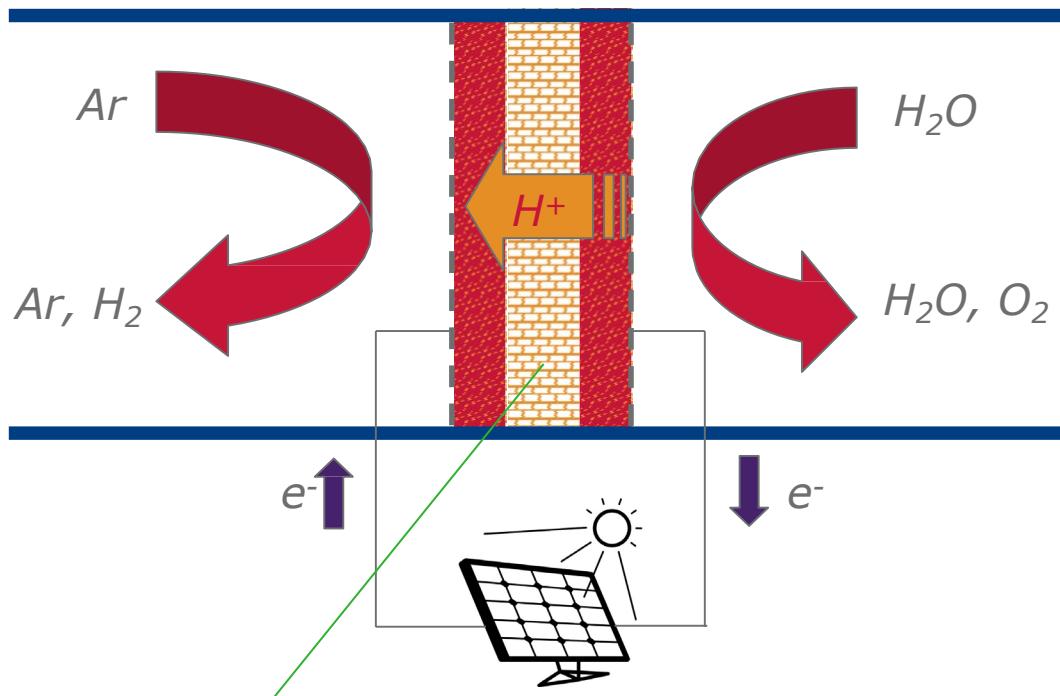
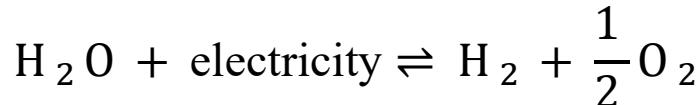
- **Multi-scale modelling: Why? and How?**
- The continuum approach
- Engineering descriptions of reaction kinetics
- Common types of chemical reactors
- Binary diffusion: A common pitfall in reaction engineering
- Brief Introduction to Systems Modelling

# PEM Fuel Cell



- $H^+$  conducting Polymer electrolyte (e.g. Nafion)
- Works between  $80^\circ\text{C}-120^\circ\text{C}$ , needs to be hydrated for good conductivity
- Conduction via hopping of  $H^+$  across covalently bonded anion groups in membrane ( $\text{SO}_3^-$  in Nafion) or H-bond formation and cleavage with water

# PEM Electrolysis Cell



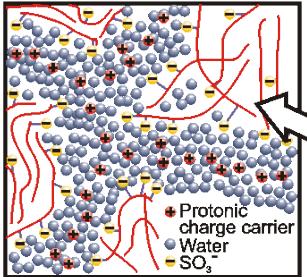
- H<sup>+</sup> conducting Polymer electrolyte (e.g. Nafion)
- Works between 80°C-120°C, needs to be hydrated for good conductivity
- Conduction via hopping of H<sup>+</sup> across covalently bonded anion groups in membrane (SO<sub>3</sub><sup>-</sup> in Nafion) or H-bond formation and cleavage with water

# The need for multi-scale modelling

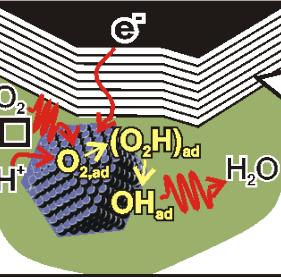
Processes to consider in Proton Exchange Membrane Cells – an (electro-)chemical reactor

## From the micro- to the macro-scales

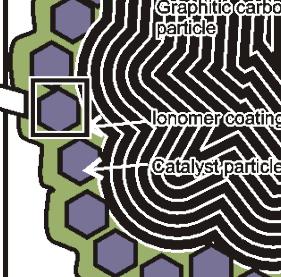
Structure of the ionomer - hydrophobic polymer backbone surrounded by water phase



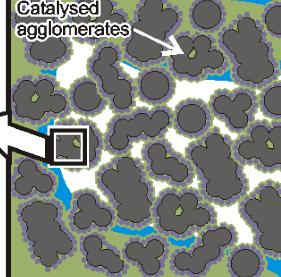
A platinum particle attached to a carbon particle substrate surrounded by ionomer



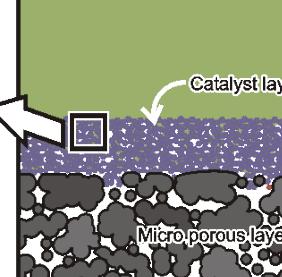
A single catalysed coated carbon particle



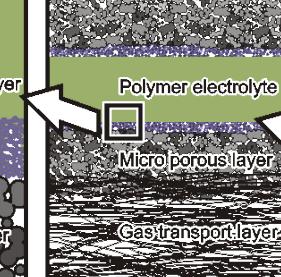
Catalyst layer showing pores and agglomerates of catalysed carbon particles



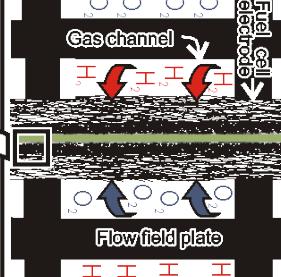
Catalyst layer and membrane



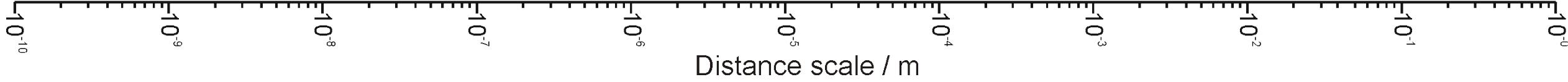
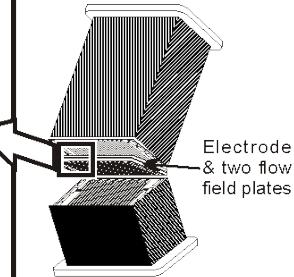
Gas transport layer, Microporous diffusion layer, composite catalyst layer and membrane



A MEA/bipolar plate combination showing feed channel and diffusion layer

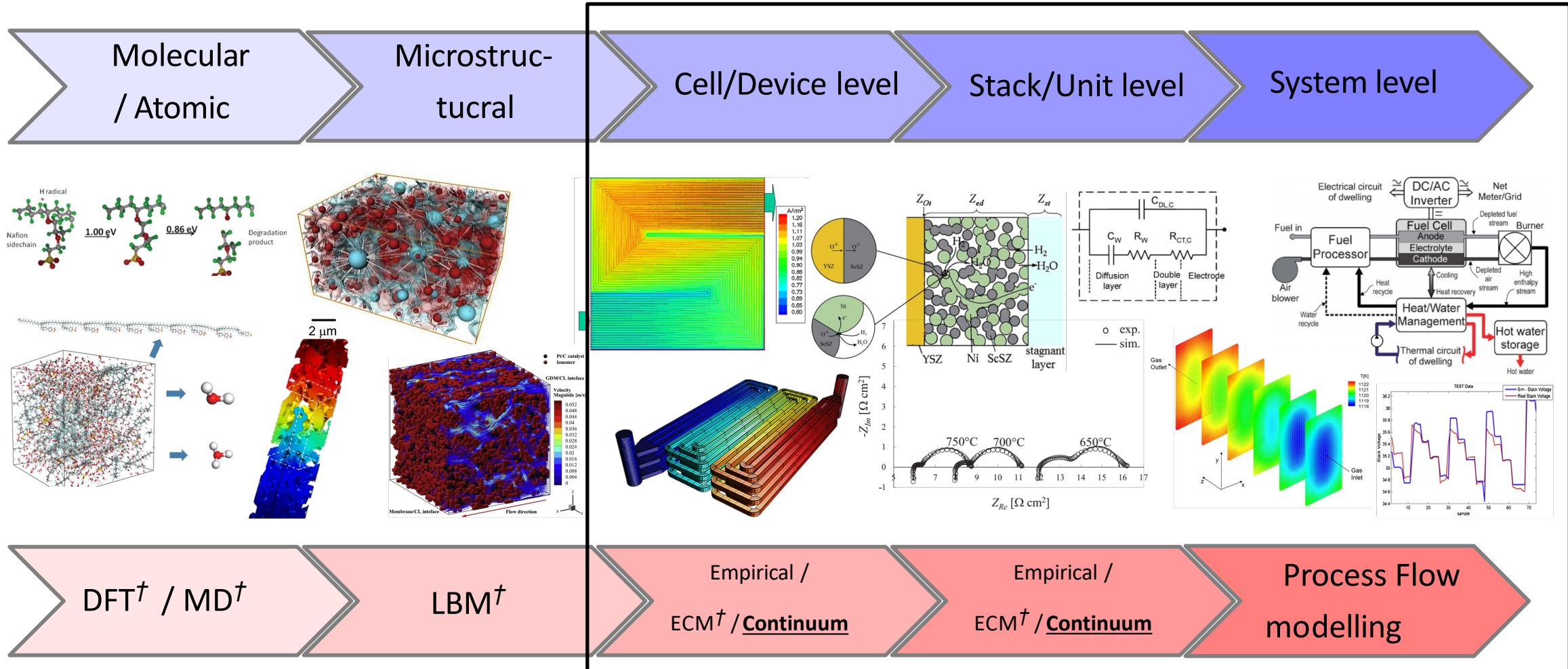


Fuel cell stack composed of multiple electrode/flow-field plate combinations



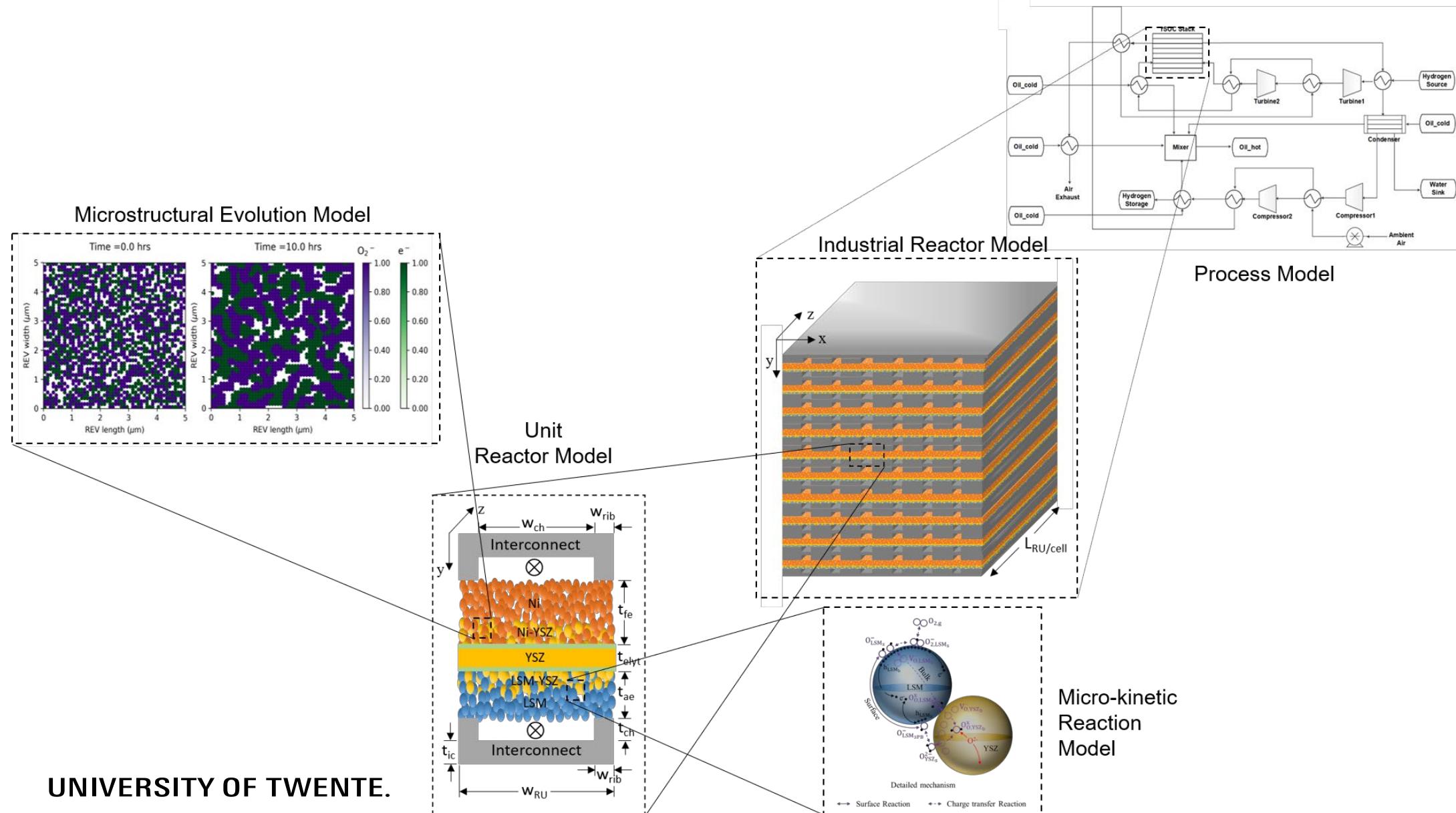
# Modelling scales and approaches

## Engineering Approaches for Real-World Applications

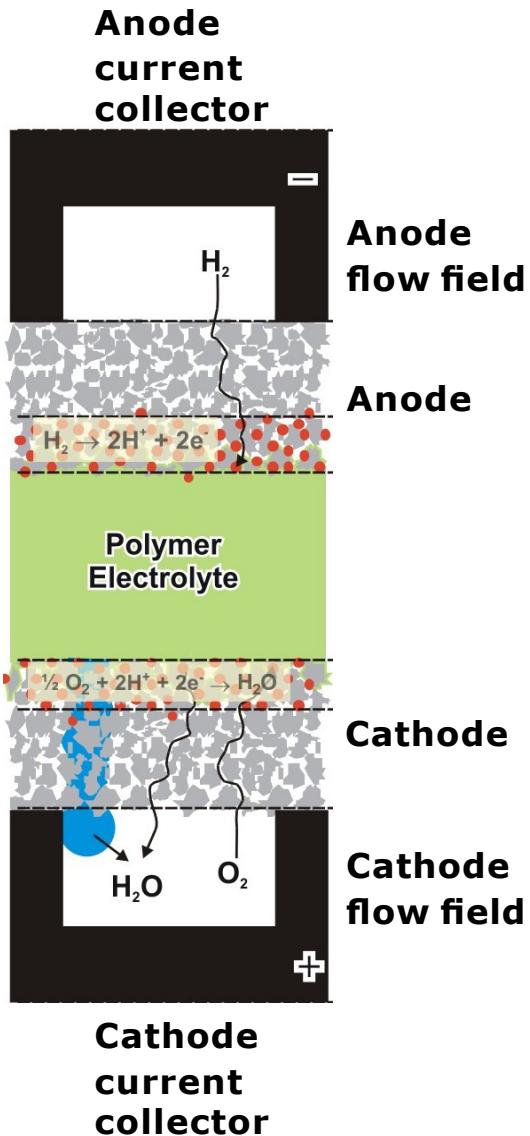


<sup>†</sup> DFT: Density Functional Theory; MD: Molecular Dynamics; LBM: Lattice Boltzmann Method; ECM: Equivalent circuit model

# Engineering Multi-scale Modelling: from surfaces to systems



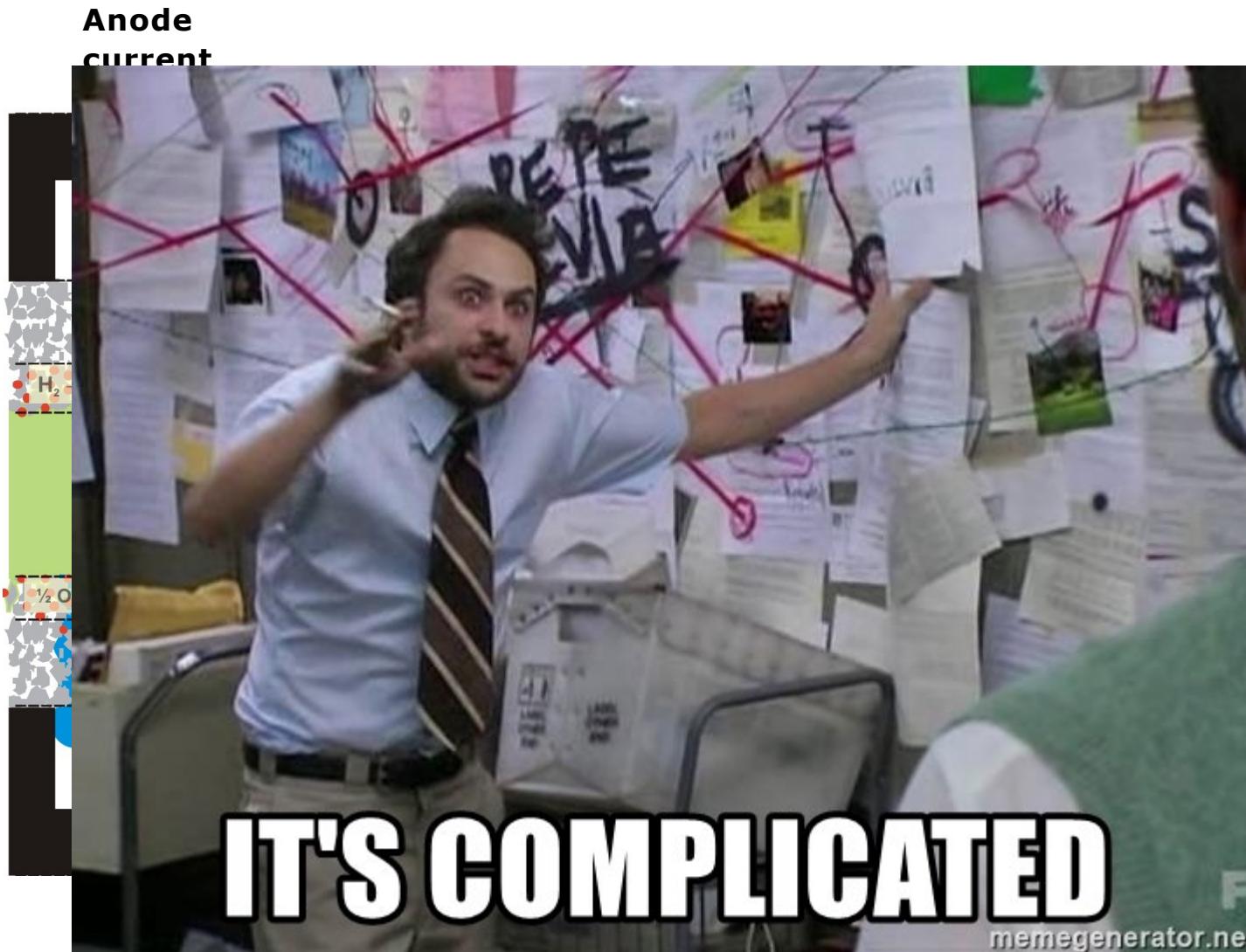
# Engineering a unit PEM cell (reactor) model



## Processes to consider

- Gas and Liquid flow through the channels and electrode pores
- Electron transport across the current collector and electrodes
- Ionic transport across the electrolyte and electrodes
- Transport of heat primarily through solid matrix
- Phase change - condensation/evaporation in the electrode pores
- Charge transfer reaction kinetics on the active sites in the electrodes

# Engineering a unit PEM cell (reactor) model



with the channels and

the current collector

electrolyte and

through solid

on/evaporation

kinetics on the

active sites in the electrodes

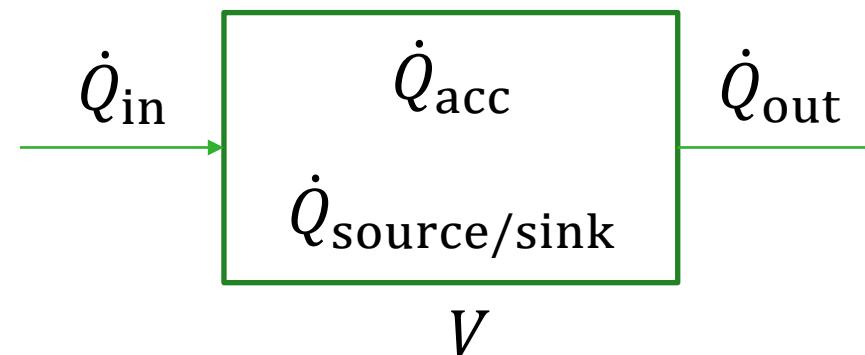
# Content

---

- Multi-scale modelling: Why? and How?
- **The continuum approach**
  - Continuity equation
  - Transport phenomena
  - Source/sink terms
- Engineering descriptions of reaction kinetics
- Common types of chemical reactors
- Binary diffusion: A common pitfall in reaction engineering
- Brief Introduction to Systems Modelling

# The Continuum Approach – Bedrock of engineering models

Law of conservation of a continuous quantity  $Q$  across a volume  $V$ :



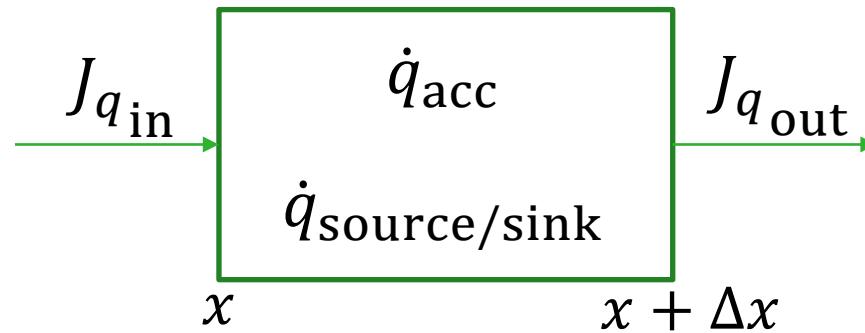
$$\dot{Q}_{\text{acc}} = \dot{Q}_{\text{in}} - \dot{Q}_{\text{out}} + \dot{Q}_{\text{source/sink}}$$

Or in terms of the volumetric quantity  $q$  ( $=Q/V$ ) and flux  $J_q$  ( $= \dot{Q}/A$ )

$$\dot{q}_{\text{acc}} = \frac{J_{q,\text{in}}A}{V} - \frac{J_{q,\text{out}}A}{V} + \dot{q}_{\text{source/sink}}$$

# Continuity Equation

Now for 1-dimensional transport along  $x$  across the control volume  $dV$



$$\frac{\partial q}{\partial t} = \frac{J_{q\text{ in}}|_x - J_{q\text{ out}}|_{x+\Delta x}}{\Delta x} + \dot{q}_{\text{source/sink}}$$

or,

$$\frac{\partial q}{\partial t} = -\frac{\partial J_q}{\partial x} + \dot{q}_{\text{source/sink}}$$

Continuity equation

# Continuity Equation

$$\frac{\partial q}{\partial t} = - \frac{\partial J_q}{\partial x} + \dot{q}_{source/sink}$$

e.g. due to (electro-)chemical reactions, phase change, etc.

Transport of  $q$

Conservation equation

$q$

Mass Conservation

Density ( $\rho$ )

Momentum Conservation

Volumetric mass flow ( $\rho u$ )

flow velocity

Energy Conservation

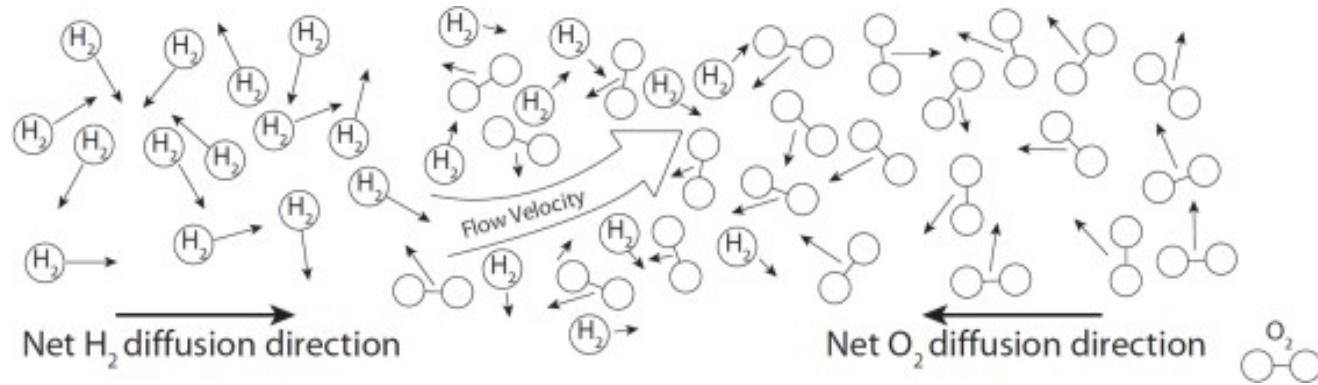
Volumetric energy density ( $\rho C_p T$ )

Charge Conservation

Charge ( $zFc$ )

concentration

# Transport phenomena



- Two primary types of transport

- Advective

Movement of a quantity due to being carried along with the flow of the bulk

$$J_{q,adv} = uq$$

- Diffusive

Movement of a quantity due to local driving forces acting directly on particles

# Diffusive Transport

---

- Basic linear law of diffusive transport of quantity q:

*Flux of q  $\propto$  -gradient of driving force of the flux*

$$J_q = -K(q)\nabla(\text{DrivingForce})$$

Material property (often obtained experimentally but perhaps can also be evaluated from microscopic simulations, e.g. DFT/MD)

K	DrivingForce
Mass	Mobility*density
Charge	Mobility*charge
Heat	Thermal Conductivity
Momentum	Dynamic Viscosity

# Diffusive Transport

---

- Mass

$$J_{c,diff} = -Mc\nabla\mu$$

Since,  $\mu = \mu^0 + RT\ln(c)$  and  $M = \frac{D}{RT}$

$$J_{c,diff} = -D\nabla c \quad \text{Fick's law}$$

- Charge

$$J_{zFc,diff} = -MzFc\nabla\tilde{\mu}$$

Since,  $\tilde{\mu} = \mu^0 + RT\ln(c) + zF\phi$ ,  $M = \frac{D}{RT}$  and  $\sigma = \frac{z^2 F^2}{RT} Dc$

$$J_{zFc,diff} = -zFD\nabla c - \sigma\nabla\phi \quad \text{Nernst-Planck Equation}$$

If  $\nabla c$  is negligible,  
UNIVERSITY OF TWENTE.

$$J_{zFc,diff} = -\sigma\nabla\phi \quad \text{Ohm's Law}$$

# Diffusive Transport

- Heat

$$J_{\rho C_p T, diff} = -k \nabla T$$

Fourier's law of heat conduction

- Momentum

$$J_{\rho u, diff} = \frac{\partial p}{\partial x} - \tau$$

Driving force for advection

$$\tau = \mu_{visc} \frac{\partial u_x}{\partial y}$$

Newton's Law of viscosity for incompressible flow

shear stress due to fluid friction (diffusive)

- Thus, total transport flux of 'q',

$$J_q = u q + J_{q, diff}$$

# Source/Sink Terms

---

- Mass and Charge
  - Due to (electro-)chemical reactions
- Heat
  - Due to (electro-)chemical reactions
  - Due to heat exchange with another body, e.g. by convection or radiation
- Momentum
  - Due to body forces, e.g. gravity, electrostatic field, wall friction, porous media effects (pore permeability and inertia)

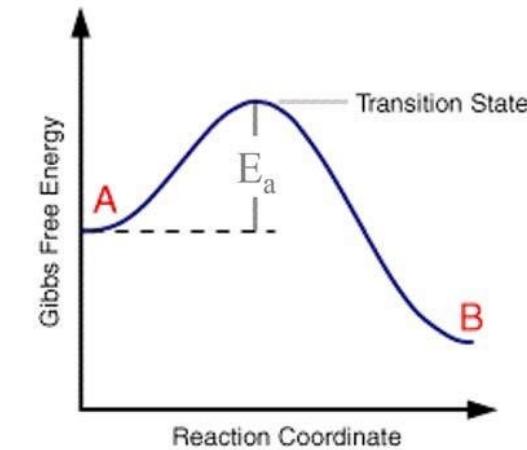
# Content

---

- Multi-scale modelling: Why? and How?
- The continuum approach
- **Engineering descriptions of reaction kinetics**
  - Global kinetics
  - Rate limiting step and quasi-equilibrium assumption
  - Elementary kinetics
- Common types of chemical reactors
- Binary diffusion: A common pitfall in reaction engineering
- Brief Introduction to Systems Modelling

# Reaction Kinetics

For a chemical reaction,  $mA \rightleftharpoons nB$



Following non-equilibrium thermodynamics,

$$r = k_f^0 \exp\left(-\frac{(\mu_{TS} - \mu_{reactants})}{RT}\right) - k_b^0 \exp\left(-\frac{(\mu_{TS} - \mu_{products})}{RT}\right)$$

$$\mu_{reactants} = m\mu_A^0 + mRT\ln(c_A)$$

$$\mu_{TS} = \mu_{TS}^0 + RT\ln(c_{TS})$$

$$\mu_{products} = n\mu_B^0 + nRT\ln(c_B)$$

# Reaction Kinetics

---

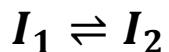
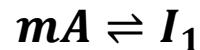
if  $c_{TS} \approx 0$  and since,  $E^{\text{act}} = \Delta G_k^0 = \mu_{TS}^0 - \mu_{k=A,B}^0$

$$r = k_f^0 \exp\left(-\frac{E_f^{\text{act}}}{RT}\right) c_A^m - k_b^0 \exp\left(-\frac{E_b^{\text{act}}}{RT}\right) c_B^n$$

$m, n \equiv \text{reaction orders}$

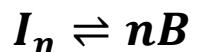
Technically, this derivation is only valid if  $\mathbf{mA} \rightleftharpoons \mathbf{nB}$  is an elementary reaction

In reality, the reaction  $\mathbf{mA} \rightleftharpoons \mathbf{nB}$  likely proceeds via a number of elementary steps,



⋮

$I \equiv \text{intermediate}$



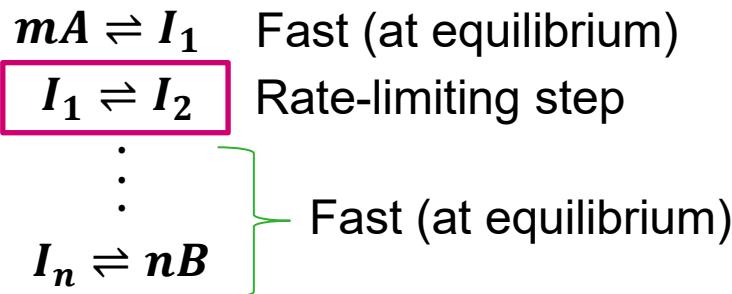
# Reaction Kinetics

---

A common engineering approach to deal with this complexity is to simply fit the reaction orders (and sometimes activation barriers) to match experimental data and is called global-kinetic modelling. Thus,

$$r = k_f^0 \exp\left(-\frac{E_f^{act}}{RT}\right) c_A^{m'} - k_b^0 \exp\left(-\frac{E_b^{act}}{RT}\right) c_B^{n'}$$

Another less empirical approach involves the assumption of a rate-limiting step and a quasi-equilibrium assumption for all other steps



# Reaction Kinetics

---

The least empirical approach, of course, is to consider all elementary steps, i.e. the entire mechanism without any assumptions. This is known as elementary-kinetic or micro-kinetic reaction modelling.

Depending on the reaction, mechanisms could involve anywhere between tens to hundreds to thousands of elementary steps!

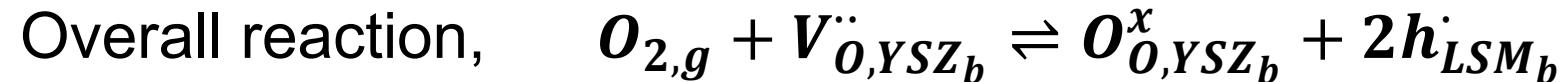
Apart from the added computational expense of simulating all of these steps, the challenge is also the correct estimation of the forward and backward rate constants for each elementary step whilst ensuring thermodynamic consistency, i.e.

At equilibrium,

$$\frac{k_f^0 \exp\left(-\frac{E_f^{act}}{RT}\right)}{k_b^0 \exp\left(-\frac{E_b^{act}}{RT}\right)} = \exp\left(-\frac{\Delta G_{reac}^0}{RT}\right)$$

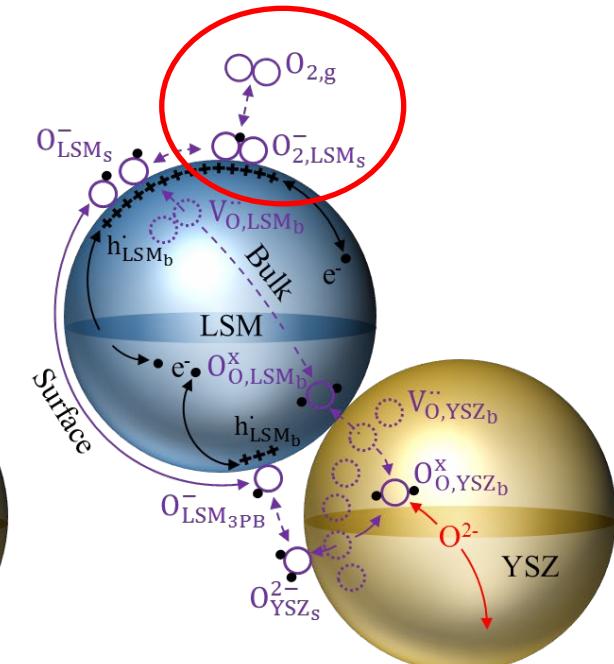
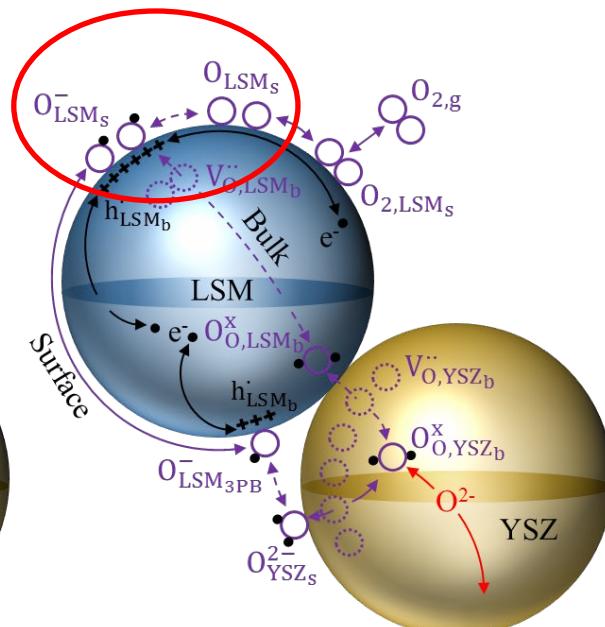
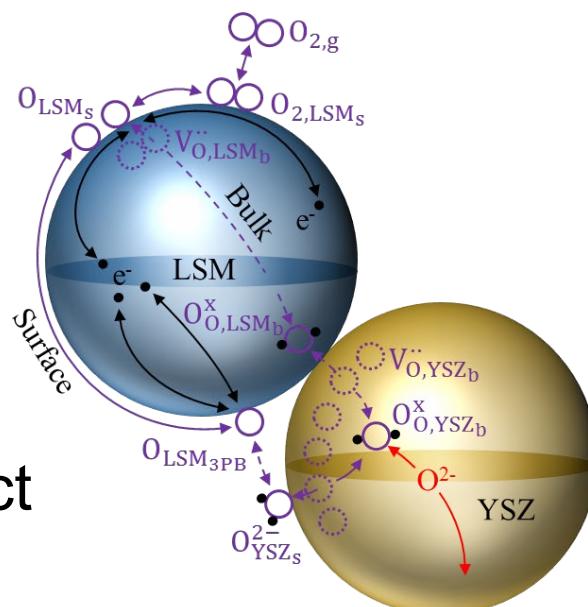
# Elementary-kinetic Reaction Modelling

An example: Electrochemical reduction of  $O_2$  on Lanthanum Strontium Manganite (LSM) and Yttria-Stabilised Zirconia (YSZ) composite electrodes



Proposed elementary-kinetic mechanisms

Can we use elementary-kinetic reaction modelling to help identify the correct mechanism?



↔ Surface Reaction

↔ Charge transfer Reaction

# Elementary-kinetic Reaction Modelling

## Kinetic Parameters

Mechanism 1	$k_f^0$	$E_f^{act}$ (kJ mol <sup>-1</sup> )
<b>Surface Pathway</b>		
$O_{2,g} + \square_{LSM_s} \rightleftharpoons O_{2,LSM_s}$	$1 \cdot 10^{-4a}$	0.0
$O_{2,LSM_s} + \square_{LSM_s} \rightleftharpoons 2O_{LSM_s}$	$5 \cdot 10^{22} \text{ cm}^2 \text{ mol}^{-1} \text{ s}^{-1}$	154.4
$O_{LSM_s} \rightleftharpoons O_{LSM_{3PB}}$	$9.5 \cdot 10^{10} \text{ s}^{-1}$	144.7
$O_{LSM_{3PB}} + \square_{YSZ_s} \rightleftharpoons O_{YSZ_s}^{2-} + \square_{LSM_s} + 2h_{LSM_b}^{\cdot}$	$7.5 \cdot 10^{18} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	154.4
$O_{YSZ_s}^{2-} + V_{O,YSZ_b}^{\cdot\cdot} \rightleftharpoons O_{O,YSZ_b}^x + \square_{YSZ_s}$	$1.8 \cdot 10^{13} \text{ s}^{-1}$	90.9
<b>Bulk Pathway</b>		
$O_{LSM_s} + V_{O,LSM_b}^{\cdot\cdot} \rightleftharpoons O_{O,LSM_b}^x + \square_{LSM_s}$	At Equilibrium	
$O_{O,LSM_b}^x \rightleftharpoons O_{O,LSM_{2PB}}^x$	$4.9 \cdot 10^7 \text{ s}^{-1}$	270.3
$O_{O,LSM_{2PB}}^x + V_{O,YSZ_b}^{\cdot\cdot} \rightleftharpoons O_{O,YSZ_b}^x + V_{O,LSM_{2PB}}^{\cdot\cdot}$	At Equilibrium	

<sup>a</sup> Sticking Coefficient

Fit Parameters

# Elementary-kinetic Reaction Modelling

## Kinetic Parameters

Mechanism 2	$k_f^0$	$E_f^{act}$ (kJ mol <sup>-1</sup> )
<b>Surface Pathway</b>		
$O_{2,g} + \square_{LSM_s} \rightleftharpoons O_{2,LSM_s}$	$1 \cdot 10^{-4a}$	0.0
$O_{2,LSM_s} + \square_{LSM_s} \rightleftharpoons 2O_{LSM_s}$	$1.9 \cdot 10^{21} \text{ cm}^2 \text{ mol}^{-1} \text{ s}^{-1}$	22.2
$O_{LSM_s} \rightleftharpoons O_{LSM_s}^- + h_{LSM_b}^i$	$5 \cdot 10^{13} \text{ cm}^2 \text{ mol}^{-1} \text{ s}^{-1}$	154.4
$O_{LSM_s}^- \rightleftharpoons O_{LSM_{3PB}}^-$	$9.5 \cdot 10^{10} \text{ s}^{-1}$	144.7
$O_{LSM_{3PB}}^- + \square_{YSZ_s} \rightleftharpoons O_{YSZ_s}^{2-} + \square_{LSM_s} + h_{LSM_b}^i$	$4.5 \cdot 10^{17} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	154.4
$O_{YSZ_s}^{2-} + V_{O,YSZ_b}^{\cdot\cdot} \rightleftharpoons O_{O,YSZ_b}^x + \square_{YSZ_s}$	$1.8 \cdot 10^{13} \text{ s}^{-1}$	90.9
<b>Bulk Pathway</b>		
$O_{LSM_s}^- + V_{O,LSM_b}^{\cdot\cdot} \rightleftharpoons O_{O,LSM_b}^x + \square_{LSM_s} + h_{LSM_b}^i$	At Equilibrium	
$O_{O,LSM_b}^x \rightleftharpoons O_{O,LSM_{2PB}}^x$	$4.9 \cdot 10^7 \text{ s}^{-1}$	270.3
$O_{O,LSM_{2PB}}^x + V_{O,YSZ_b}^{\cdot\cdot} \rightleftharpoons O_{O,YSZ_b}^x + V_{O,LSM_{2PB}}^{\cdot\cdot}$	At Equilibrium	

<sup>a</sup> Sticking Coefficient

Fit Parameters

# Elementary-kinetic Reaction Modelling

## Kinetic Parameters

Mechanism 3	$k_f^0$	$E_f^{act}$ (kJ mol <sup>-1</sup> )
<b>Surface Pathway</b>		
$O_{2,g} + \square_{LSM_s} \rightleftharpoons O_{2,LSM_s}^- + h_{LSM_b}^.$	$1 \cdot 10^{-4a}$	0
$O_{2,LSM_s}^- + \square_{LSM_s} \rightleftharpoons 2O_{LSM_s}^- + h_{LSM_b}^.$	$2.6 \cdot 10^{26} \text{ cm}^2 \text{ mol}^{-1} \text{ s}^{-1}$	190
$O_{LSM_s}^- \rightleftharpoons O_{LSM_{3PB}}^-$	$9.5 \cdot 10^{10} \text{ s}^{-1}$	144.7
$O_{LSM_{3PB}}^- + \square_{YSZ_s} \rightleftharpoons O_{YSZ_s}^{2-} + \square_{LSM_s} + h_{LSM_b}^.$	$7.5 \cdot 10^{17} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	144.7
$O_{YSZ_s}^{2-} + V_{O,YSZ_b}^{\cdot\cdot} \rightleftharpoons O_{O,YSZ_b}^x + \square_{YSZ_s}$	$1.8 \cdot 10^{13} \text{ s}^{-1}$	90.9
<b>Bulk Pathway</b>		
$O_{LSM_s}^- + V_{O,LSM_b}^{\cdot\cdot} \rightleftharpoons O_{O,LSM_b}^x + \square_{LSM_s} + h_{LSM_b}^.$	At Equilibrium	
$O_{O,LSM_b}^x \rightleftharpoons O_{O,LSM_{2PB}}^x$	$4.9 \cdot 10^7 \text{ s}^{-1}$	270.3
$O_{O,LSM_{2PB}}^x + V_{O,YSZ_b}^{\cdot\cdot} \rightleftharpoons O_{O,YSZ_b}^x + V_{O,LSM_{2PB}}^{\cdot\cdot}$	At Equilibrium	

<sup>a</sup> Sticking Coefficient

# Elementary-kinetic Reaction Modelling

**Thermodynamic Parameters  
to ensure thermodynamic  
consistency**

Fit  
Parameters

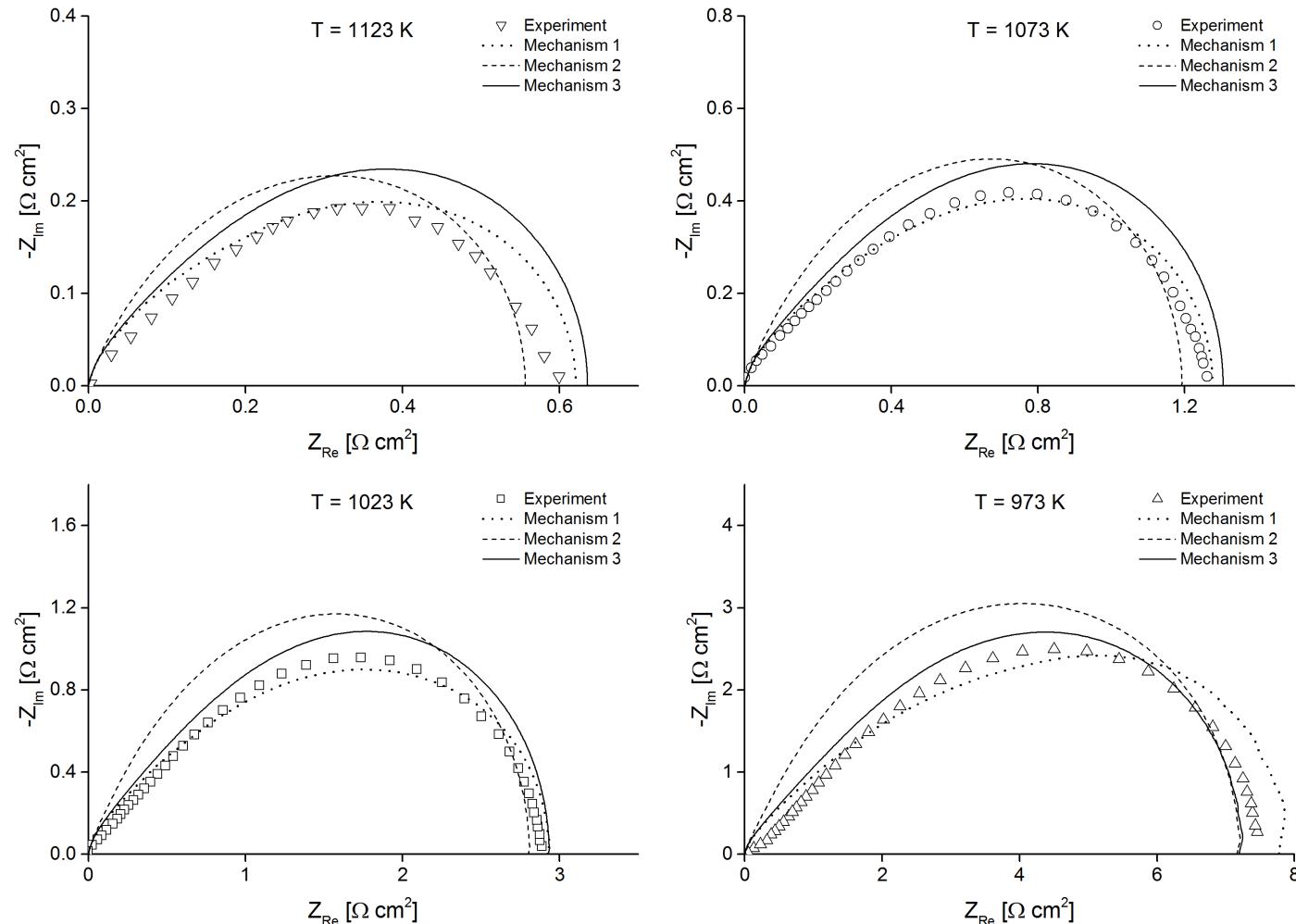
Species, $k$	$h_k$ (kJ mol $^{-1}$ )			$s_k$ (J K $^{-1}$ mol $^{-1}$ )		
	Mech 1	Mech 2	Mech 3	Mech 1	Mech 2	Mech 3
<b>Gas phase</b>						
$O_2$		25			246	
<b>LSM phase</b>						
$\square_{LSM_s}$		0			0	
$O_{2,LSM_s}$		-74.38			182.45	
$O_{2,LSM_s}^-$		-		-74.38	-	182.45
$O_{LSM_s}$		-40			91.22	
$O_{LSM_s}^-$		-165		-93.65	-	91.22
$O_{LSM_{3PB}}^-$		-165		-93.65	-	91.22
<b>LSM bulk</b>						
$V_{O,LSM_b}$		0			0	
$O_{O,LSM_b}^x$		-148.24			91.22	
<b>YSZ surface</b>						
$\square_{YSZ_s}$		0			0	
$O_{YSZ_s}^{2-}$		-236			91.22	
<b>YSZ bulk</b>						
$V_{O,YSZ_b}^{..}$		0			0	
$O_{O,YSZ_b}^x$		-236			91.22	

# Elementary-kinetic Reaction Modelling

## Model Calibration

All three mechanisms fit the data well. Does that mean all three mechanisms are valid?

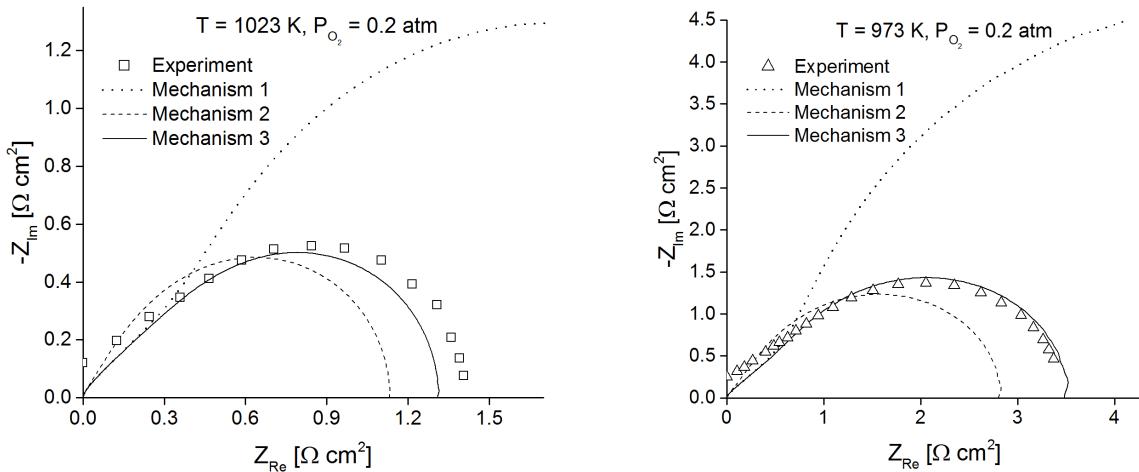
Comparison of Mechanisms against data from Barbucci et al.



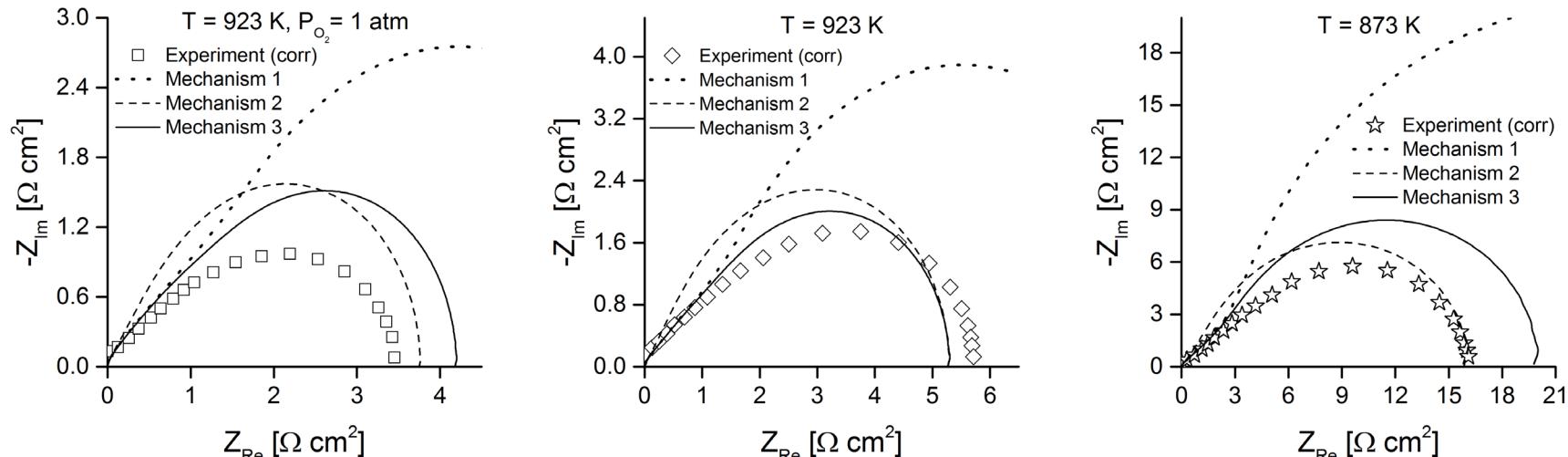
# Elementary-kinetic Reaction Modelling

Comparison of Mechanisms against data from Cronin et al.

## Model Testing



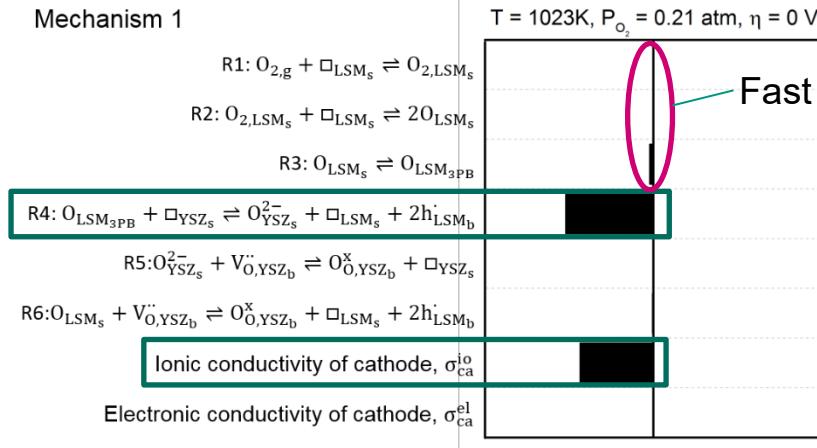
Comparison of Mechanisms against data from Nielsen et al.



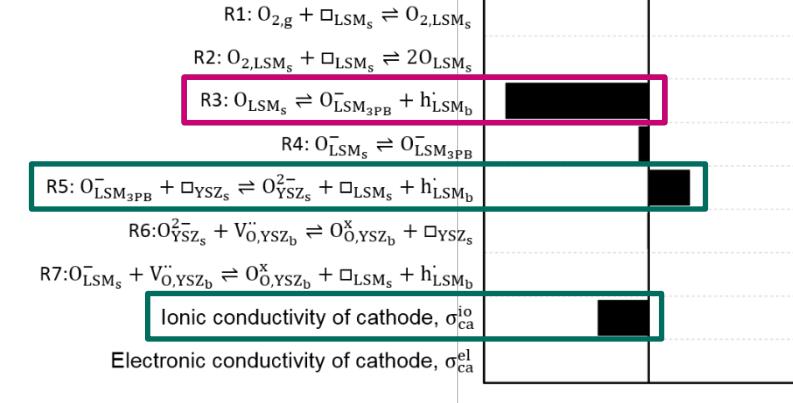
# Elementary-kinetic Reaction Modelling

## Sensitivity Analysis

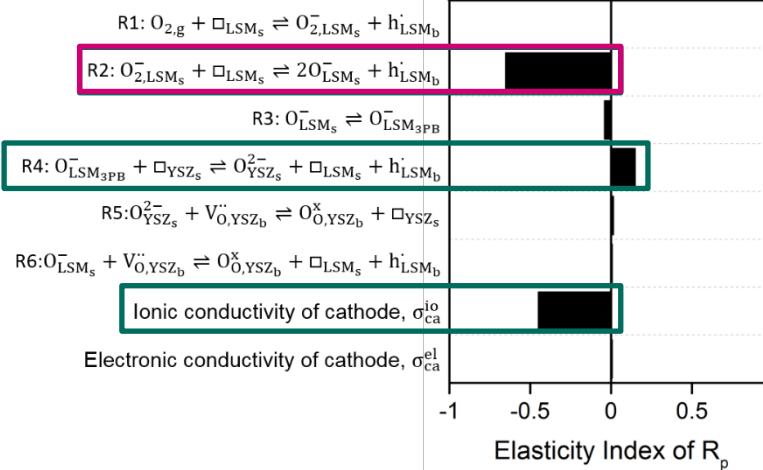
Mechanism 1



Mechanism 2



Mechanism 3



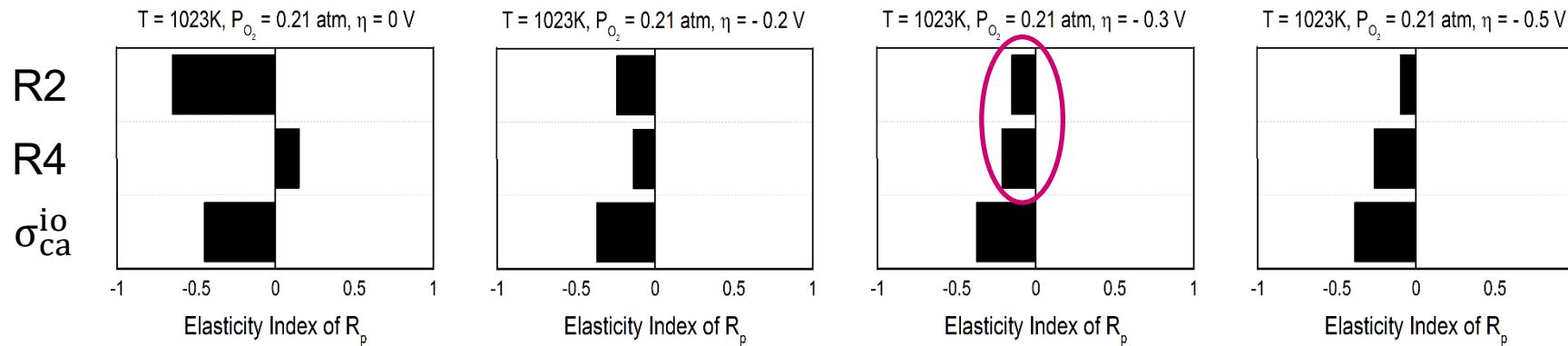
With this knowledge,  
what would you tell an  
experiment to look for in  
order to decide between  
mechanisms 2 and 3?

Taken from: A. Banerjee, O. Deutschmann, *J Catalysis*, **346**, 30–49 (2017).

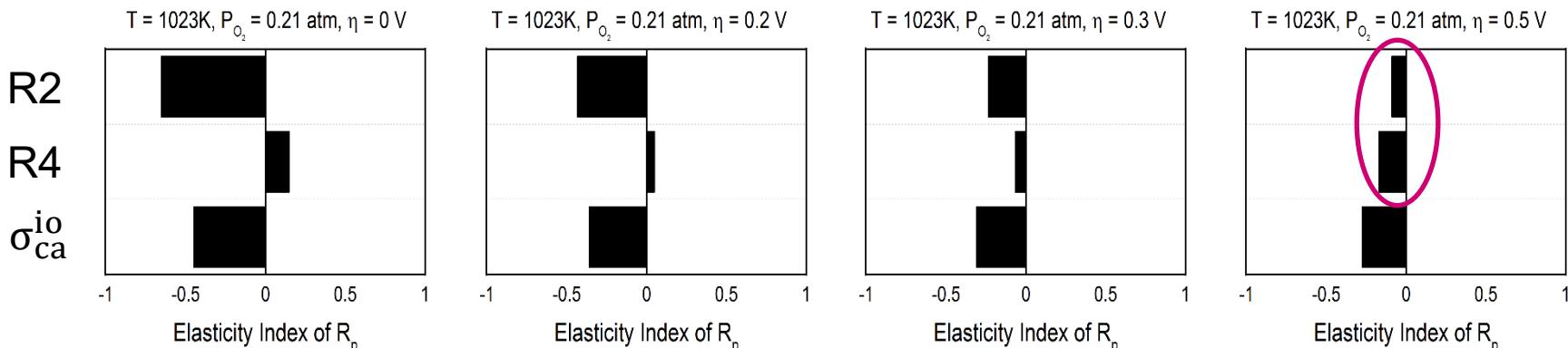
# Elementary-kinetic Reaction Modelling

## Sensitivity Analysis – Switch over of Rate Limiting Step

→ “Fuel Cell” mode



→ “Electrolyser” mode



# Link to download Python code

---

<https://github.com/aayanb90/SMvsFicks>

# Content

---

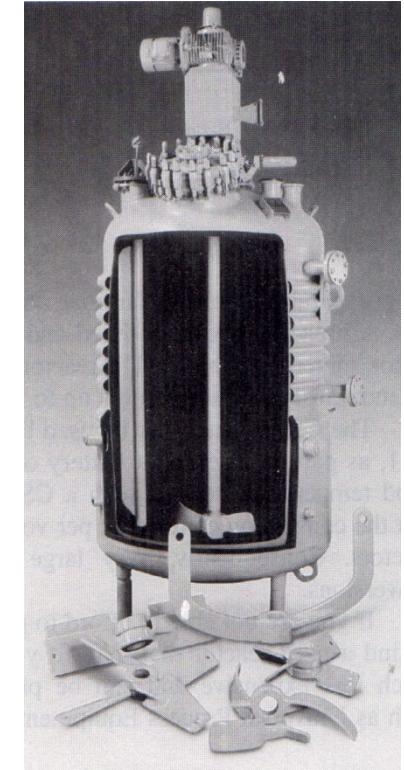
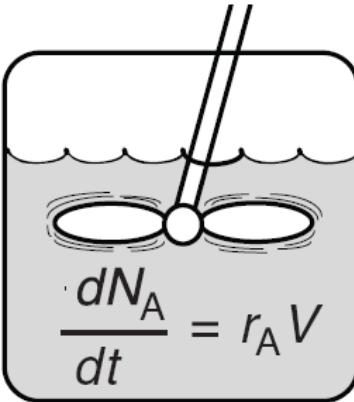
- Multi-scale modelling: Why? and How?
- The continuum approach
- Engineering descriptions of reaction kinetics
- **Common types of chemical reactors**
  - Batch
  - CSTR
  - Plug
  - Packed/Fixed Bed
    - Porous media transport
    - Transport inside the catalyst pellet
- Binary diffusion: A common pitfall in reaction engineering
- Brief Introduction to Systems Modelling

# Types of Chemical Reactors

## Batch Reactor

Key features

- Closed system, i.e. no flow
- Well-mixed, i.e. no gradients



Thus applying continuity equation,

Mass:  $\frac{\partial \rho}{\partial t} = -\frac{\partial J_\rho^0}{\partial x} + \dot{r}_V$

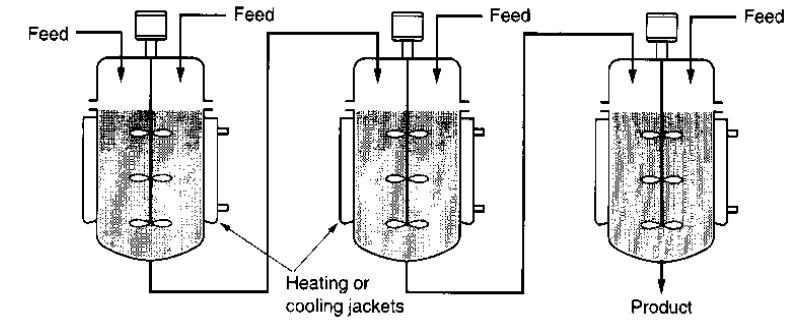
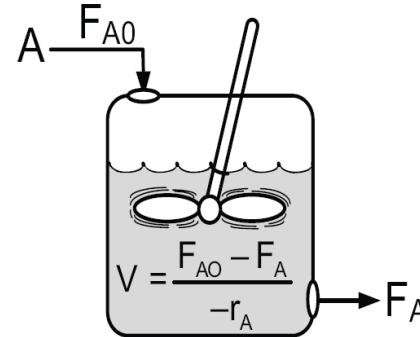
Energy:  
(adiabatic)  $\frac{\partial(\rho C_p T)}{\partial t} = -\frac{\partial J_{\rho C_p T}^0}{\partial x} + \dot{q}_V(\dot{r}_V)$

# Types of Chemical Reactors

## Continuously Stirred Tank Reactor (CSTR)

Key features

- Open system
- Well-mixed, i.e. no gradients



Thus applying continuity equation,

Mass:

$$\frac{\partial \rho_A}{\partial t} = \frac{F_{A,in} - F_{A,out}}{V} + -\frac{\partial J_\rho}{\partial x}^0 + \dot{r}_V$$

$F \equiv$  mass flow rate

$V \equiv$  reactor volume

Energy:  
(adiabatic)

$$\frac{\partial (\rho C_p T)}{\partial t} = \frac{\dot{H}_{A,in} - \dot{H}_{A,out}}{V} - \frac{\partial J_{\rho C_p T}}{\partial x}^0 + \dot{q}_V (\dot{r}_V)$$

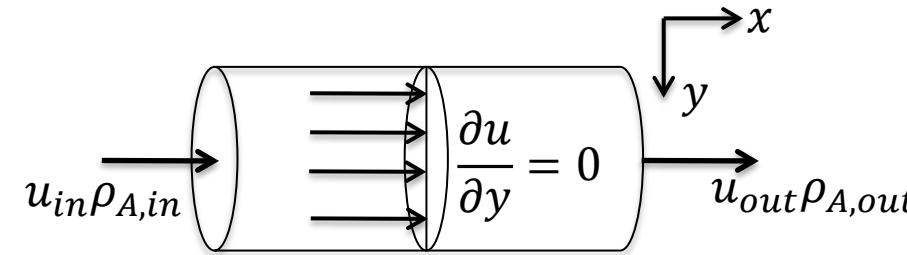
$\dot{H} \equiv$  enthalpy rate

# Types of Chemical Reactors

## Plug Flow Reactor (PFR)

Key features

- Open system
- Only axial gradients (i.e. in direction of flow)



Thus applying continuity equation,

$$\text{Mass: } \frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial x} \left( u\rho - D \frac{\partial \rho}{\partial x} \right) + \dot{r}_V$$

$$\text{Energy: (adiabatic)} \quad \frac{\partial(\rho C_p T)}{\partial t} = -\frac{\partial}{\partial x} \left( u(\rho C_p T) - k \frac{\partial T}{\partial x} \right) + \dot{q}_V (\dot{r}_V)$$

$$\text{Momentum: } \frac{\partial(\rho u)}{\partial t} = -\frac{\partial}{\partial x} \left( u(\rho u) + \frac{\partial p}{\partial x} - \mu_{visc} \frac{\partial u}{\partial y} \right)$$



Polyethylene reactor; this 16-in inner-diameter reactor is designed to operate at 35,000 psi and 600°F; in operation, this reactor is in a vertical configuration. Courtesy of Autoclave Engineers, Division of Snap-tite, Inc.

# Types of Chemical Reactors

## Packed-bed/Fixed-bed Reactor

Key features

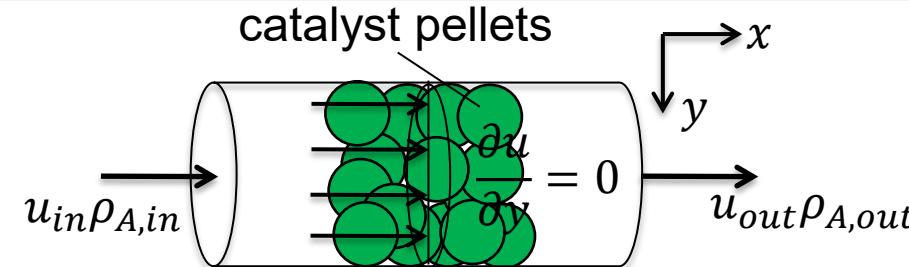
- Open system
- Plug flow assumption: Only axial gradients (i.e. in direction of flow)

Thus applying continuity equation, it is clear the plug flow equations would hold (at least outside the bed),

$$\text{Mass: } \frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial x} \left( u\rho - D \frac{\partial \rho}{\partial x} \right) + \dot{r}_V$$

$$\text{Energy: } \frac{\partial(\rho C_p T)}{\partial t} = -\frac{\partial}{\partial x} \left( u(\rho C_p T) - k \frac{\partial T}{\partial x} \right) + \dot{q}_V (\dot{r}_V)$$

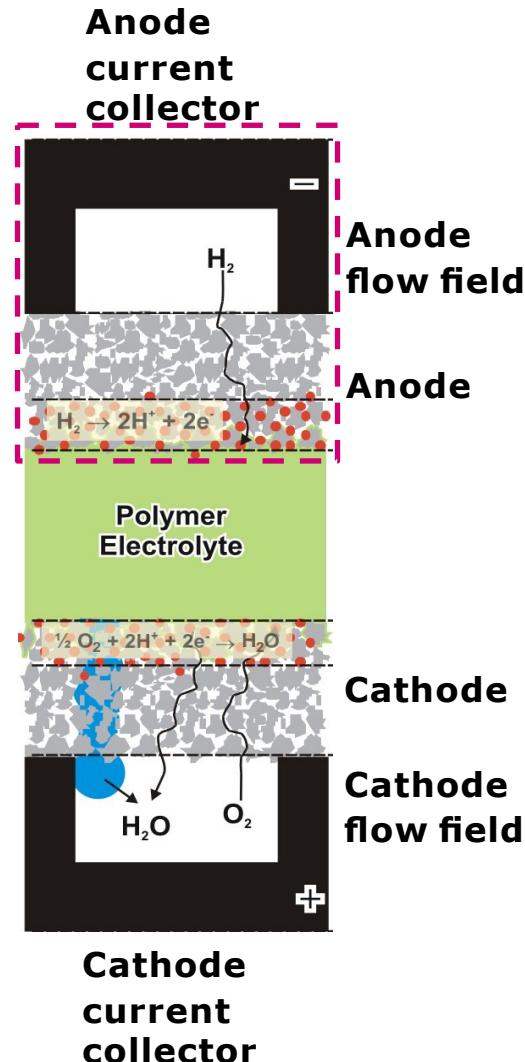
$$\text{Momentum: } \frac{\partial(\rho u)}{\partial t} = -\frac{\partial}{\partial x} \left( u(\rho u) + \frac{\partial p}{\partial x} - \mu_{visc} \frac{\partial u}{\partial y} \right)$$



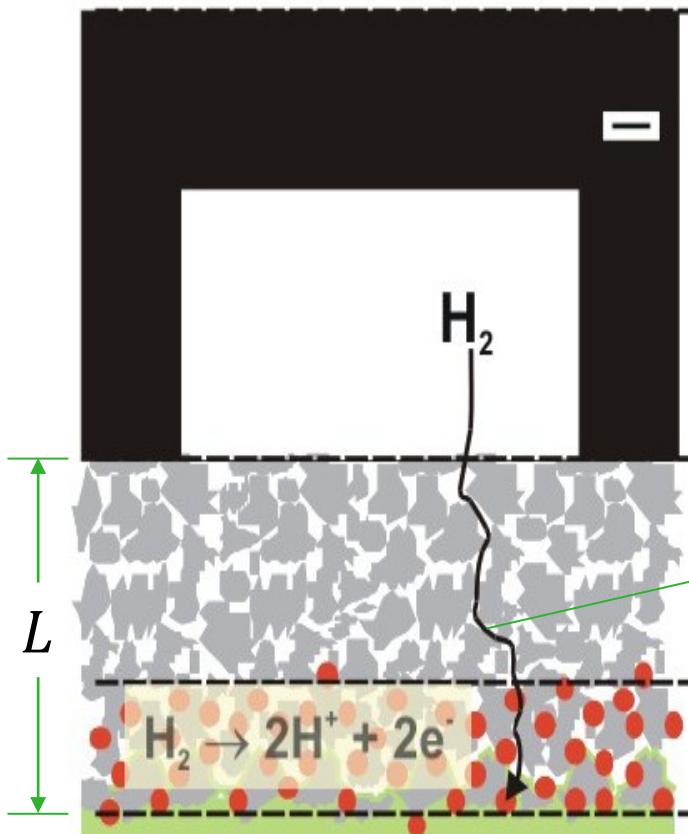
But how do we deal with transport inside the porous packed bed?

# Porous Media Transport

PEM Cell - Twin fixed-bed reactors separated by a membrane



# Porous Media Transport



Superficial velocity  $\left( = u_{pore} \frac{\epsilon}{\tau_{pore}} \right)$

- Obtained by modifying the momentum continuity (Navier-Stokes) equation to include additional linear (Darcy) and non-linear (Forchheimer) source terms to account for pore-scale effects
- UNIVERSITY OF TWENTE.

$$\frac{\partial(eq)}{\partial t} = -\frac{\partial J_q^{eff}}{\partial x} + \dot{q}_{source/sink}$$

$= \epsilon$  for conservation of  $q$  in pore phase and  $1 - \epsilon$  for solid phase

$$\text{Porosity, } \epsilon = \frac{V_{pore}}{V_{total}}$$

A longer, more “tortuous” path needs to be taken by  $H_2$  through the pores due to the random distribution of solid and pore phases

$$\text{Tortuosity, } \tau = \frac{L_{tortuous}}{L}$$

$$J_q^{eff} = uq + J_{q,diff} \cdot f(e, \tau)$$

Commonly,  $f(e, \tau) = \frac{e}{\tau_{solid/pore}^2}$

$e = \epsilon, \text{ pore}$   
 $1 - \epsilon, \text{ solid}$

However, many more complex and empirical correlations exist for  $f(e, \tau)$

# Types of Chemical Reactors

## Packed-bed/Fixed-bed Reactor

Key features

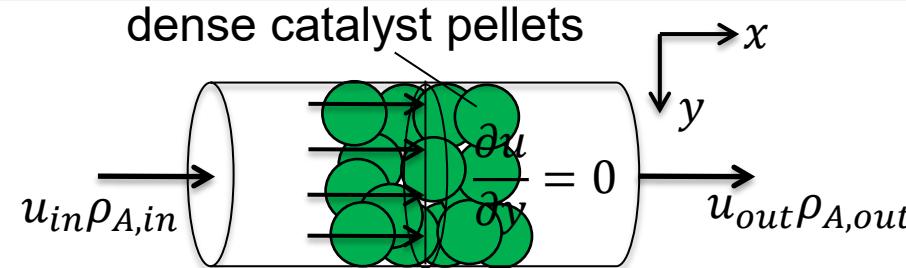
- Open system
- Plug flow assumption: Only axial gradients (i.e. in direction of flow)

Now applying porous media transport theory inside the bed and assuming dense catalyst pellets, for the fluid phase we get,

Mass:  $\frac{\partial(\epsilon\rho)}{\partial t} = -\frac{\partial}{\partial x}\left(u\rho - D \cdot f(e, \tau) \frac{\partial\rho}{\partial x}\right) + \dot{r}_V$  But what happens if the pellets are also porous?

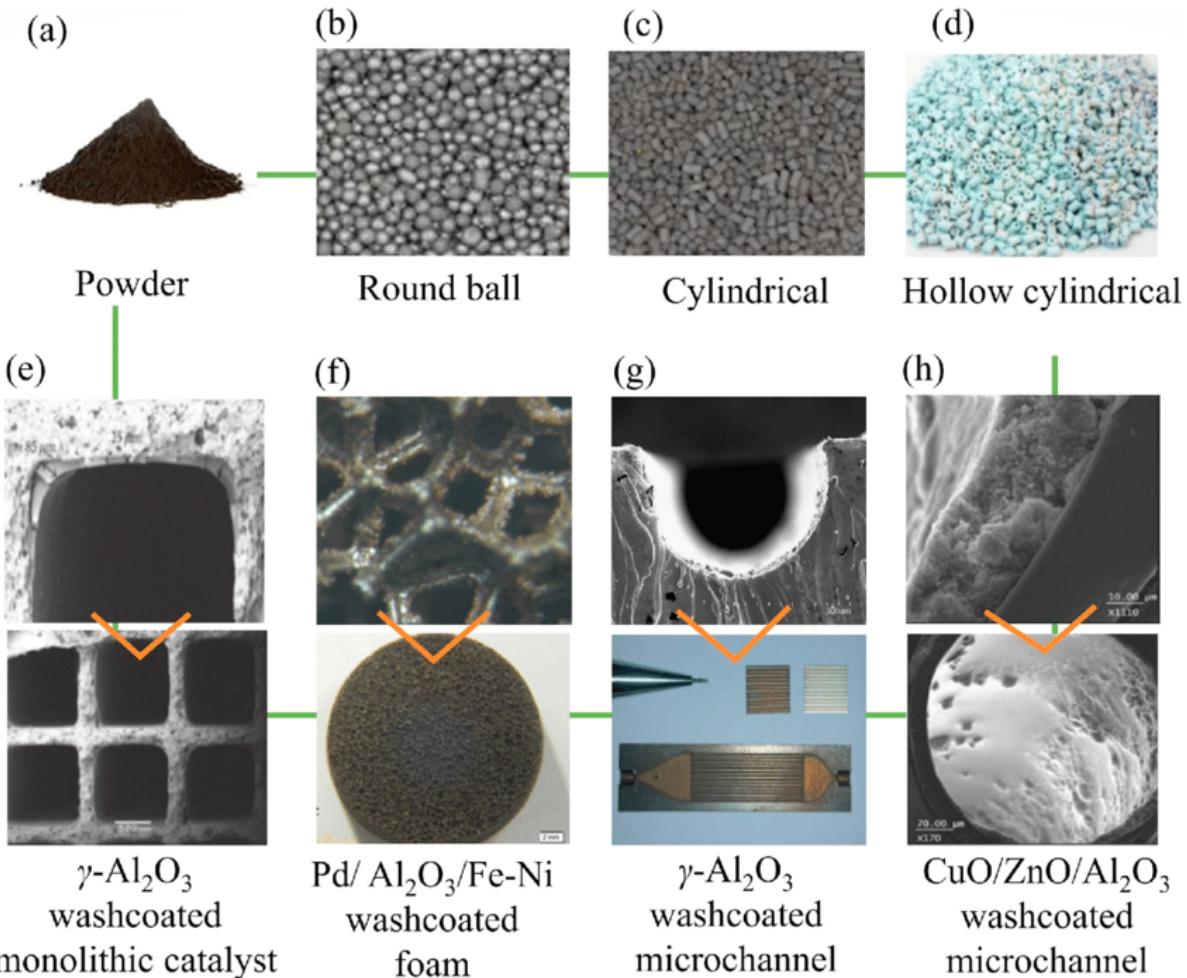
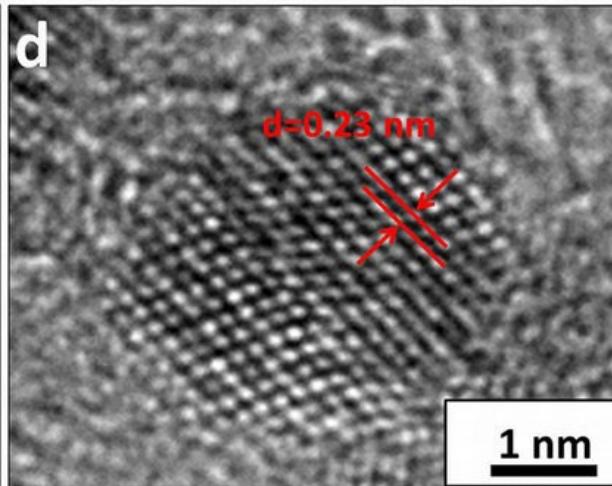
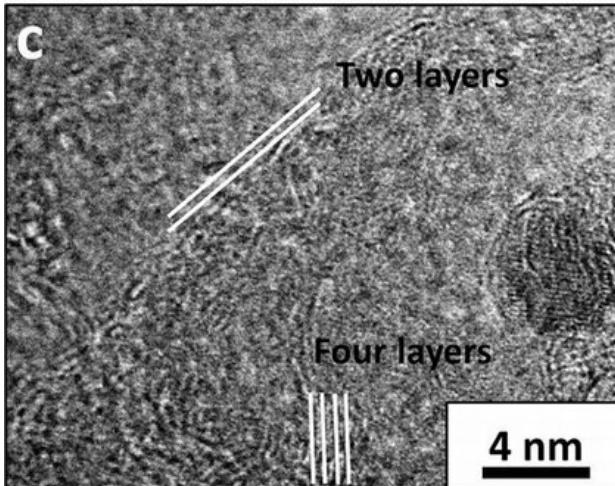
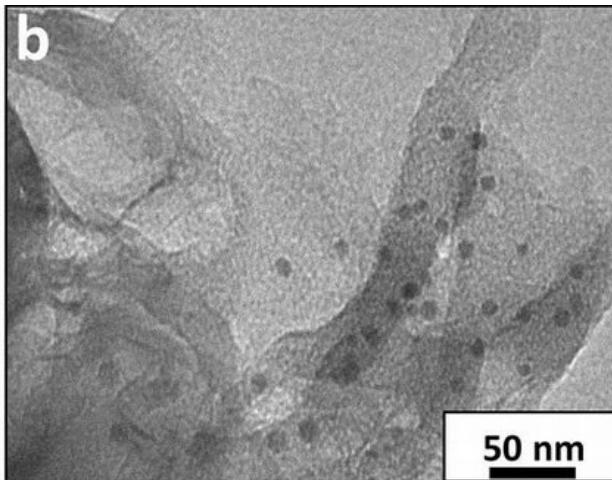
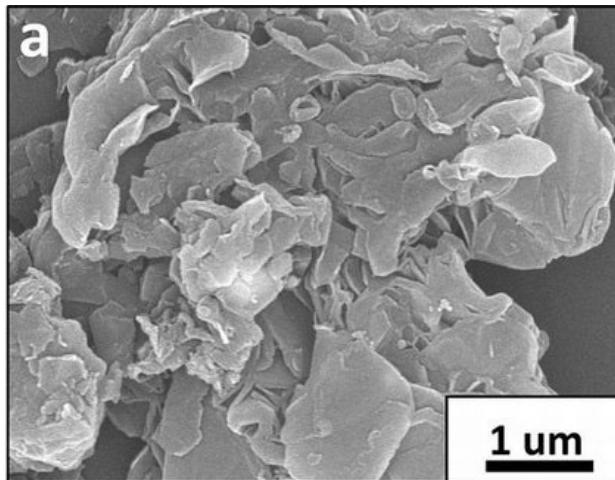
Energy:  $\frac{\partial(\epsilon\rho C_p T)}{\partial t} = -\frac{\partial}{\partial x}\left(u(\rho C_p T) - k \cdot f(e, \tau) \frac{\partial T}{\partial x}\right) + \dot{q}_V(\dot{r}_V)$

Momentum:  $\frac{1}{\epsilon} \frac{\partial(\rho u)}{\partial t} = -\frac{\partial}{\partial x}\left(\frac{1}{\epsilon^2} u(\rho u) + \frac{\partial p}{\partial x}\right) + \dot{s}_V$  where,  $\dot{s}_V = -\frac{\mu_{visc}}{\kappa_p} u - \frac{\rho}{\kappa_i} u^2$



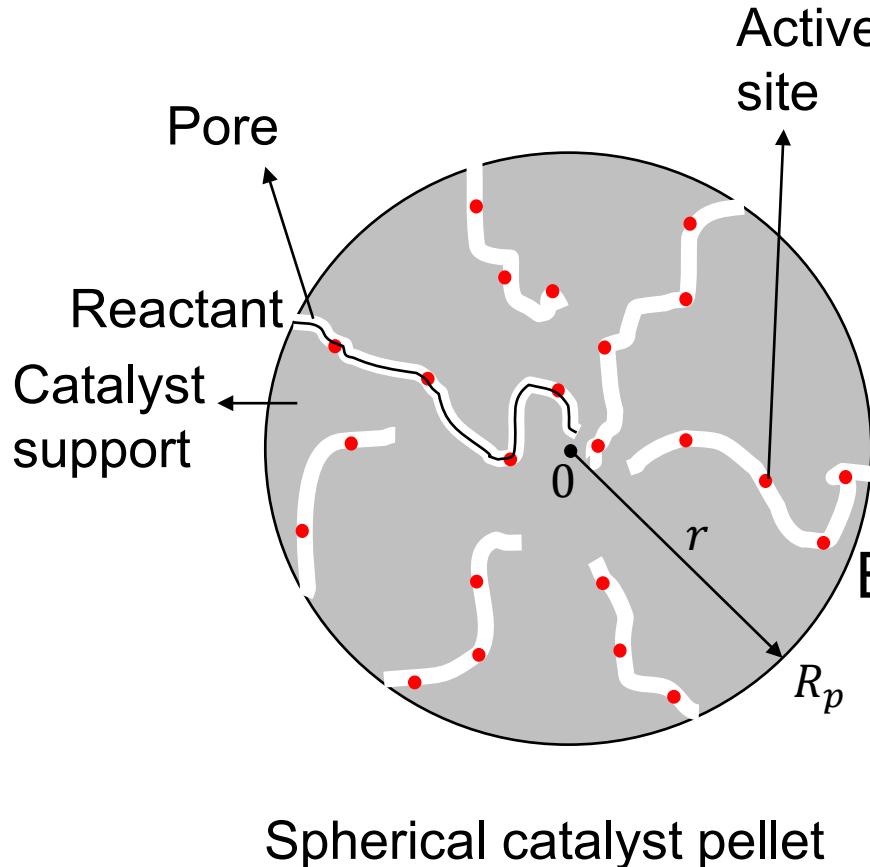
# Types of Chemical Reactors

## Packed-bed/Fixed-bed Reactor – Transport inside the catalyst pellet



# Types of Chemical Reactors

## Packed-bed/Fixed-bed Reactor – Transport inside the catalyst pellet



Mass:

$$\frac{\partial(\epsilon \rho_p)}{\partial t} = -\frac{1}{r^2} \frac{\partial}{\partial r} \left( -D \cdot f(e_p, \tau_p) r^2 \frac{\partial \rho_p}{\partial r} \right) + \dot{r}_V$$

Boundary Conditions:

Dirichlet: At  $r=R_p$ ,  $\rho_p = \rho$

Neumann: At  $r=0$ ,  $\frac{\partial \rho_p}{\partial r} = 0$  (symmetry)

Energy:

$$\frac{\partial(\epsilon \rho_p C_P T_p)}{\partial t} = -\frac{1}{r^2} \frac{\partial}{\partial r} \left( -k \cdot f(e_p, \tau_p) r^2 \frac{\partial T_p}{\partial r} \right) + \dot{q}_V (\dot{r}_V)$$

Boundary Conditions:

Dirichlet: At  $r=R_p$ ,  $T_p = T$

Neumann: At  $r=0$ ,  $\frac{\partial T_p}{\partial r} = 0$  (symmetry)

# Types of Chemical Reactors

## Packed-bed/Fixed-bed Reactor

Key features

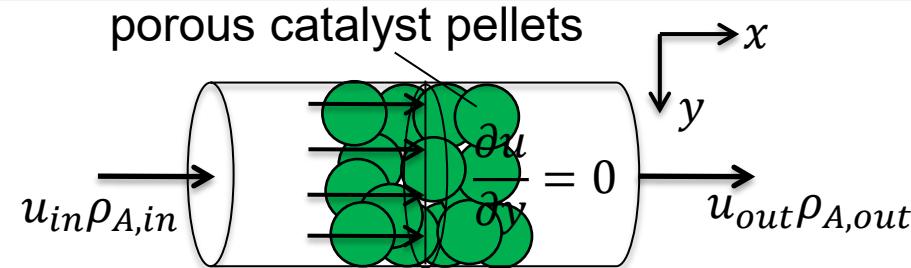
- Open system
- Plug flow assumption: Only axial gradients (i.e. in direction of flow)

For the fluid phase,

Mass:  $\frac{\partial(\epsilon\rho)}{\partial t} = -\frac{\partial}{\partial x}\left(u\rho - D \cdot f(e, \tau) \frac{\partial\rho}{\partial x}\right) + \dot{r}_V$  where,  $\dot{r}_V = J_{\rho,p}\Big|_{r=R_p} \cdot \frac{A_{p,surf,tot}}{V}$

Momentum:  $\frac{1}{\epsilon} \frac{\partial(\rho u)}{\partial t} = -\frac{\partial}{\partial x}\left(\frac{1}{\epsilon^2} u(\rho u) + \frac{\partial p}{\partial x}\right) + \dot{s}_V$  where,  $\dot{s}_V = -\frac{\mu_{visc}}{\kappa_p} u - \frac{\rho}{\kappa_i} u^2$

Energy:  $\frac{\partial(\epsilon\rho C_p T)}{\partial t} = -\frac{\partial}{\partial x}\left(u(\rho C_p T) - k \cdot f(e, \tau) \frac{\partial T}{\partial x}\right) + \dot{q}_V$   
(adiabatic) where,  $\dot{q}_V = J_{\rho C_P T, p}\Big|_{r=R_p} \cdot \frac{A_{p,surf,tot}}{V}$



# Content

---

- Multi-scale modelling: Why? and How?
- The continuum approach
- Engineering descriptions of reaction kinetics
- Common types of chemical reactors
- **Binary diffusion: A common pitfall in reaction engineering**
  - Describing diffusion in a binary system (Fick's law)
  - Describing multi-species diffusion (Maxwell-Stefan model)
  - Fick's vs Maxwell-Stefan
- Brief Introduction to Systems Modelling

# Binary diffusion – a common pitfall in reaction engineering

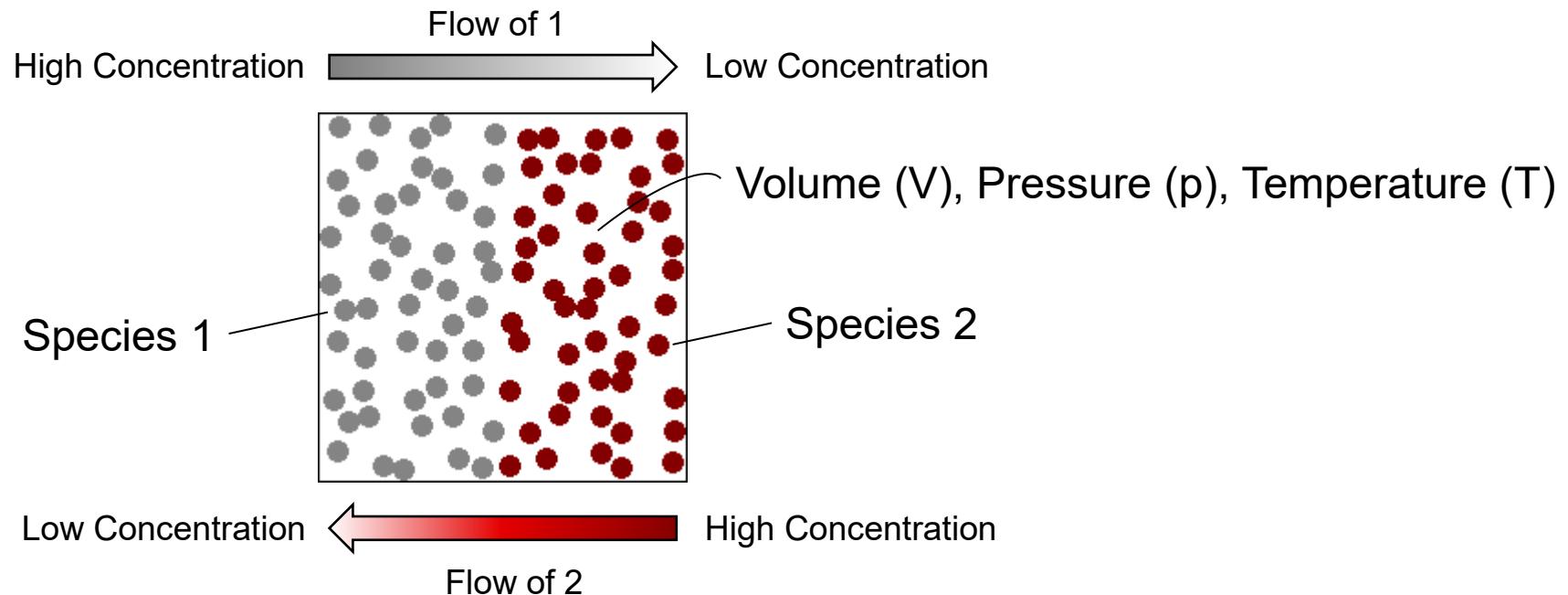
---

- Binary diffusion implies the transport of two species, e.g. 1 and 2, due to collisions/interactions with each other
- Fick's law and the Nernst-Planck equation, describing diffusion of uncharged and charged species respectively, are strictly only valid for binary systems as we will see in the coming slides
- So then what happens for a simple (and very common) reaction system  
 $mA + nB \rightleftharpoons yC$ ?

Is binary diffusion still valid? Let's investigate!

# Describing diffusion in a binary system

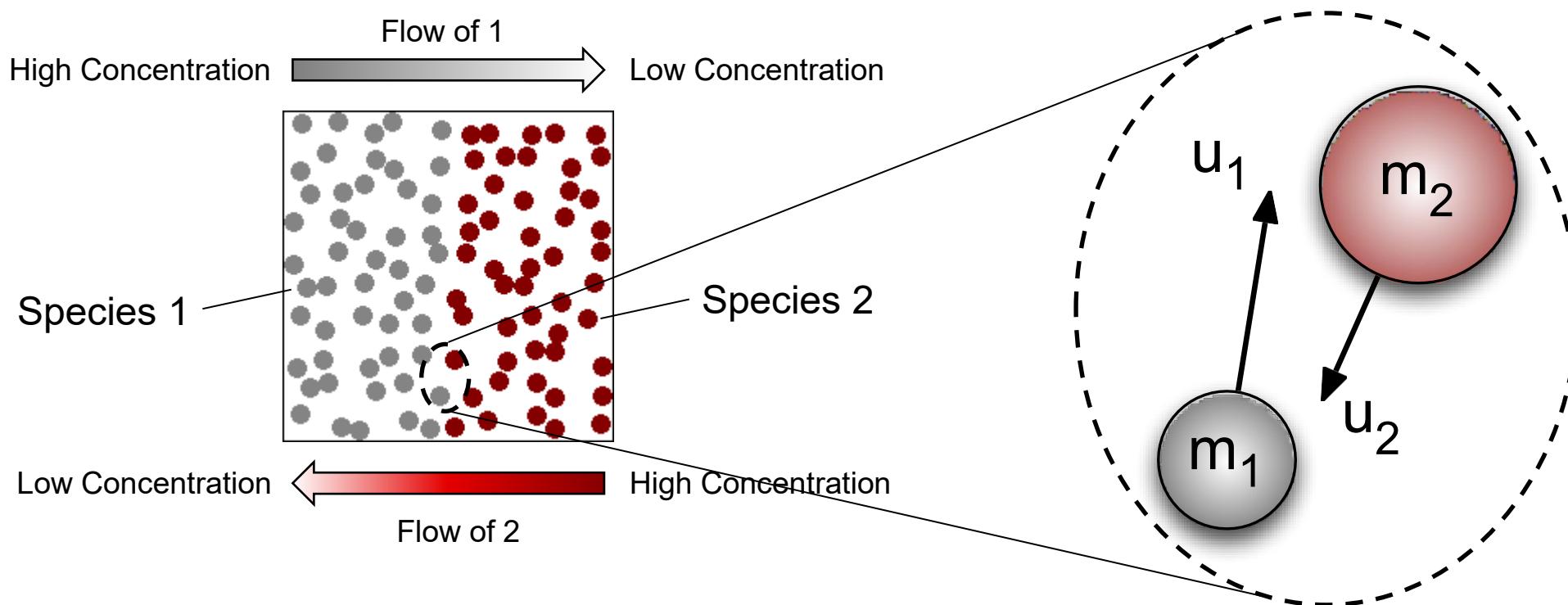
Consider 2 species colliding with each other in a closed volume ( $V$ ) with constant pressure ( $p$ ) and constant temperature ( $T$ )



Diffusion describes the flow of each species down the slope of their concentration gradient (i.e. from high to low)

# Describing diffusion in a binary system

Let us now zoom into a single collision between 1 and 2



We can use our understanding of force, momentum and energy conservation to describe the physics of this collision

# Describing diffusion in a binary system

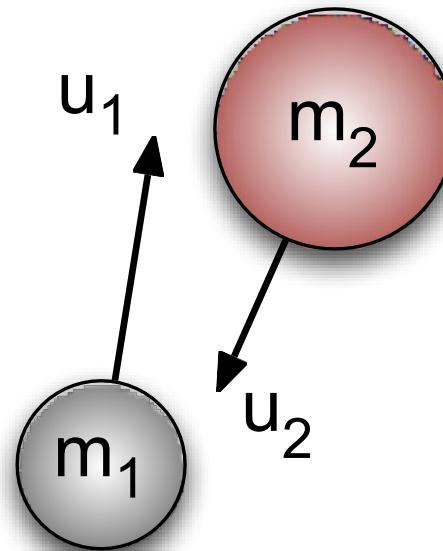
First let us evaluate the trajectories of 1 and 2 post-collision

Conservation of linear momentum (elastic collision):

$$m_1(u_1 - u_{f1}) + m_2(u_2 - u_{f2}) = 0$$

Conservation of kinetic energy (elastic collision):

$$m_1(u_1^2 - u_{f1}^2) + m_2(u_2^2 - u_{f2}^2) = 0$$



Therefore, solving for the final velocities,

$$u_{f1} = \frac{u_1(m_1 - m_2) + 2m_2 u_2}{m_1 + m_2},$$

$$u_{f2} = \frac{u_2(m_2 - m_1) + 2m_1 u_1}{m_1 + m_2}$$

Gives the momentum exchanged in the collision as

$$\begin{aligned} m_1(u_1 - u_{f1}) &= m_1 u_1 - \frac{m_1}{m_1 + m_2} (u_1(m_1 - m_2) + 2m_2 u_2), \\ &= \frac{2m_1 m_2 (u_1 - u_2)}{m_1 + m_2} \end{aligned}$$

# Describing diffusion in a binary system

But what causes this collision in the first place?

The answer lies in Newton's second law of motion.

For species 1,

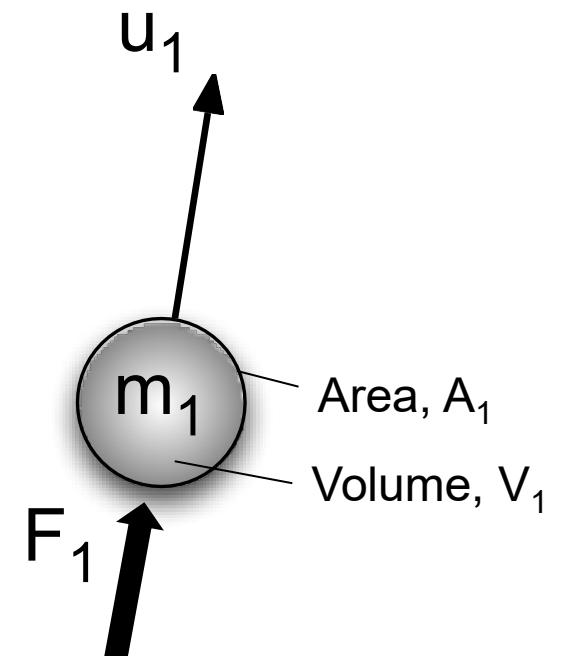
Force acting on 1 (cause) = Rate of change of momentum of 1 (effect)

Therefore,

$$F_1 = \int_{A_1} p_1 dA_1 = \frac{2}{m_1 + m_2} m_1 m_2 (u_1 - u_2)$$

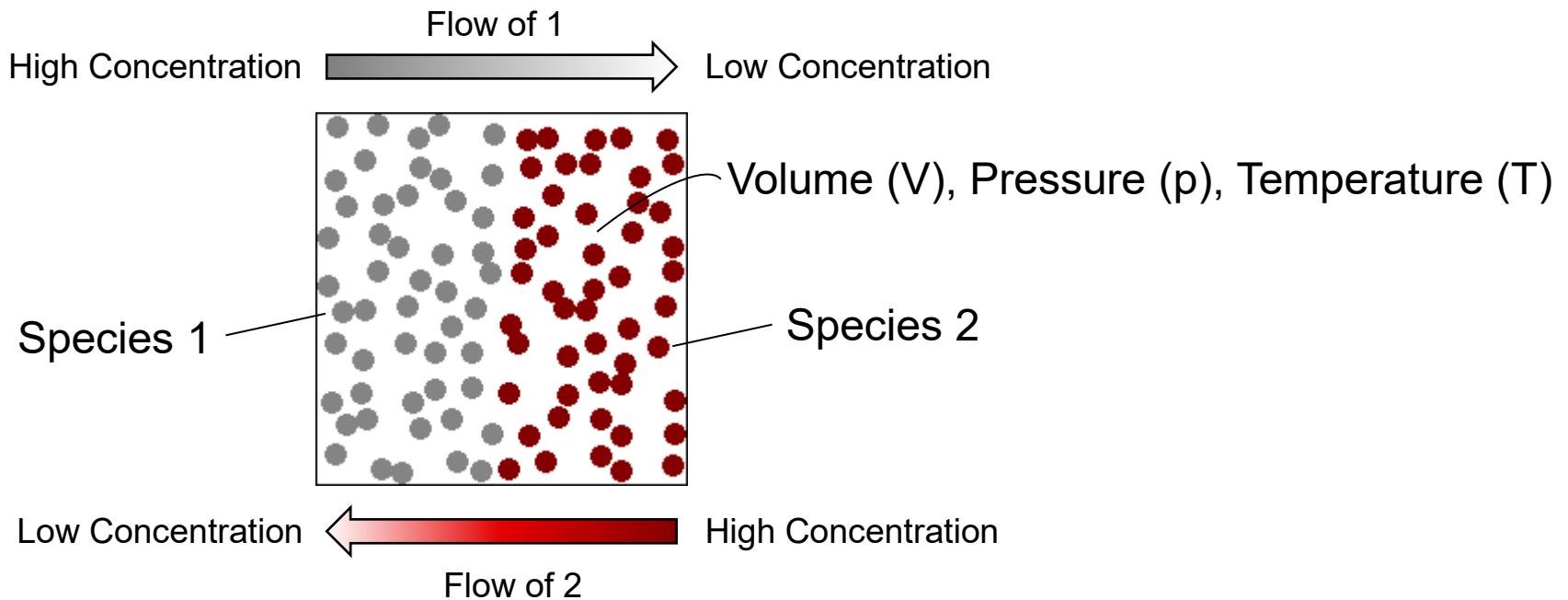
Pressure acting on 1

Force-momentum  
balance for a single  
species 1 particle



Now we can go back to the many particle system and write the equivalent force-momentum balance for all species 1 particles due to collisions between 1 and 2

# Describing diffusion in a binary system



Force-momentum balance for all species 1 particles due to collisions between 1 and 2

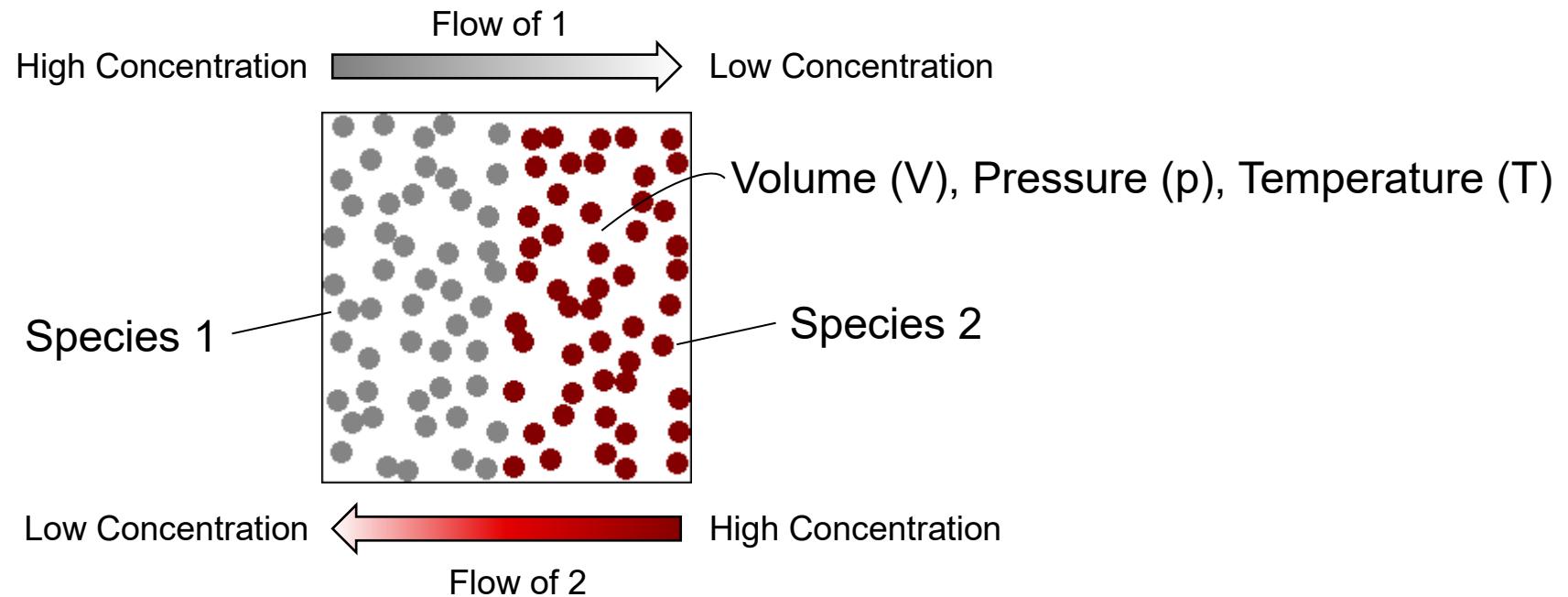
$$\int_V -\nabla p_1 dV = \int_V f_{12} \frac{c_1 c_2 (u_1 - u_2)}{c_T}$$

total gas concentration ( $= p/RT$ )

$$\text{where, } f_{12} = 2 \frac{MW_1 MW_2}{MW_{12}}$$

/  
average molecular weight of 1 and 2

# Describing diffusion in a binary system

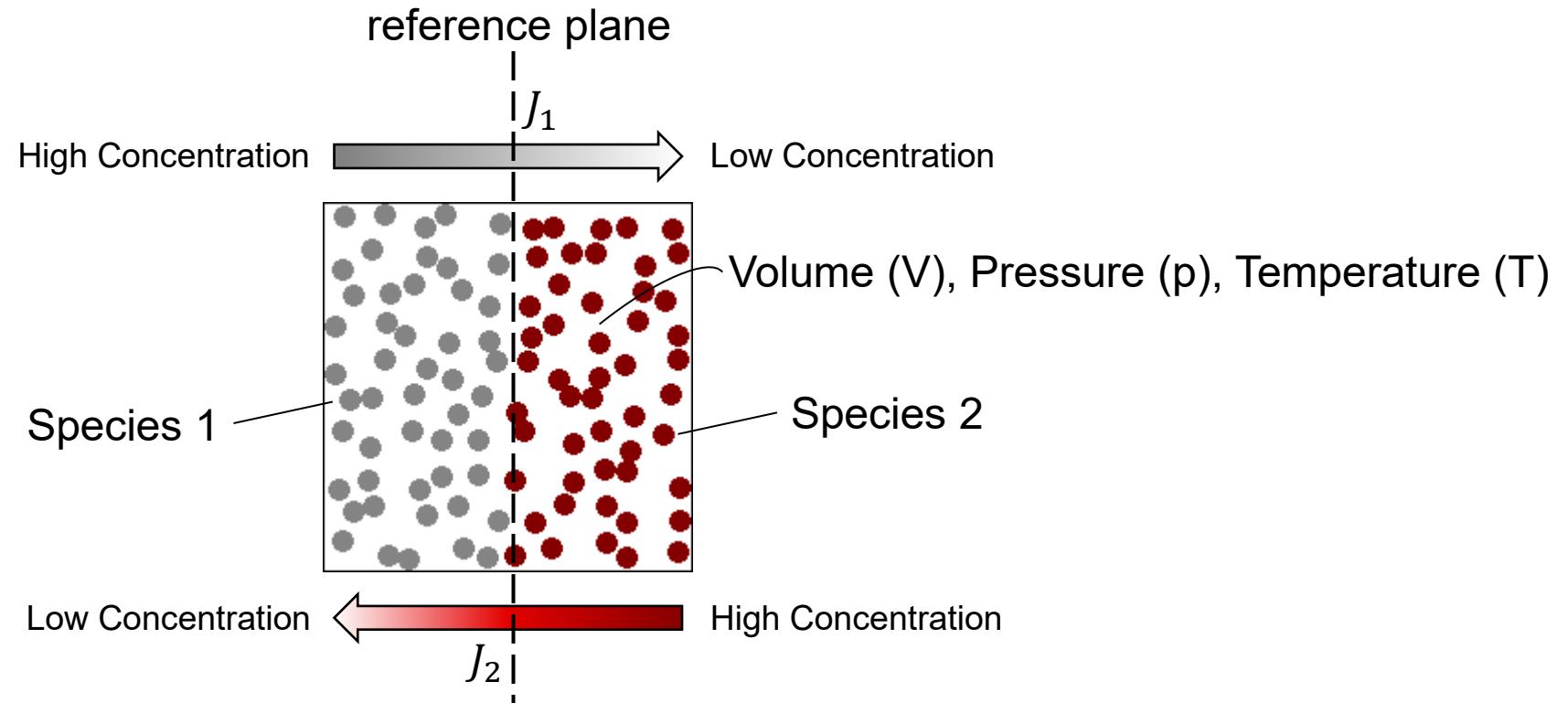


Now dividing by  $V$  and defining a “binary diffusion coefficient” as  $D_{12} = \frac{RT}{f_{12}}$ ,

$$-\frac{1}{RT} \nabla(p_1) = -\nabla(c_1) = \frac{c_1 c_2 (u_1 - u_2)}{c_T D_{12}}$$

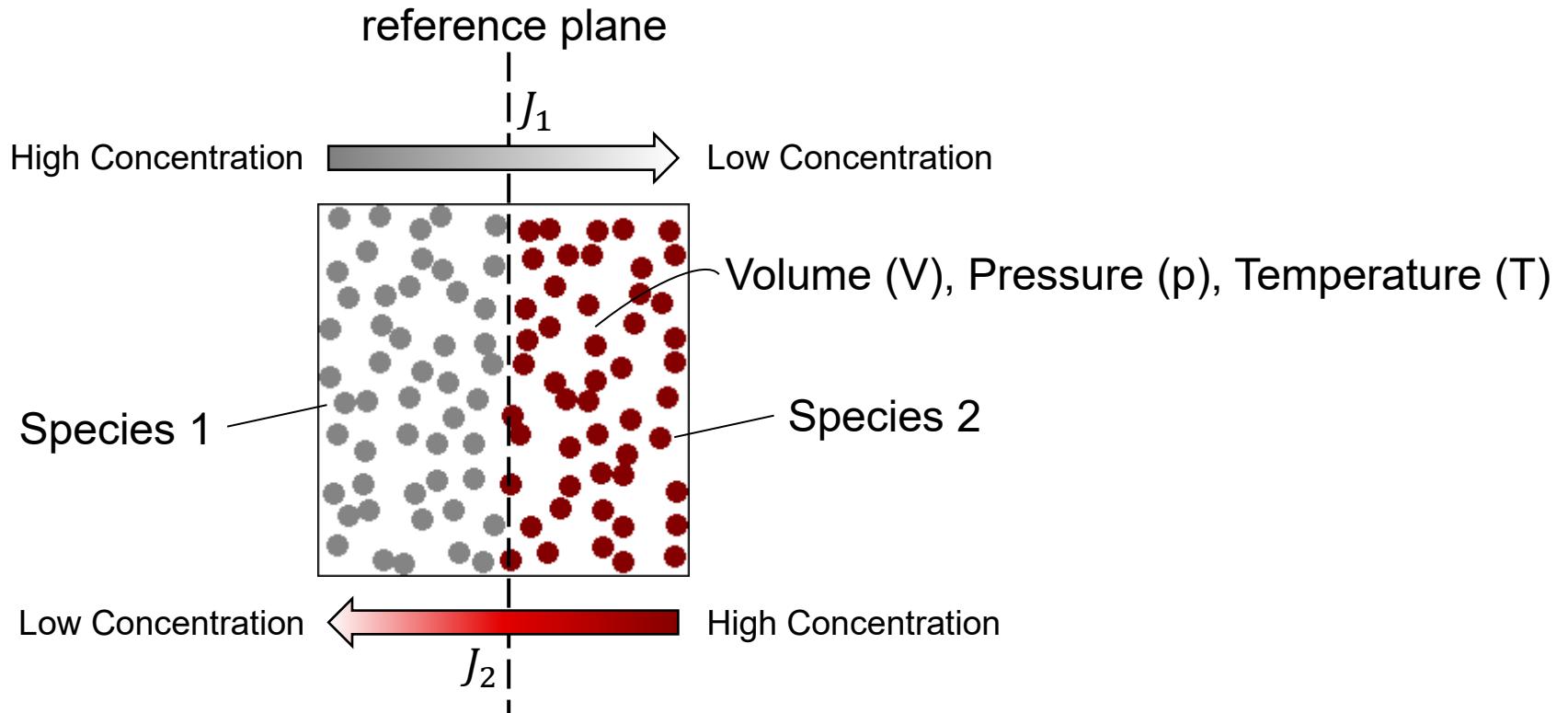
# Describing diffusion in a binary system

To quantify the rate at which species 1 and 2 are diffusing, we count the amount of species 1 and 2 crossing an arbitrary plane across the centre of the closed volume



Here,  $J_1$  and  $J_2$  are fluxes of species 1 and 2 crossing the reference plane with units of  $\frac{mol}{m^2-s}$

# Describing diffusion in a binary system

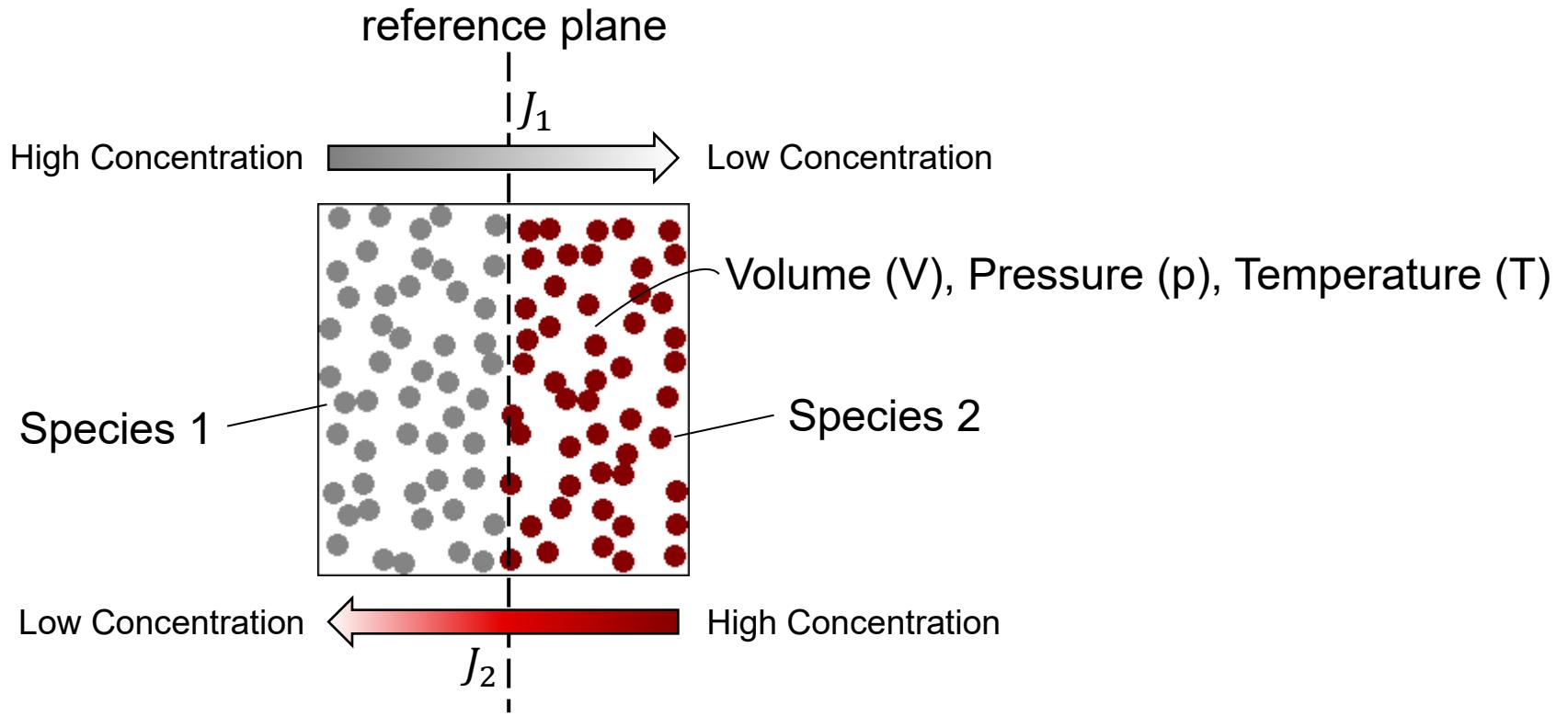


$$\text{Thus, } J_1 \left[ \frac{\text{mol}}{\text{m}^2 - \text{s}} \right] = c \left[ \frac{\text{mol}}{\text{m}^3 - \text{s}} \right] \cdot u \left[ \frac{\text{m}}{\text{s}} \right]$$

$$\text{And, } -\nabla(c_1) = \frac{J_1 c_2 - J_2 c_1}{c_T D_{12}}$$

where,  $J_1 = c_1 u_1$  and  $J_2 = c_2 u_2$

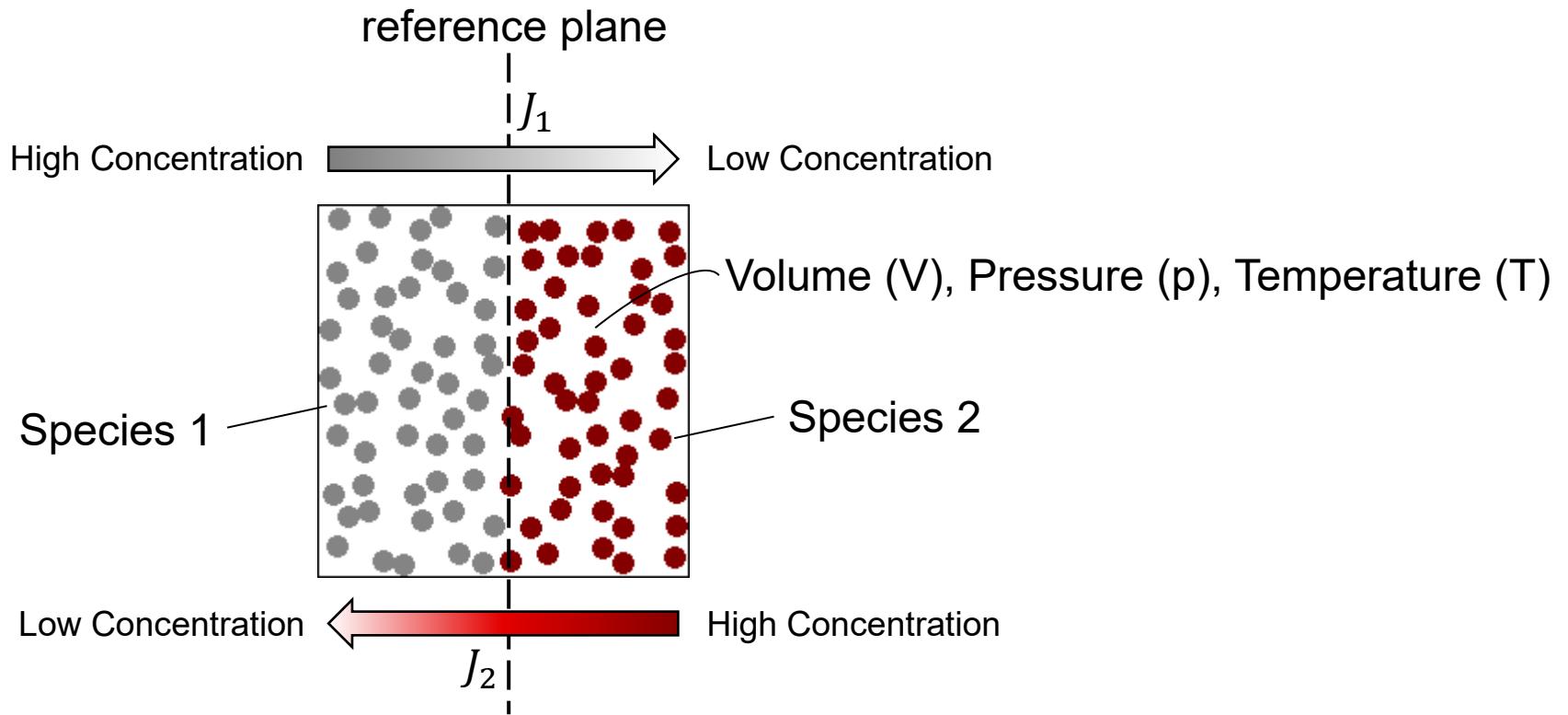
# Describing diffusion in a binary system



Now defining mole fractions  $X_1 = \frac{c_1}{c_T}$  and  $X_2 = \frac{c_2}{c_T}$ , we get

$$-\nabla(c_1) = \frac{(J_1 X_2 - J_2 X_1)}{D_{12}}$$

# Describing diffusion in a binary system

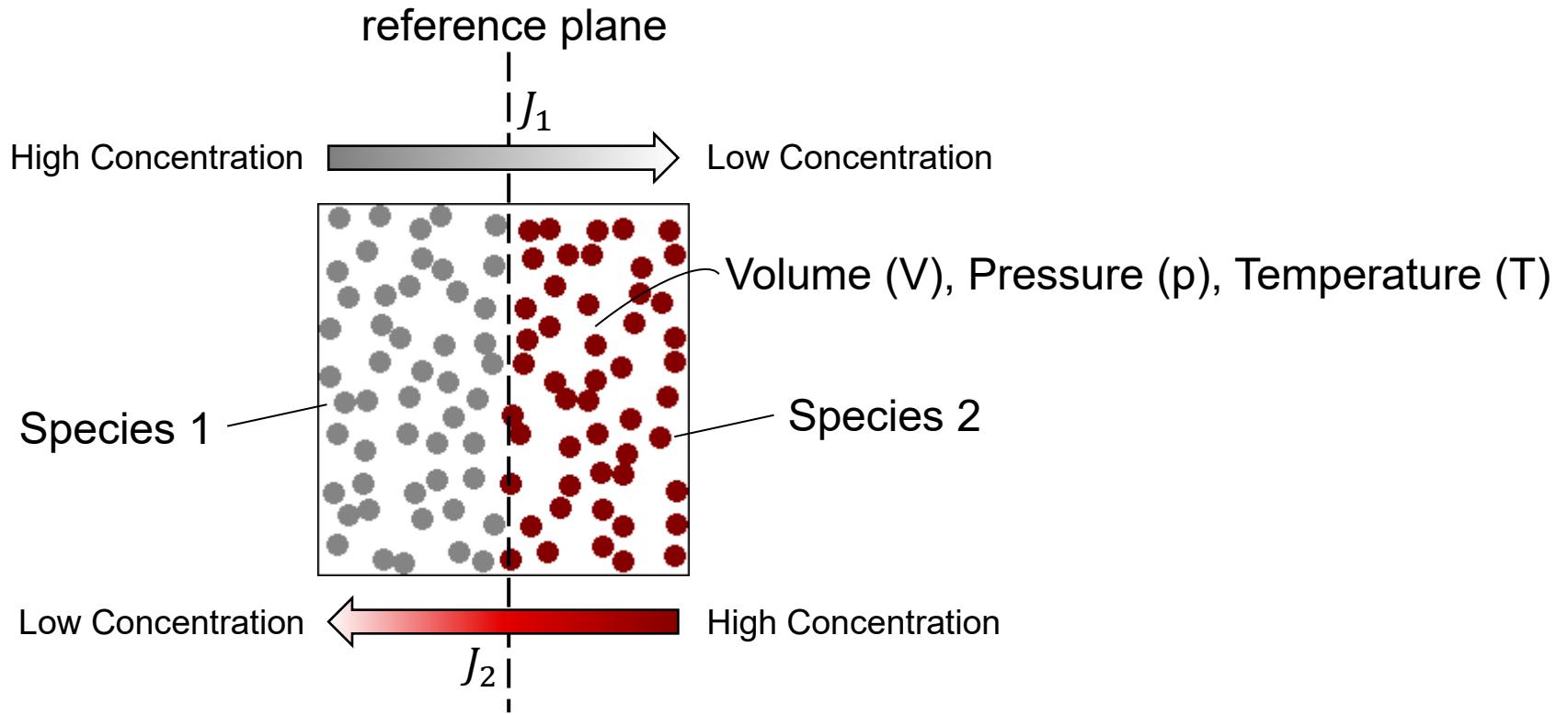


Since the pressure ( $p$ ) is constant across the volume ( $V$ ), the total amount of species 1 and 2 particles on either side of the reference plane must be equal at any given time

$$\text{Thus, } J_1 = -J_2$$

$$\text{Also, since } c_1 + c_2 = c_T, X_1 + X_2 = 1$$

# Describing diffusion in a binary system



$$\text{Therefore, } J_1(1 - X_1) + J_1X_1 = -D_{12}\nabla(c_1)$$

$$\Rightarrow \boxed{J_1 = -D_{12}\nabla c_1}$$

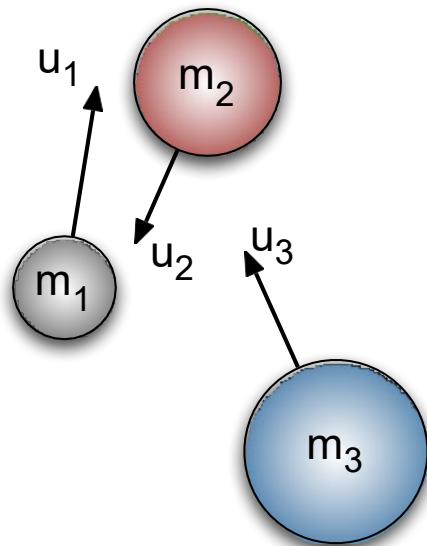
Fick's law of  
binary diffusion

# Describing multi-species diffusion

We have seen that Fick's law is simply the result of conserving force, momentum and energy from collisions between two species

But what happens when there are more than two species?

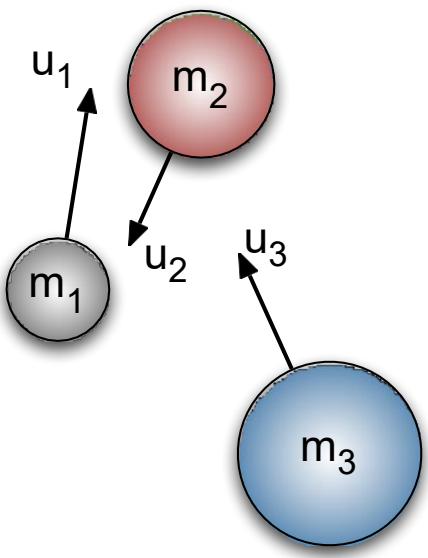
To investigate, let us now apply the same approach to a three-species (ternary) system



It is clear that aside from collisions between species 1-2, we must also consider collisions between species 1-3 and species 2-3

# Describing multi-species diffusion

Thus, following the same force-momentum balance approach as for a binary system,



$$-\nabla(c_1) = \frac{c_1 c_2 (u_1 - u_2)}{c_T D_{12}} + \frac{c_1 c_3 (u_1 - u_3)}{c_T D_{13}}$$

$$-\nabla(c_2) = \frac{c_1 c_2 (u_1 - u_2)}{c_T D_{12}} + \frac{c_2 c_3 (u_2 - u_3)}{c_T D_{23}}$$

Or, in terms of fluxes,

$$-\nabla(c_1) = \frac{(J_1 X_2 - J_2 X_1)}{D_{12}} + \frac{(J_1 X_3 - J_3 X_1)}{D_{13}}$$

$$-\nabla(c_2) = \frac{(J_1 X_2 - J_2 X_1)}{D_{12}} + \frac{(J_2 X_3 - J_3 X_2)}{D_{23}}$$

# Describing multi-species diffusion

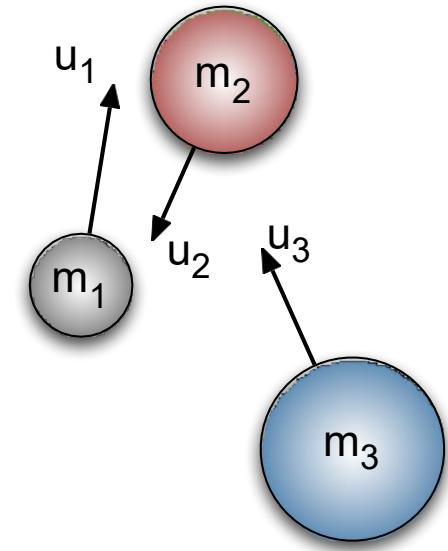
This force-momentum balance approach can be generalised to obtain the Maxwell-Stefan diffusion model for n-species systems,

$$-\nabla(c_i) = \sum_{k \neq i}^N \frac{J_i X_k - J_k X_i}{D_{ik}}$$

Going back to the 3-species diffusion equation

$$-\nabla(c_1) = \frac{(J_1 X_2 - J_2 X_1)}{D_{12}} + \frac{(J_1 X_3 - J_3 X_1)}{D_{13}}$$

$$-\nabla(c_2) = \frac{(J_1 X_2 - J_2 X_1)}{D_{12}} + \frac{(J_2 X_3 - J_3 X_2)}{D_{23}}$$

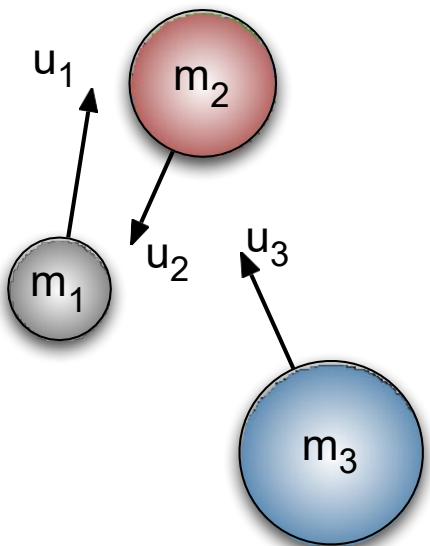


We see that solving for the diffusive fluxes  $J_1$ ,  $J_2$  and  $J_3$  are not as trivial as for a binary system and requires considerable mathematical effort including matrix inversions. Thus, it is often implemented numerically especially for when there are more than 3-species

# Describing multi-species diffusion

---

Skipping the complex mathematics, the diffusive fluxes in a 3-species system are given as



$$J_1 = -C \left( \frac{1}{D_{23}} + BX_1 \right) \nabla c_1 - BCX_1 \nabla c_2$$

$$J_2 = -CBX_2 \nabla c_1 - C \left( \frac{1}{D_{13}} + AX_2 \right) \nabla c_2$$

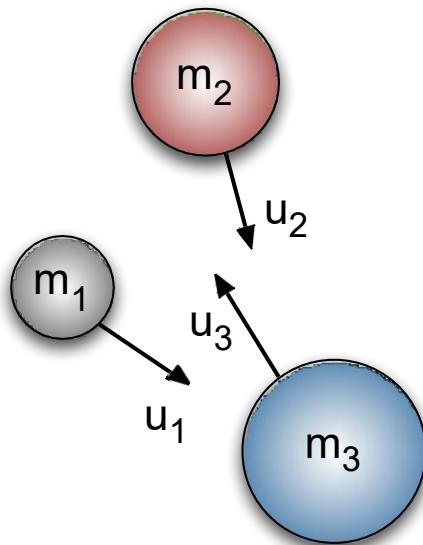
$$J_3 = -(J_1 + J_2)$$

$$\text{where, } A = \left( \frac{1}{D_{12}} - \frac{1}{D_{13}} \right), \quad B = \left( \frac{1}{D_{12}} - \frac{1}{D_{23}} \right),$$

$$C = \frac{D_{13}D_{23}}{1 + AD_{13}X_2 + BD_{23}X_1}$$

# Describing multi-species diffusion

Due to this computational complexity, we often look to ignore collisions between 1-2, for example, in a dilute solution where solute concentrations (1 and 2) is very low compared to the solvent (3),



$$c_1 \ll c_3 ; c_2 \ll c_3 ; c_3 \approx c_T$$

$$\text{or, } X_1 \ll X_3 ; X_2 \ll X_3 ; X_3 \approx 1$$

$$-\nabla(c_1) = \frac{(J_1 X_2 - J_2 X_1)}{D_{12}} + \frac{(J_1 X_3 - J_3 X_1)}{D_{13}}$$

$$-\nabla(c_2) = \frac{(J_1 X_2 - J_2 X_1)}{D_{12}} + \frac{(J_2 X_3 - J_3 X_2)}{D_{23}}$$

We can then get back Fick's law for each flux,

$$J_1 = -D_{13} \nabla(c_1) ; J_2 = -D_{23} \nabla(c_2)$$

But how often is this dilute solution assumption valid?

# Comparison of Fick's and Maxwell-Stefan diffusion

---

If we compare the diffusive flux equations for a 2-species vs 3-species system without the dilute solution assumption,

2-species system:  $J_1 = -D_{12}\nabla c_1$  [Fick's diffusion model]

3-species system:  $J_1 = -C \left( \frac{1}{D_{23}} + BX_1 \right) \nabla c_1 - BCX_1 \nabla c_2$  where,  $A = \left( \frac{1}{D_{12}} - \frac{1}{D_{13}} \right)$ ,  $B = \left( \frac{1}{D_{12}} - \frac{1}{D_{23}} \right)$

[Maxwell-Stefan diffusion model]

$$C = \frac{D_{13}D_{23}}{1 + AD_{13}X_2 + BD_{23}X_1}$$

There are two major observations:

1. The diffusion coefficients for a 3-species system are a complex function of the binary diffusion coefficients
2. The diffusion flux of a species in a 3-species system does not only depend on its own concentration gradient

# Comparison of Fick's and Maxwell-Stefan diffusion

The first observation is particularly important as this affects the definition of two commonly used dimensionless numbers used to compare diffusive mass transport to reaction kinetics, e.g.

Damkohler Number:  $Da_{II} = \frac{kC_0^{n-1}}{(D/L^2)}$  - checks for external mass transport limitations

Thiele Modulus:  $\phi = \frac{V_p}{A_p} \sqrt{\frac{kC_0^{n-1}}{D \cdot \left(\frac{\epsilon}{\tau}\right)}}$

How do we estimate D?

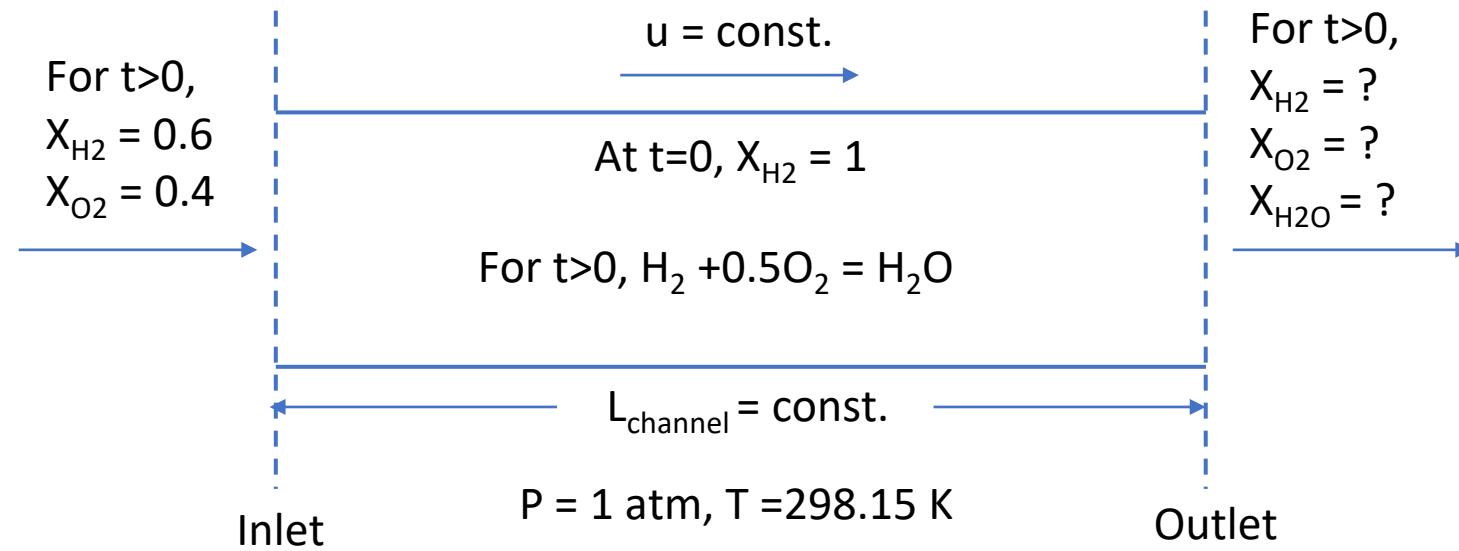
In the absence of Knudsen diffusion, for a binary system, D is simply the binary diffusion coefficient

However, for more than 2 components, as we have seen calculating the value of D is not trivial without the dilute solution assumption

# Comparison of Fick's and Maxwell-Stefan diffusion

Let us now investigate the validity of the dilute solution assumption (and in turn, Fick's law) by studying a simple 3-species reaction system

Problem definition:

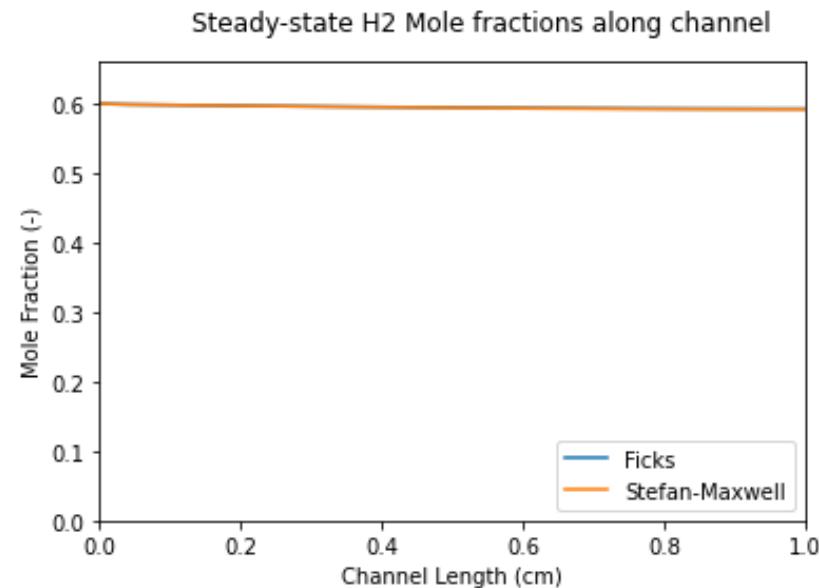
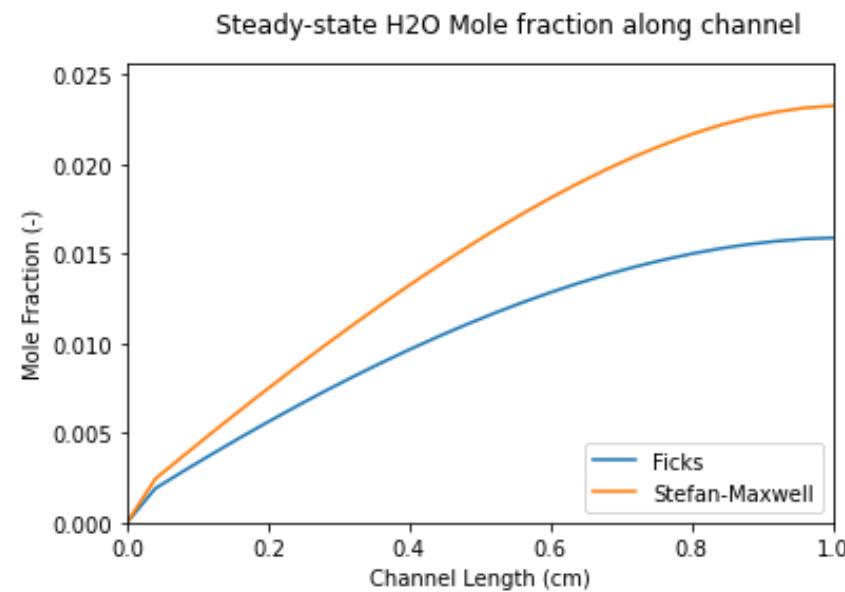
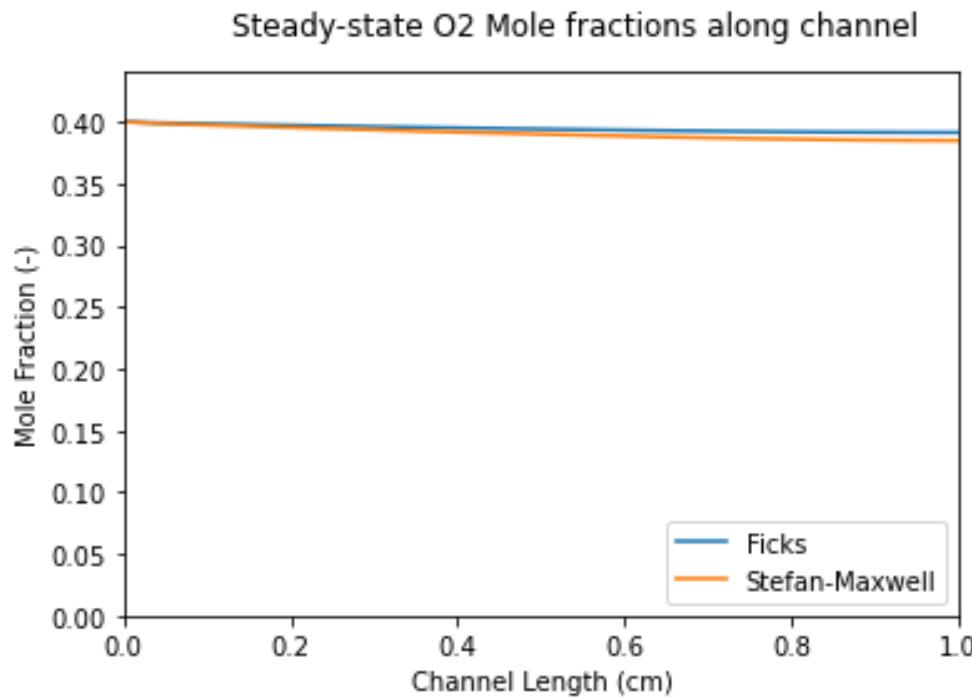


Objective : To compare steady-state mole fraction profiles of  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$  along the channel obtained using Fick's vs Maxwell-Stefan diffusion models for different  $\text{H}_2\text{O}$  yields

For Fick's diffusion model, we assume  $\text{H}_2$  to be the “solvent/background”, thus  $\text{O}_2\text{-H}_2\text{O}$  collisions are neglected

# Comparison of Fick's and Maxwell-Stefan diffusion

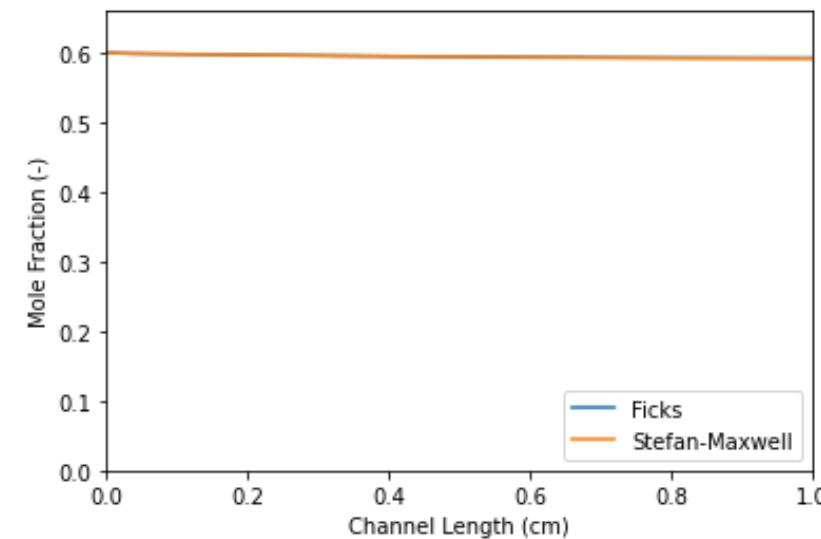
Results: For low H<sub>2</sub>O yield  
(k\_reac = 1e-1)



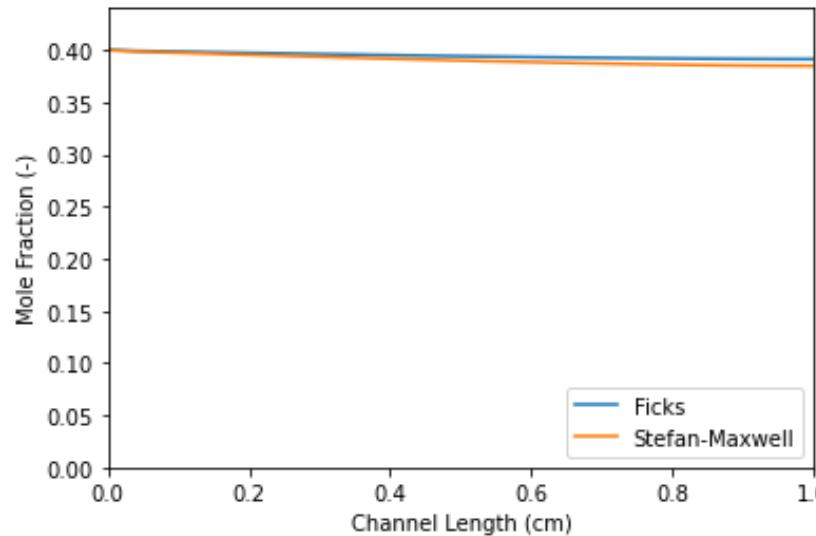
# Results: For low H<sub>2</sub>O yield

$$Relative\ Error\ (\%) = \frac{abs(Mol\ frac_{Ficks} - Mol\ frac_{SM})}{Mol\ frac_{SM}} \cdot 100$$

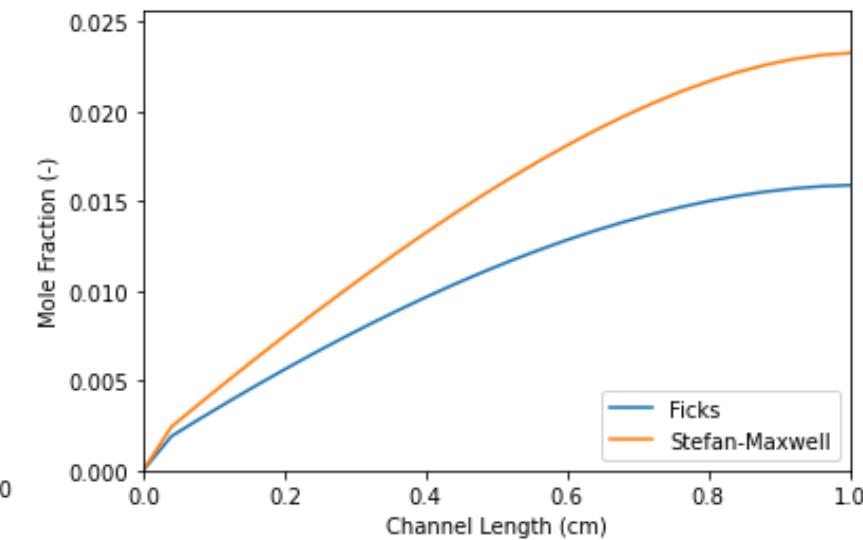
Steady-state H<sub>2</sub> Mole fractions along channel



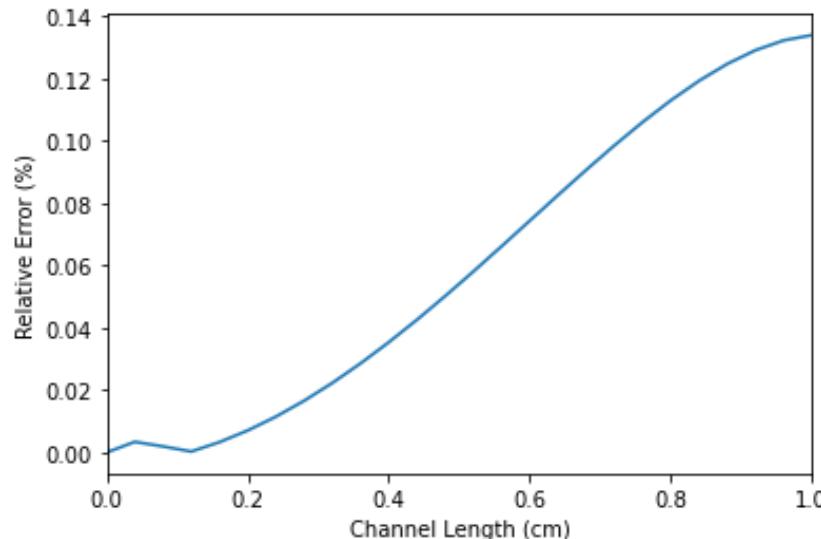
Steady-state O<sub>2</sub> Mole fractions along channel



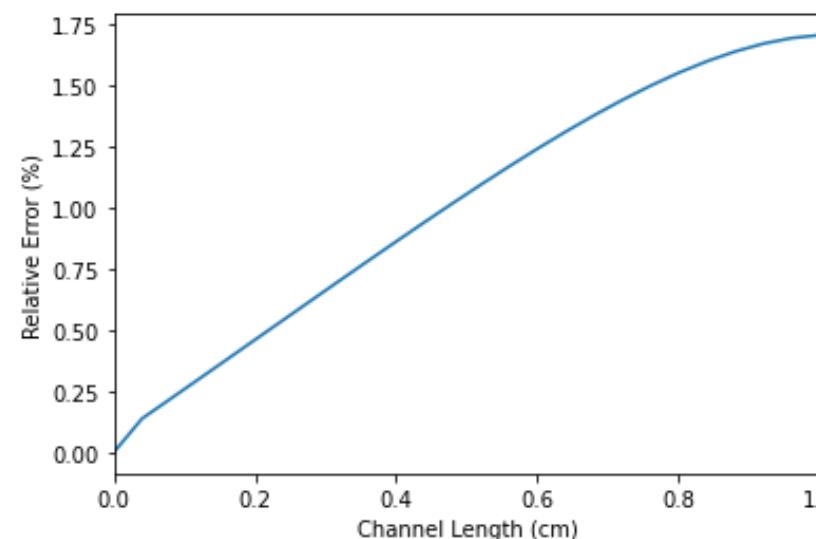
Steady-state H<sub>2</sub>O Mole fraction along channel



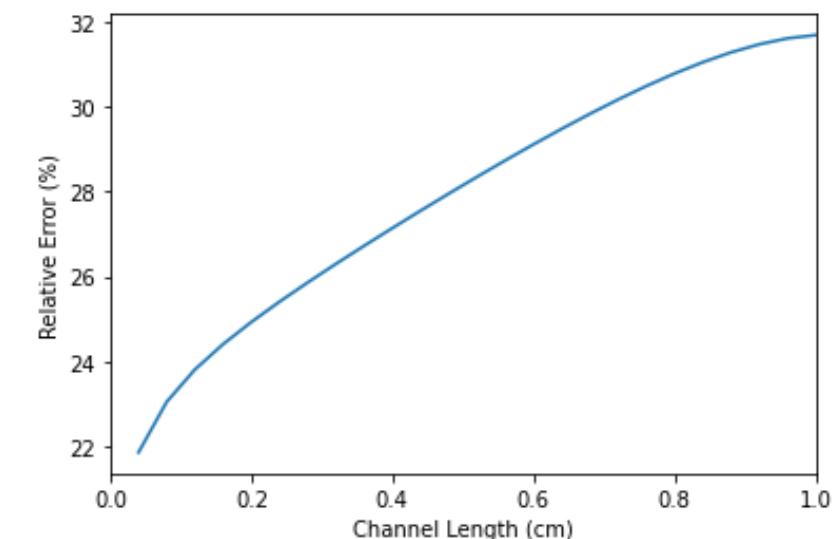
Steady-state Error in H<sub>2</sub> Mole fractions along channel



Steady-state Error in O<sub>2</sub> Mole fractions along channel

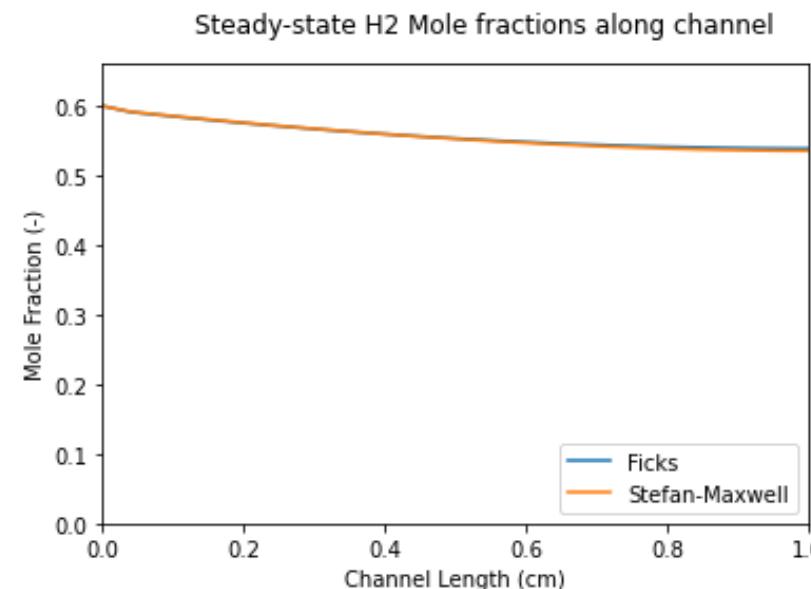
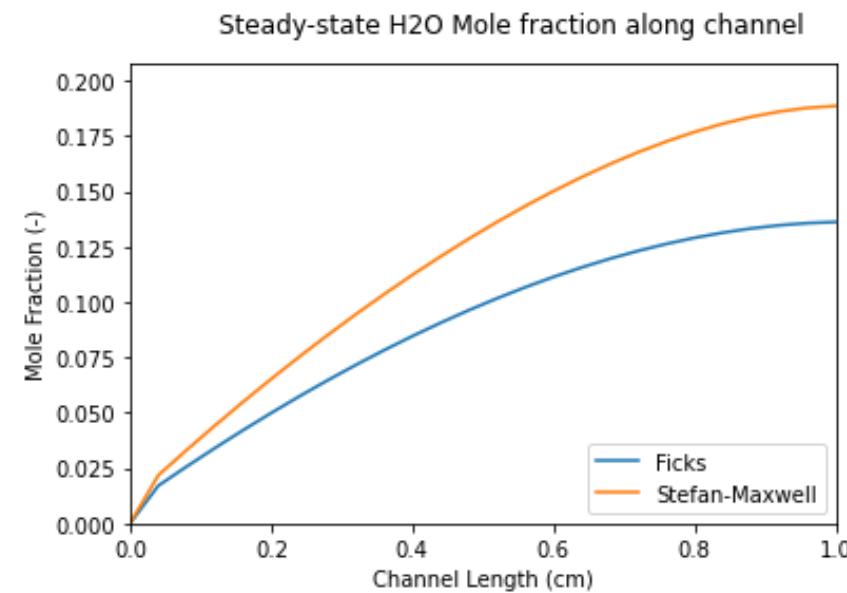
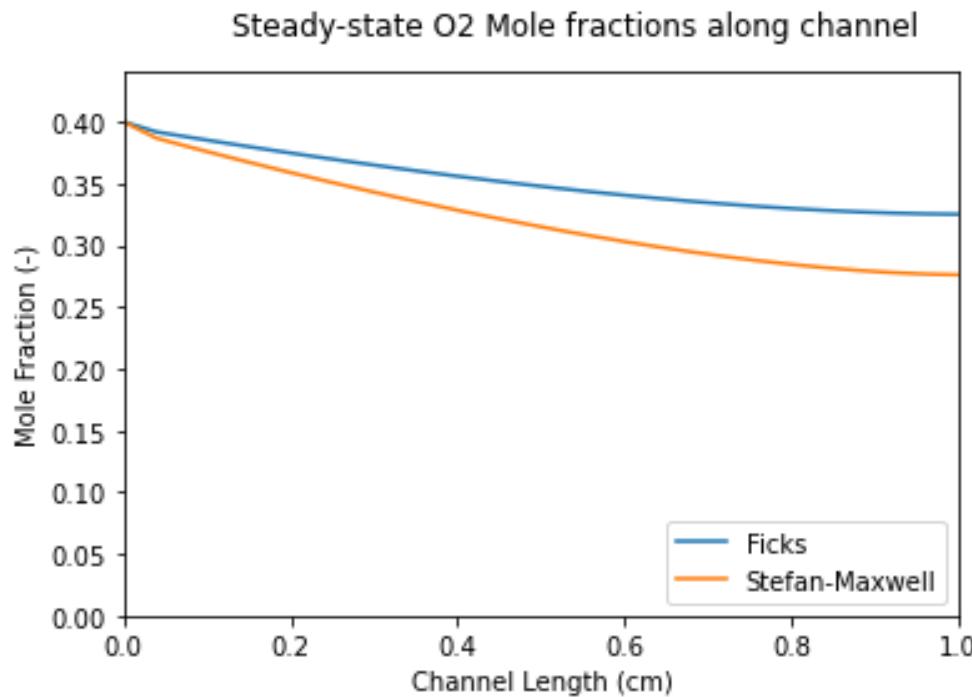


Steady-state Error in H<sub>2</sub>O Mole fraction along channel



# Comparison of Fick's and Maxwell-Stefan diffusion

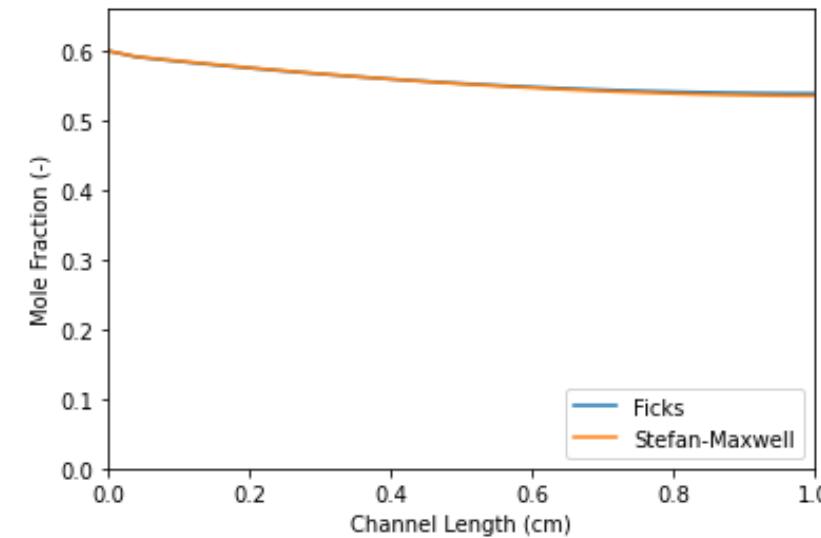
Results: For medium H<sub>2</sub>O yield  
(k\_reac = 1)



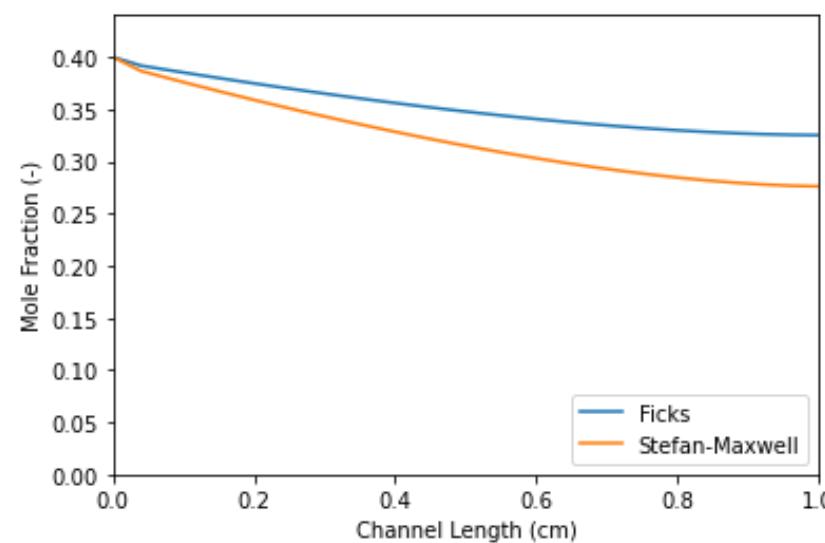
# Results: For mid H<sub>2</sub>O yield

$$Relative\ Error\ (\%) = \frac{abs(Mol\ frac_{Ficks} - Mol\ frac_{SM})}{Mol\ frac_{SM}} \cdot 100$$

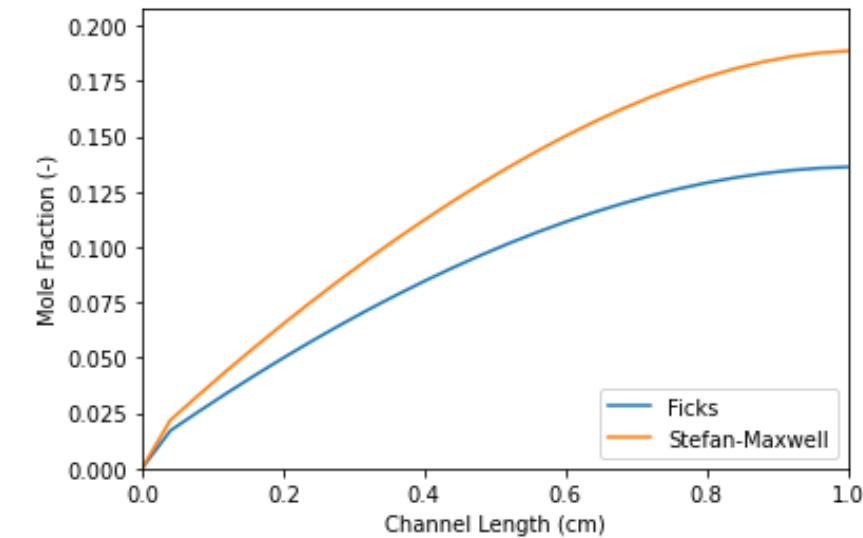
Steady-state H<sub>2</sub> Mole fractions along channel



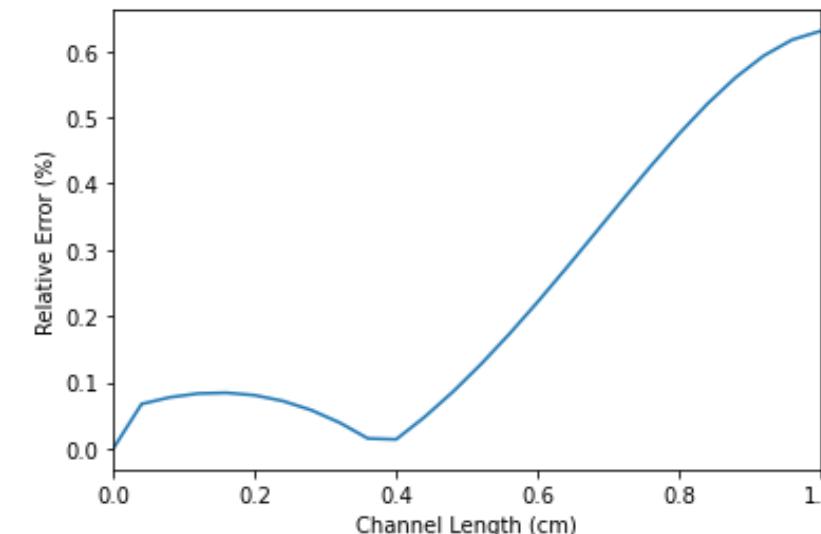
Steady-state O<sub>2</sub> Mole fractions along channel



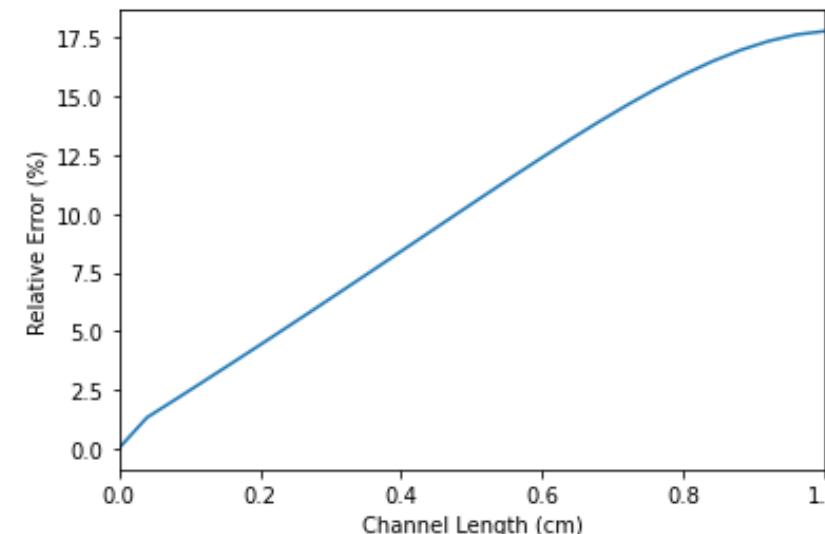
Steady-state H<sub>2</sub>O Mole fraction along channel



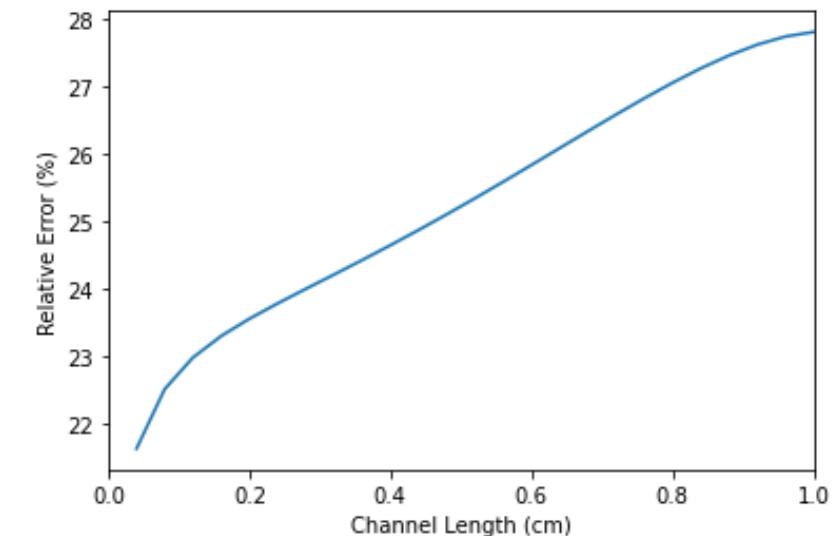
Steady-state Error in H<sub>2</sub> Mole fractions along channel



Steady-state Error in O<sub>2</sub> Mole fractions along channel

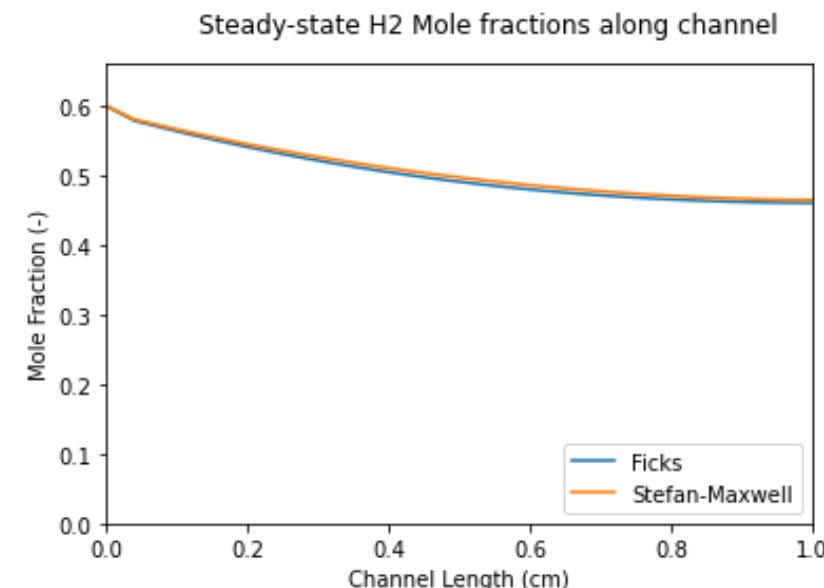
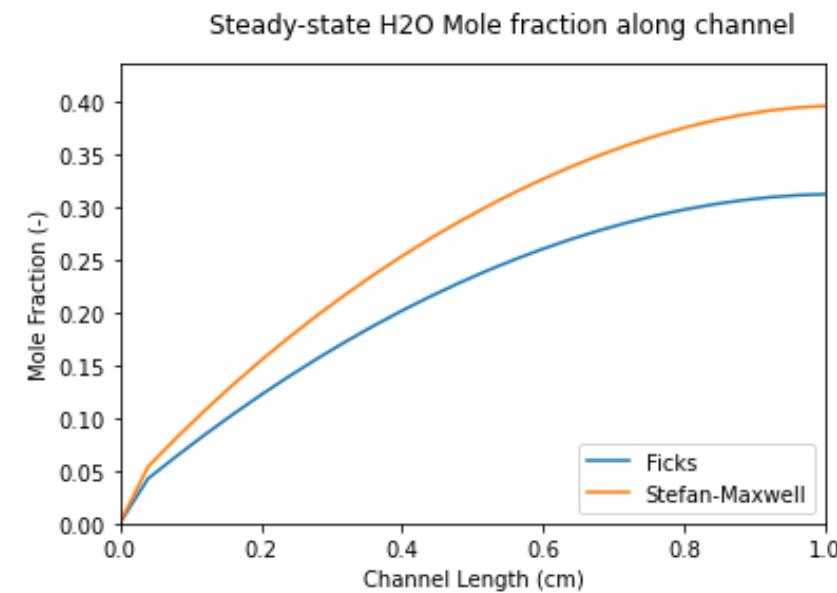
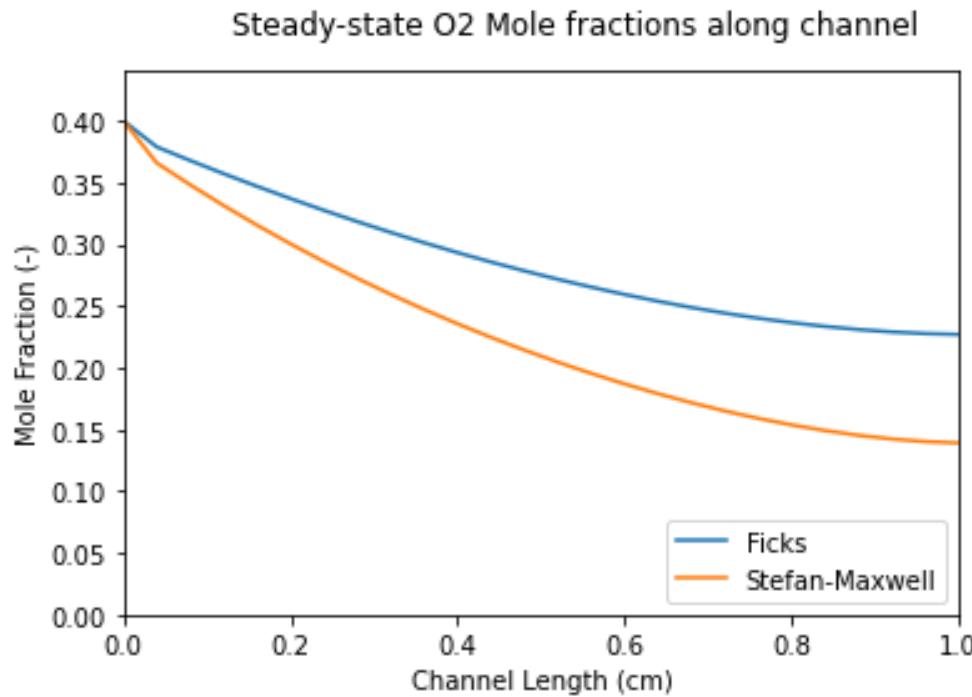


Steady-state Error in H<sub>2</sub>O Mole fraction along channel



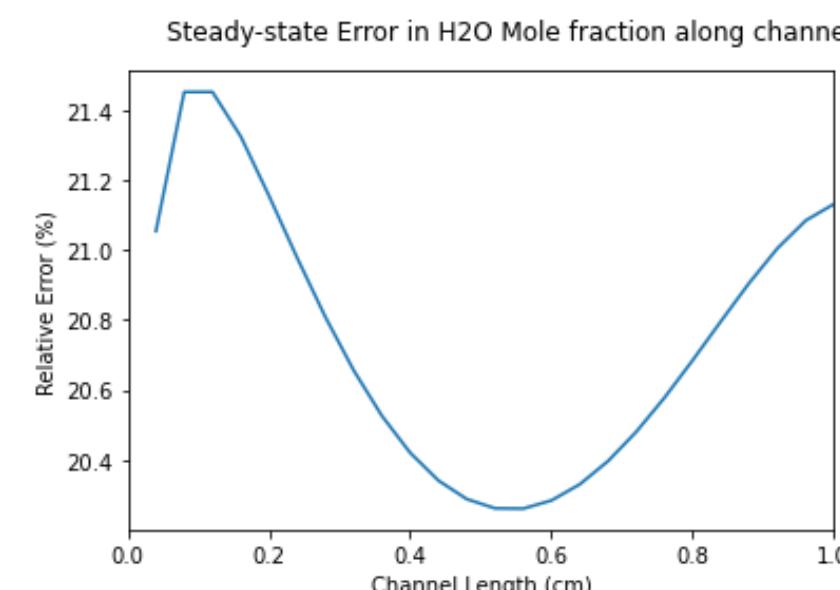
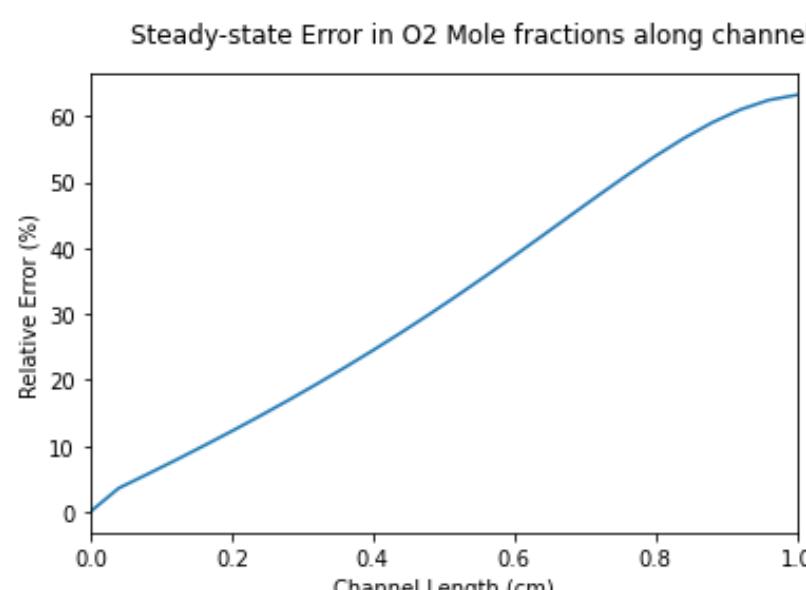
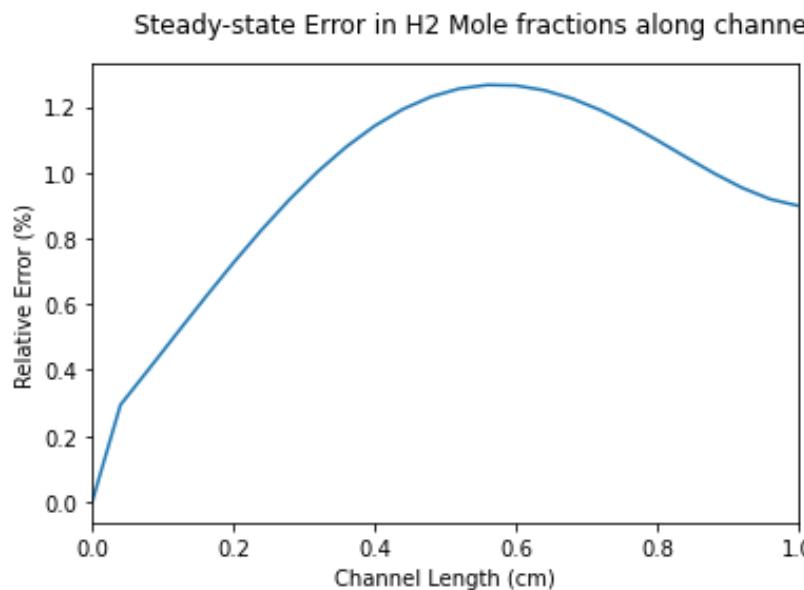
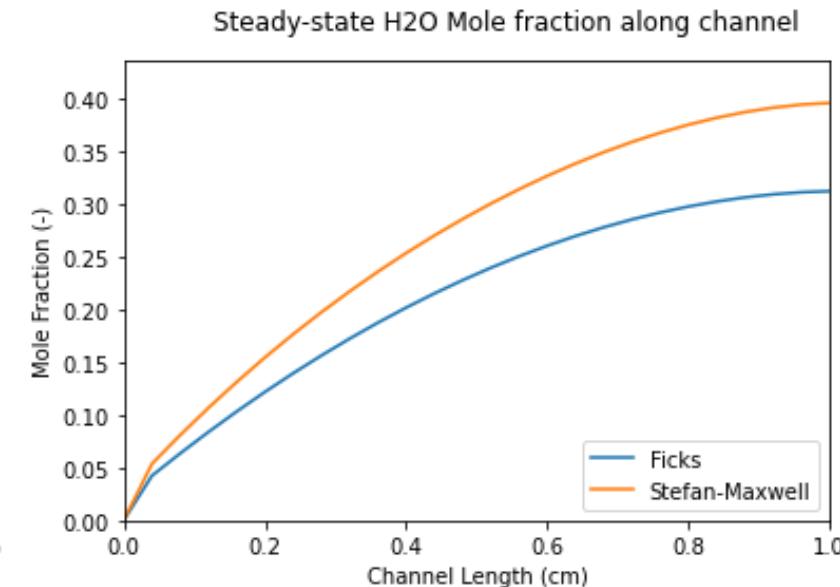
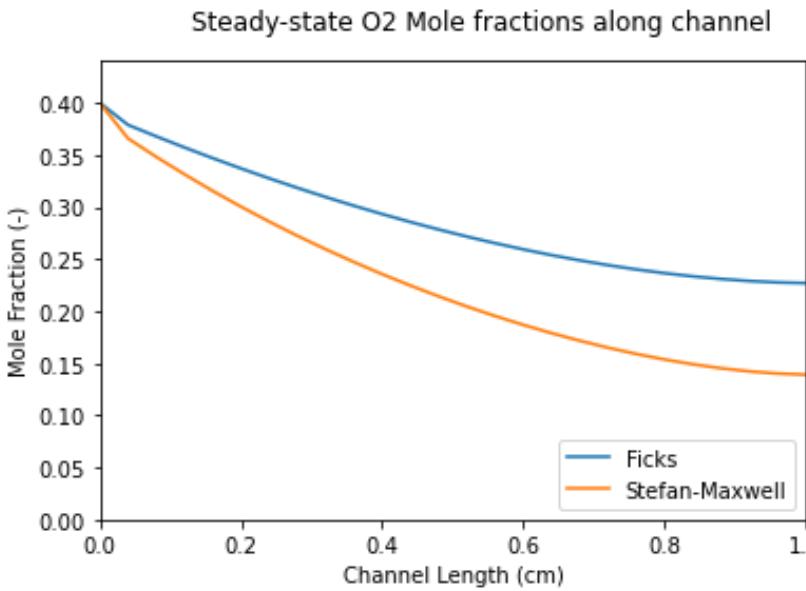
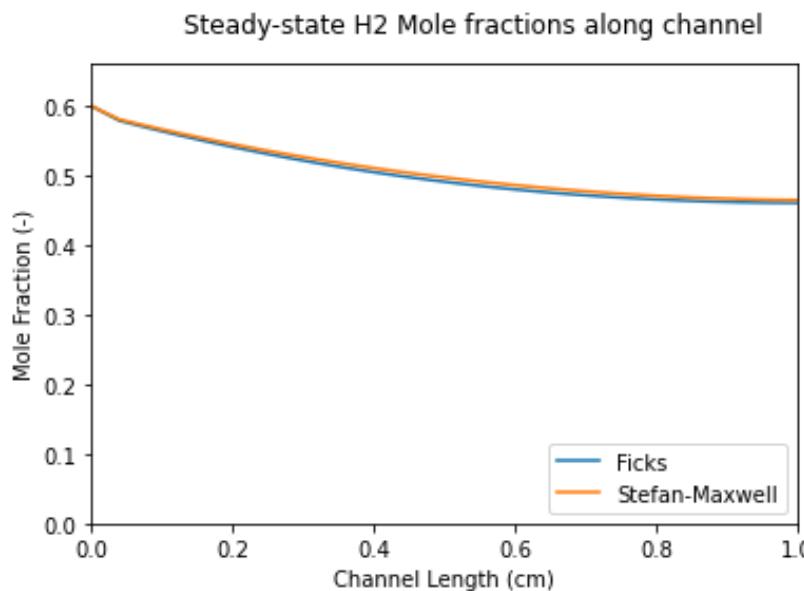
# Comparison of Fick's and Maxwell-Stefan diffusion

Results: For high H<sub>2</sub>O yield  
(k\_reac = 3)

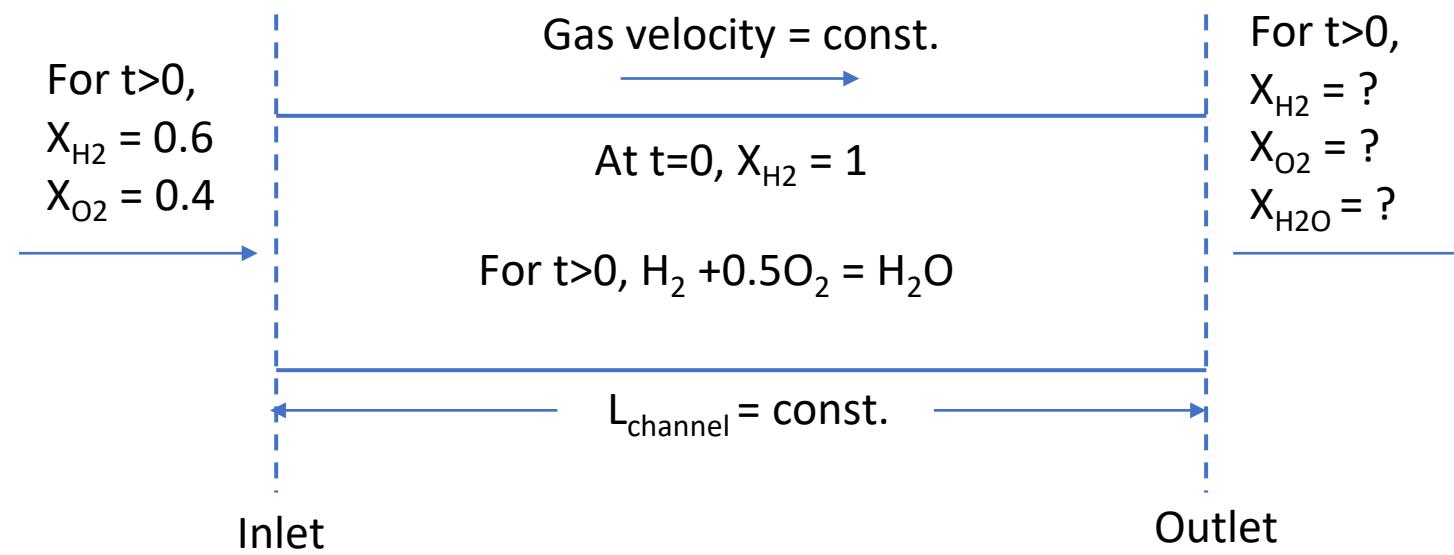


# Results: For high H<sub>2</sub>O yield

$$Relative\ Error\ (\%) = \frac{abs(Mol\ frac_{Ficks} - Mol\ frac_{SM})}{Mol\ frac_{SM}} \cdot 100$$



# Comparison of Fick's and Maxwell-Stefan diffusion



$\text{H}_2$  is assumed to be the “solvent/background” for the Ficks diffusivity calculations

$\text{H}_2\text{O}$ Yield according to M-S diffusion model	$D_{\text{O}_2}$			$D_{\text{H}_2\text{O}}$		
	$D_{\text{O}_2,\text{H}_2}$ [m <sup>2</sup> /s]	$D_{\text{O}_2,M-S}$ [m <sup>2</sup> /s]	$\frac{D_{\text{O}_2,\text{H}_2}}{D_{\text{O}_2,M-S}}$	$D_{\text{H}_2\text{O},\text{H}_2}$ [m <sup>2</sup> /s]	$D_{\text{H}_2\text{O},M-S}$ [m <sup>2</sup> /s]	$\frac{D_{\text{H}_2\text{O},\text{H}_2}}{D_{\text{H}_2\text{O},M-S}}$
2.3%	$8.14 \times 10^{-5}$	$7.94 \times 10^{-5}$	1.02	$9.05 \times 10^{-5}$	$4.77 \times 10^{-5}$	1.9
18.8%	$8.14 \times 10^{-5}$	$6.6 \times 10^{-5}$	1.24	$9.05 \times 10^{-5}$	$6.1 \times 10^{-5}$	1.48
39.6%	$8.14 \times 10^{-5}$	$5.02 \times 10^{-5}$	1.62	$9.05 \times 10^{-5}$	$7.63 \times 10^{-5}$	1.19

# Short Summary on Fick's vs Maxwell-Stefan diffusion

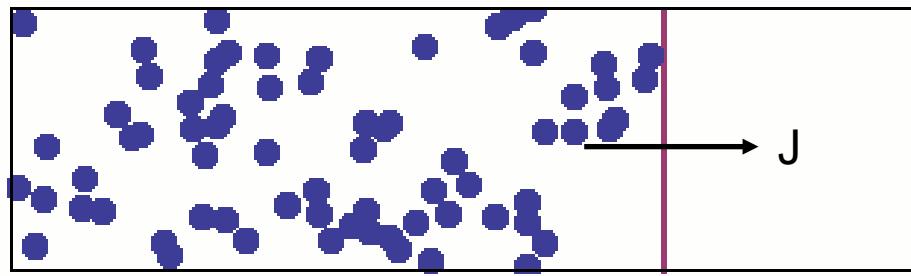
---

- Fick's law can be obtained simply by a force, momentum and energy balance of two-species collisions
- Generalising this force, momentum and energy balance to collisions between n-species leads to the Maxwell-Stefan diffusion model
- Thus, Fick's diffusion model is just a special case of the Maxwell-Stefan diffusion model applied to a 2-species system
- Dilute solution is an oft-made assumption to allow diffusion in multi-species systems to be evaluated using Fick's law and thereby calculate mass transport parameters like thiele modulus using the binary diffusion coefficient
- However, we need to be careful with this approximation as it can lead to substantial errors in estimating the real diffusion coefficient and thereby the correct thiele modulus

# One More Thing...

---

What about a single-species system?



Would the use of Fick's binary diffusion model to calculate the flux  $J$  be valid here?

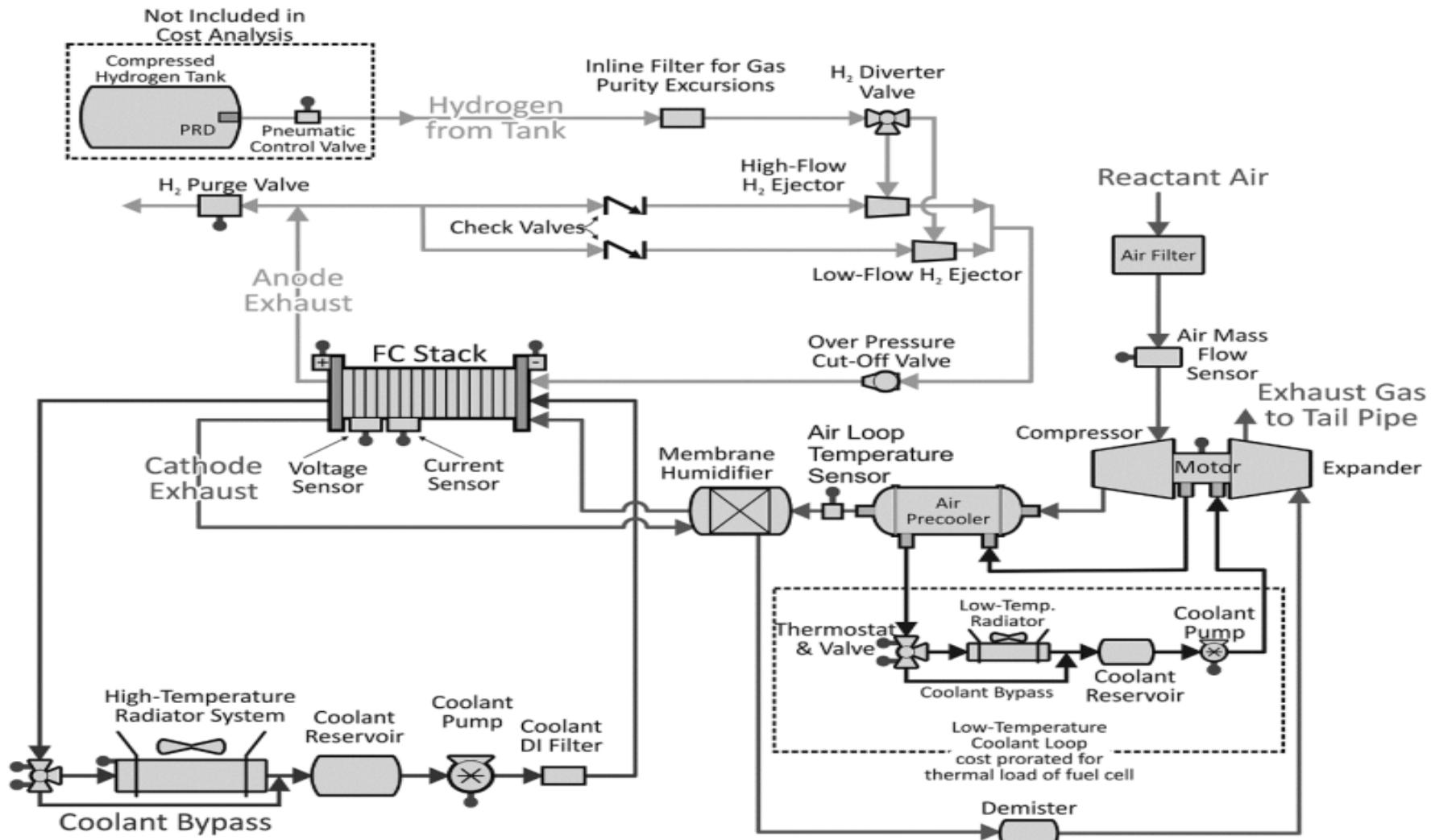
# Content

---

- Multi-scale modelling: Why? and How?
- The continuum approach
- Engineering descriptions of reaction kinetics
- Common types of chemical reactors
- Binary diffusion: A common pitfall in reaction engineering
- **Brief Introduction to Systems Modelling**

# Systems Modelling

## PEM Cell and its associated balance-of-plant



# Systems Modelling

---

- Modelling systems can be extremely complex and time consuming.
- Many systems have been modelled extensively in the past, *i.e.*, petrochemical plants → software exists to speed up the process.
- For new technology this is less developed.
- Common system modelling software include:
  - gPROMS
  - Matlab Simulink
  - Aspen Plus

# Systems Modelling

---

- Software like Aspen Plus are useful since they already have various models for balance-of-plant components embedded in them such as for heat exchangers, compressors, blowers, etc.
- Typically most (if not all) component models are 0-dimensional to facilitate quick computation and dynamic multi-variate optimisation
- The basic idea is to track mass and energy flows through the system to determine product yields and losses/inefficiencies

$$\text{Mass balance: } \sum F_{\text{system,in}} = \sum F_{\text{system,out}}$$

$$\text{Energy balance: } \sum \dot{H}_{\text{system,in}} = \sum \dot{H}_{\text{system,out}} + W_{\text{out}} + \text{Heat lost to surroundings}$$