# 2-D ion transport modelling of water desalination by reverse osmosis (RO) considering the real membrane effect

**Fernan Martinez**
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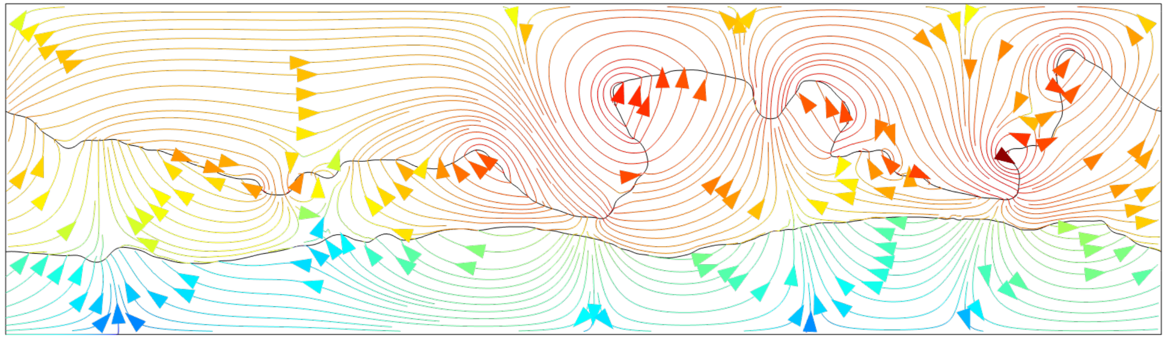

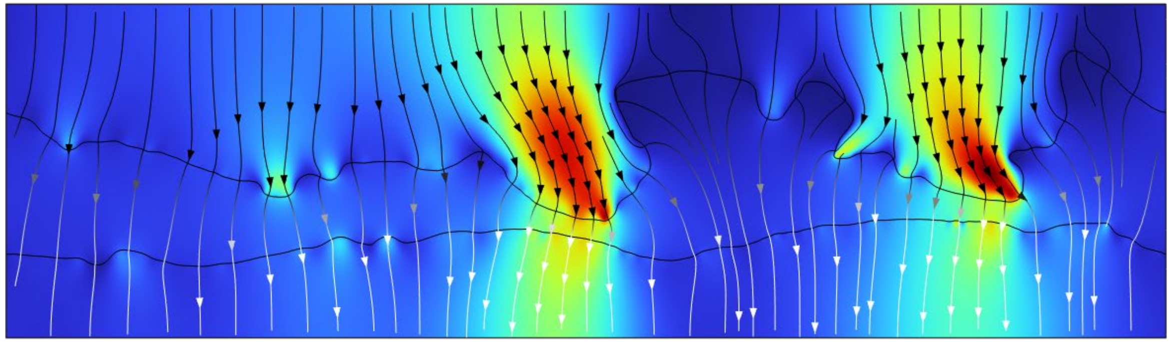

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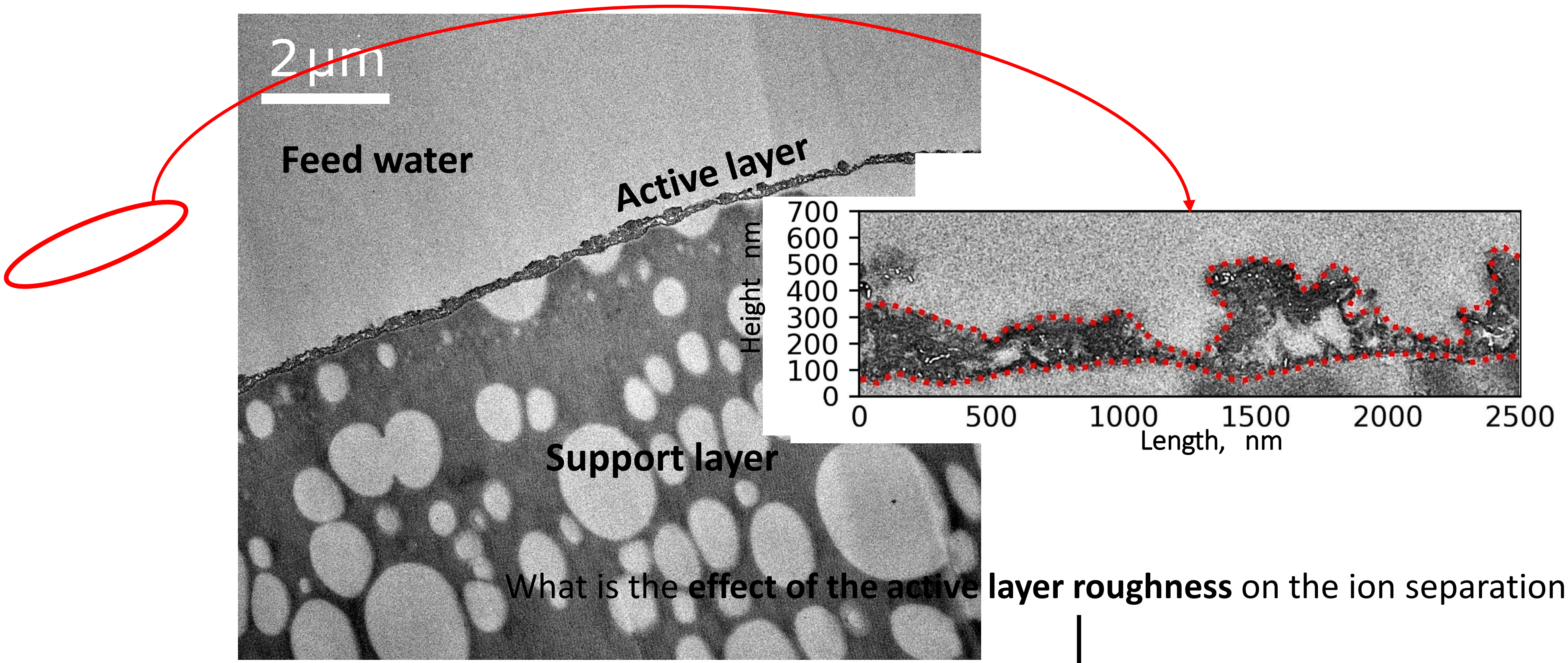
# Describing the problem



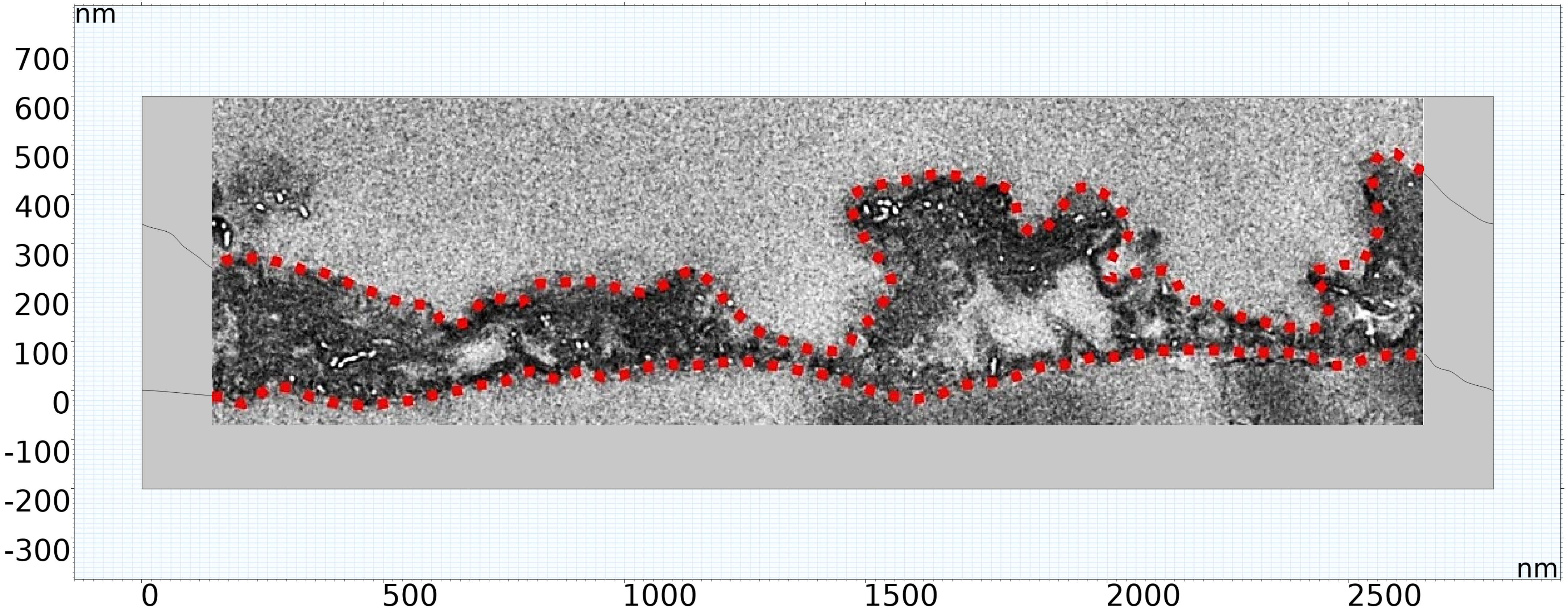

What is the **effect of the active layer roughness** on the ion separation?

↓

Compute $\boldsymbol{Na^+}$ and $\boldsymbol{Cl^-}$ transport through the

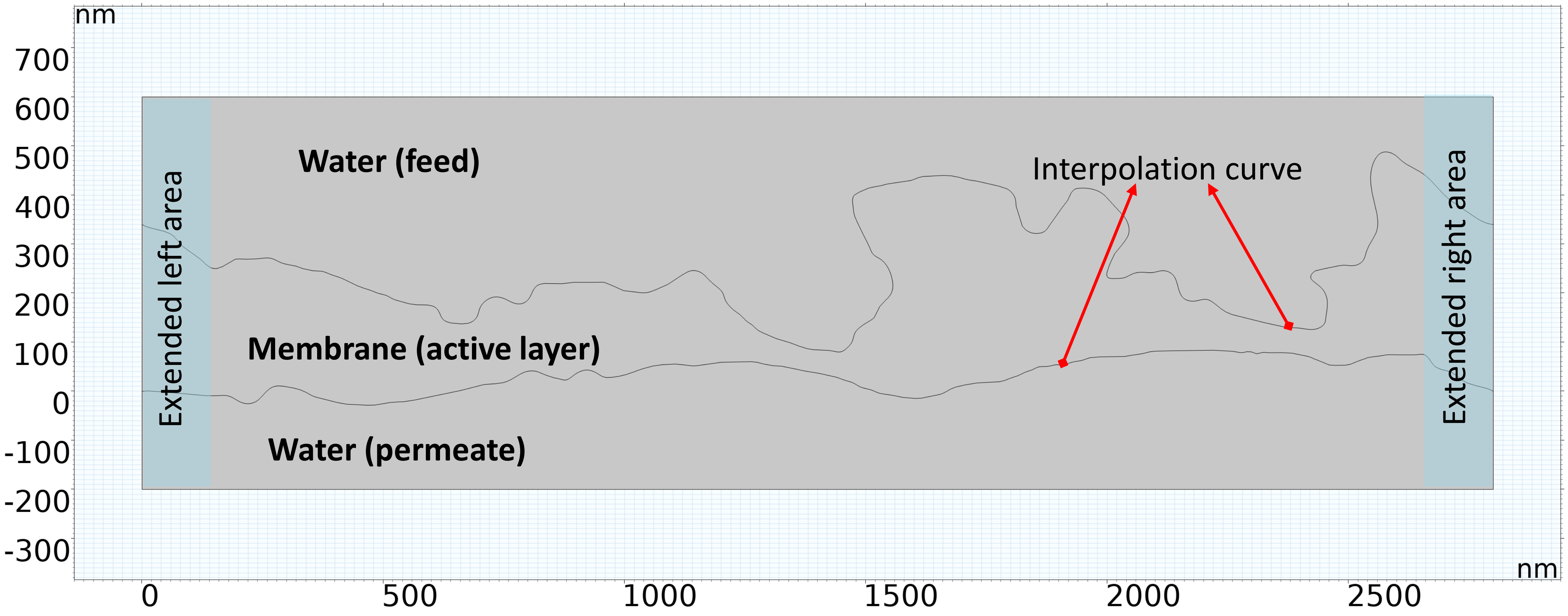
<u>active layer with real 2-D geometry</u>

# Geometry



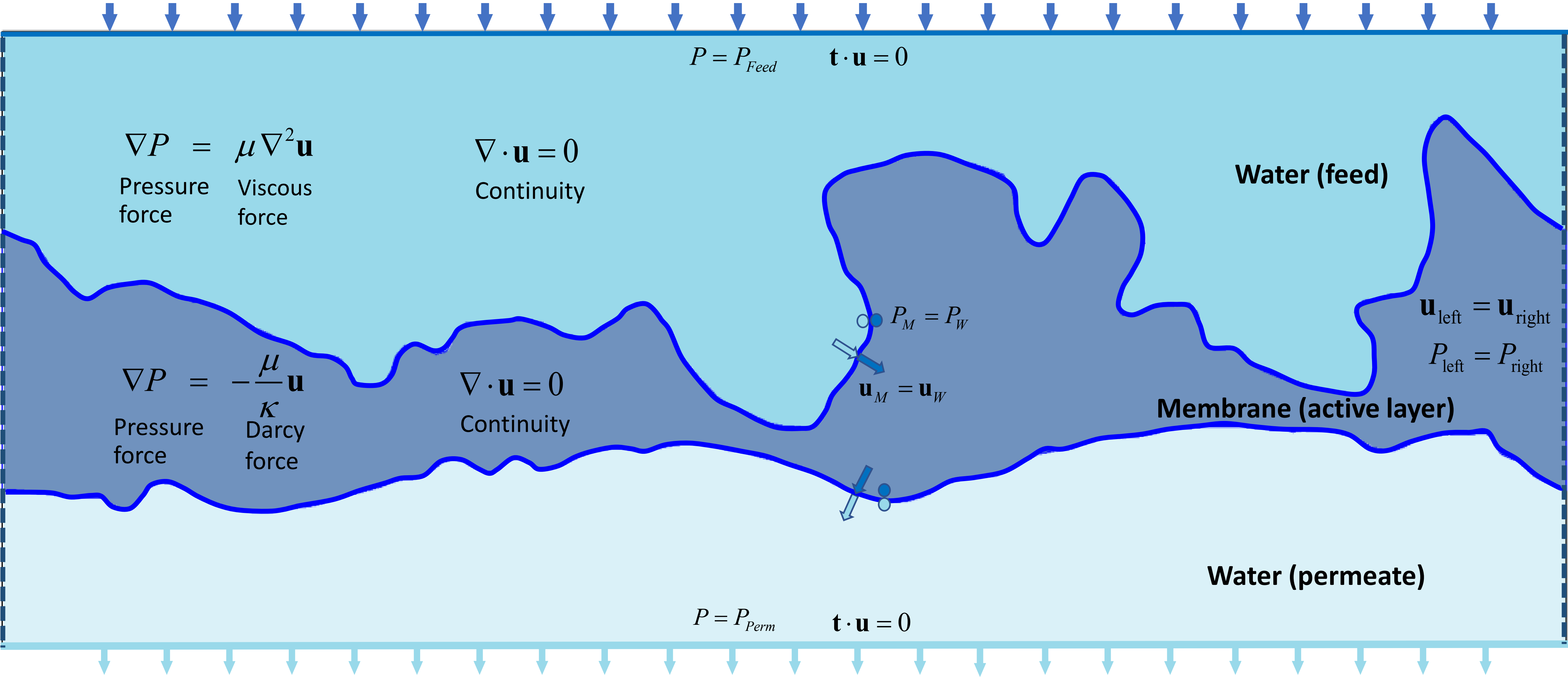
nm
700
600
500
400
300
200
100
0
-100
-200
-300
nm
0
500
1000
1500
2000
2500

# Geometry


nm
700
600
500
400
300
200
100
0
-100
-200
-300
Water (feed)
Interpolation curve
Extended left area
Extended right area
Membrane (active layer)
Water (permeate)
nm
0
500
1000
1500
2000
2500

# Model description. Transport of water: creeping flow

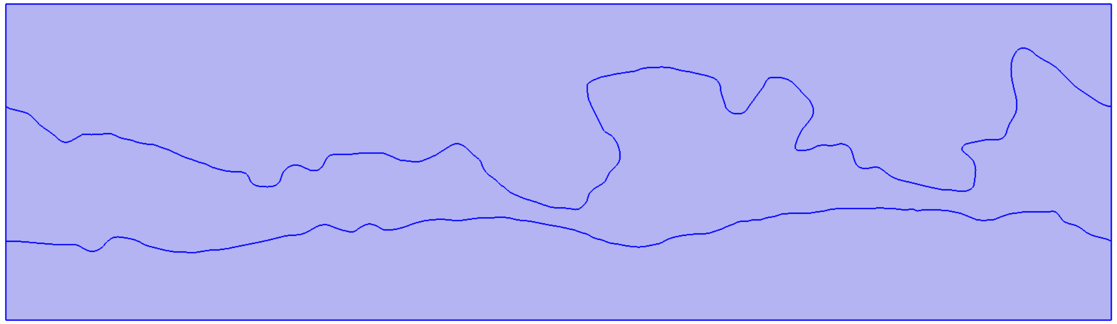
## Transport of water (u, *P*)



# Model implementation. Transport of water: creeping flow

- Creeping Flow *(spf)*
  - Feed and permeate properties
  - Initial Values 1
  - Wall 1
  - Porous Medium
    - Fluid
    - Porous Membrane
  - Inlet pressure feed
  - Outlet pressure permeate
  - Periodic Flow Condition

**Domain selection:** all domains



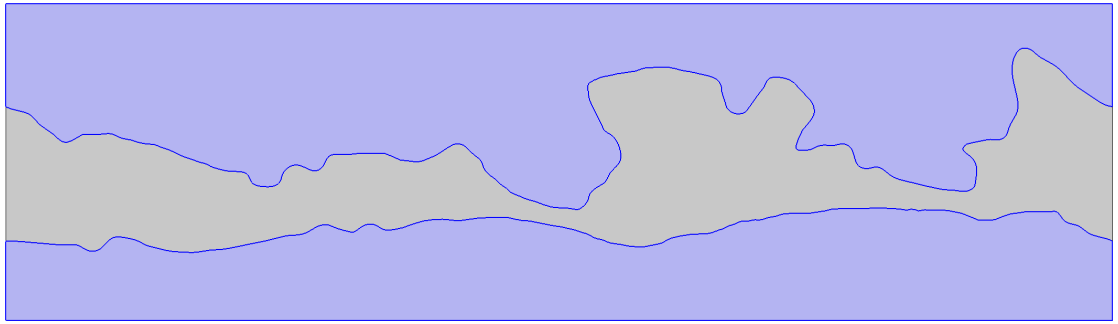
Dependent Variables

| | |
|---|---|
| Velocity field: | u |
| Velocity field components: | u |
| | v |
| | ~~w~~ |
| Pressure: | p |

# Model implementation. Transport of water: creeping flow

- Creeping Flow *(spf)*
  - Feed and permeate properties
  - Initial Values 1
  - Wall 1
  - Porous Medium
    - Fluid
    - Porous Membrane
  - Inlet pressure feed
  - Outlet pressure permeate
  - Periodic Flow Condition

**Domain selection:** feed and permeate domain



Fluid Properties

Density:

$\rho$ User defined

rho = 997 kg/m³

Constitutive relation

Specify dynamic viscosity

$\mu$ User defined

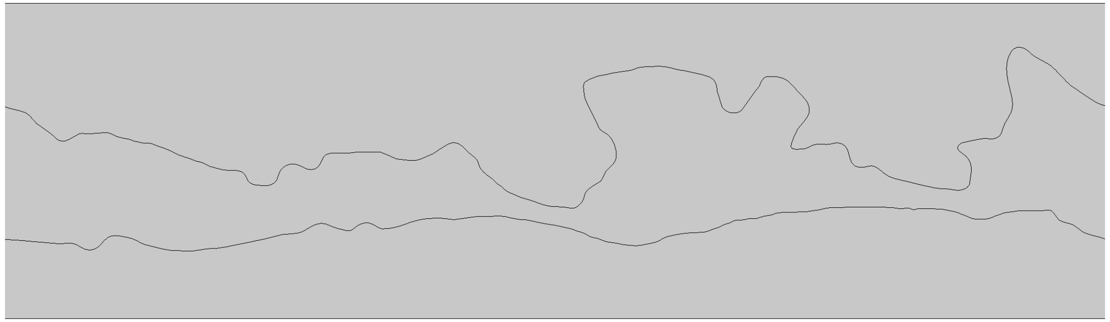
mu = 8.016E-4 Pa·s

# Model implementation. Transport of water: creeping flow

- Creeping Flow *(spf)*
  - Feed and permeate properties
  - Initial Values 1
  - Wall 1
  - Porous Medium
    - Fluid
    - Porous Membrane
  - Inlet pressure feed
  - Outlet pressure permeate
  - Periodic Flow Condition

Wall 1 → Overridden by → Inlet pressure feed, Outlet pressure permeate, Periodic Flow Condition

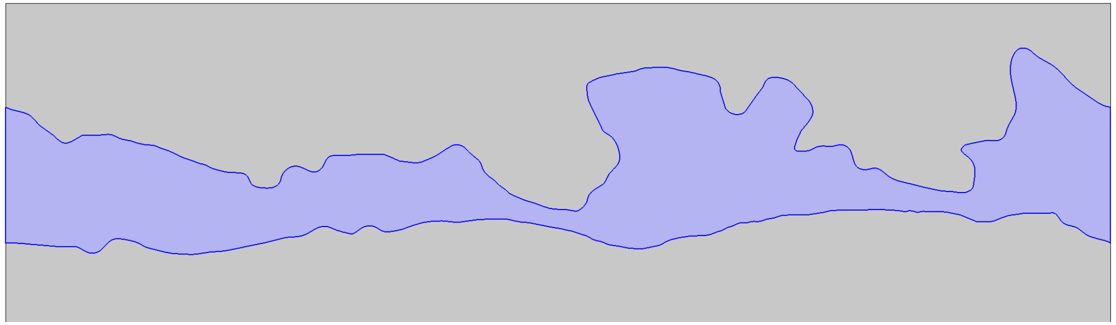
**Boundary selection:** all boundaries were overridden



# Model implementation. Transport of water: creeping flow

- Creeping Flow *(spf)*
  - Feed and permeate properties
  - Initial Values 1
  - Wall 1
  - Porous Medium
    - Fluid
    - Porous Membrane
  - Inlet pressure feed
  - Outlet pressure permeate
  - Periodic Flow Condition

**Domain selection:** membrane



Matrix Properties

Porosity:

$\epsilon_p$ User defined

epse = 0.05 1

Permeability model:

Permeability

Permeability:

$\kappa$ User defined

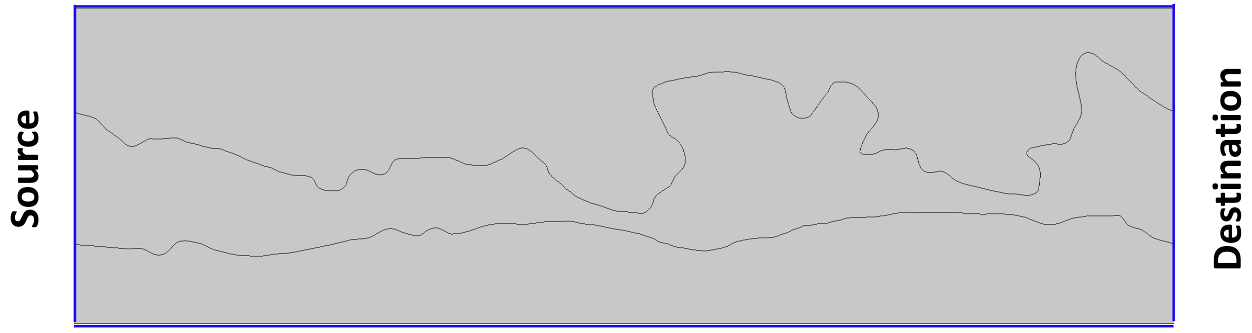
Kperm_mem = 5.344E-22 $m^2$

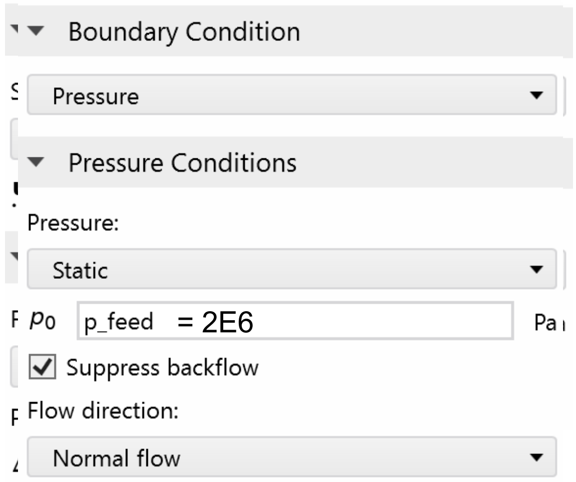
Isotropic

# Model implementation. Transport of water: creeping flow

- Creeping Flow *(spf)*
  - Feed and permeate properties
  - Initial Values 1
  - Wall 1
  - Porous Medium
    - Fluid
    - Porous Membrane
  - Inlet pressure feed
  - Outlet pressure permeate
  - Periodic Flow Condition

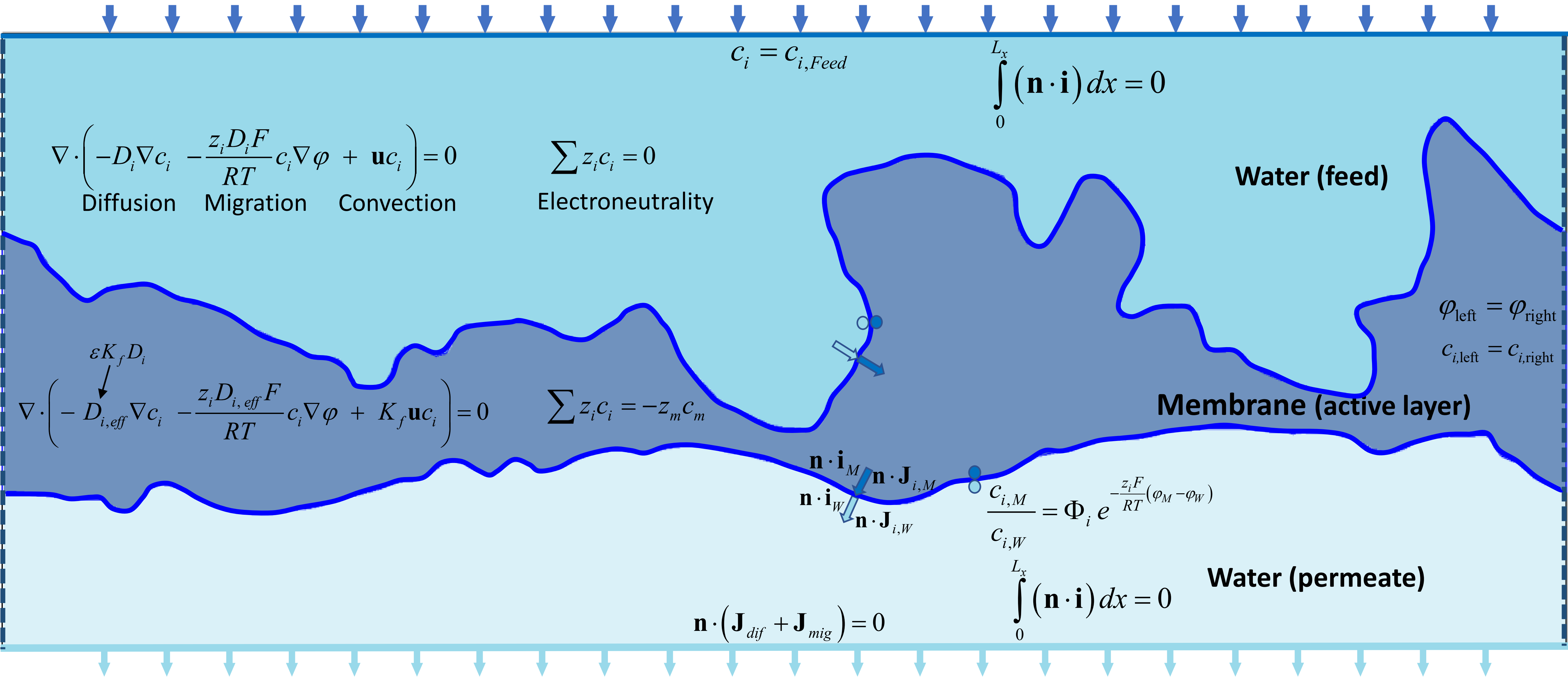
**Boundaries selection:** external boundaries



# Model description. Transport of species: tertiary current distribution, Nernst-Plank

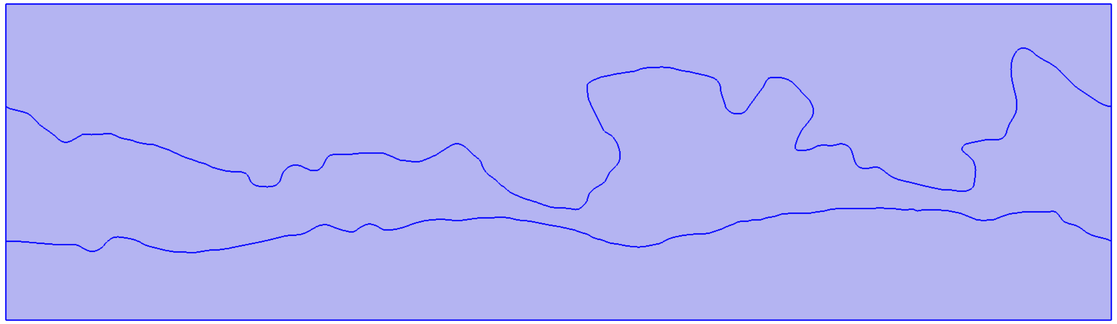
## Transport of *$Na^+$* and *$Cl^-$* ($c_i$, φ)



# Model implementation. Transport of species: tertiary current distribution, Nernst-Plank

- Tertiary Current Distribution, Nernst-Planck *(tcd)*
  - Species Charges
  - Electrolyte Liquid (Feed and Permeate)
  - No Flux
  - Insulation
  - Initial Values Membrane
  - Initial Values Feed
  - Initial Values Permeate
  - Ion Exchange Membrane
    - Equation View
  - Concentration feed
  - Only convection on permate
  - Periodic Condition
  - Electrolyte Current Feed
  - Electrolyte Current Permeate
  - Electrolyte Potential in one point

**Domain selection:** all domains



**Dependent Variables**

| | |
|---|---|
| Number of species: | 2 |
| Concentrations: | c_cl |
| | c_na |
| Electrolyte potential: | V |
| Electric potential: | dummy |

# Transport of species: tertiary current distribution, Nernst-Plank

- Tertiary Current Distribution, Nernst-Planck *(tcd)*
  - Species Charges
  - Electrolyte Liquid (Feed and Permeate)
  - No Flux
  - Insulation
  - Initial Values Membrane
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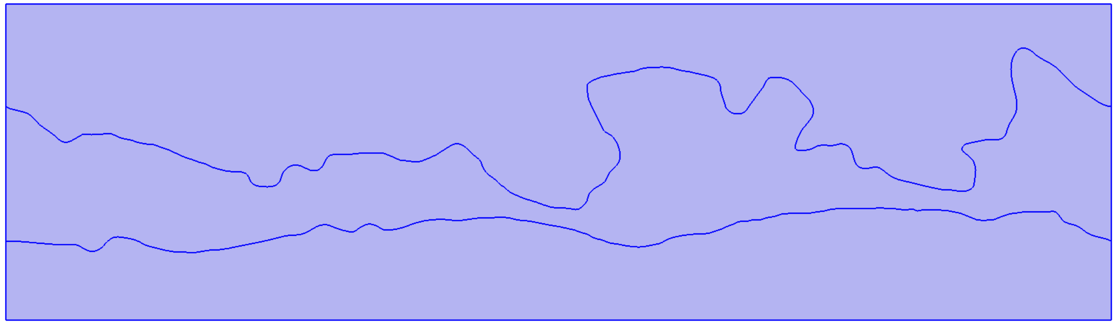
  - Periodic Condition
  - Electrolyte Current Feed
  - Electrolyte Current Permeate
  - Electrolyte Potential in one point

**Domain selection:** all domains



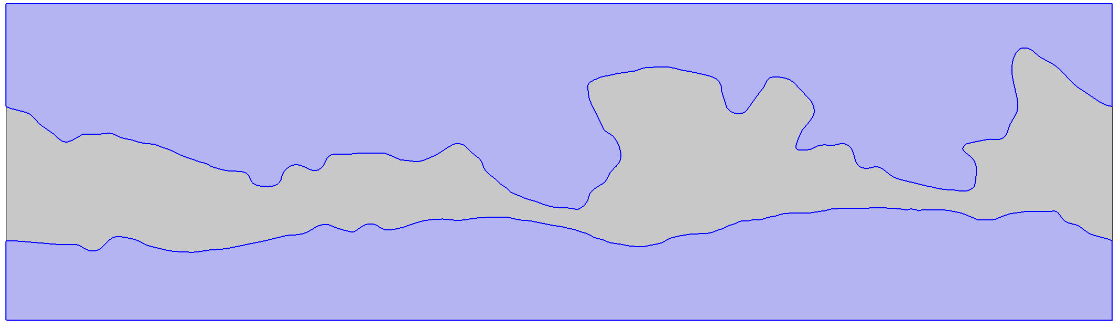
**Charge**

| | | |
|---|---|---|
| $z_{c\_cl}$ | z_cl = -1 | 1 |
| $z_{c\_na}$ | z_na = 1 | 1 |

# Transport of species: tertiary current distribution, Nernst-Plank

- Tertiary Current Distribution, Nernst-Planck *(tcd)*
  - Species Charges
  - Electrolyte Liquid (Feed and Permeate)
  - No Flux
  - Insulation
  - Initial Values Membrane
  - Initial Values Feed
  - Initial Values Permeate
  - Ion Exchange Membrane
    - Equation View
  - Concentration feed
  - Only convection on permate
  - Periodic Condition
  - Electrolyte Current Feed
  - Electrolyte Current Permeate
  - Electrolyte Potential in one point

**Domain selection:** feed and permeate



**Diffusion**

Material:

None

Diffusion coefficient:

$D_{c\_cl}$ User defined

D_cl = 2.032E-9 $m^2/s$

Isotropic

Diffusion coefficient:

$D_{c\_na}$ User defined

D_na = 1.334E-9 $m^2/s$

Isotropic

**Migration in Electric Field**

Mobility:

Nernst-Einstein relation

$$u_{m,i} = \frac{D_i}{RT}$$

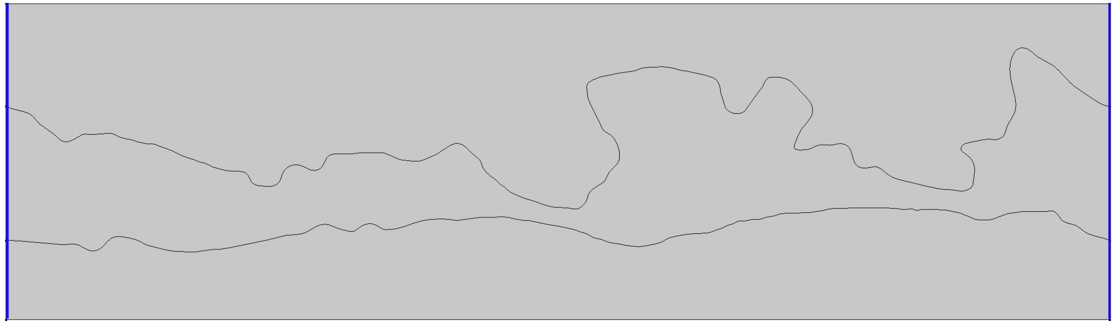
**Convection**

Velocity field:

**u** Velocity field (spf)

- Tertiary Current Distribution, Nernst-Planck *(tcd)*
  - Species Charges
  - Electrolyte Liquid (Feed and Permeate)
  - No Flux
  - Insulation
  - Initial Values Membrane
  - Initial Values Feed
  - Initial Values Permeate
  - Ion Exchange Membrane
    - Equation View
  - Concentration feed
  - Only convection on permate
  - Periodic Condition
  - Electrolyte Current Feed
  - Electrolyte Current Permeate
  - Electrolyte Potential in one point

**Boundaries selection:** only lateral



**Equation**

Show equation assuming:

Study 1: Flow and Solutes 2D, Statior

$$-\mathbf{n}\cdot(\mathbf{J}_i+\mathbf{u}c_i)=0$$

**Convection**

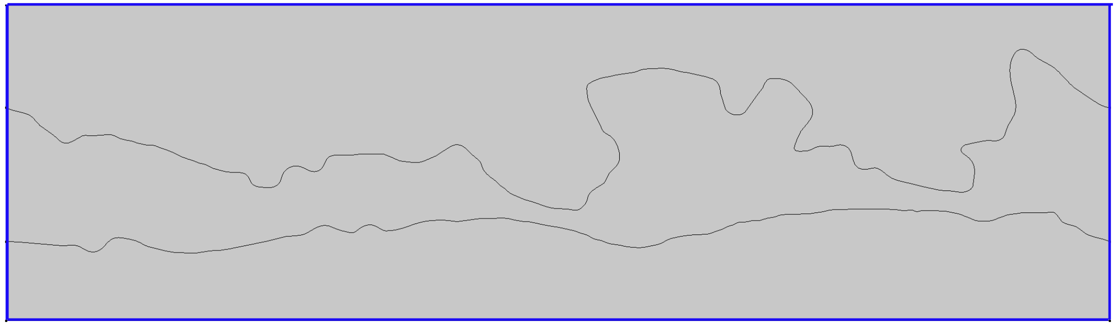
☑ Include

# Transport of species: tertiary current distribution, Nernst-Plank

- Tertiary Current Distribution, Nernst-Planck *(tcd)*
  - Species Charges
  - Electrolyte Liquid (Feed and Permeate)
  - No Flux
  - Insulation
  - Initial Values Membrane
  - Initial Values Feed
  - Initial Values Permeate
  - Ion Exchange Membrane
    - Equation View
  - Concentration feed
  - Only convection on permate
  - Periodic Condition
  - Electrolyte Current Feed
  - Electrolyte Current Permeate
  - Electrolyte Potential in one point

Insulation → Overridden by → Periodic Condition, Electrolyte Current Feed, Electrolyte Current Permeate

**Boundaries selection:** external boundaries



# Transport of species: tertiary current distribution, Nernst-Plank

- Tertiary Current Distribution, Nernst-Planck *(tcd)*
  - Species Charges
  - Electrolyte Liquid (Feed and Permeate)
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  - Initial Values Permeate
  - Ion Exchange Membrane
    - Equation View
  - Concentration feed
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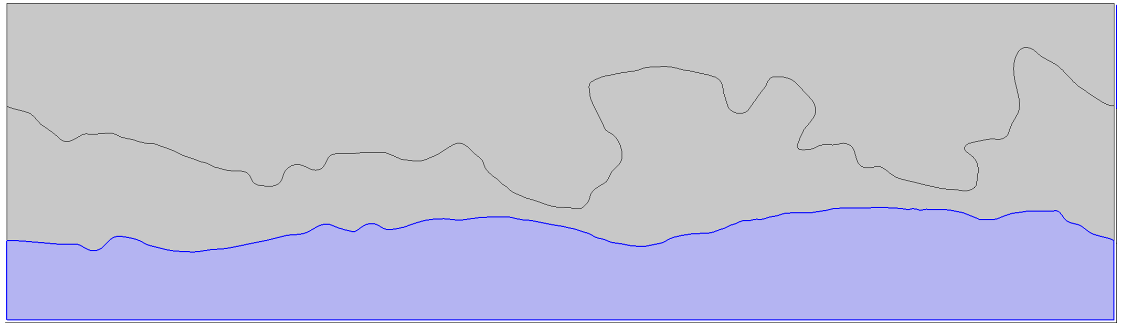
  - Periodic Condition
  - Electrolyte Current Feed
  - Electrolyte Current Permeate
  - Electrolyte Potential in one point

**Domain selection:** all domains

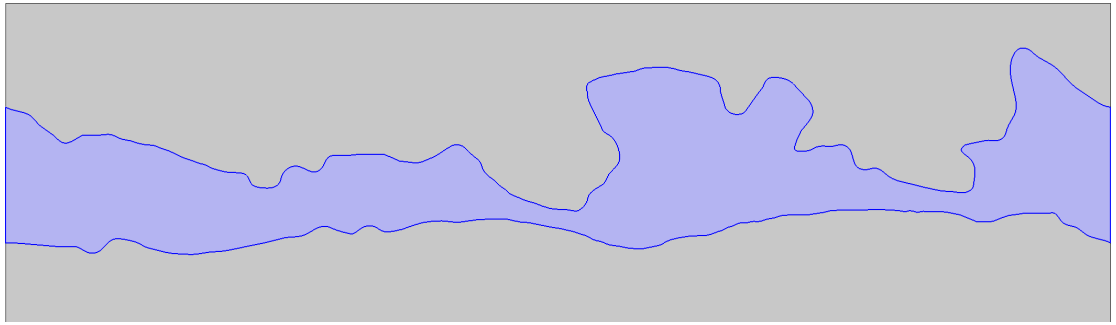
Imposed values on each domain



# Transport of species: tertiary current distribution, Nernst-Plank

- Tertiary Current Distribution, Nernst-Planck *(tcd)*
  - Species Charges
  - Electrolyte Liquid (Feed and Permeate)
  - No Flux
  - Insulation
  - Initial Values Membrane
  - Initial Values Feed
  - Initial Values Permeate
  - Ion Exchange Membrane
    - Equation View
  - Concentration feed
  - Only convection on permate
  - Periodic Condition
  - Electrolyte Current Feed
  - Electrolyte Current Permeate
  - Electrolyte Potential in one point

**Domain selection:** membrane



**Ion Exchange Membrane Properties**

Fixed space charge:

$\rho_{fix}$ F_const*z_mem*c_mem = -1.93E5 C/m³

☑ Apply Donnan boundary conditions

**Convection**

Velocity field:

**u** User defined

| | | |
|---|---|---|
| u*Kf = U*0.2 | x | m/s |
| v*Kf = V*0.2 | y | |

**Diffusion**

Material:

None

Diffusion coefficient:

$D_{c\_cl}$ User defined

D_cl*epse*Kf = 2.032E-11 m²/s

Isotropic

Diffusion coefficient:

$D_{c\_na}$ User defined

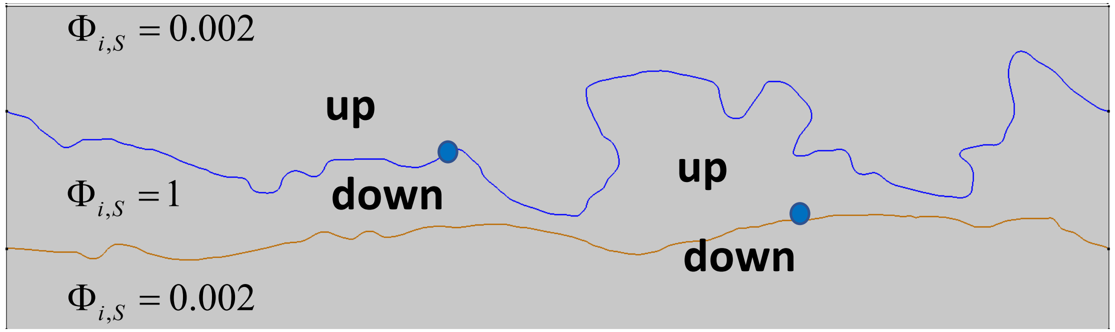
D_cl*epse*Kf = 1.334E-11 m²/s

Isotropic

# Transport of species: tertiary current distribution, Nernst-Plank

- Tertiary Current Distribution, Nernst-Planck *(tcd)*
  - Species Charges
  - Electrolyte Liquid (Feed and Permeate)
  - No Flux
  - Insulation
  - Initial Values Membrane
  - Initial Values Feed
  - Initial Values Permeate
  - Ion Exchange Membrane
    - Equation View
  - Concentration feed
  - Only convection on permate
  - Periodic Condition
  - Electrolyte Current Feed
  - Electrolyte Current Permeate
  - Electrolyte Potential in one point

**Constraint on the interface (boundary) feed/active layer**



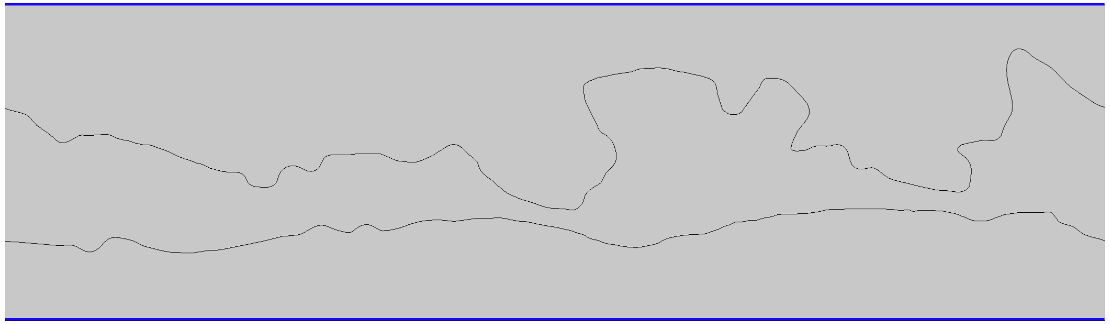

- Concentration on the boundary (feed/active layer)

$$\mathrm{up}(\Phi_{i,S}\, c_i) \exp\left( -\frac{z_i F}{RT}(\varphi_M - \varphi_W) \right)\Bigg|_{\mathrm{up}} - \mathrm{down}(\Phi_{i,S}\, c_i) \exp\left( -\frac{z_i F}{RT}(\varphi_M - \varphi_W) \right)\Bigg|_{\mathrm{down}}$$

# Transport of species: tertiary current distribution, Nernst-Plank

- Tertiary Current Distribution, Nernst-Planck *(tcd)*
  - Species Charges
  - Electrolyte Liquid (Feed and Permeate)
  - No Flux
  - Insulation
  - Initial Values Membrane
  - Initial Values Feed
  - Initial Values Permeate
  - Ion Exchange Membrane
    - Equation View
  - Concentration feed
  - Only convection on permate
  - Periodic Condition
  - Electrolyte Current Feed
  - Electrolyte Current Permeate
  - Electrolyte Potential in one point

**Boundary selection:** inlet and outlet



**Equation**

Show equation assuming:

Study 1: Flow and Solutes 2D, Stationary solı

$c_i = c_{0,i}$

**Concentration**

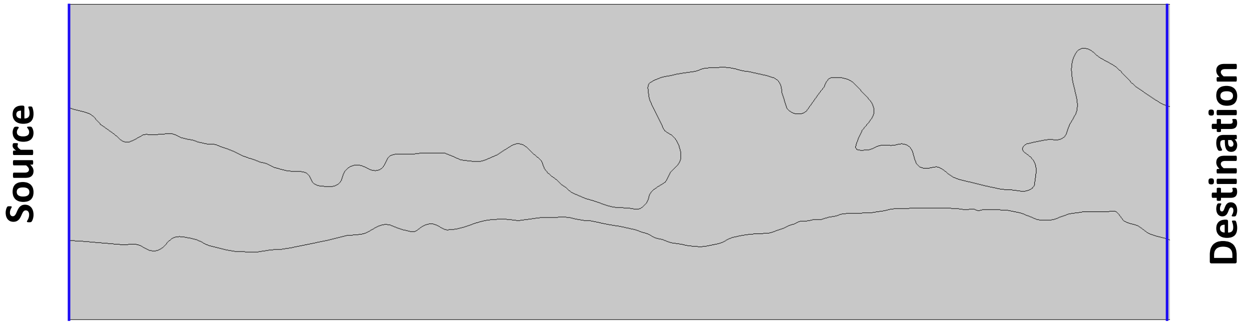
☑ Species c_cl

$c_{0,c\_cl}$ cf_cl = 500 mol/m$^3$

# Transport of species: tertiary current distribution, Nernst-Plank

- Tertiary Current Distribution, Nernst-Planck *(tcd)*
  - Species Charges
  - Electrolyte Liquid (Feed and Permeate)
  - No Flux
  - Insulation
  - Initial Values Membrane
  - Initial Values Feed
  - Initial Values Permeate
  - Ion Exchange Membrane
    - Equation View
  - Concentration feed
  - Only convection on permate
  - Periodic Condition
  - Electrolyte Current Feed
  - Electrolyte Current Permeate
  - Electrolyte Potential in one point

**Boundary selection:** only lateral




Equation

Show equation assuming:

Study 1: Flow and Solutes 2D, Laminar Flow

$\phi_{l\text{src}} = \phi_{l\text{dst}}$

$c_{i,\text{src}} = c_{i,\text{dst}}$

$-\mathbf{n}_{\text{src}} \cdot (\mathbf{J}_i + \mathbf{u}c_i)_{\text{src}} = \mathbf{n}_{\text{dst}} \cdot (\mathbf{J}_i + \mathbf{u}c_i)_{\text{dst}}$

Periodic Condition

☑ Apply for electrolyte phase

Potential difference:

$\phi_{l,\text{src}} - \phi_{l,\text{dst}}$ 0

☐ Apply for electrode phase

# Transport of species: tertiary current distribution, Nernst-Plank

- Tertiary Current Distribution, Nernst-Planck *(tcd)*
  - Species Charges
  - Electrolyte Liquid (Feed and Permeate)
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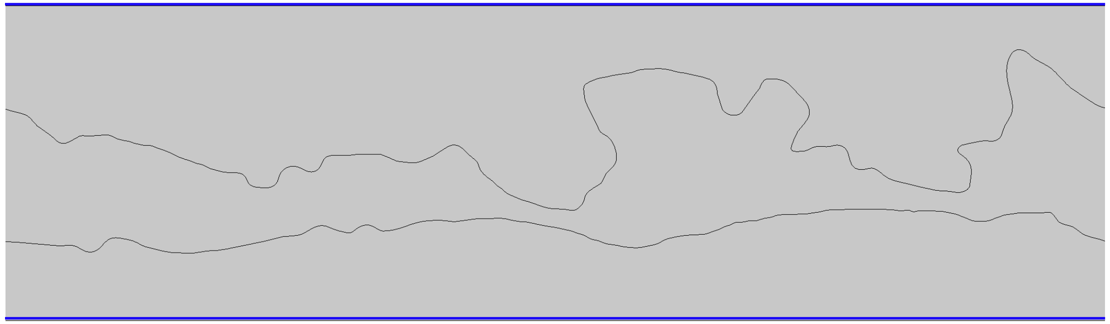
  - Periodic Condition
  - Electrolyte Current Feed
  - Electrolyte Current Permeate
  - Electrolyte Potential in one point

**Boundary selection:** feed and permeate



**Equation**

Show equation assuming:

Study 1: Flow and Solutes 2D, Laminar Flow

$$-\int_{\partial\Omega} \mathbf{i}_l \cdot \mathbf{n} dl = i_{l,average} \int_{\partial\Omega} dl$$

**Electrolyte Current**

Average current density

Inward electrolyte current density:

$i_{l,average}$ 0 A/m²

Boundary electrolyte potential initial value:

$\phi_{l,bnd,init}$ 1e-6[V] V

# Solution strategy

**Build model**

Creeping flow

Tertiary current distribution

**Step 1**

Solving (*u, v, p*)

Solution (*u*, v, *p*)

**Step 2**

Solving (*c_na, c_cl, V*)

**Auxiliary sweep**

c_mem = -0.01 [mM]

↓ Solution

c_mem = -1 [mM]

↓ Solution

c_mem = -10 [mM]

↓ Solution

⋮

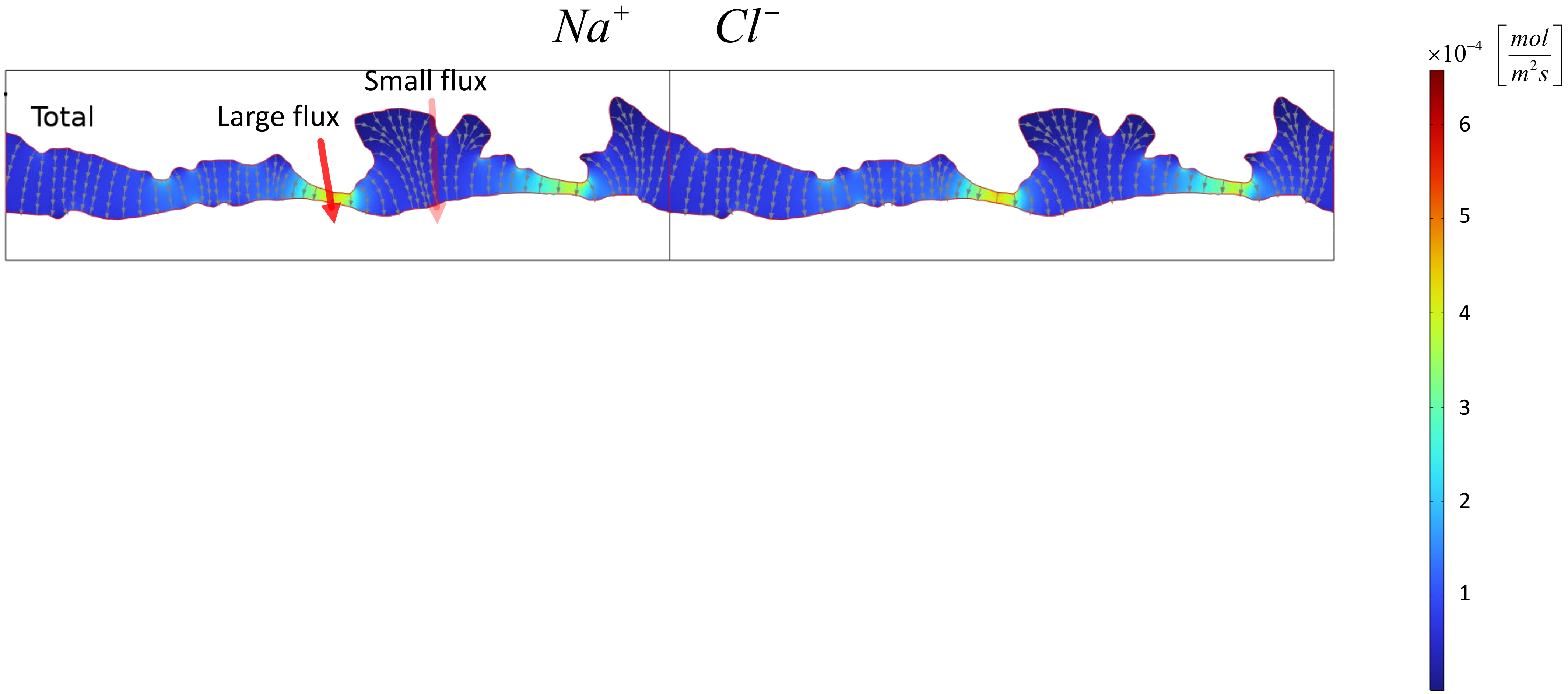
c_mem = -200 [mM]

**Results**

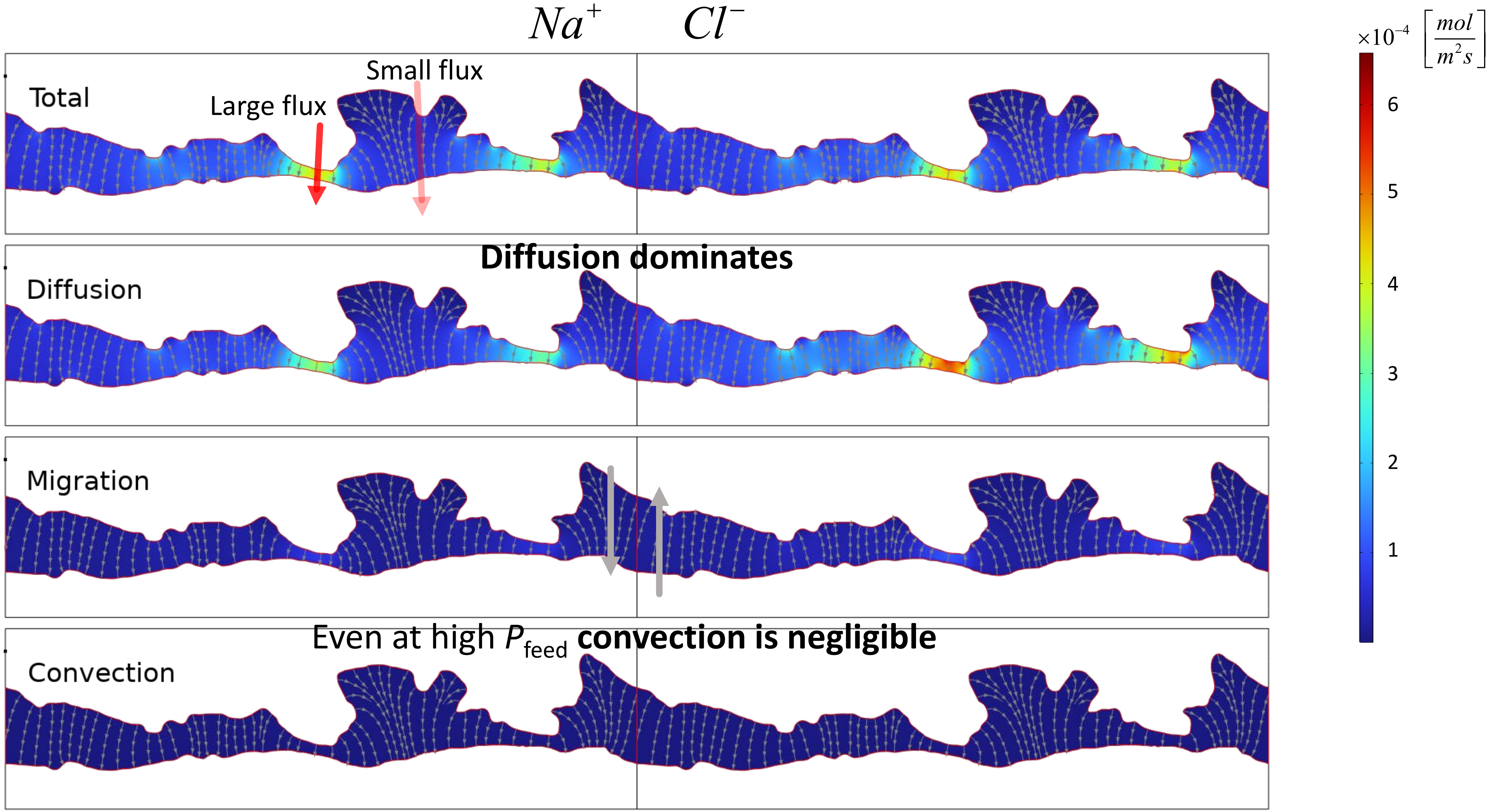
**Solution**

**(*c_na, c_cl, V, u, v, p*)**

# 2-D Model. Results - Fluxes in uncharged membrane (-0.01 mM)



# 2-D Model. Results - Fluxes in uncharged membrane (-0.01 mM)

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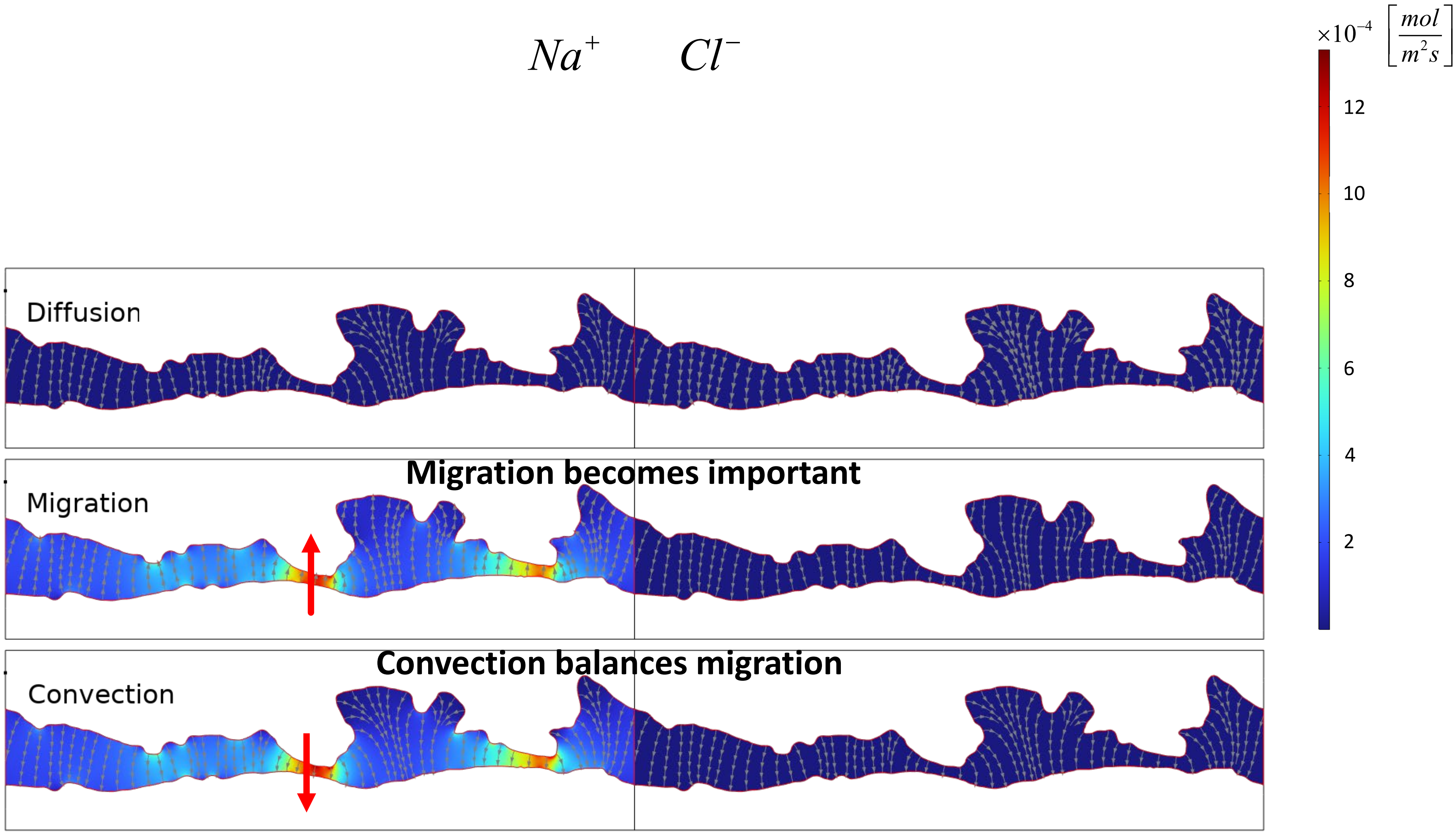
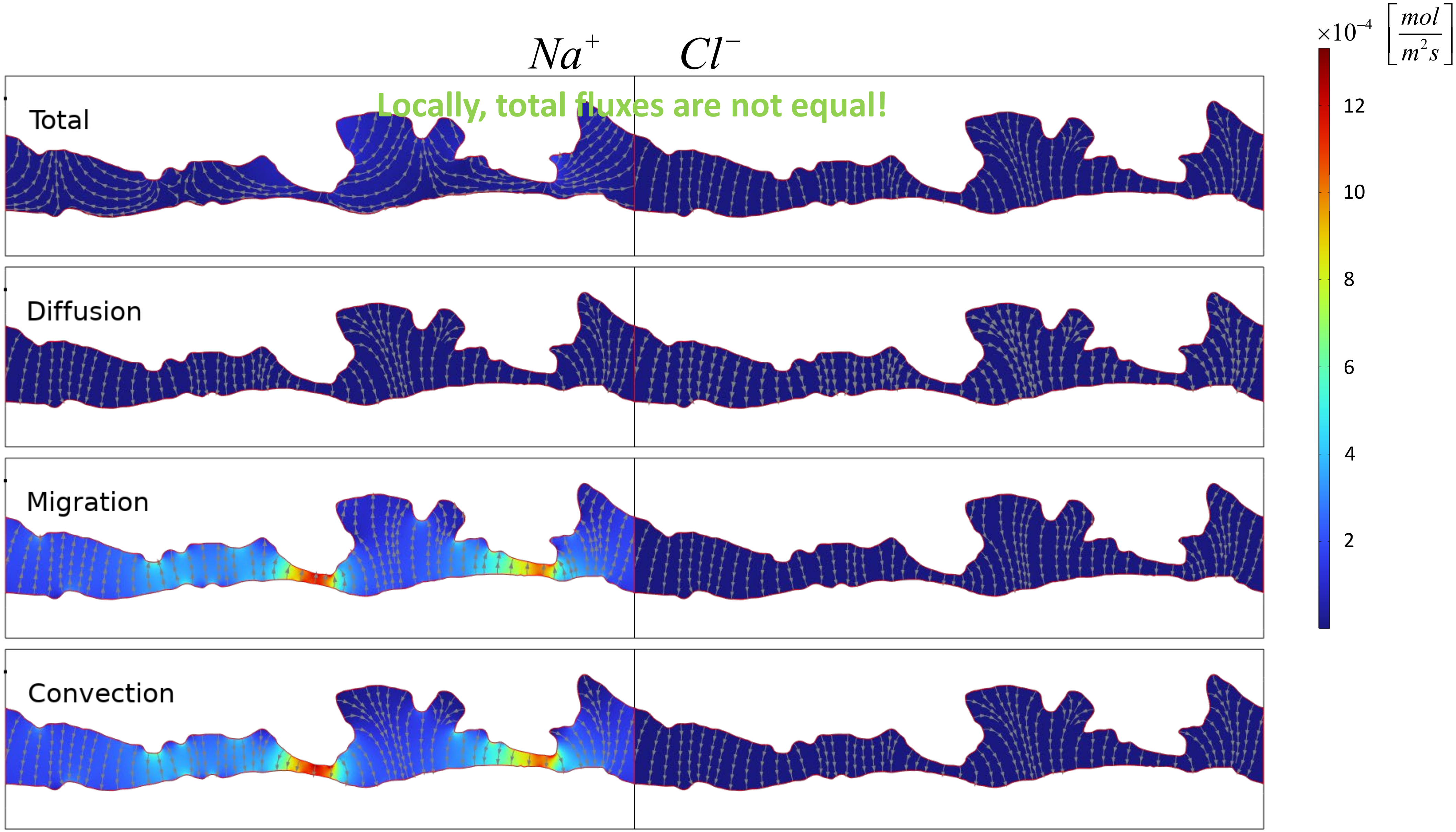
# 2-D Model. Results - Fluxes in charged membrane (-200 mM)

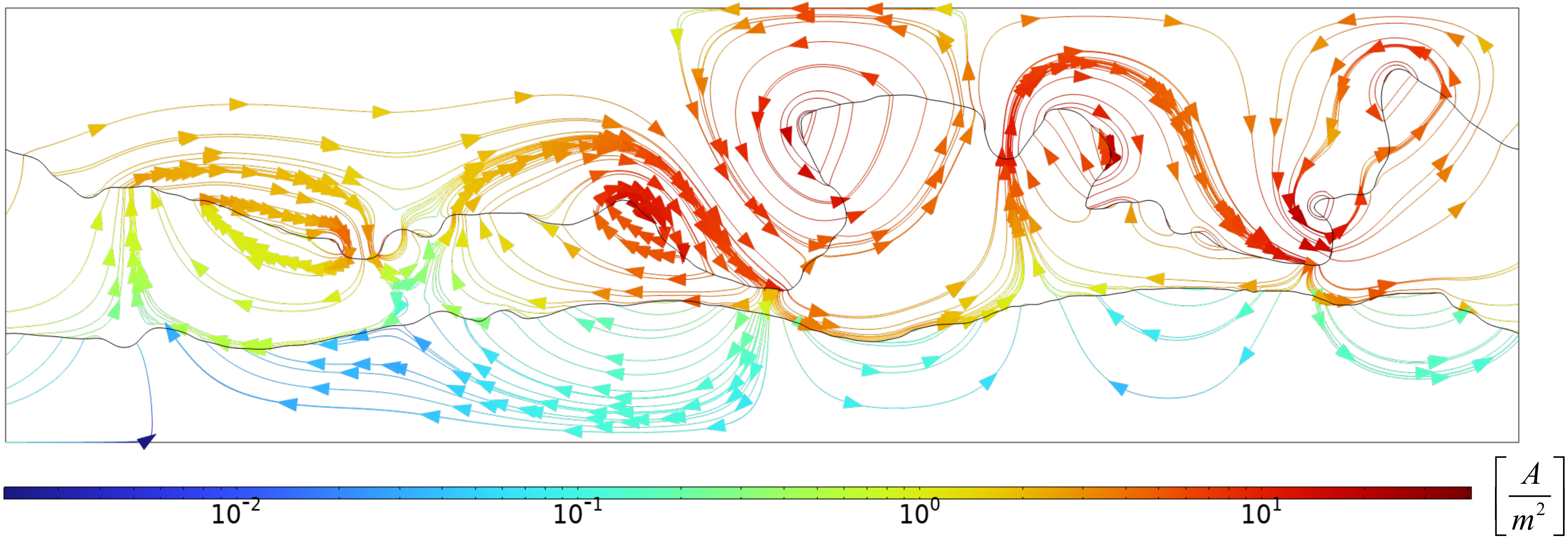


# 2-D Model. Results - Fluxes in charged membrane (-200 mM)



# 2-D Model. Ionic current density

**There are ionic currents in the 2-D membrane**




**Closed current circuits (insulation)**

Desalination 565 (2023) 116876

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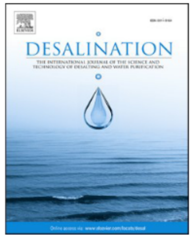



# Two-dimensional model of ion transport in composite membranes active layers with TEM-scanned morphology

Fernan David Martinez-Jimenez [a,*], Valentina-Elena Musteata [b], Santiago Cespedes-Zuluaga [a], Bastiaan Blankert [a], Cristian Picioreanu [a]

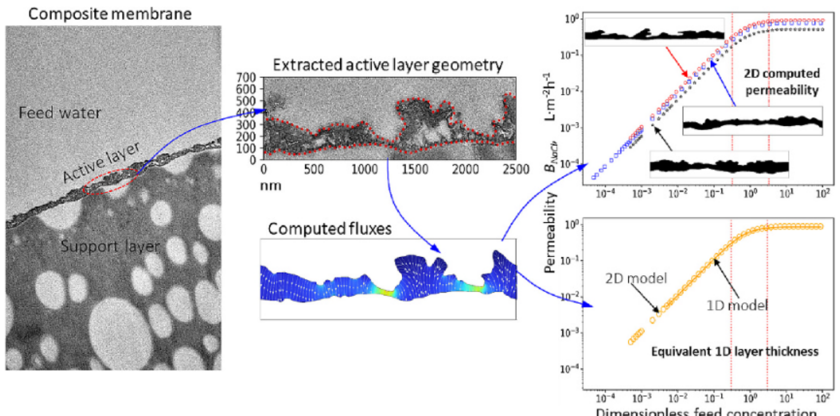
[a] *Environmental Science & Engineering Program (EnSE), Biological and Environmental Science and Engineering Division (BESE) and Water Desalination and Reuse Center (WDRC), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia*

[b] *KAUST Core Labs, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia*

## HIGHLIGHTS

- A 2D solution-friction model reveals new effects of active layer on ion permeability.
- Ionic current loops may develop inside and around the active layer.
- Different transport mechanisms are dominant in different conditions.
- An equivalent 1D active layer thickness leads to the same permeability as in 2D.
- The equivalent thickness can be computed from images of the active layer.

## GRAPHICAL ABSTRACT

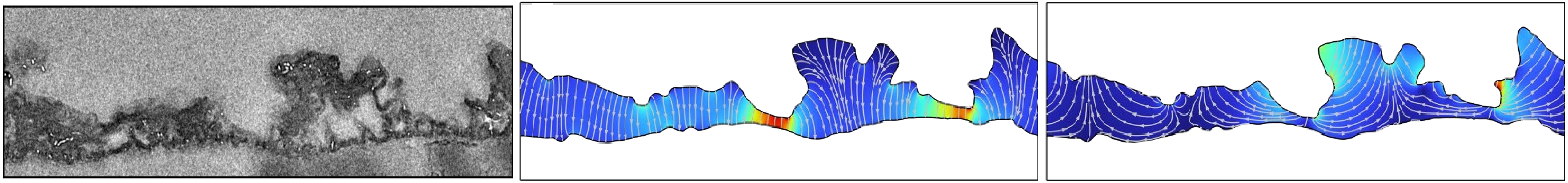


# Key messages

**1.** The response of the 2-D model to variations in flux and salinity can be represented by a 1-D model using an appropriate *equivalent membrane thickness.*

**2.** We provided a method to compute the *equivalent membrane thickness* from images of membrane active layer.

**3.** The 2-D model revealed *the possibility of circular ionic currents*.



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جامعة الملك عبدالله للعلوم والتقنية
King Abdullah University of Science and Technology
Water Desalination and Reuse Center

# 6TH PHYSICS OF MEMBRANE PROCESSES WORKSHOP

**November 13 - 16 , 2023**

King Abdullah University of Science and Technology (KAUST), Saudi Arabia

PMP PHYSICS OF MEMBRANE PROCESSES

جامعة الملك عبدالله للعلوم والتقنية
King Abdullah University of Science and Technology

**Scan the code to learn more about the workshop**

**wdrc.conferences@kaust.edu.sa**

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- Fundamentals of membrane transport processes
- Theory and computer applications in **COMSOL**
- Experimental aspects of transport phenomena in membranes, from small-scale to system-level

# Thank you

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**Article**

**PMP 6th conference**

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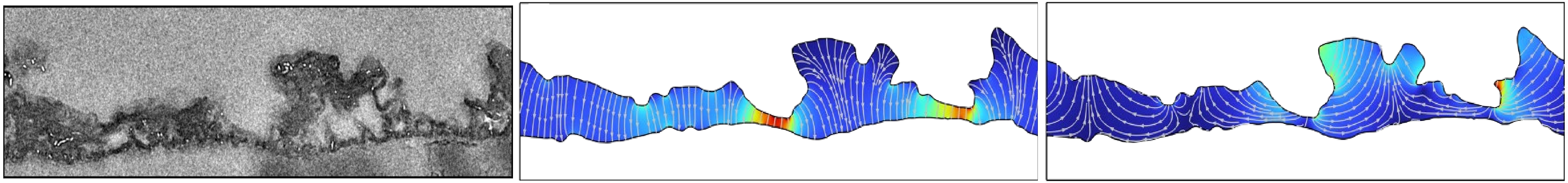
# SUPPLEMENTARY INFORMATION



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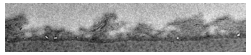
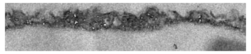
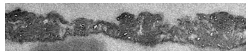
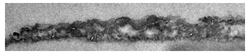
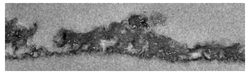
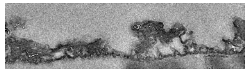
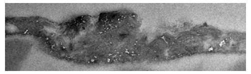
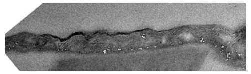
# Ideal 1D and equivalent active layer thickness L3, for all active layer geometries

| **Active layer** | **Geometry** | **Average 2D thickness $L_1$, nm** | **Relative standard deviation of $L_1$, $\sigma/L_1$** | **Reference 1D thickness $L_B$, nm** | **Reference 1D thickness $L_A$, nm** | **Equivalent thickness $L_3$, nm** |
|---|---|---|---|---|---|---|
|  | **a** | 181 | 0.29 | 149 | 154 | 149 |
|  | **b** | 175 | 0.35 | 125 | 130 | 131 |
|  | **c** | 160 | 0.27 | 128 | 132 | 128 |
|  | **d** | 270 | 0.27 | 224 | 231 | 220 |
|  | **e** | 198 | 0.23 | 165 | 170 | 165 |
|  | **f** | 250 | 0.38 | 177 | 183 | 178 |
|  | **g** | 221 | 0.51 | 129 | 133 | 129 |
|  | **h** | 324 | 0.40 | 239 | 247 | 239 |
|  | **i** | 214 | 0.34 | 179 | 185 | 180 |

# Feed and permeate:

$$\nabla \cdot \left( -D_i \nabla c_i - \frac{z_i D_i F}{RT} c_i \nabla \varphi + \mathbf{u} c_i \right) = 0$$

$$\mathbf{J}_i = -D_i \nabla c_i - \frac{z_i D_i F}{RT} c_i \nabla \varphi + \mathbf{u} c_i$$

$$\mathbf{i} = F \sum_i z_i \mathbf{J}_i$$

$$\sum_i z_i c_i = 0$$

# Membrane:

$$\nabla \cdot \left( -D_{i,eff} \nabla c_i \;\; - \frac{z_i D_{i,eff} F}{RT} c_i \nabla \varphi \; + K_f \mathbf{u} c_i \right) = 0$$

$$\mathbf{J}_i = -D_{i,eff} \nabla c_i \;\; - \frac{z_i D_{i,eff} F}{RT} c_i \nabla \varphi \; + K_f \mathbf{u} c$$

$$\mathbf{i} = F \sum_i z_i \mathbf{J}_i$$

$$z_M c_M + \sum_i z_i c_i = 0$$

# Brinkman

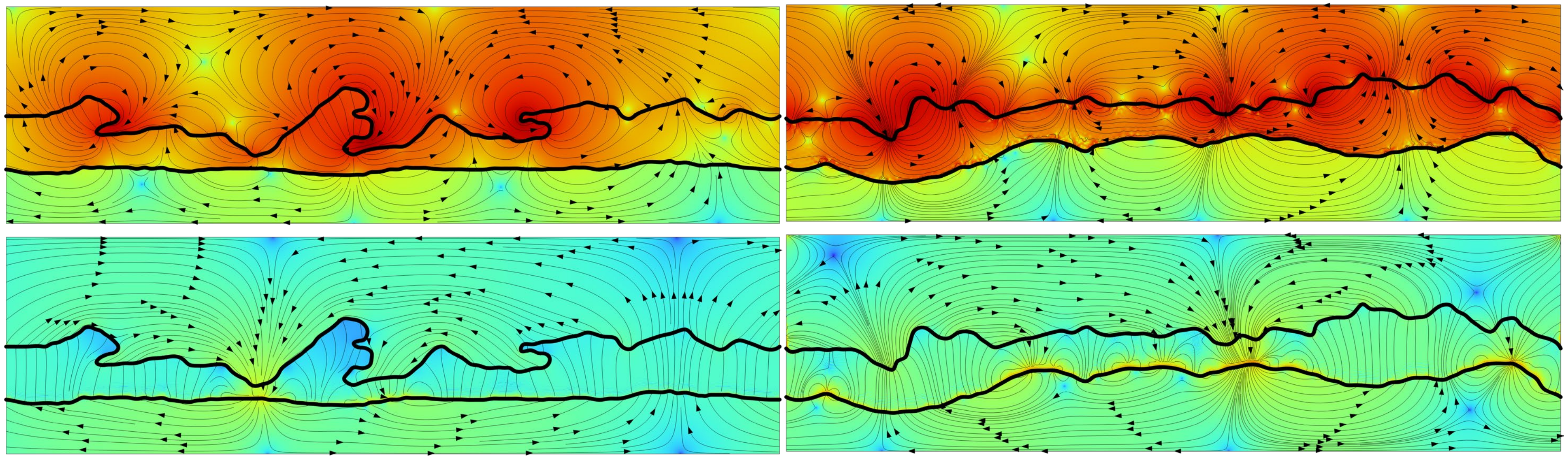
$$\underbrace{\frac{1}{\varepsilon^2}\rho(\mathbf{u}\cdot\nabla)\mathbf{u}}_{\text{Inertial force}} = -\underbrace{\nabla p}_{\text{Pressure force}} + \underbrace{\frac{\mu}{\varepsilon}\nabla^2\mathbf{u}}_{\text{Viscous force}} - \underbrace{\frac{\mu}{\kappa}\mathbf{u}}_{\text{Darcy force}} + \underbrace{RT\sum_i \frac{c_i}{D_i}(\mathbf{u}_i - \mathbf{u})}_{\text{Electroosmotic force}}$$

$$\frac{1}{\varepsilon^2}\rho(\mathbf{u}\cdot\nabla)\mathbf{u} = -\nabla p + \frac{\mu}{\varepsilon}\nabla^2\mathbf{u} - \frac{\mu}{\kappa}\mathbf{u} + RT\sum_i \frac{c_i}{D_i}(\mathbf{u}_i - \mathbf{u})$$

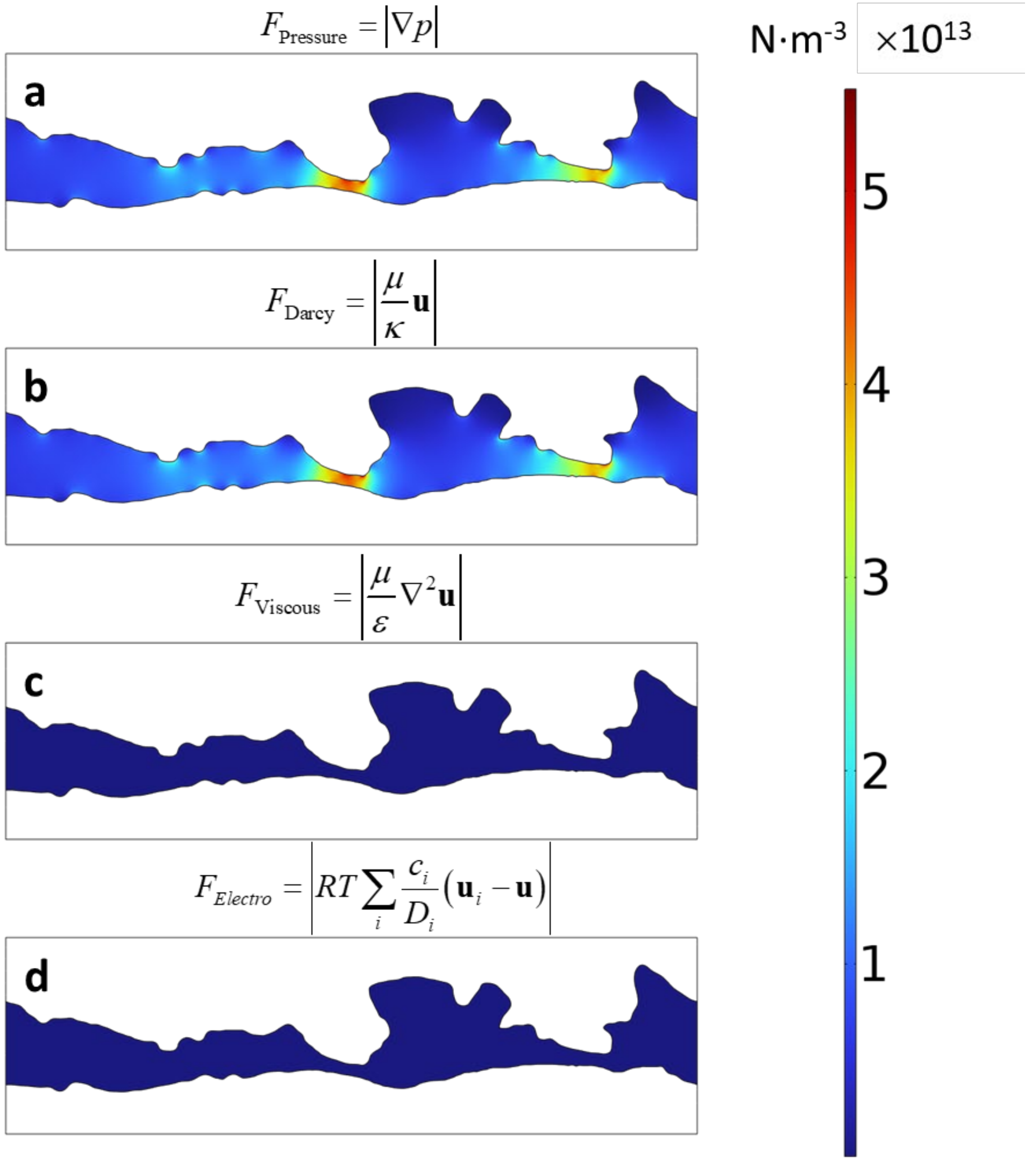
# 2-D Model. Ionic current density

-200 mM

-0.01 mM



# Comparison between the magnitudes of forces affecting water permeation through the active layer:



# 2-D Model. Water transports in the membrane. SD or SF?

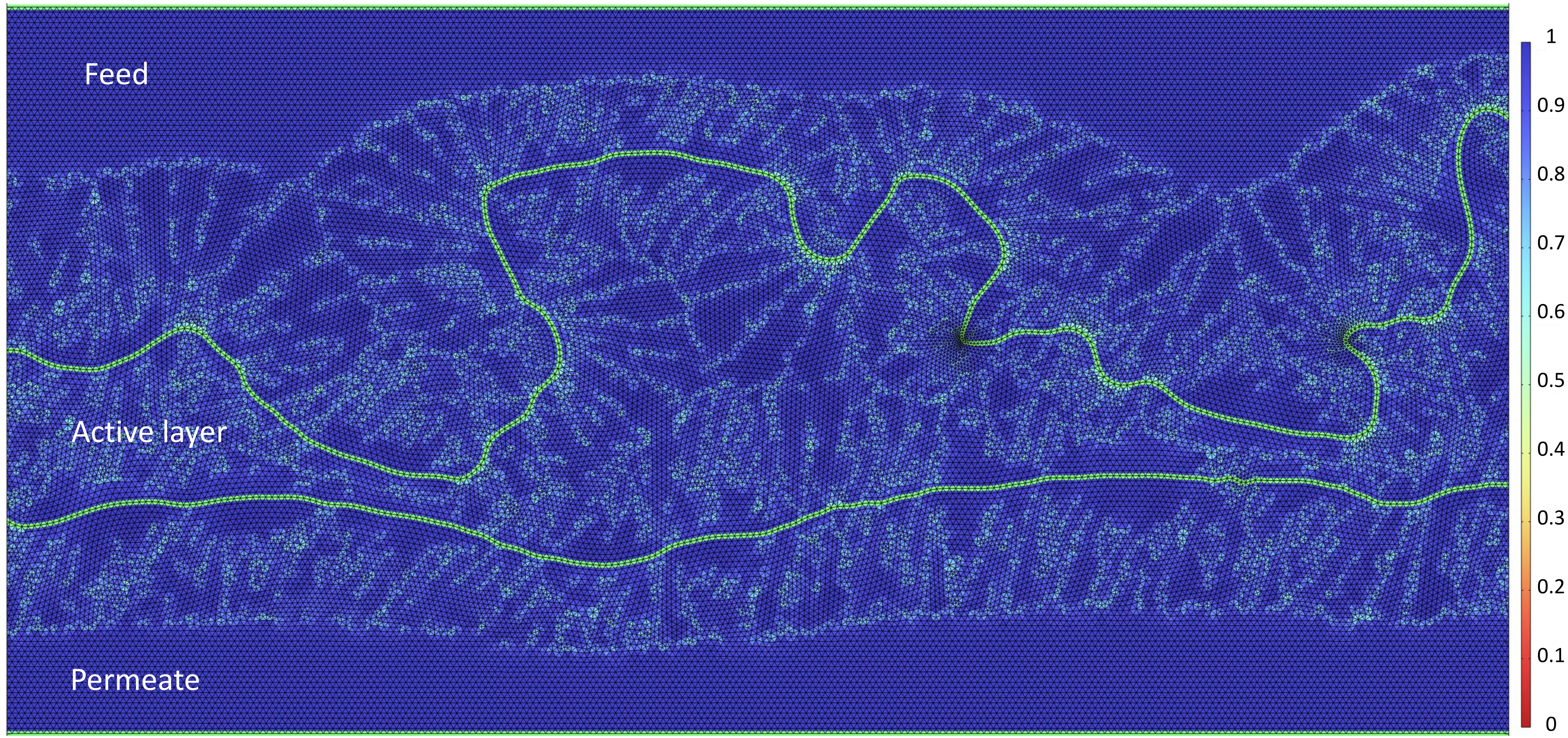
**SD model is equivalent to the Darcy equation when the osmotic pressure gradient is negligible**

$$\mathbf{u} = -\frac{\kappa}{\mu}\nabla p \quad \Rightarrow \quad J_W \propto \frac{dp}{dx}$$

$$J_W = A\left(\Delta p - \sigma \Pi\right) \quad \Rightarrow \quad J_W \propto \frac{dp}{dx}$$

strong water/membrane partitioning

# Figure SI 4



# Model implementation. Transport of water: creeping flow

- Creeping Flow *(spf)*
  - Feed and permeate properties
  - Initial Values 1
  - Wall 1
  - Porous Medium
    - Fluid
    - Porous Membrane
  - Inlet pressure feed
  - Outlet pressure permeate
  - Periodic Flow Condition

**Domain selection:** all domains

Imposed values on each domain