Modeling hydrophobicity in a porous fuel cell electrode

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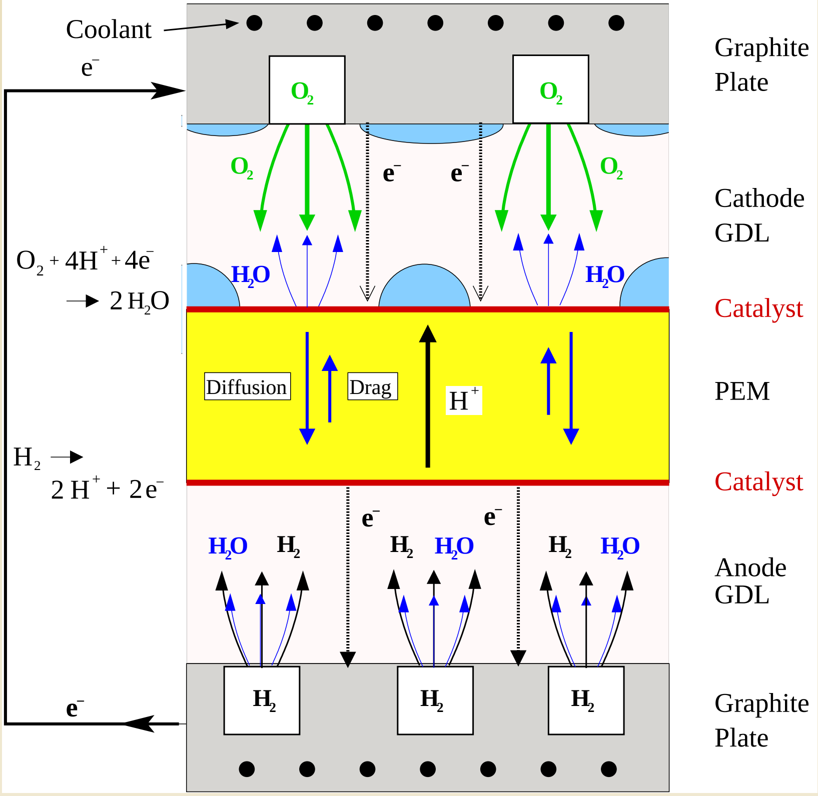
Motivation: Water management

Water management is critical to fuel cell performance, and its impact is pervasive:

- reactant water may appear in liquid or vapour form
- membrane must be fully hydrated to maintain conductivity
- both cathode and anode input streams are humidified
- liquid water must be removed, otherwise flooding can occur in the
  - catalyst: blocking reaction sites
  - electrode: blocking reactant gas diffusion



Water transport is also integrally connected with thermal management!

Our aim:

To develop a model for multicomponent, multiphase heat and mass transfer in a porous gas diffusion layer (GDL), focusing on **liquid water**

Questions:

- Does liquid water hinder performance by blocking pores leading to the catalyst layer?
- Does liquid water clog the flow channels?
- How can PEMFC design be altered to improve water transport?
- How does hydrophobicity (Teflon) affect water transport?

Outline

1. Modelling multiphase flow in porous media:
   - unsaturated flow
   - hydrophobic media
   - condensation

   . . . focusing on the cathode gas diffusion layer

2. Our GDL model

3. Numerical simulations

4. Summary and future work

1. Multiphase flow in porous media

A great deal of work has been done on modelling porous media in soil hydrology, oil reservoir simulation, and other engineering applications.

In **PEM fuel cells**, the GDL (carbon fibre paper) is distinguished from other "usual" porous media (soil, rock, sand) in several ways:

	GDL	**Soil/rock**
Porosity (ε)	0.70–0.80	0.10–0.40
Permeability (K, cm^2)	10^{-7}–10^{-9}	10^{-7}–10^{-13}
Length scale (cm)	0.05	10^1–10^3
Anisotropy	up to 10	1
Derived time scales (sec):		
convective	3×10^{-6}	3×10^{4}
diffusive	9×10^{-3}	9×10^{3}
Péclet number	3×10^{3}	3×10^{-1}

1.1. Unsaturated flow

Single-phase (saturated) flow in porous media is typically modelled using

Darcy's Law: $$\vec{U} = -\frac{K}{\varepsilon\mu}\,\nabla P$$

where $\vec{U}$ = fluid velocity (cm/s)

P = pressure (g/cm s^2)

K = permeability (cm^2)

μ = viscosity (g/cm s)

ε = porosity

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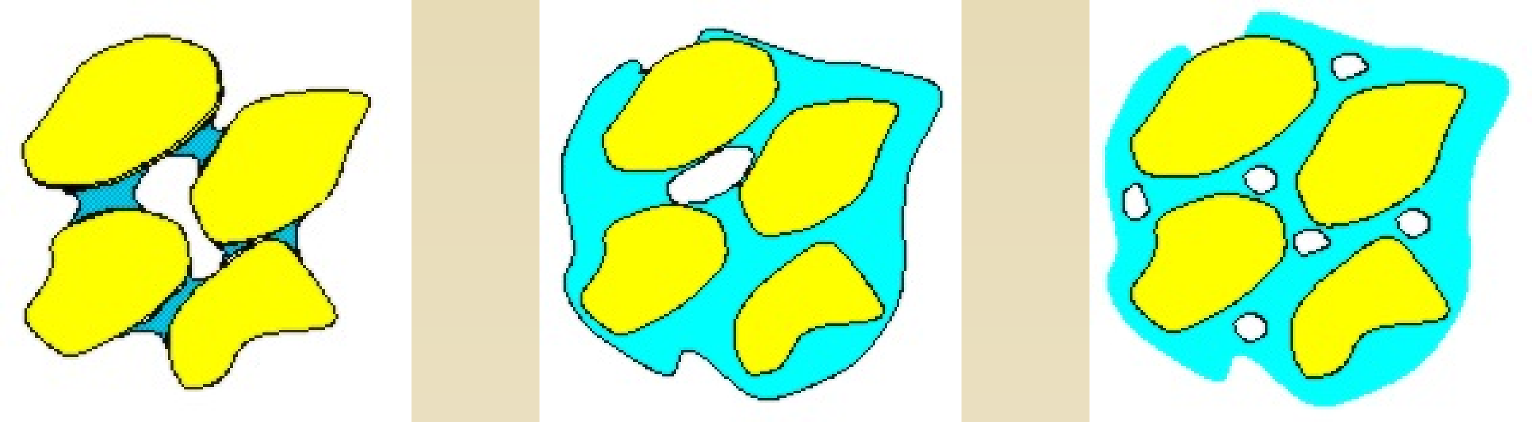
μ = viscosity (g/cm s)
ε = porosity

Generalization to **unsaturated** flows:

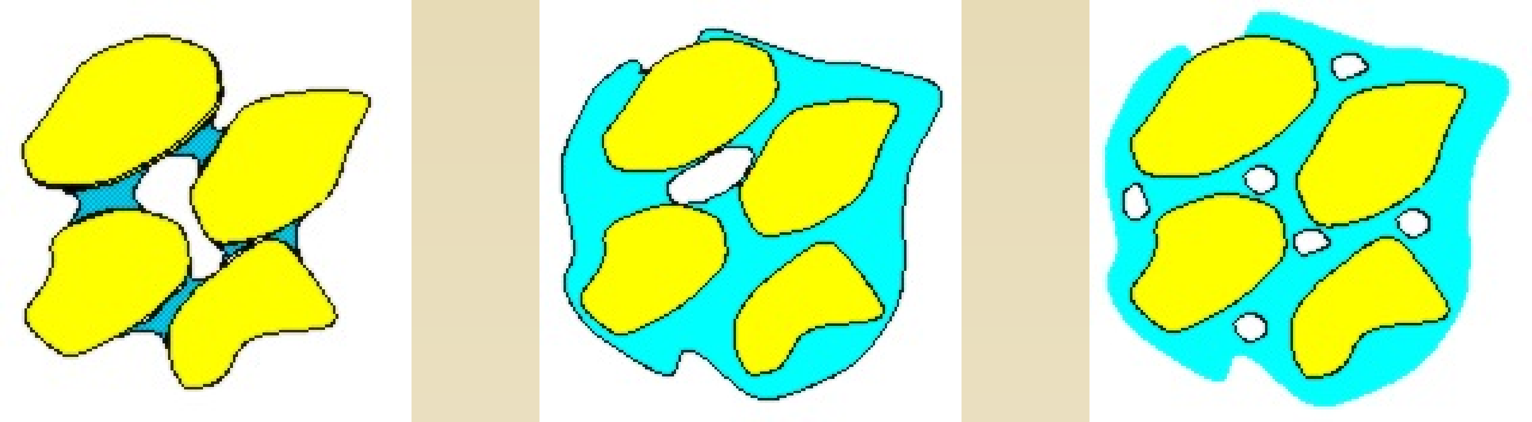
Modified Darcy's Law: $$\vec{U} = -\frac{K\ k_{rel}(s)}{\varepsilon\mu}\nabla P$$

where s = liquid volume fraction or "saturation"
$(1-s)$ = gas volume fraction
$k_{rel}(s)$ = relative permeability

$(s \approx 0)$ $\longrightarrow$ increasing s $\longrightarrow$ $(s \approx 1)$



$(s \approx 0)$ ⟶ increasing s ⟶ $(s \approx 1)$



In unsaturated flows, pressure is dominated by **capillary effects**

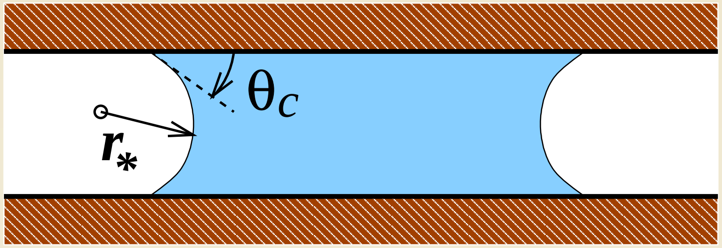
$$P \approx P_c = \frac{2\gamma\cos\theta_c}{r_*} = \gamma\cos\theta_c\,\sqrt{\varepsilon/K}\;\mathcal{J}(s)$$

where γ = surface tension (g/s^2)

θ_c = liquid contact angle

$\mathcal{J}(s)$ = scaled capillary pressure function

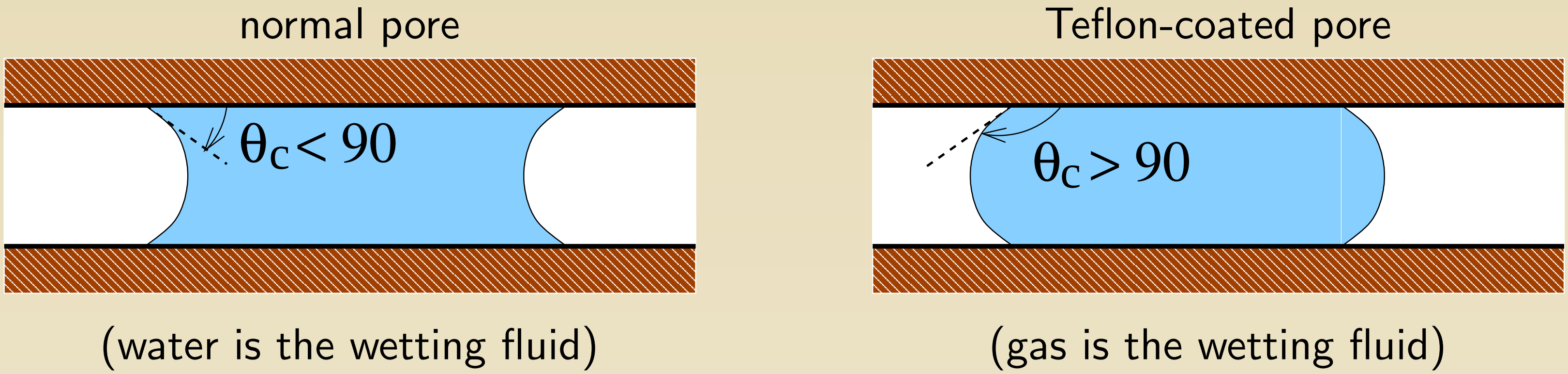
cylindrical pore



r_* = radius of curvature

1.2. Hydrophobic media

The catalyst layer and portions of the GDL are typically impregnated with **Teflon** to improve liquid water transport:



Three primary effects of hydrophobicity:

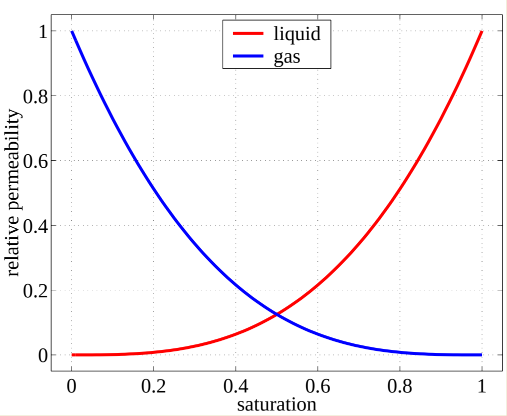
1. relative permeabilities for gas and water, $k_{rel}(s)$

2. capillary pressure function, $\mathcal{J}(s)$:

- a "residual saturation" s_o, below which water is immobile
- much larger gradients

3. boundary effects, where water "beads" on hydrophobic surfaces

1. Relative permeability:



"Usual" media (soil, rock)

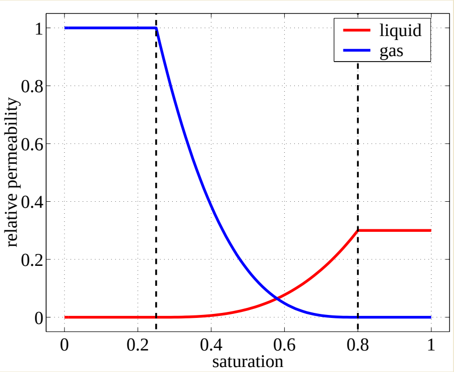
$$k_{rel,\ell}(s) = s^3$$
$$k_{rel,g}(s) = (1-s)^3$$

Based on Craig's "Rules of Thumb" [Craig, 1971; Anderson, 1987]:

$$k_{rel,\ell}(s) = k_{max}\ \tilde{s}^3 \qquad k_{rel,g}(s) = (1-\tilde{s})^3 \qquad \text{where } \tilde{s} = \begin{cases} 0, & \text{if } 0 \le s < s_o \\ \frac{s-s_o}{s_1-s_o}, & \text{if } s_o \le s \le s_1 \\ 1, & \text{if } s_1 < s \le 1 \end{cases}$$

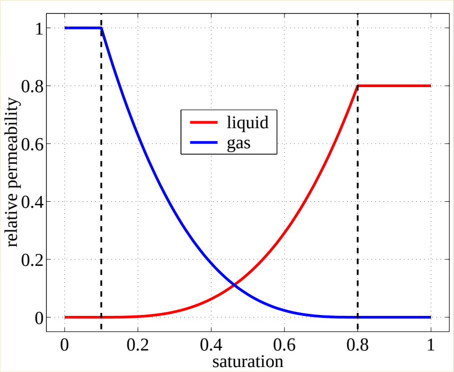
$\tilde{s}$ = reduced saturation
s_o = residual saturation
s_1 = max. saturation
k_{max} = max. permeability

Water-wet



$$k_{max} \lessapprox 0.3, \quad s_o \gtrapprox 0.25$$

Gas-wet (hydrophobic)



$$k_{max} \lessapprox 0.5-1.0, \quad s_o \lessapprox 0.1$$

2. Capillary pressure function: [Anderson, 1987]

– **hydrophilic:** the usual cubic Leverett function

$$\mathcal{J}(s) = 1.417(1-s) - 2.120(1-s)^2 + 1.263(1-s)^3$$

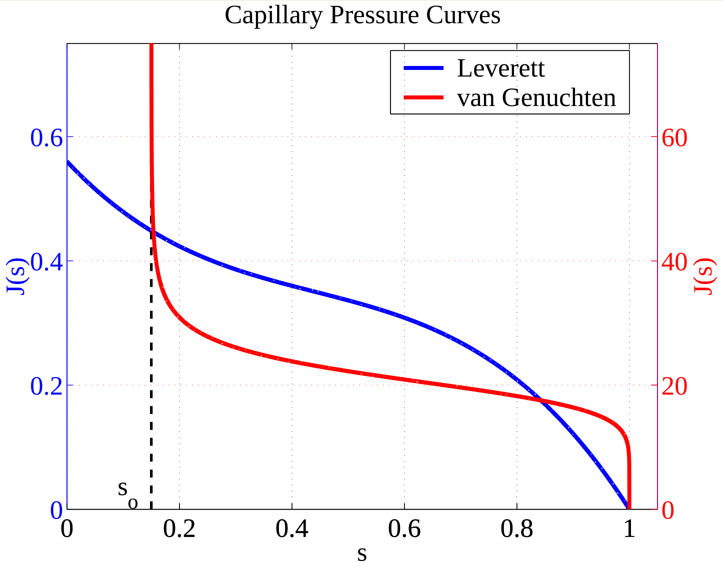
2. Capillary pressure function: [Anderson, 1987]

- **hydrophilic:** the usual cubic Leverett function

$$\mathcal{J}(s) = 1.417(1-s) - 2.120(1-s)^2 + 1.263(1-s)^3$$

- **hydrophobic:** van Genuchten function

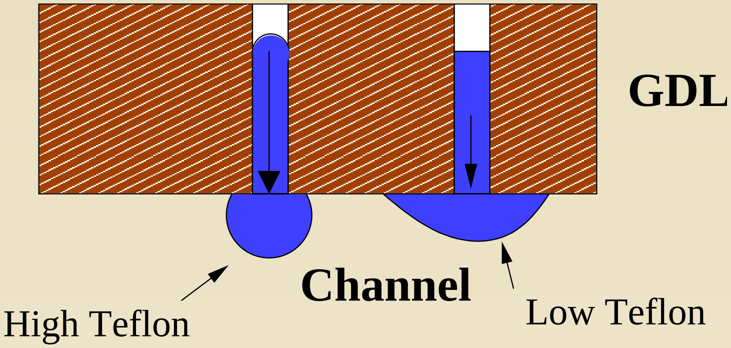
$$\mathcal{J}(s) = \begin{cases} b\left[\tilde{s}^{-1/a_2} - 1\right]^{1/a_1}, & \text{if } 0 < \tilde{s} \leq 1 \\ 0, & \text{otherwise} \end{cases}$$



3. Boundary effects:

- the usual seepage or “Signorini” boundary condition: $P_c(\text{channel}) = 0$
  [Signorini, 1959; Slodička, 1998]

- **Question:** How should this be modified to incorporate the beading effect seen on Teflonated surfaces?



1.3. Condensation

Two approaches to incorporating phase change:

1. Mixture models:

- liquid + vapour is treated as a single phase or "fog"
- "quality" variable determines liquid mass fraction from local saturation temperature

[Wang, Wang & Chen, 2001], [Kermani, JMS & Gerber, 2003] **(poster)**

2. Condensation source terms:

- liquid and vapour are treated as separate phases
- condensation appears via source terms in the equations

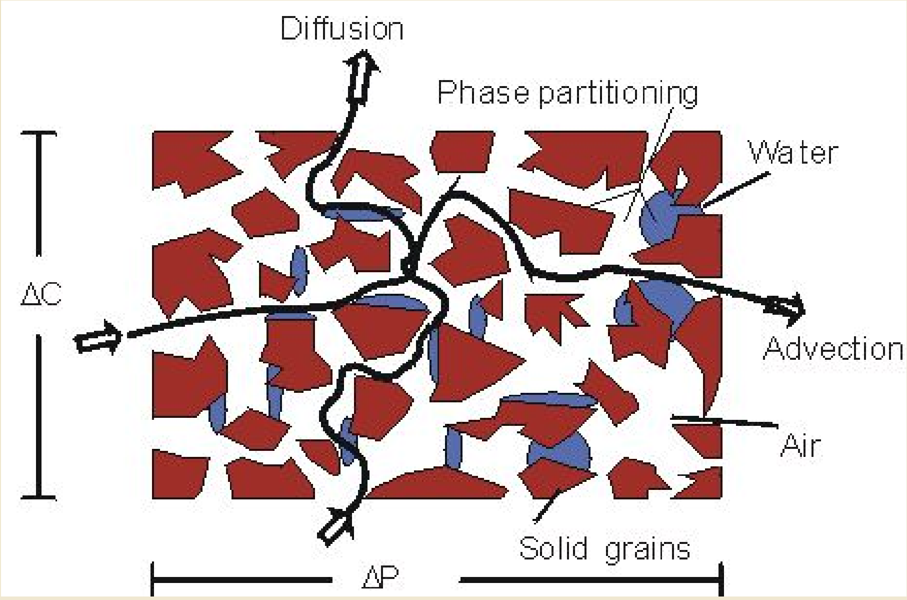
[Natarajan & Nguyen, 2001]

2. Our GDL model

Flow in the GDL of a PEM fuel cell cathode, consists of

- **gas phase:** a multicomponent mixture (typically humidified air, $O_2 + H_2O + N_2$), driven by a combination of diffusion and advection
- **liquid phase:** driven by capillary pressure gradients

concentration gradient



pressure gradient

Assumptions:

- two-dimensional (ignore along-the-channel variations)
- gravity is negligible
- thermal equilibrium
- GDL is homogeneous and isotropic
- gas: ideal, Darcy's Law, Maxwell-Stefan
- liquid: capillary-driven
- catalyst layer is an interface, with reaction handled using Tafel equation
- all product water generated in gas phase

Species and mixture C_1 (O_2), C_2 (H_2O), C_3 (N_2)

concentrations: $C = C_1 + C_2 + C_3$

Conservation laws: (single-phase only)

$$\rho_t + \nabla \cdot \left(\rho \vec{U}_g\right) = 0$$

gas mixture ($\rho = MC$)

$$(C_1)_t + \nabla \cdot \underbrace{\left(C_1 \vec{U}_g + \vec{J}_1\right)}_{\vec{N}_1 = \text{total flux}} = 0$$

reactant

$$(C_2)_t + \nabla \cdot \left(C_2 \vec{U}_g + \vec{J}_2\right) = 0$$

water vapour

$$(\overline{\rho c} T)_t + \nabla \cdot \left(\overline{\rho c U} T - \kappa \nabla T\right) = \frac{i^2}{\sigma}$$

energy

Constitutive relations: (single-phase only)

Diffusive flux:
(Maxwell-Stefan)

$$-\nabla \left(\frac{C_i}{C}\right) = \sum_{j=1}^{3} \frac{C_j \vec{J}_i - C_i \vec{J}_i}{C^2 D_{ij}}$$

Darcy's Law:
(ideal gas)

$$\vec{U}_g = -\frac{K}{\varepsilon \mu_g} \nabla (CRT)$$

Species and mixture concentrations: C_1 (O_2), C_2 (H_2O), C_3 (N_2)

$$C = C_1 + C_2 + C_3$$

Conservation laws: (two-phase)

$$((1-s)\rho)_t + \nabla \cdot \left(\rho \vec{U}_g\right) = -M\Gamma$$

gas mixture ($\rho = MC$)

$$((1-s)C_1)_t + \nabla \cdot \left(C_1 \vec{U}_g + \vec{J}_1\right) = 0$$

reactant

$$((1-s)C_2)_t + \nabla \cdot \left(C_2 \vec{U}_g + \vec{J}_2\right) = -\Gamma$$

water vapour

$$(\overline{\rho c} T)_t + \nabla \cdot \left(\overline{\rho c U} T - \kappa \nabla T\right) = \frac{i^2}{\sigma} + h_{\ell g}\Gamma$$

energy

$$s_t + \nabla \cdot (s\vec{U}_\ell) = \Gamma / C_\ell$$

liquid water

Constitutive relations: (two-phase)

Diffusive flux: $$-\nabla\left(\frac{C_i}{C}\right)=\sum_{j=1}^{3}\frac{C_j\vec{J}_i-C_i\vec{J}_i}{C^2D_{ij}}$$

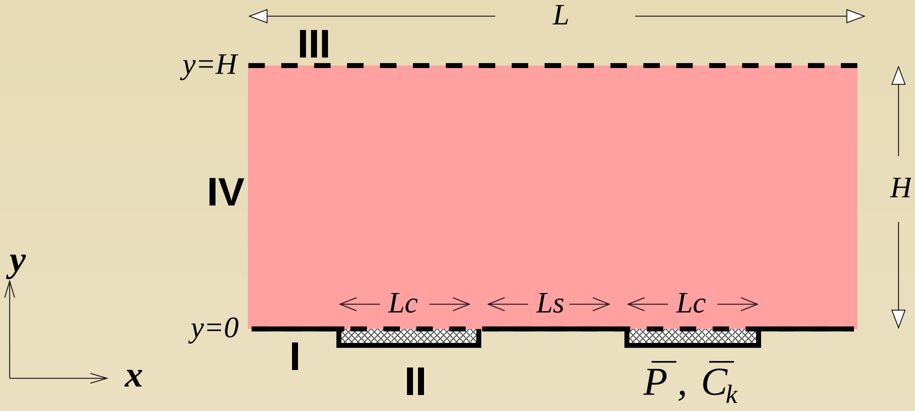
Darcy's Law (gas): $$\vec{U}_g=-\frac{K\,k_{rel,g}(s)}{\varepsilon\mu_g}\nabla(CRT)$$

Darcy's Law (liquid): $$\vec{U}_\ell=-\frac{K\,k_{rel,\ell}(s)}{\varepsilon\mu_\ell}\nabla P_\ell$$

Capillary pressure: $$P_\ell=P_g+\gamma\cos\theta_c\,\sqrt{\varepsilon/K}\cdot\mathcal{J}(s)\qquad(\theta_c\approx 108^o)$$

Condensation rate: $$\Gamma=\begin{cases}H^+(1-s)(C_2-C_2^{sat}(T)), & \text{if } C_2\geq C_2^{sat}(T)\\ H^-s(C_2-C_2^{sat}(T)), & \text{if } C_2<C_2^{sat}(T)\end{cases}$$

Model domain:



Dimensions: $L_c = 0.1$ cm, $L_s = 0.1$ cm, $H = 0.05$ cm

Boundary conditions:

I. landing area, no flow

II. channel inflow, seepage condition

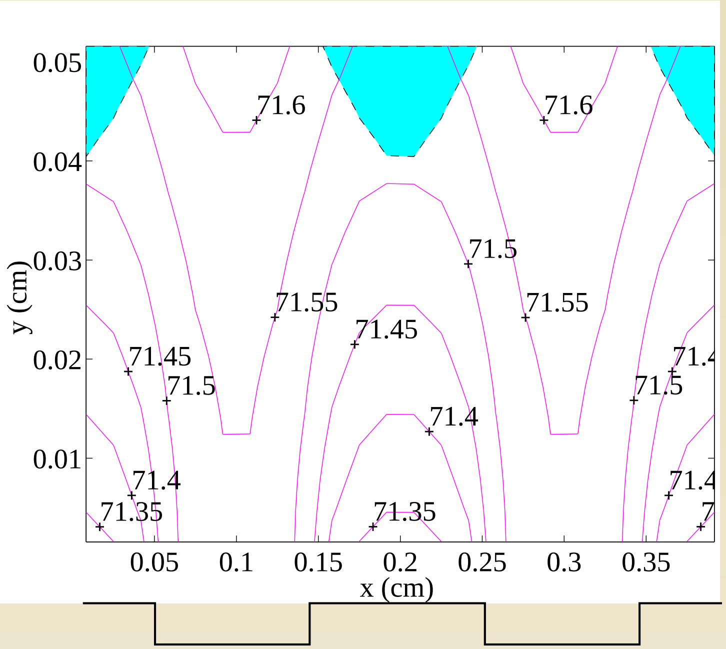
III. catalyst layer, reaction source terms, no gas flux into PEM

IV. periodic

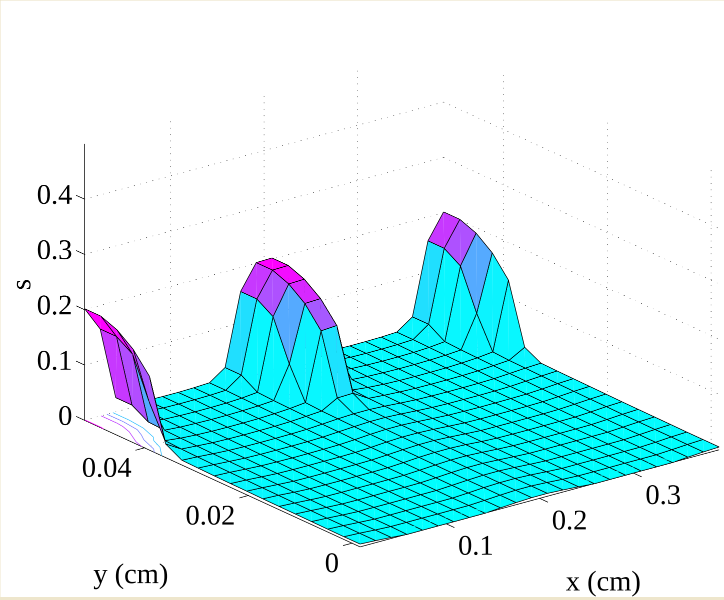
3. Numerical simulations

Cathode fed with humidified air at 70^{o}C:

Temperature contours and condensing regions

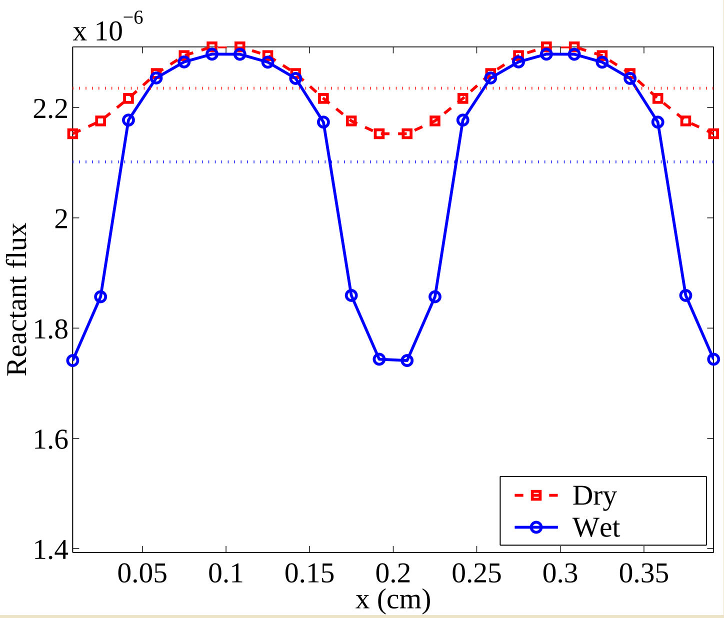


Saturation



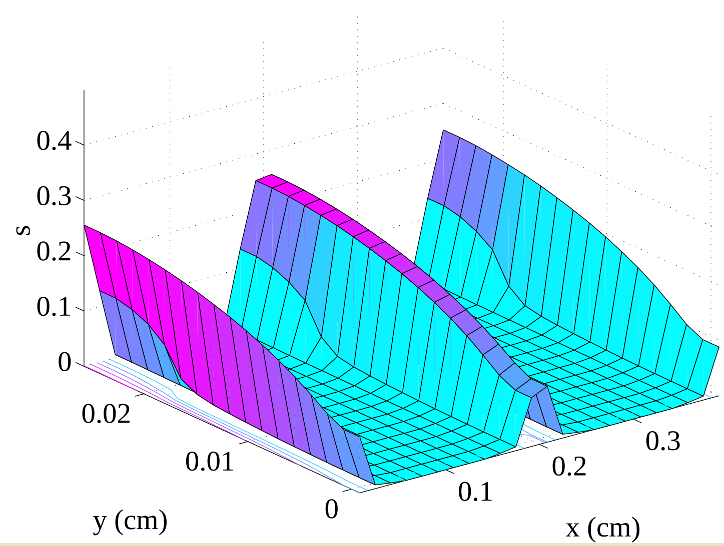
Performance measure: Reactant (O_2) flux at the catalyst is proportional to local current density

Comparison of dry and wet run

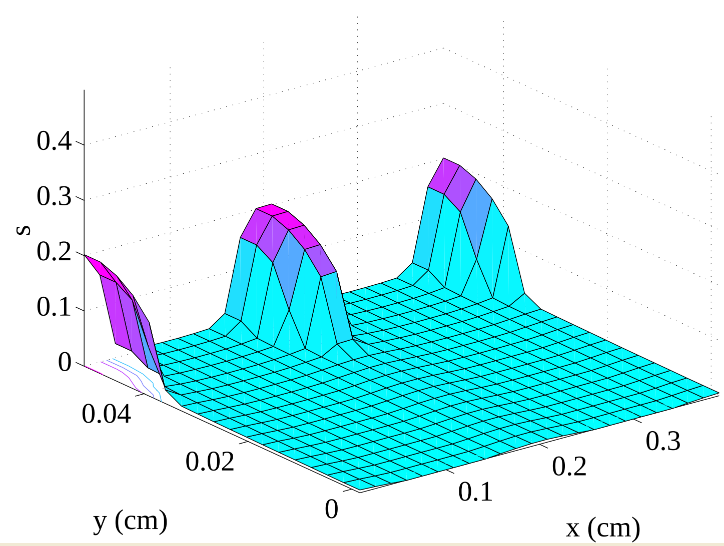


Effect of changing GDL thickness on water distribution

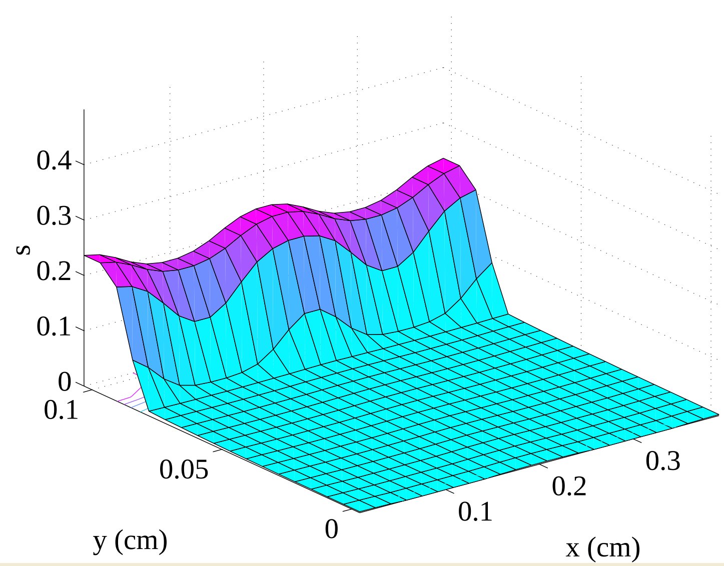
$H = 0.025$ cm



$H = 0.05$ cm



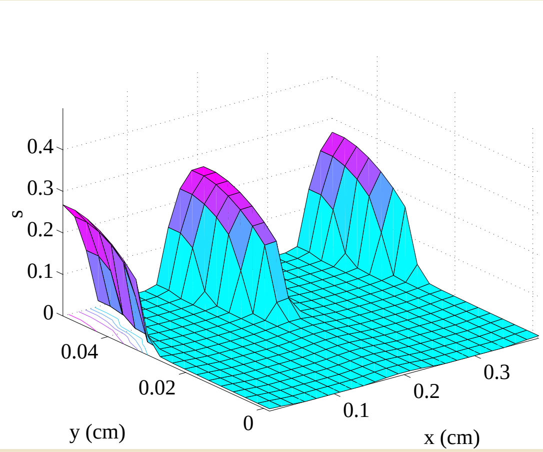
$H = 0.10$ cm



Effect of changes in the Capillary Function:

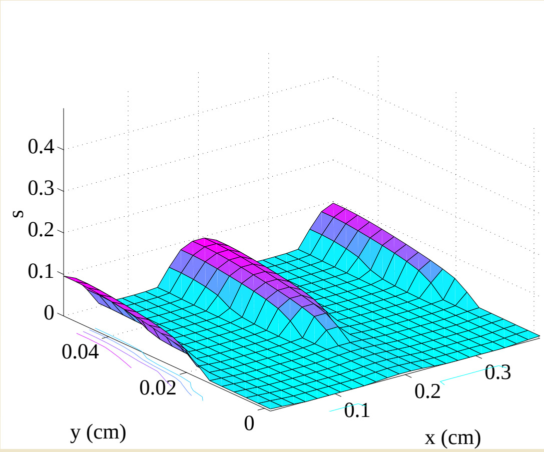
- hydrophobicity $\Longrightarrow$ faster water transport
- immobile saturation $\Longrightarrow$ sharper gradients

Hydrophilic



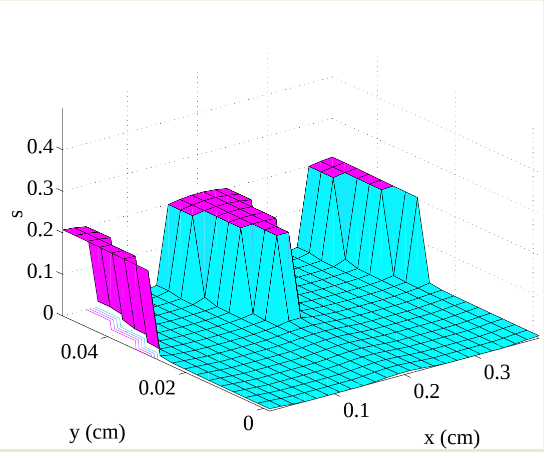
[movie]

Hydrophobic, $s_o = 0.01$



[movie]

Hydrophobic, $s_o = 0.1$



[movie]

4. Summary

- developed a model for multiphase flow and condensation in a PEM fuel cell cathode

- studied the influence of liquid water on condensing regions

- hydrophobicity and its effect on liquid transport

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Future work:

- more complete study of hydrophobicity
- incorporation of boundary effects
- fingering instabilities? [Philip, 1975; Nieber et al., 2000] ← gravity-driven!
- couple with along-the-channel (1+1) model [Berg et al., 2003]

References

[1] W. G. Anderson. Wettability literature survey – Part 4: Effects of wettability on capillary pressure. *J. Petrol. Technol.*, pages 1283–1299, Oct. 1987.

[2] W. G. Anderson. Wettability literature survey – Part 5: The effects of wettability on relative permeability. *J. Petrol. Technol.*, pages 1453–1468, Nov. 1987.

[3] P. Berg, K. Promislow, J. St.-Pierre, J. Stumper, and B. Wetton. Water management in PEM fuel cells. Unpublished, 2003.

[4] M. J. Kermani, J. M. Stockie, and A. G. Gerber. Condensation in the cathode of a PEM fuel cell. In *Proceedings of the Eleventh Annual Conference of the CFD Society of Canada*, Vancouver, BC, May 28-30 2003. To appear.

[5] D. Natarajan and T. V. Nguyen. A two-dimensional, two-phase, multicomponent, transient model for the cathode of a proton exchange membrane fuel cell using conventional gas distributors. *J. Electrochem. Soc.*, 148(12):A1324–A1335, 2001.

[6] J. L. Nieber, T. W. J. Bauters, T. S. Steenhuis, and J.-Y. Parlange. Numerical simulation of experimental gravity-driven unstable flow in water repellent sand. *J. Hydrol.*, 231-232:295–307, 2000.

[7] J. R. Philip. Stability analysis of infiltration. *Soil Sci. Soc. Amer. Proc.*, 39:1049–1053, 1975.

[8] A. Signorini. Questioni di elasticità non linearizzata e semilinearizzata. *Rend. Mat. e Appl., Serie 5*, 18:95–139, 1959.

[9] M. Slodička. Finite elements in modeling of flow in porous media: How to describe wells. *Acta Math. Univ. Comen.*, 67(1):197–214, 1998.

[10] Z. H. Wang, C. Y. Wang, and K. S. Chen. Two-phase flow and transport in the air cathode of proton exchange membrane fuel cells. *J. Power Sources*, 94(1):40–50, 2001.