Geometrical constraints for membrane polarization

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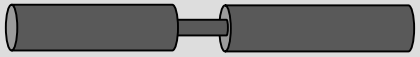
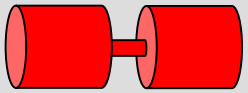
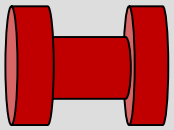
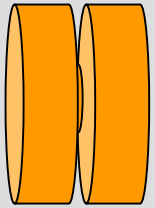


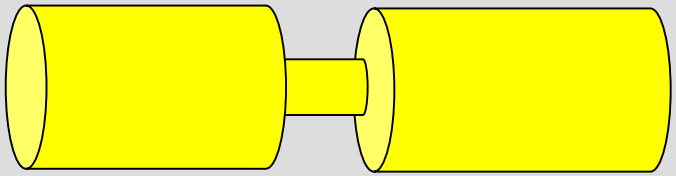
Exploration of parameter space

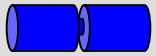
- Pore radii
- Pore lengths
- L/R ratios



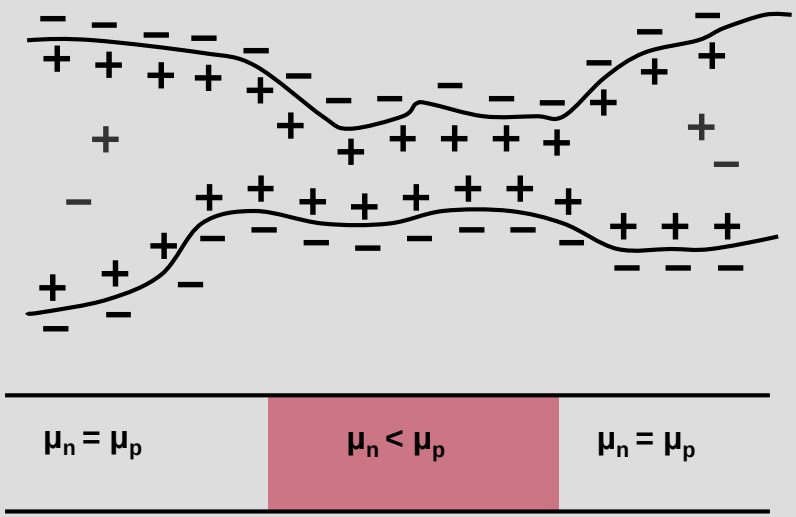


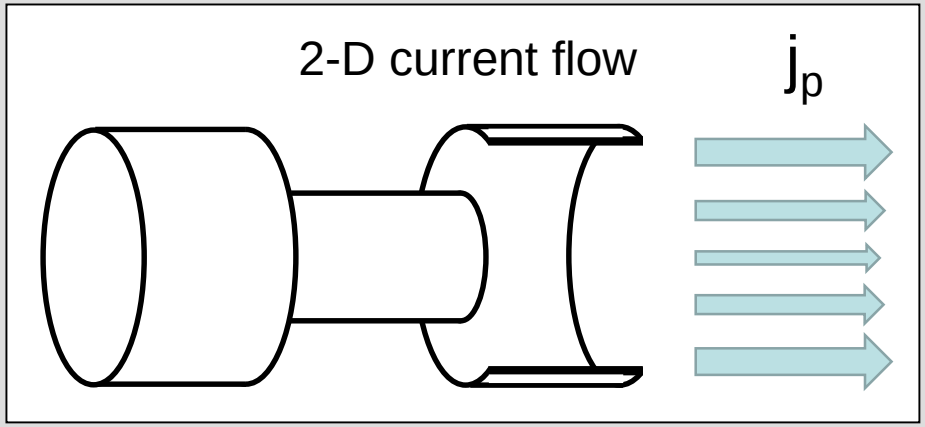






Extended membrane polarization model





Marshall and Madden (1959)

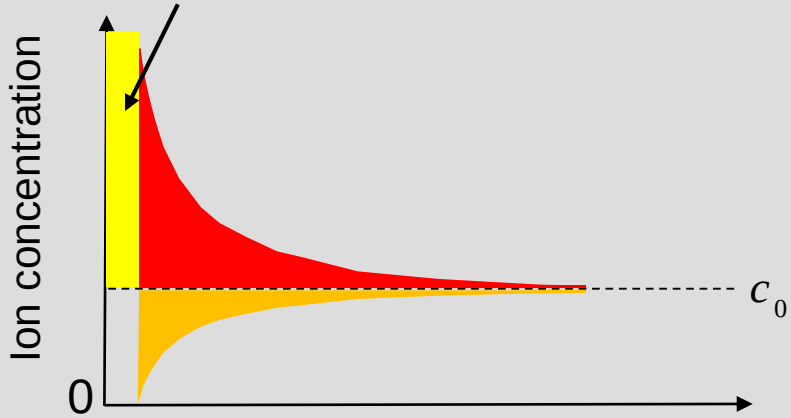
Different charge transport due to

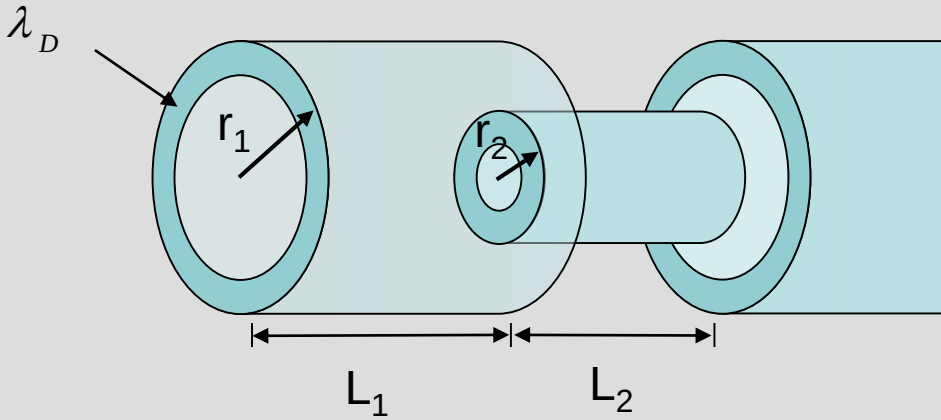
- charge densities
- geometry

Electrical double layer (EDL)

Different charge transport through different ion concentrations

Stern layer: partition coefficient





Integrate concentration over pore radius.

Model parameters

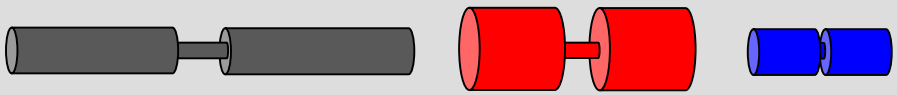
Property	Symbol	Value
Length of pore 1	L_1	$500\ \mu m$
Length of pore 2	L_2	$5\ \mu m$
Radius of pore 1	r_1	$200\ nm$
Radius of pore 2	r_2	$20\ nm$
Ion concentration	c_0	$1\ mol/m^3$
pH	pH	6
Mobility of all ions	$\mu_{p1} = \mu_{p2} = \mu_{n1} = \mu_{n2}$	$5 \cdot 10^{-8} m^2/(Vs)$
Temperature	T	$293\ K$
Zeta-potential	ζ	$-75mV$
Partition coefficient	f_Q	$0,2$

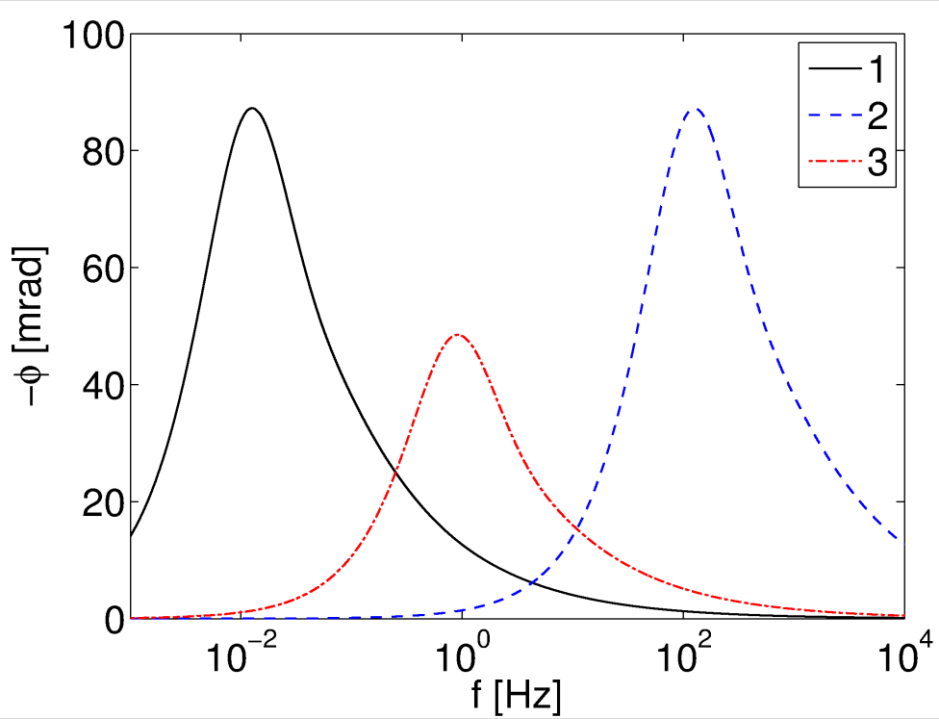
Geometrical parameters

Fluid properties

EDL properties

Sample phase spectra





	1	2	3
R1 (nm)	200	200	1000
R2 (nm)	20	20	20
L1(Micrometer)	500	5	50
L2 (Micrometer)	5	0,05	0,5

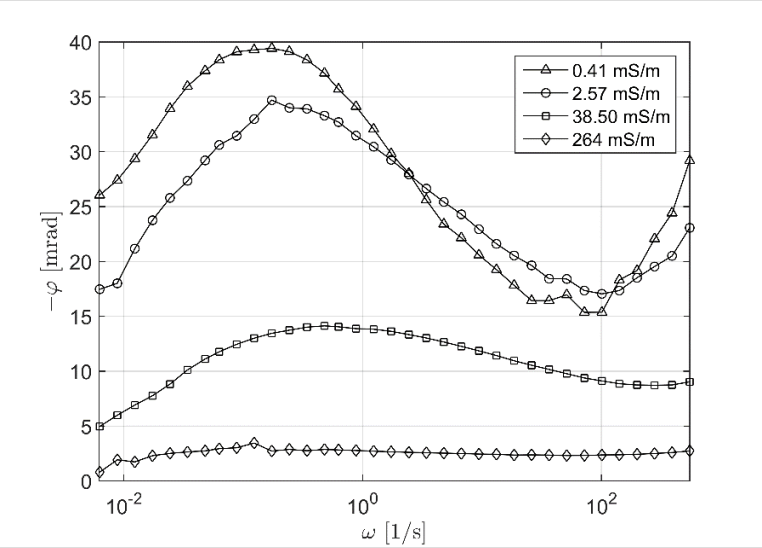
Scope

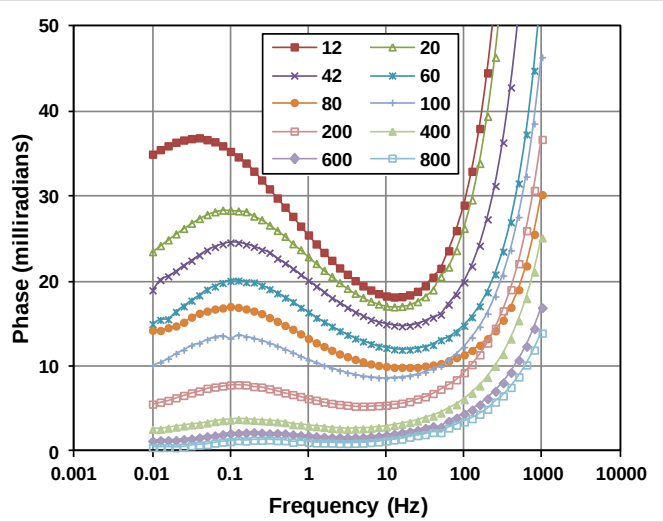
- Constraints on
  - Pore radii
  - Pore lengths
  - L/r ratios

… to simulate measured phase spectra

- Are the required geometries „realistic“

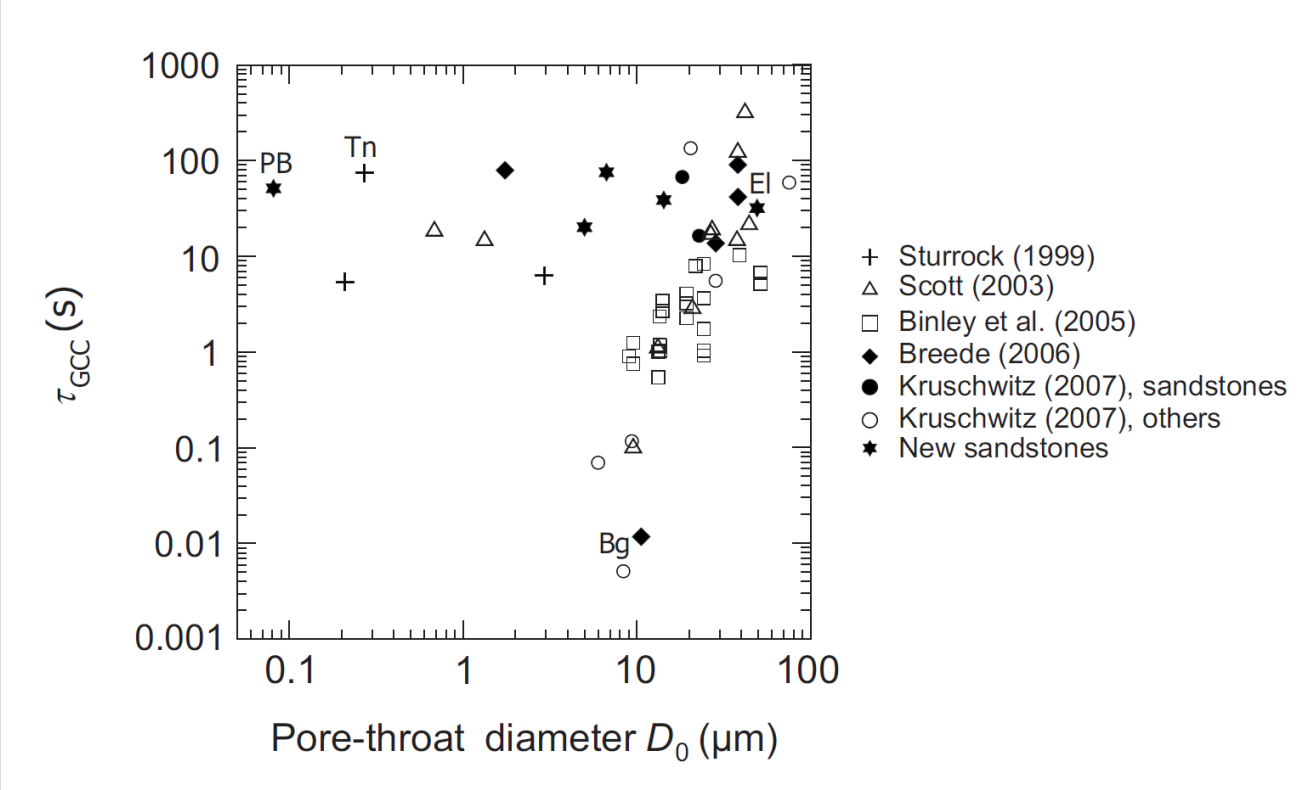
„Typical“ phase spectra of sandstones





Joseph et al. (2015)

Range of relaxation time scales of sandstones

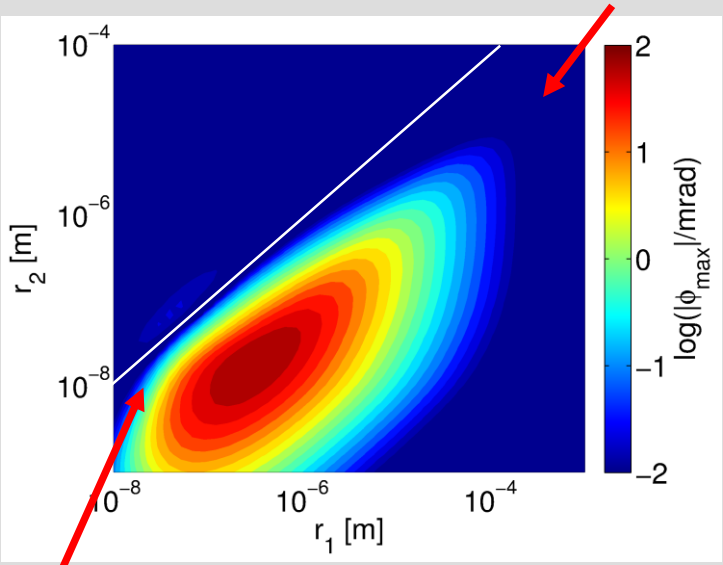


Kruschwitz et al. (2010)

Exploration of parameter space Part 1: pore radii

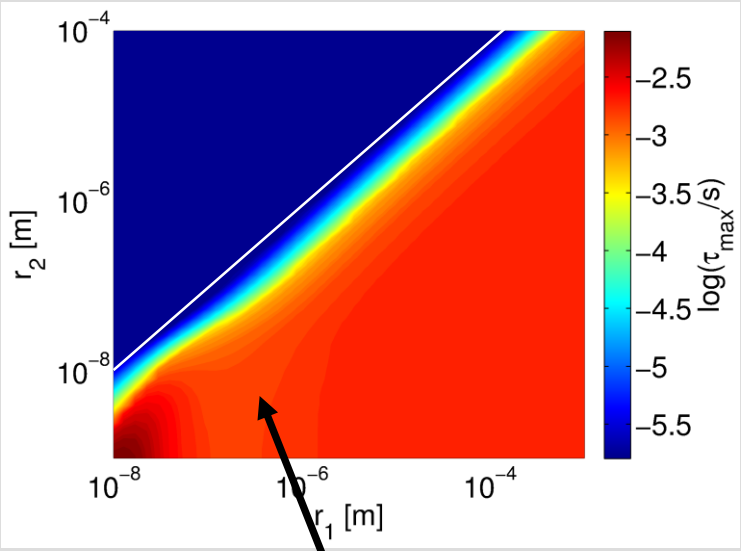
Phase shift

Pore radii too large,
no phase shift



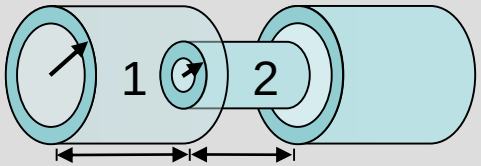
No symmetry
because L different

Relaxation time



Relaxation time independent
of pore radii

Lengths fixed, radii vary

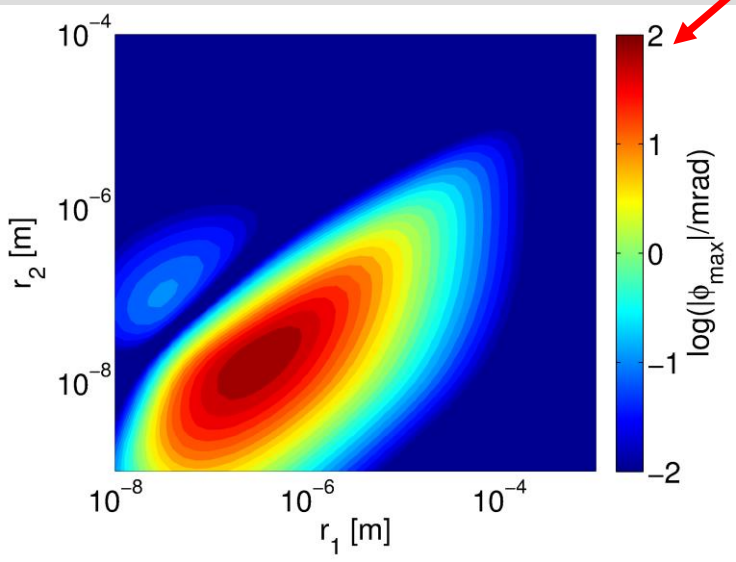


5 µm 0.05 µm

Exploration of parameter space Part 1: pore radii

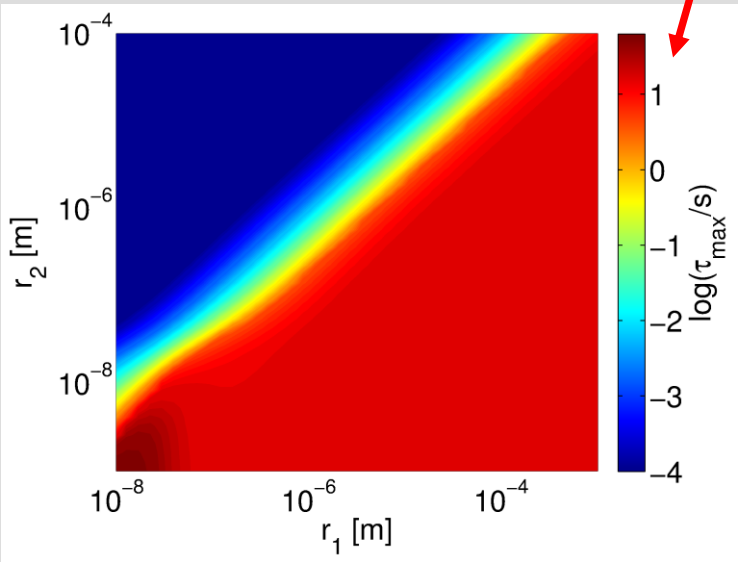
Phase shift

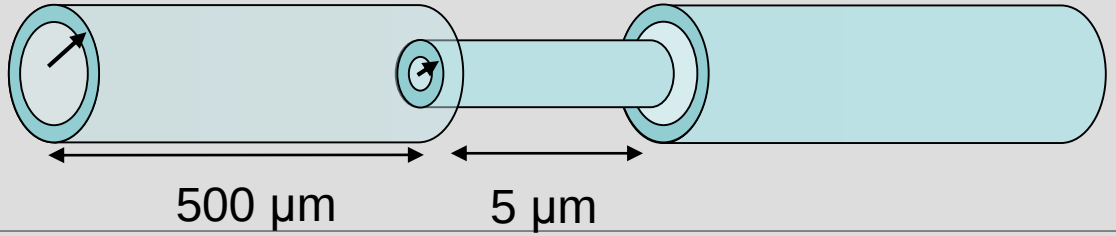
Maximum phase shift unchanged



Relaxation time

Relaxation times much larger





Summary pore radii

Minimum pore radius in the range << 1 µm to produce measurable phase shifts

Time scale fairly independent of pore radii

Are small pore radii relevant ?

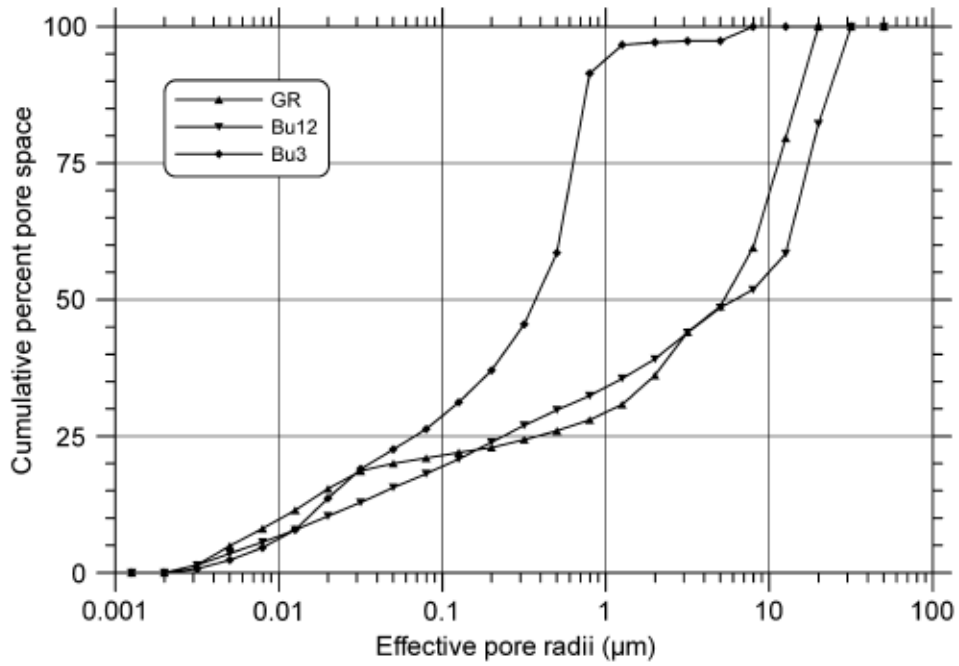


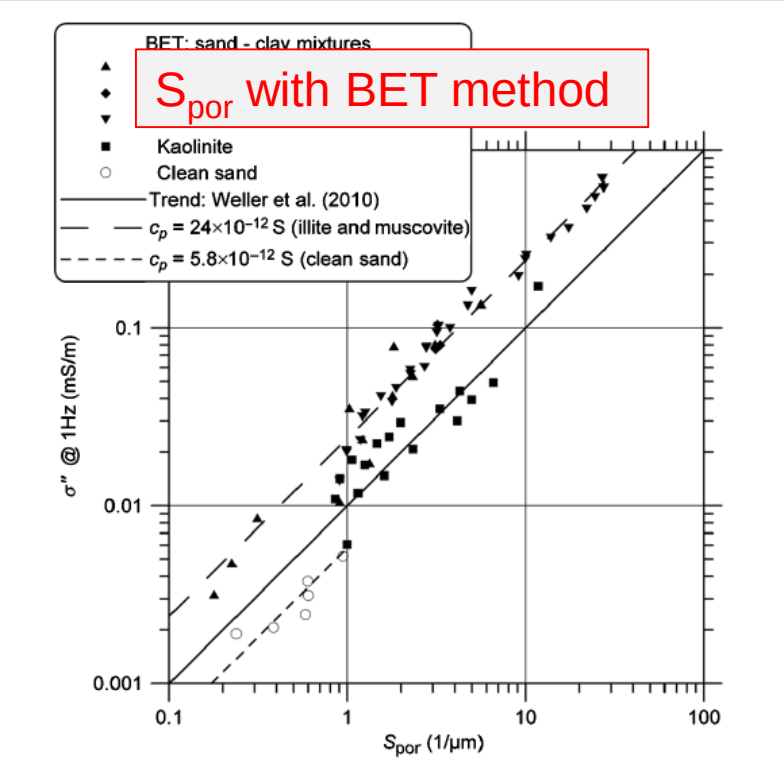
Figure 2. Mercury injection curves for the sandstone samples GR, Bu12, and Bu3.

Weller et al. (2011)

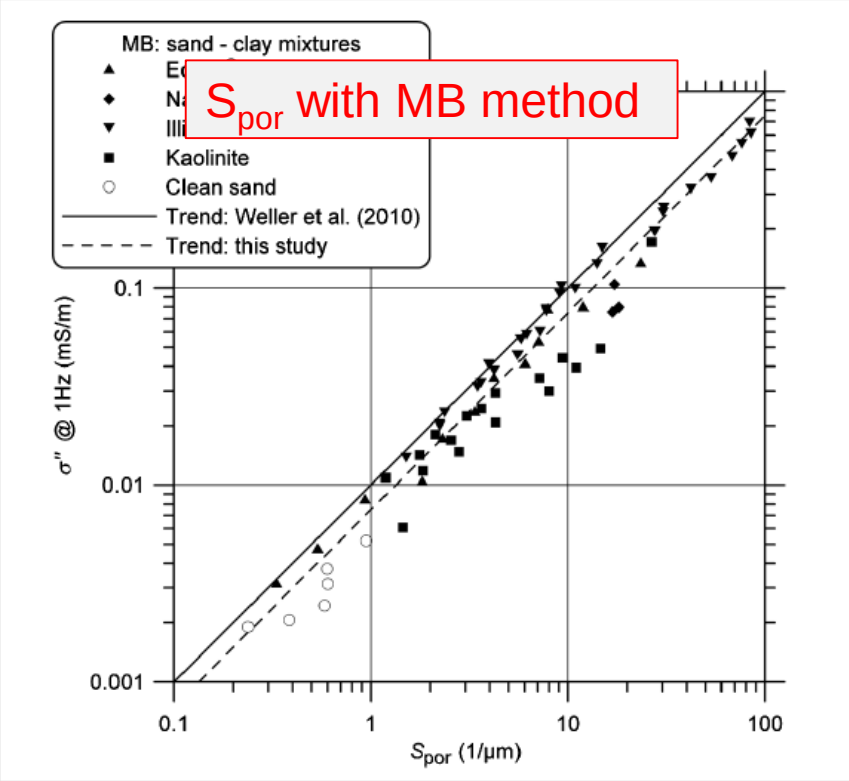
Even 10 nm pores occupy a significant portion of the volume

Are small pore radii relevant ?

Correlations of S_{por} with σ“



S_{por} with BET method



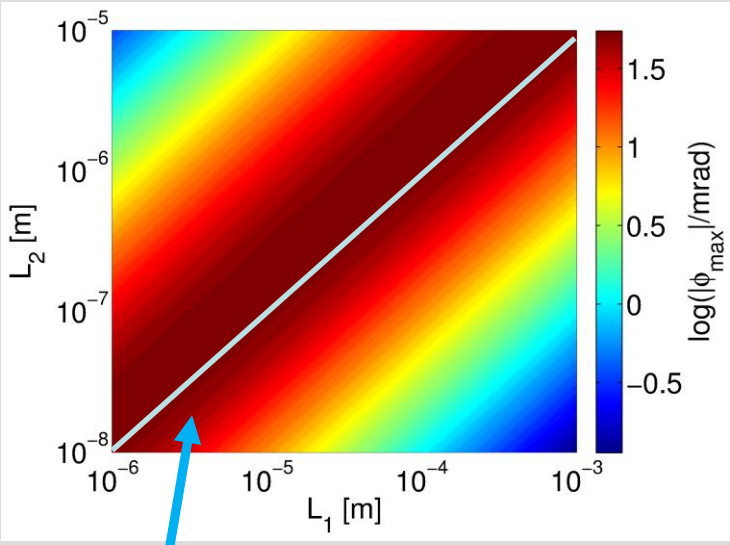
S_{por} with MB method

Weller et al. (2015)

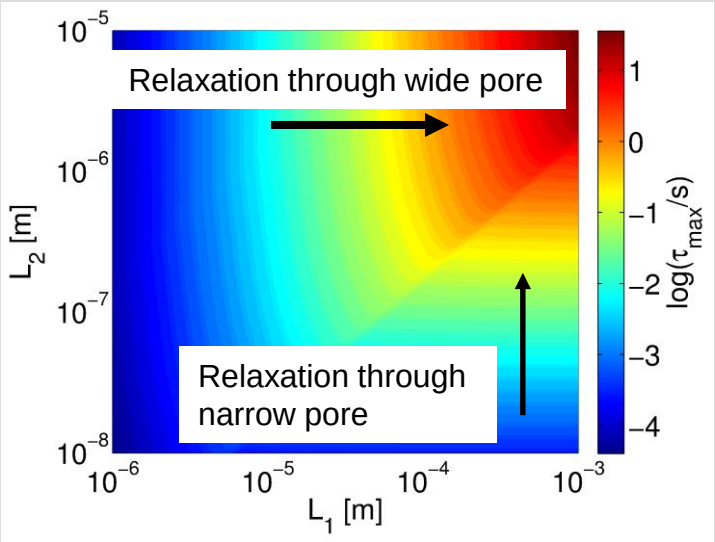
MB (high resolution) better correlation → small pore radii

Exploration of parameter space 2: pore length

Phase shift

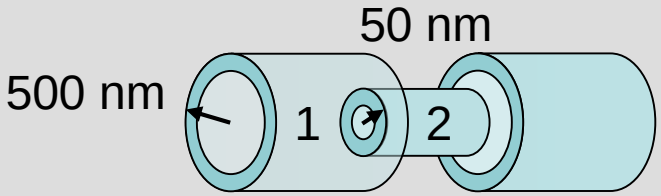


Relaxation time

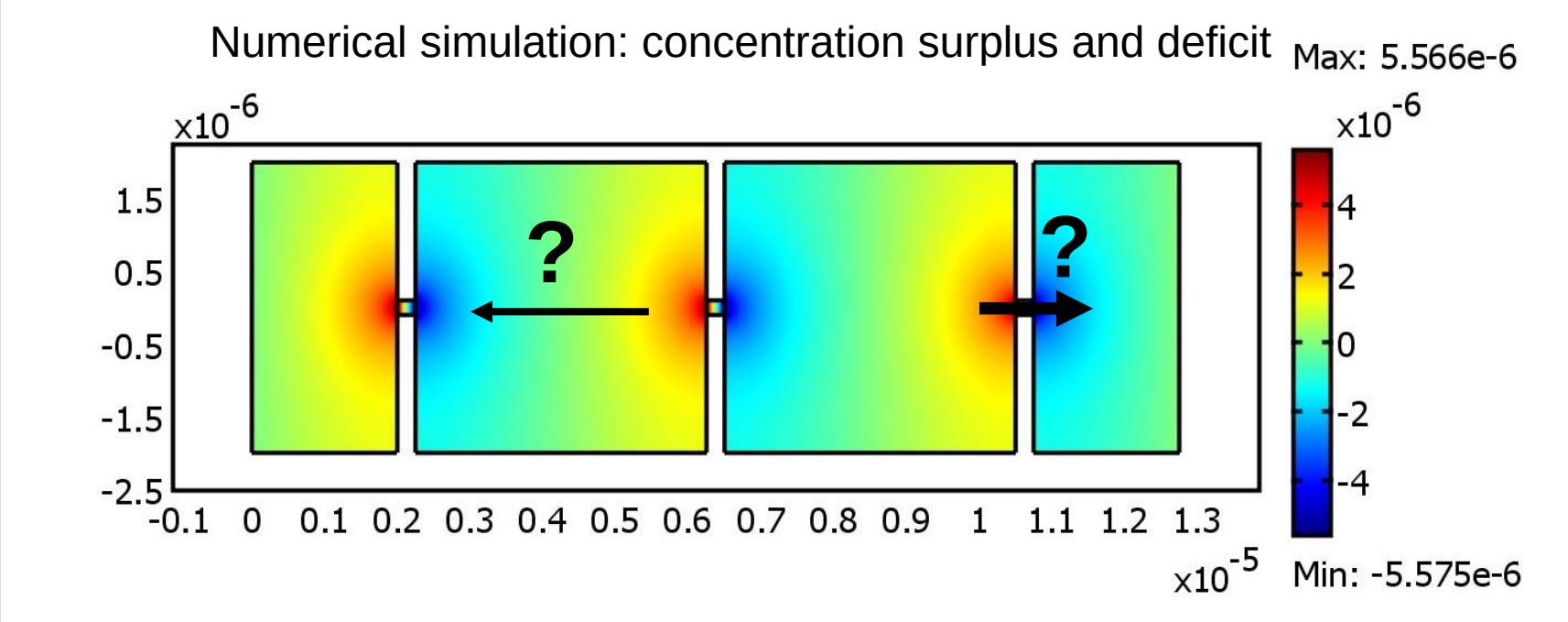


$$\sqrt{\frac{L_1}{L_2}} = 10 = \frac{r_1}{r_2}$$

Pore radii fixed, lengths varied

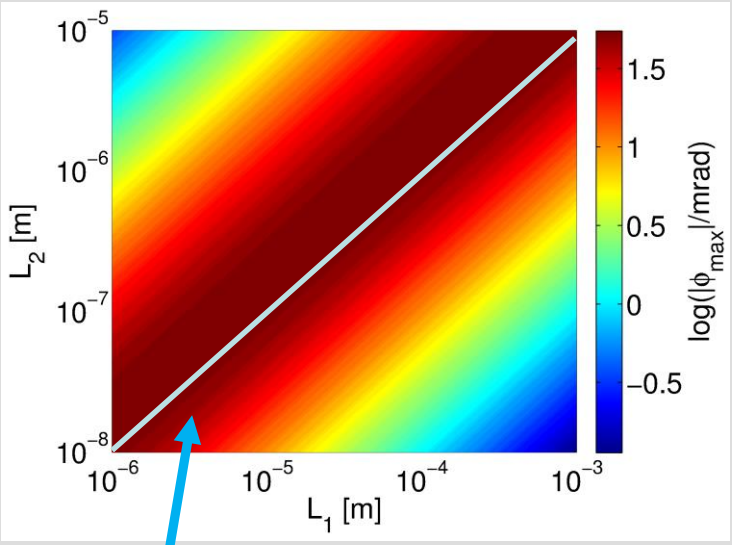


Excursion: Relaxation of concentration gradients

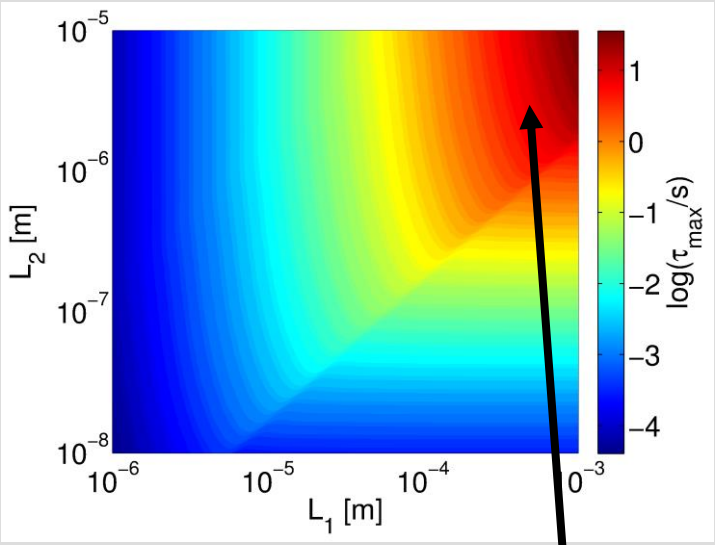


Exploration of parameter space 2: pore length

Phase shift

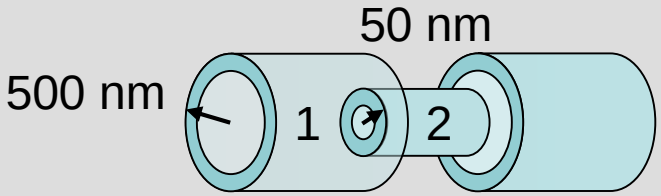


Relaxation time



$$\sqrt{\frac{L_1}{L_2}} = 10 = \frac{r_1}{r_2}$$

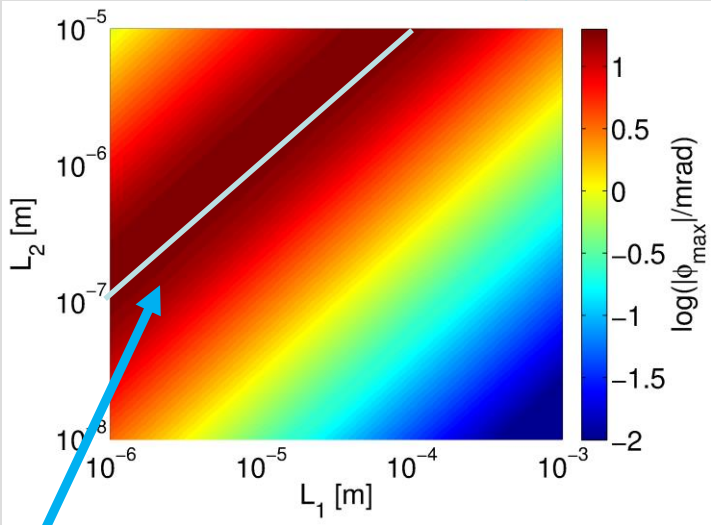
Pore radii fixed, lengths varied



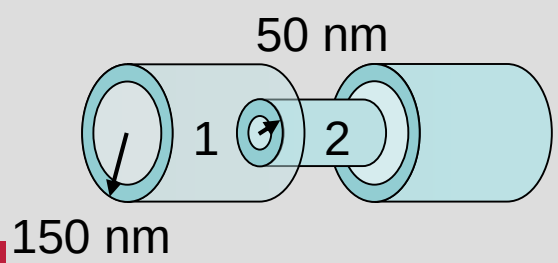
Large length – large time scale

Exploration of parameter space 2: pore length

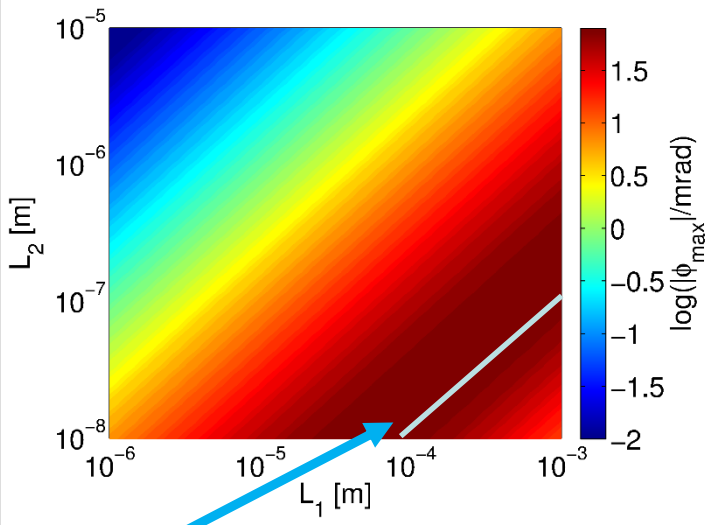
Phase shift



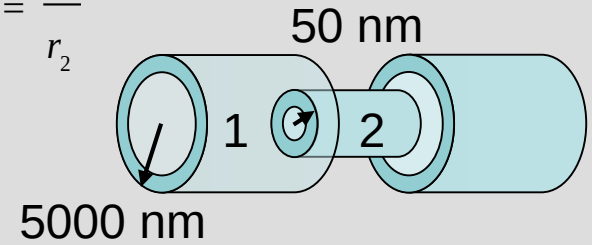
$$\sqrt{\frac{L_1}{L_2}} = 3 = \frac{r_1}{r_2}$$



Phase shift



$$\sqrt{\frac{L_1}{L_2}} = 100 = \frac{r_1}{r_2}$$



Summary pore length

Pore length controls time scale

Optimum length ratio connected to radius ratio:

$$\sqrt{\frac{L_1}{L_2}} = \frac{r_1}{r_2}$$

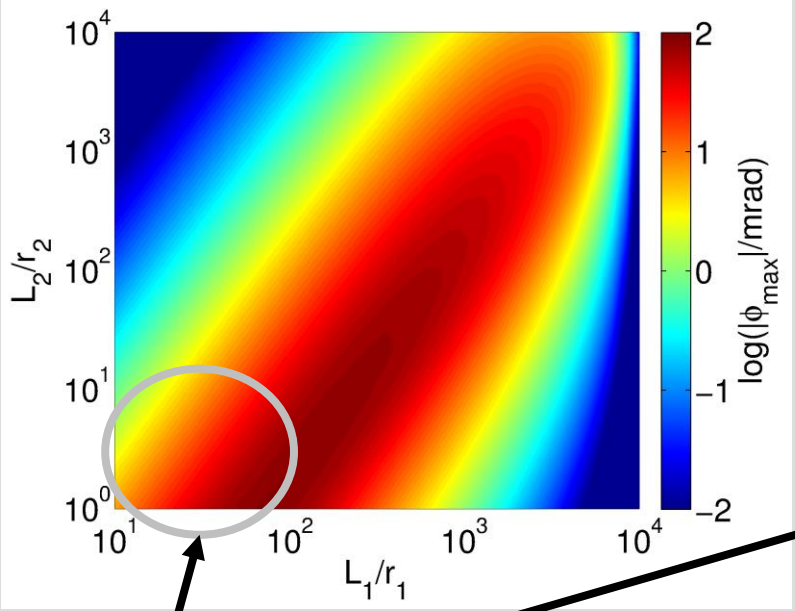
Length and radii:

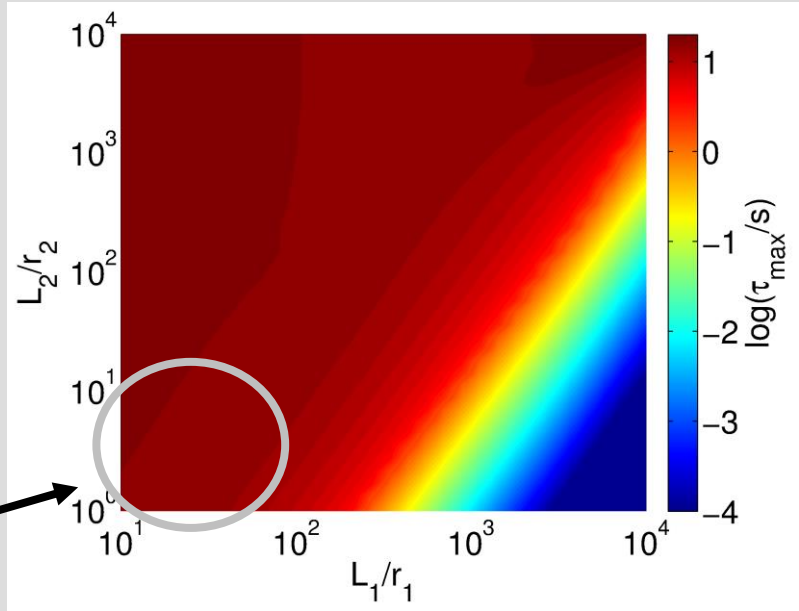
„Small“ radii required for large phase shifts

„Large“ length required for large time scale (> 1s)

Large L/r ratio required ?

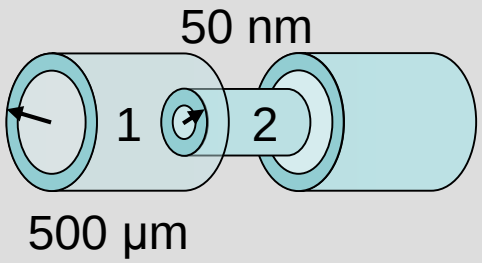
Exploration of parameter space Part 3: L/r





Moderate L/r ratios,
large phase shift,
large time scales

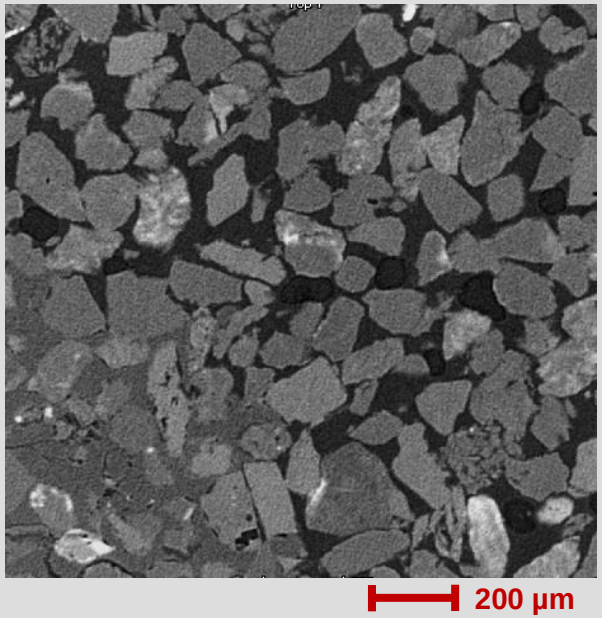
Fix L_1 and r_2



Can L/r ratios be constrained?

Figure 1. Micrographs of thin sections of the samples (a) GR with the size $850 \times 690\ \mu m^2$, (b) Bu12 with the size $850 \times 690\ \mu m^2$, and (c) Bu3 with the size $2125 \times 1700\ \mu m^2$.

Weller et al. (2011)



Bairlein et al. (2016)

Describing real pore space not trivial
Current high-resolution methods do not give information on L

Conclusions

- Wide range of time scales and phase shifts simulated
- Membrane polarization Not particular for long time scales
- Pore length controls time scale
- Pore radii AND length control phase shift

$$\sqrt{\frac{L_1}{L_2}} = \frac{r_1}{r_2}$$

- No evidence that these are „unrealistic“

Acknowlegdements

Matthias Bücker

DFG (Ho1506/23-1)

Thank you for your attention