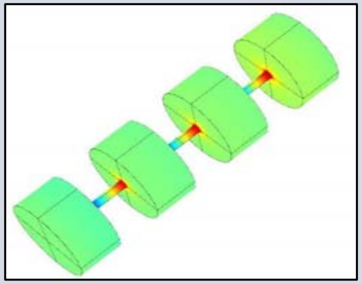
Presented at the COMSOL Conference 2008 Hannover



Microscale Modelling of the Frequency Dependent Resistivity of Porous Media

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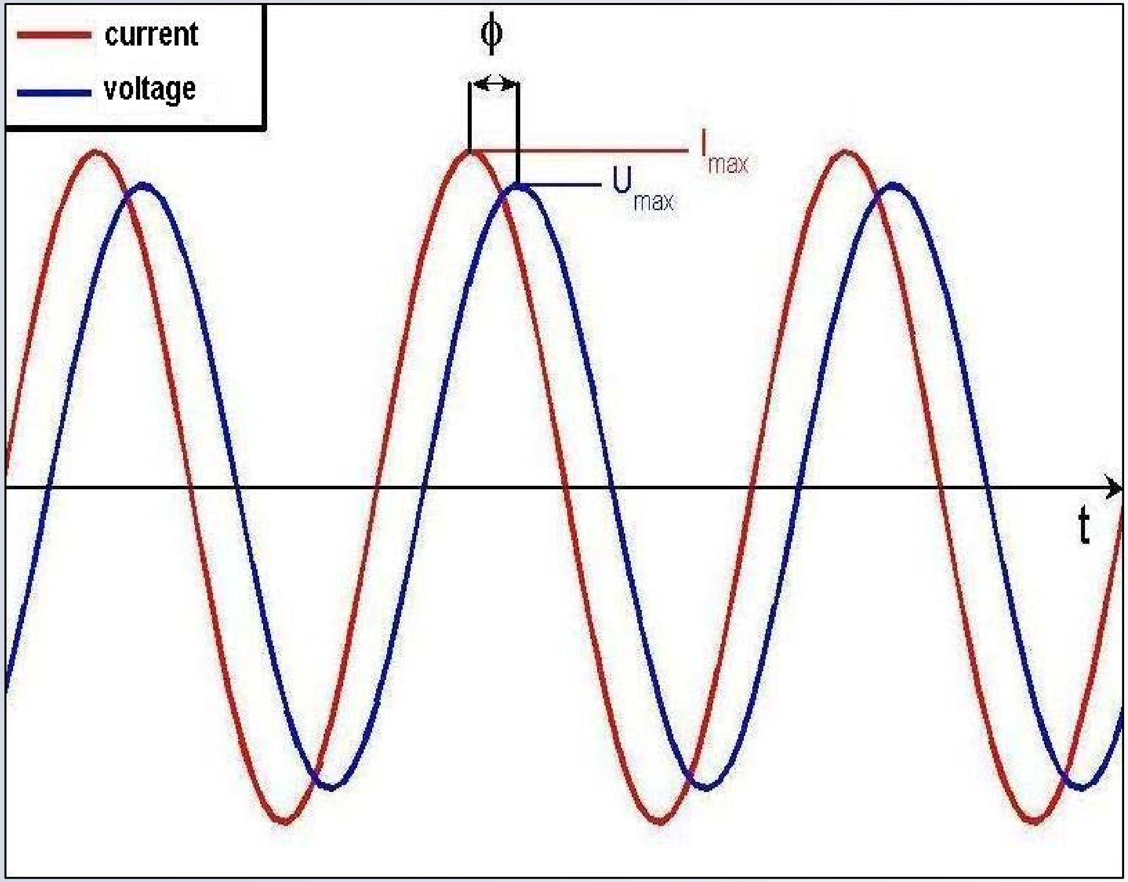
Content

- motivation
- theory and modelling idea
- governing equations
- model verification
- first parameter studies
- outlook

Motivation

In geophysics:



$$\rightarrow \begin{cases} |R(f)| \\ \varphi_R(f) \end{cases}$$

= Spectral Induced Polarisation (SIP) (=Impedance Spectroscopy)

Motivation

SIP-properties:

$$\left|R(f)\right|, \varphi_R(f)$$

(empirical relations)

→ structural properties (pore radius, inner surface area,...)

→ hydraulic conductivity

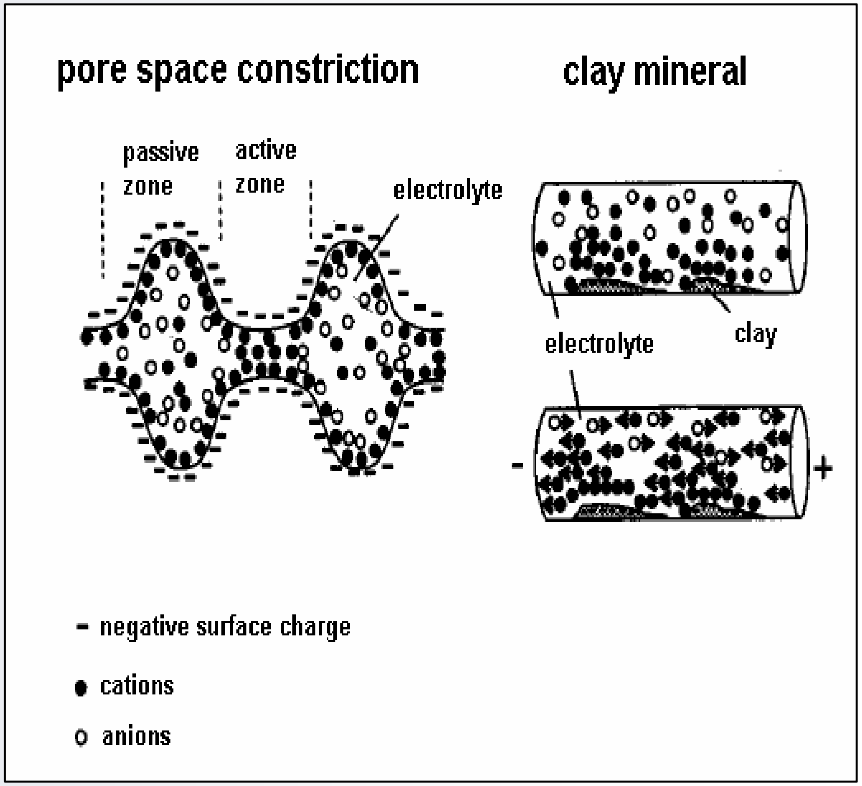
State of the Art:

- experimental results
- empirical models (equivalent circuits: Cole-Cole etc.)
- theoretical models describing simple pore systems (M&M, SNP,...)

-> numerical simulation required

IP-Effect

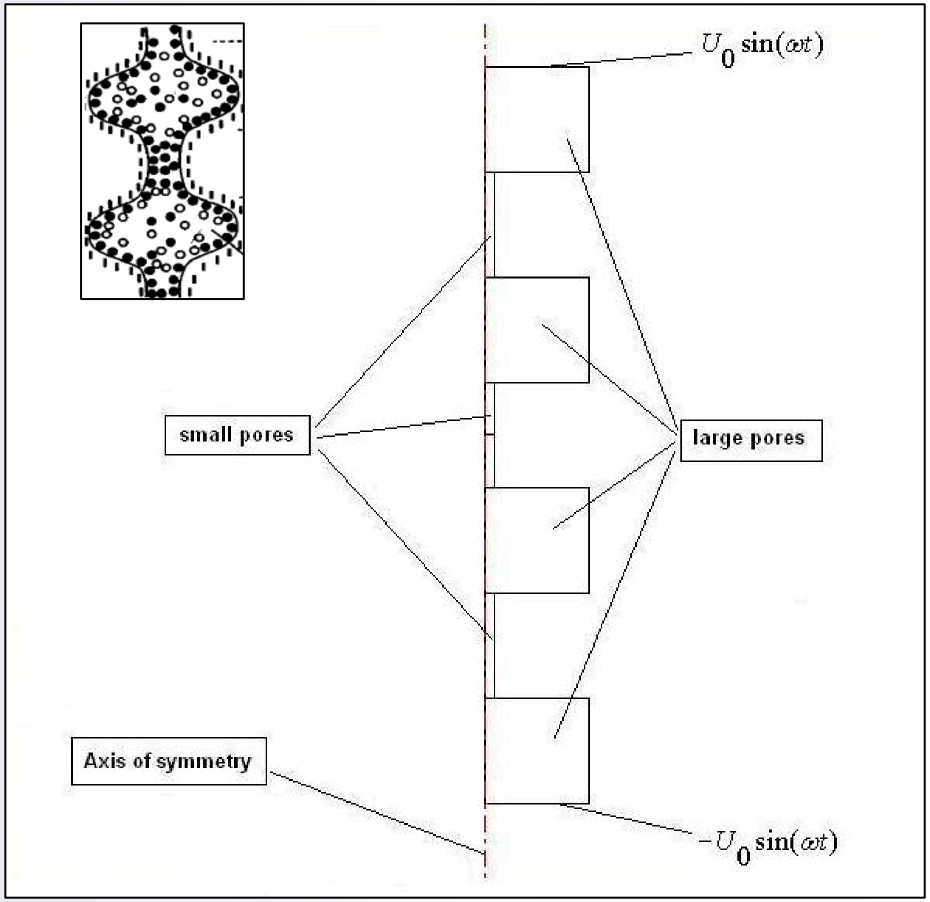
- cations bound by negative surface charges
- pore space constriction is equivalent to ion selective membrane
- small pores=active zone
- large pores=passive zone



Modelling Parameters

- modelling with Comsol-Multiphysics (FEM-Software)
- 2D axial symmetric model for cylindrical 3D problem
- sequence of smaller and larger pores
- applied alternating voltage
- M&M: different mobilities for anions and cations in the smaller pores :

$$\mu_p \neq \mu_n$$



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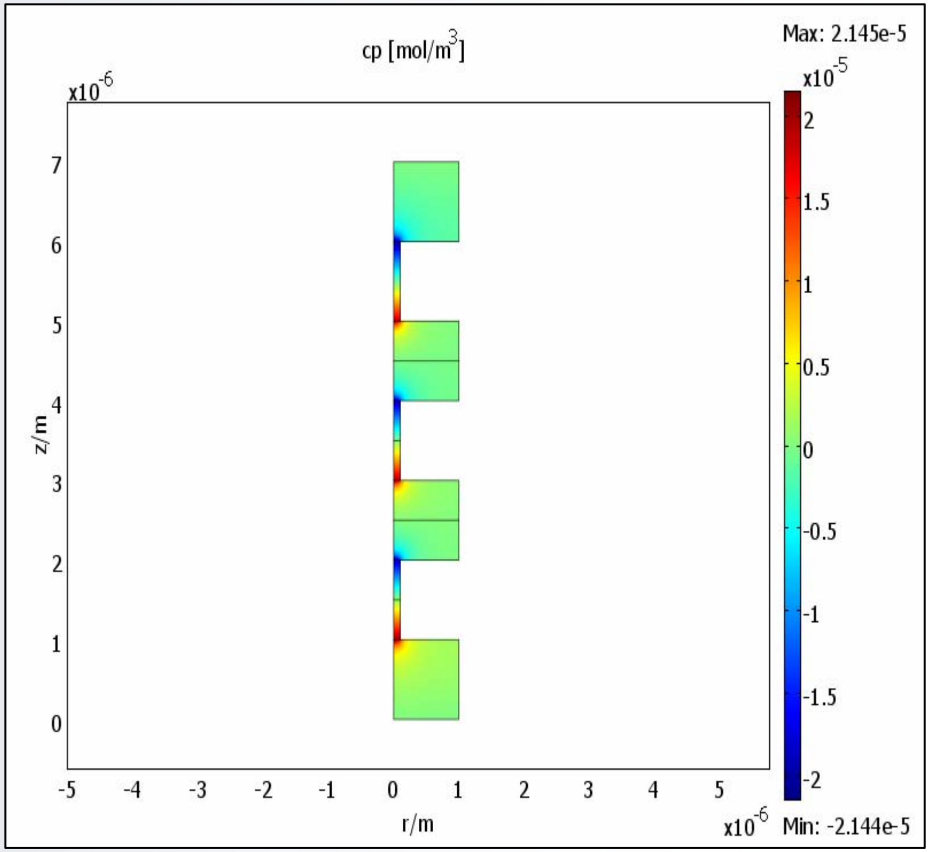

Excess concentration of cations at $\omega t = \frac{\pi}{2}$

Governing Equations (time domain)

Equations for anion (index *n*) and cation (index *p*) movement driven by diffusion and migration in an external electric field according to Marshall and Madden (1959):

(Z-I)	$\frac{\partial}{\partial t}C_p = D_p \Delta C_p + \nabla\left[\mu_p C_p \nabla U\right]$	=continuity equation for C_p
(Z-II)	$\frac{\partial}{\partial t}C_n = D_n \Delta C_n - \nabla\left[\mu_n C_n \nabla U\right]$	=continuity equation for C_n
(Z-III)	$\Delta U = \frac{F}{\varepsilon}(C_n - C_p)$	=Poisson's equation for the potential U

Einstein relation: $D_{p/n} = \frac{\mu_{p/n} k_B T}{e}$

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Einstein relation: $$D_{p/n} = \frac{\mu_{p/n} k_B T}{e}$$

Constants:

$D_{p/n}$	diffusion coefficients
$\mu_{p/n}$	ion mobilities
F	Faraday's constant
k_B	Boltzmann's constant
e	elementary charge
T	temperature
ε	permittivity

Time-Harmonic Approach

Determination of frequency dependent quantities if sinusoidal voltage is applied
->assumption of harmonic time dependence

This means:

$$C_p = c_{p0} + c_p \cdot e^{i\omega t}$$

$$C_n = c_{n0} + c_n \cdot e^{i\omega t}$$

$$U = u \cdot e^{i\omega t}$$

with

$$c_p, c_n, u \in \mathbb{C}$$

$$\dot{c}_p = \dot{c}_n = \dot{u} = 0$$

$$c_{p0}, c_{n0} = const$$

Further assumptions:

- small electric field and excess-concentrations
  -> quadratic terms neglected
- equal concentrations without applied voltage: $c_{p0} = c_{n0} = c$

Governing Equations (frequency domain)

Linearised equations according to Marshall and Madden (1959):

(F-I)
$$i\omega c_p = D_p \Delta c_p + \nabla \left[\mu_p c \nabla u \right]$$

(F-II)
$$i\omega c_n = D_n \Delta c_n - \nabla \left[\mu_n c \nabla u \right]$$

(F-III)
$$\Delta u = \frac{F}{\varepsilon}(c_n - c_p)$$

Einstein relation:

$$D_{p/n} = \frac{\mu_{p/n} k_B T}{e}$$

- equations are no longer time dependent
- c_p, c_n, u contain information about amplitude and phase
- more efficient calculation of frequency dependent quantities

Application Modes / Boundary Conditions

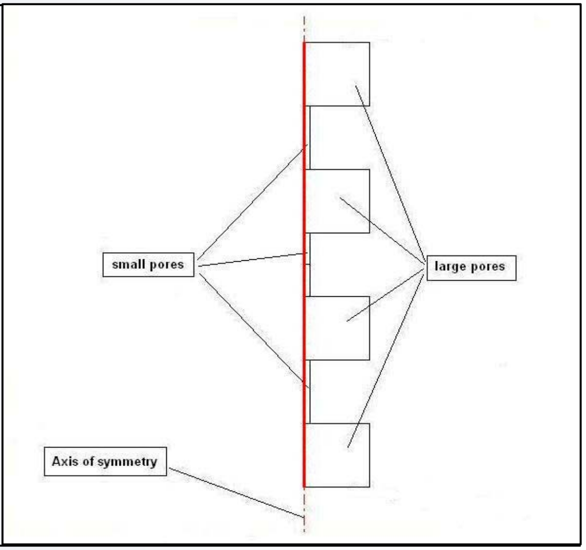
Application Modes: continuity equations (c_p, c_n) -> Electrokinetic Flow (chekf)
Poisson's equation (u) -> Electrostatics (emes)

Boundary Conditions:

u : axial symmetry

c_p : axial symmetry

c_n : axial symmetry



- equations solved for frequencies $f = 10^{-3} \ldots 10^{6}\, Hz$
- procedure: $I = |I| e^{i\varphi} e^{i\omega t}$ -> $R = U/I$ -> $|R(f)|, \varphi_R(f)$

Application Modes / Boundary Conditions

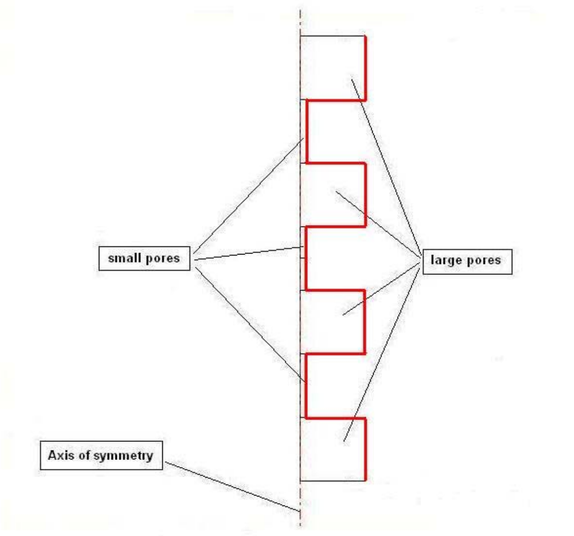
Application Modes: continuity equations (c_p, c_n) -> Electrokinetic Flow (chekf)
Poisson's equation (u) -> Electrostatics (emes)

Boundary Conditions:

u : zero charge / symmetry

c_p : insulation / symmetry

c_n : insulation / symmetry



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Application Modes / Boundary Conditions

Application Modes: continuity equations (c_p, c_n) -> Electrokinetic Flow (chekf)
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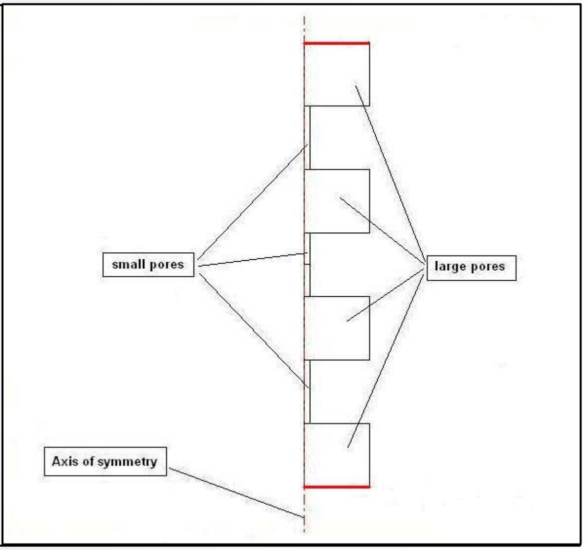
Boundary Conditions:

$$u = \pm i \cdot const$$

$$c_p = 0$$

$$c_n = 0$$



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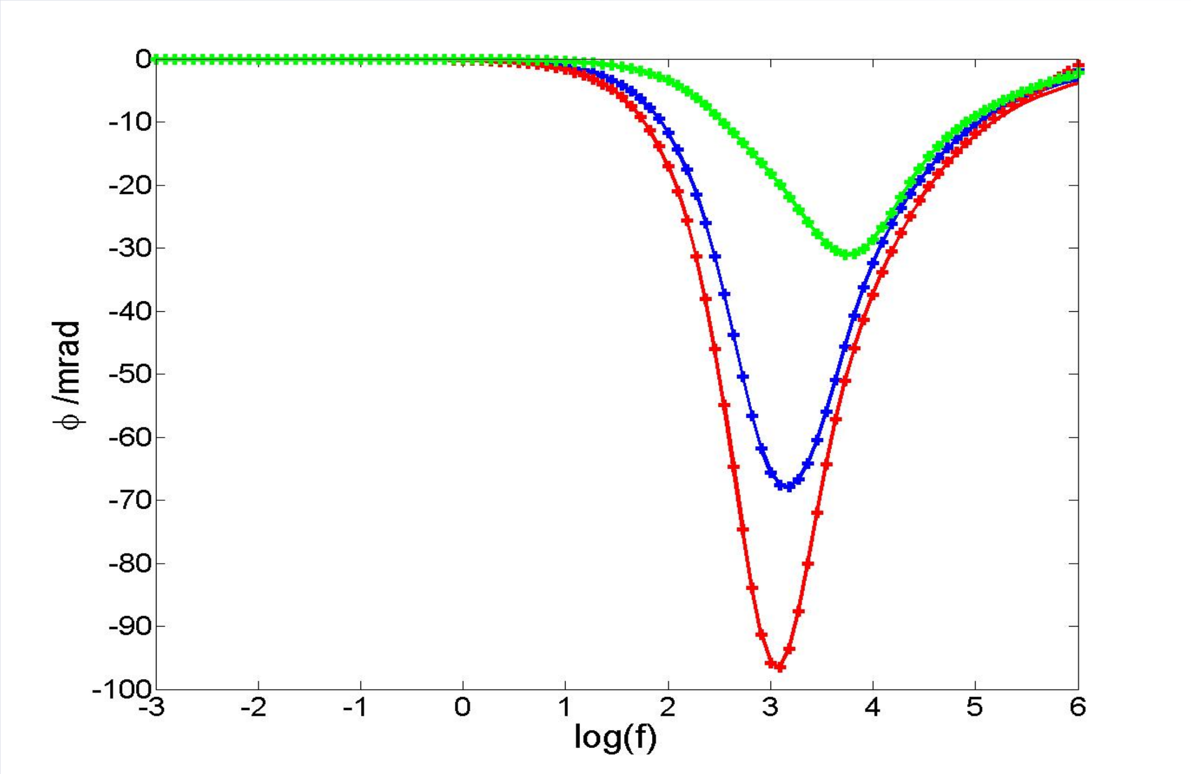
Verification - 1D

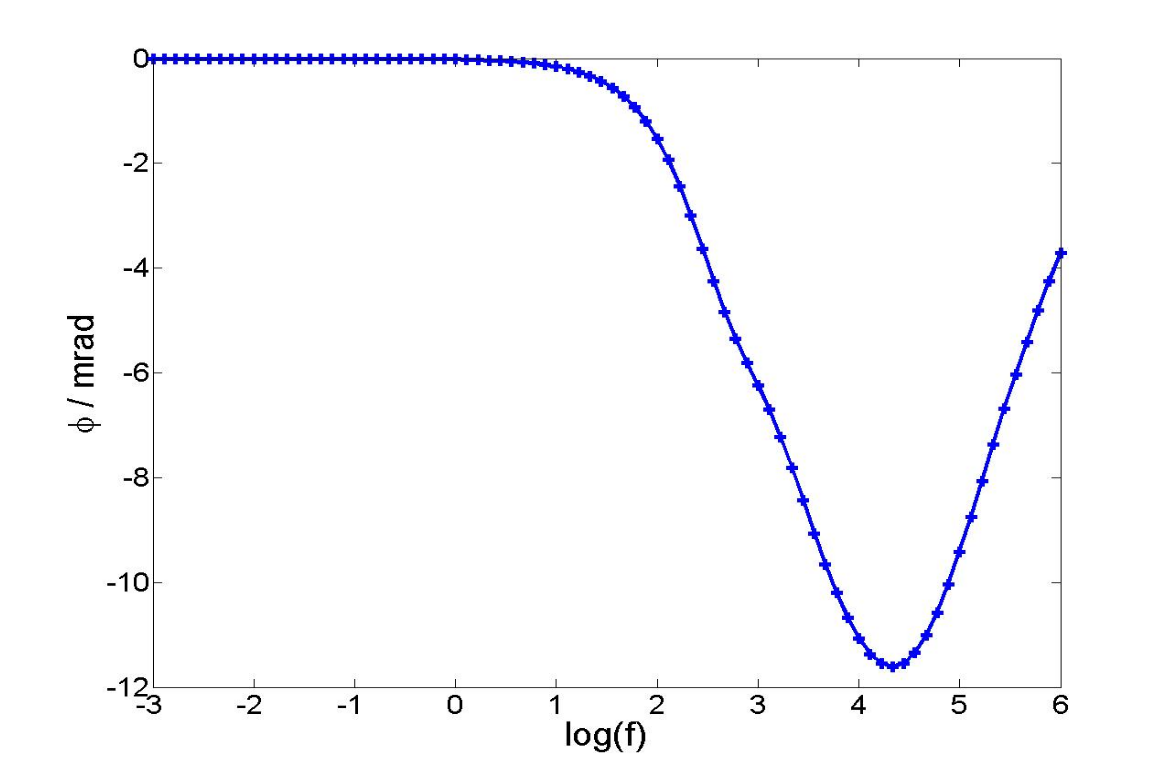


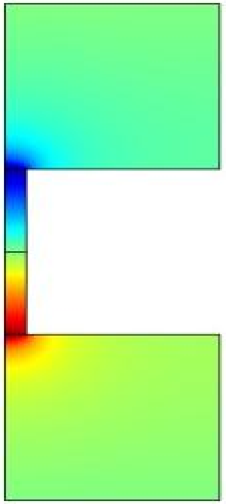
Blue:
L1=1µm
L2=1µm
Red:
L1=1.5µm
L2=0.5µm
Green:
L1=0.5µm
L2=1.5µm

1:passive zone
2:active zone

Crosses: 1D Comsol model
Solid line: analytical solution according to Marshall and Madden

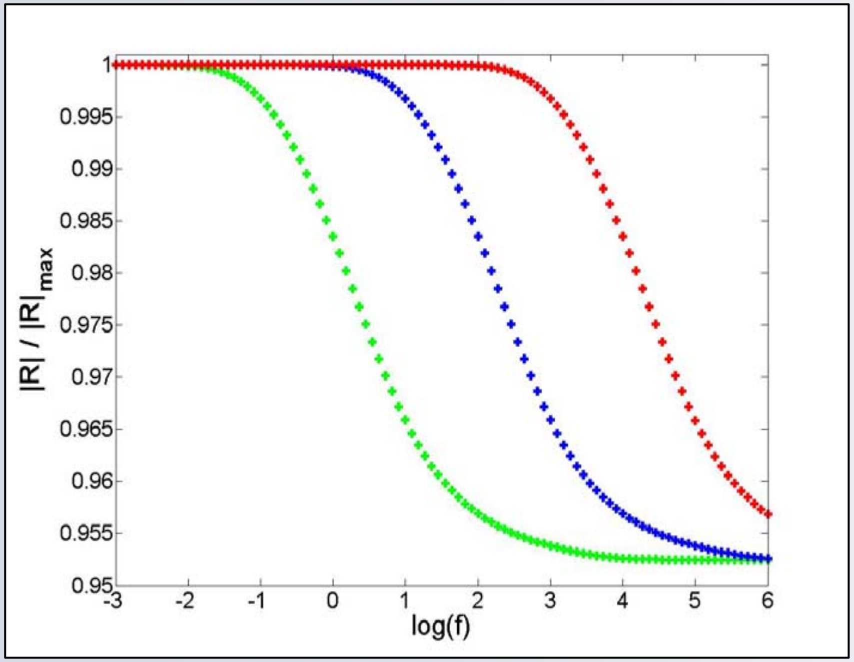
Verification - 3D

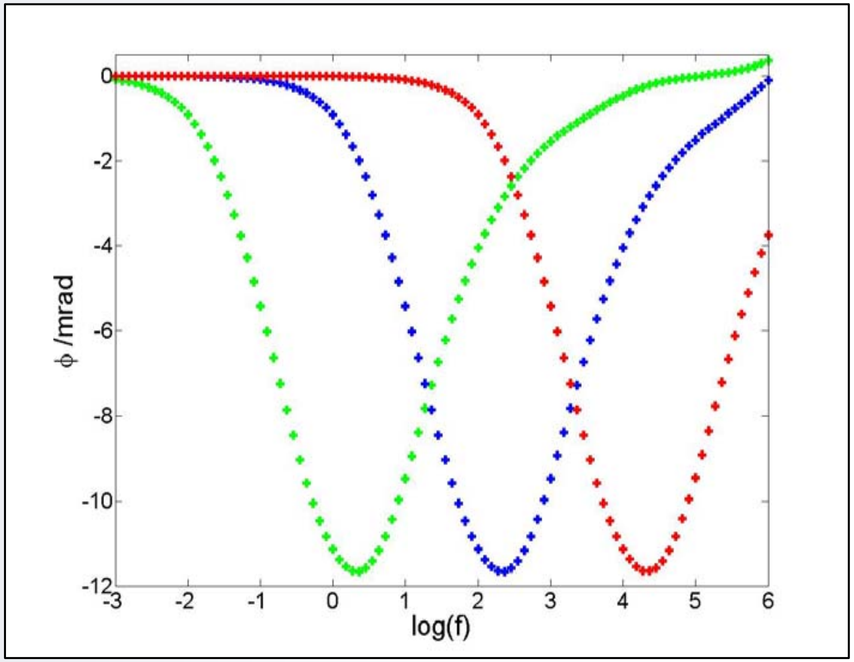




Crosses: 2D axial symmetric model
Solid line: 3D model

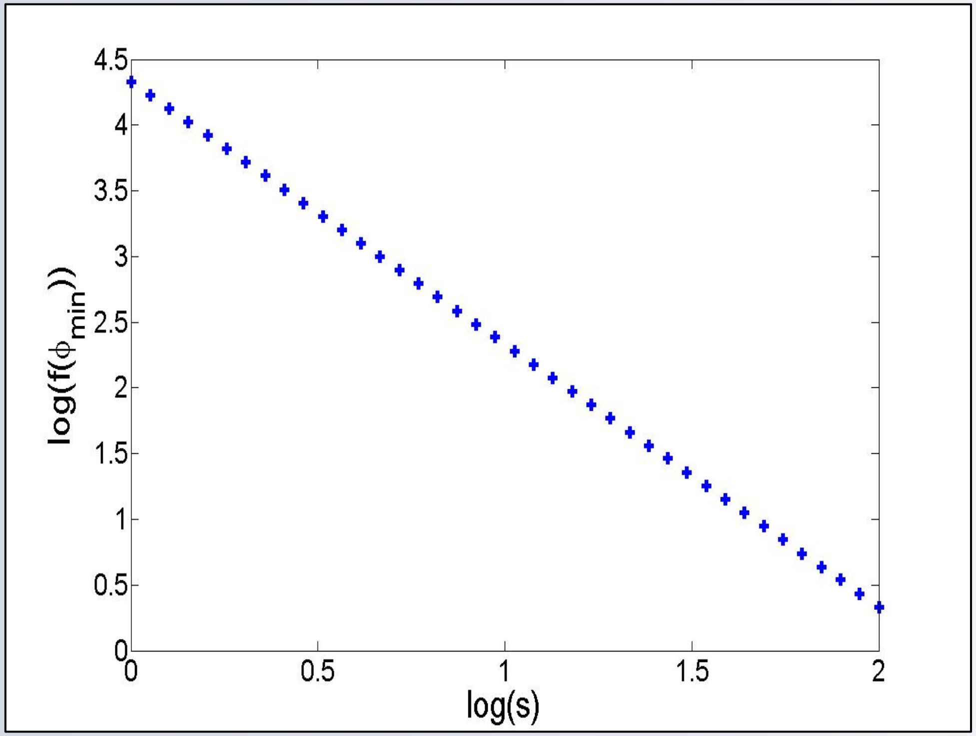
Results – 3D





Red (basic model): pore length 1µm, pore radius 0.1µm (small pores) und 1µm (large pores)
Blue: scaled geometry x10
Green: scaled geometry x100

Results – 3D



Dependence of the phase minimum on the scale factor (with regard to the basic model)

-> $$f(\varphi_{\min}) \sim (s)^{-1.9997}$$

cf. Titov et al. (2002):

$$f(\varphi_{\min}) \sim l_2^{-2}$$

$l_2 \triangleq$ length of the narrow pores

Conclusion

Approach verified by:

1. qualitatively good agreement between modelled and experimental results
2. agreement between 2D axial symmetric model and 3D model
3. agreement between 1D model and analytical solution according to Marshall and Madden
4. agreement between the results of frequency dependent calculations and those of time dependent calculations (Blaschek und Hördt, 2007)

Outlook

- studies of the influence of

    1. geometric properties (lengths, radii)
    2. electrolyte properties (mobilities, concentrations)

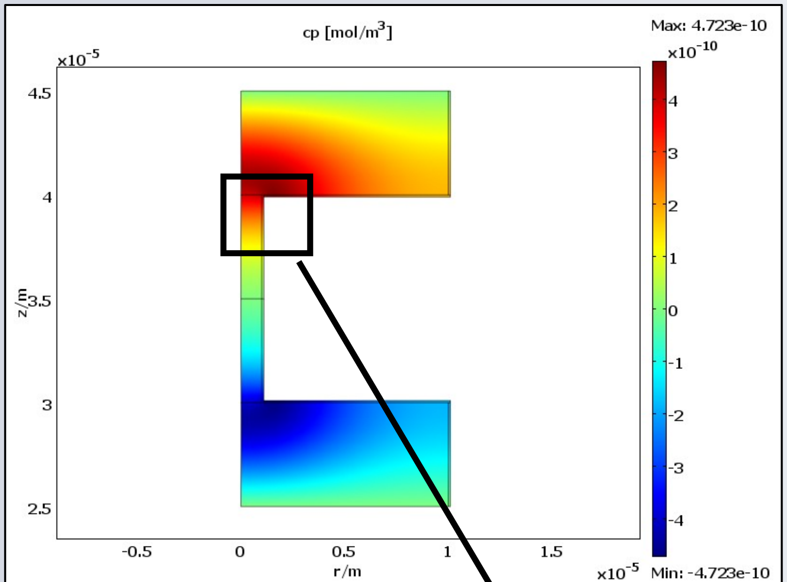
- more realistic model - IP as a surface effect
  For this purpose:

    - set surface charges?
    - set mobilities close to the pore wall?
    - set a concentration profile close to the pore wall?

  Problem: harmonic functions vs. constant surface quantities

Outlook

Reduced anion mobility at the pore walls:



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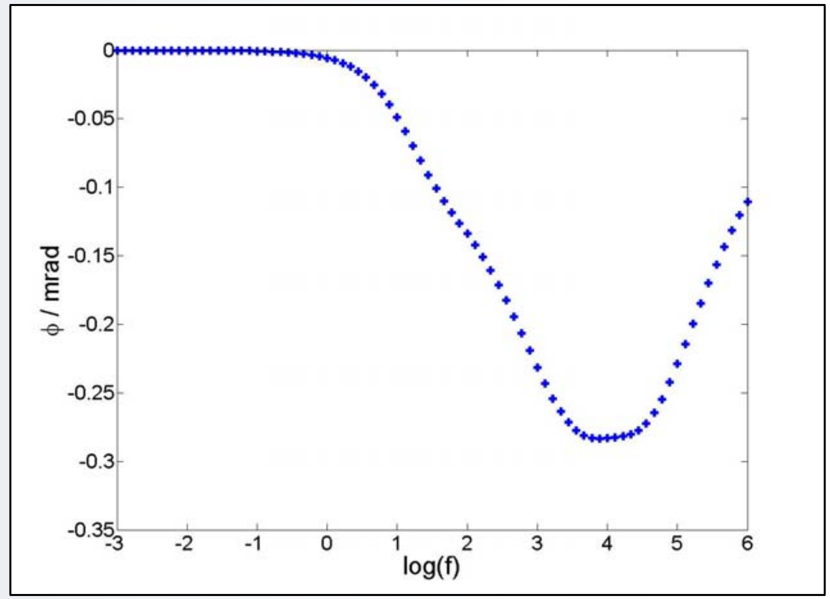

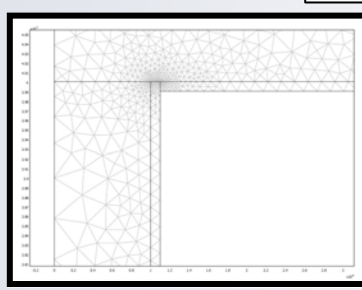

Problem: many mesh-elements

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1. Marshall, D.J. and Madden, T.K., Induced Polarization, a study of its causes, *Geophysics*, **24 (4)**, 790-816 (1959)

2. Blaschek, R. and Hördt, A., Numerical modeling of the IP-effect at the pore scale, *4th International Symposium on Three-Dimensional Electromagnetics*, Freiberg, Germany, (September 27-30, 2007)

3. Titov, K., Komarov, V., Tarasov, A. and Levitski, A., Theoretical and experimental study of time domain-induced polarization in water-saturated sands, *Journal of Applied Geophysics*, **50** ,417-433 (2002)

Thanks for your attention!