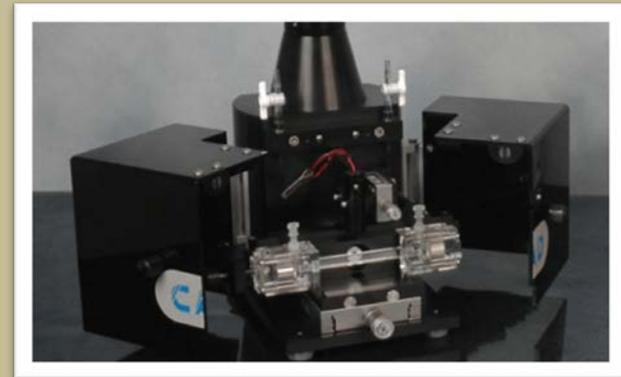
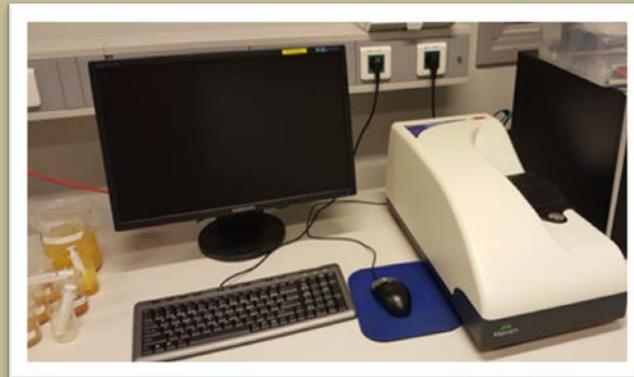
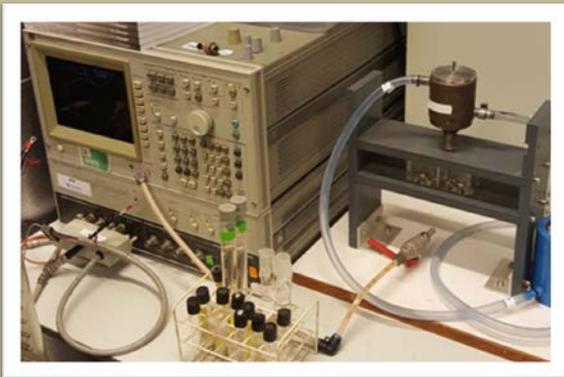
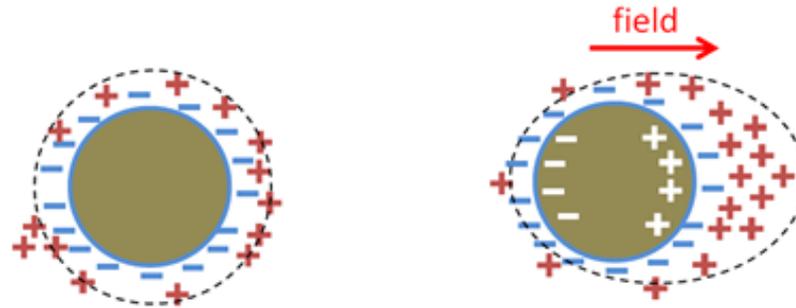


Electrokinetic response of (mainly) porous media



Electrokinetics : Polarization and mobility



When an electric field is applied to a colloidal particle, an electric dipole $\mathbf{P} = \alpha \mathbf{E}$ is formed and the particle has an electrophoretic mobility μ_0 .
In general:

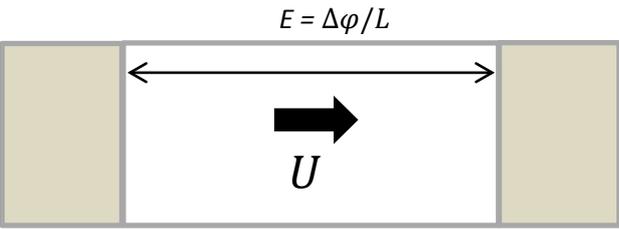
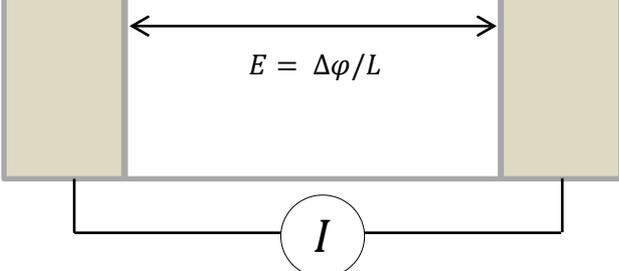
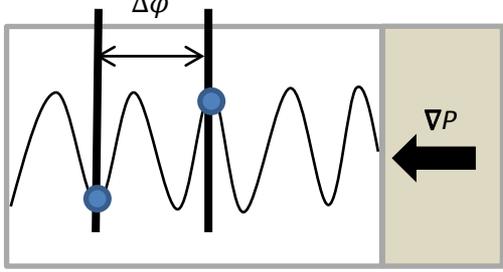
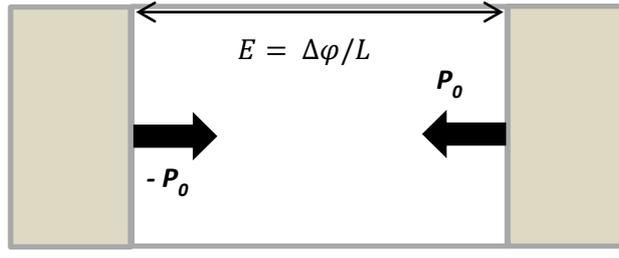
$$\begin{aligned} \mu_0 &= f(\alpha) \\ \alpha &= f(\mu_0) \end{aligned} \quad \rightarrow \quad \begin{array}{l} \text{information about :} \\ \text{particle charge, size, Stern layer} \end{array}$$

General expressions for μ_0 and α are available, for all surface charges and ionic strengths and several particle shapes.

[1] Chassagne, C., and D. Bedeaux. "The dielectric response of a colloidal spheroid." *Journal of colloid and interface science* 326.1 (2008): 240-253.

[2] Chassagne, C., F. Mietta, and J. C. Winterwerp. "Electrokinetic study of kaolinite suspensions." *Journal of Colloid and Interface Science* 336.1 (2009): 352-359.

Electrokinetic measurements

suspensions	Electrophoretic mobility (EM)	$\mu_{EM} = \left(\frac{U}{E} \right)_{\Delta P=0}$	
all	Conductivity	$\sigma = f(\alpha) = \left(\frac{I}{E} \right)_{\Delta P=0}$	
slurries	Colloid Vibration Potential (CVP)	$\left(\frac{\Delta\phi}{\Delta P} \right)_{I=0} = \mu_{CVP} \frac{\phi_s}{\sigma} \frac{\Delta\rho}{\rho}$	
slurries	Electrokinetic Sonic Amplitude (ESA)	$\left(\frac{P_0}{E} \right)_{\Delta P=0} = \mu_{ESA} \phi_s \frac{z_S z_B}{z_S + z_B} \frac{\Delta\rho}{\rho}$	

Research questions

question 1 :

$$\mu_{EM} = \mu_{CVP} = \mu_{ESA} ?$$

question 2 :

How can the electric conductivity $\sigma = f(\alpha)$ be expressed as function of independently measurable parameters for suspensions, slurries and soils?

suspensions	Electrophoretic mobility (EM)	$\mu_{EM} = \left(\frac{U}{E} \right)_{\Delta P=0}$
all	Conductivity	$\sigma = f(\alpha) = \left(\frac{I}{E} \right)_{\Delta P=0}$
slurries	Colloid Vibration Potential (CVP)	$\left(\frac{\Delta\phi}{\Delta P} \right)_{I=0} = \mu_{CVP} \frac{\phi_s}{\sigma} \frac{\Delta\rho}{\rho}$
slurries	Electrokinetic Sonic Amplitude (ESA)	$\left(\frac{P_0}{E} \right)_{\Delta P=0} = \mu_{ESA} \phi_s \frac{z_S z_B}{z_S + z_B} \frac{\Delta\rho}{\rho}$

entropy production: $\sigma_{tot} = \sigma_E + (\sigma_g + \sigma_P)^{bar}$

$$\sigma_E = \frac{\mathbf{I} \cdot \mathbf{E}}{T}$$

$$\sigma_g^{bar} = \frac{1}{T} \mathbf{g} \cdot \mathbf{J}^{bar} = 0$$

$$\sigma_P^{bar} = \frac{1}{T} \frac{\nabla P}{\rho} \cdot \mathbf{J}^{vol}$$

independent of frame of reference

total mass flow is zero in barycentric frame of reference :
 $\mathbf{J}^{bar} = 0$

total mass flow in volume-fixed frame of reference:
 $\mathbf{J}^{vol} = \Delta\rho\phi_s \mathbf{U}^{vol}$; where \mathbf{U}^{vol} is the velocity of particle in volume-fixed frame of reference

$$\mathbf{J}^{vol} = b_{PP} \frac{\nabla P}{\rho} + b_{PE} \mathbf{E}$$

$$\mathbf{I} = b_{EP} \frac{\nabla P}{\rho} + b_{EE} \mathbf{E}$$

$$\mathbf{U}^{vol} = d_{PP} \Delta\rho\phi_s \frac{\nabla P}{\rho} + d_{PE} \mathbf{E}$$

$$\mathbf{I} = d_{EP} \Delta\rho\phi_s \frac{\nabla P}{\rho} + d_{EE} \mathbf{E}$$

electric conductivity:

$$b_{EE} = d_{EE} = \sigma$$

electrophoretic mobility:

$$d_{PE} = \mu_{CVP} = \left(\frac{U^{vol}}{E} \right)_{\nabla P=0} = \left(\frac{U^{lab} - (U_{vol})^{lab}}{E} \right)_{\nabla P=0}$$

no acoustic wave \rightarrow no volume flow: $(U_{vol}^{lab})_{\nabla P=0} = 0$

$$\mu_{CVP} = \mu_{EM}$$

Link CVP / EM : $(E)_{I=0} = \frac{-\mu_{EM}}{\sigma} \frac{\Delta\rho}{\rho} \phi_s (\nabla P)_{I=0}$

Research question 1

It can similarly be demonstrated that:

$$(1 - \phi_s) \underbrace{\mu_0}_{\text{theory}} = \underbrace{\mu_{EM} = \mu_{CVP}}_{\text{zero volume flux}} = \frac{\rho}{\rho_w} \underbrace{\mu_{ESA}}_{\text{zero mass flux}}$$

years of debate...

"In their 1999 paper Dukhin and co-workers asserted that for CVP and CVI measurements, the "correct inertial frame is the laboratory frame of reference, [...]"

The relationship (Eq. (1.4)) between the ESA and the dynamic mobility, which is derived in Appendix A, is based on the use of a laboratory frame of reference. If this were not the case and as Dukhin asserts, the frame of reference moves back and forth with some part of the measuring device, there would be an alternating inertial force in the governing equations." [O'Brien et al., Coll. and Surf. A, 2003]

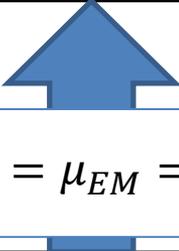
[1] Chassagne, C., and D. Bedeaux. "Reciprocal relations in electroacoustics." *The Journal of chemical physics* 141.4 (2014): 044703.

[2] Gourdin-Bertin, Simon, et al. "Onsager's reciprocal relations in electrolyte solutions. I. Sedimentation and electroacoustics." *The Journal of chemical physics* 143.6 (2015): 064708.

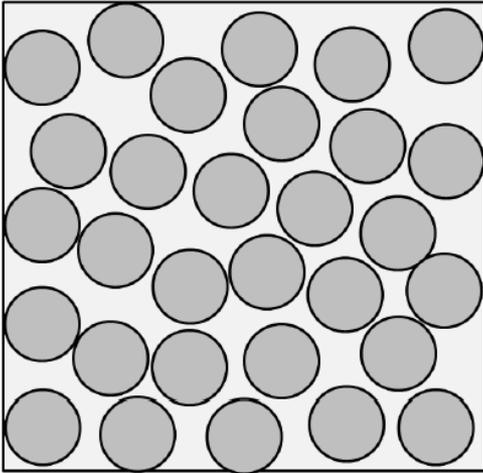
[3] Gourdin-Bertin, S., and C. Chassagne. "Onsager's reciprocal relations for electroacoustic and sedimentation: Application to (concentrated) colloidal suspensions." *The Journal of chemical physics* 142.19 (2015): 194706.

Future electrokinetic measurements

Caution should be taken regarding the frame of reference to link the different fluxes!

porous media	Streaming Potential (SP)	$\left(\frac{\Delta\varphi}{\Delta P}\right)_{I=0} = \frac{\varepsilon_0 \varepsilon_r}{\eta \sigma} \zeta$	“open” system
<div style="text-align: center;">  <div style="border: 1px solid blue; padding: 5px; display: inline-block;"> $\mu_{CVP} = \mu_{EM} = \frac{\varepsilon_0 \varepsilon_r}{\eta} \zeta$ </div> </div>			how to reconcile SP and CVP in case μ_{EM} is more complex?
slurries	Colloid Vibration Potential (CVP)	$\left(\frac{\Delta\varphi}{\Delta P}\right)_{I=0} = \frac{\mu_{CVP}}{\sigma} \frac{\Delta\rho}{\rho} \phi_s$	“closed” system

Research question 2 for porous media



The porous media is seen as packed, immobile spheres in an electrolyte.

In this case:

$$\mu_0 = 0$$

- a) How to correlate α to the electric conductivity σ ?
- b) How to correlate α to relevant system parameters?

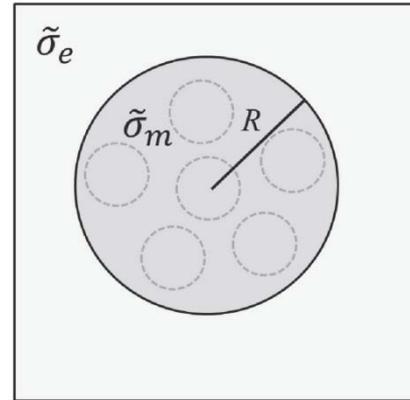
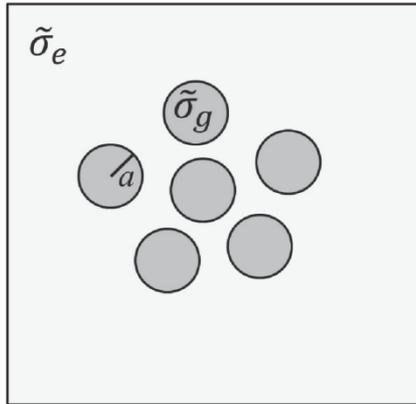
Note: for convenience, the dipolar coefficient β will be used instead of the polarizability α :

$$\alpha = 4\pi\epsilon_0\epsilon_e a^3 \beta$$

$\epsilon_0\epsilon_e$ is the dielectric permittivity of water

a is the radius of a sphere

How to correlate β to the electric conductivity σ



$$\tilde{\Psi}_{out} = -\mathbf{E} \cdot \mathbf{r} \left[1 - N\tilde{\beta} \left(\frac{a}{r} \right)^3 \right]$$

$$\tilde{\Psi}_{out} = -\mathbf{E} \cdot \mathbf{r} \left[1 - \tilde{\beta}_m \left(\frac{R}{r} \right)^3 \right]$$

$$\tilde{\beta}_m = \tilde{\beta} \frac{Na^3}{R^3} = \tilde{\beta} \phi_s$$

$$\tilde{\sigma}_m(\omega) = \tilde{\sigma}_e(\omega) \frac{1 + 2\phi_s \tilde{\beta}(\omega)}{1 - \phi_s \tilde{\beta}(\omega)}$$

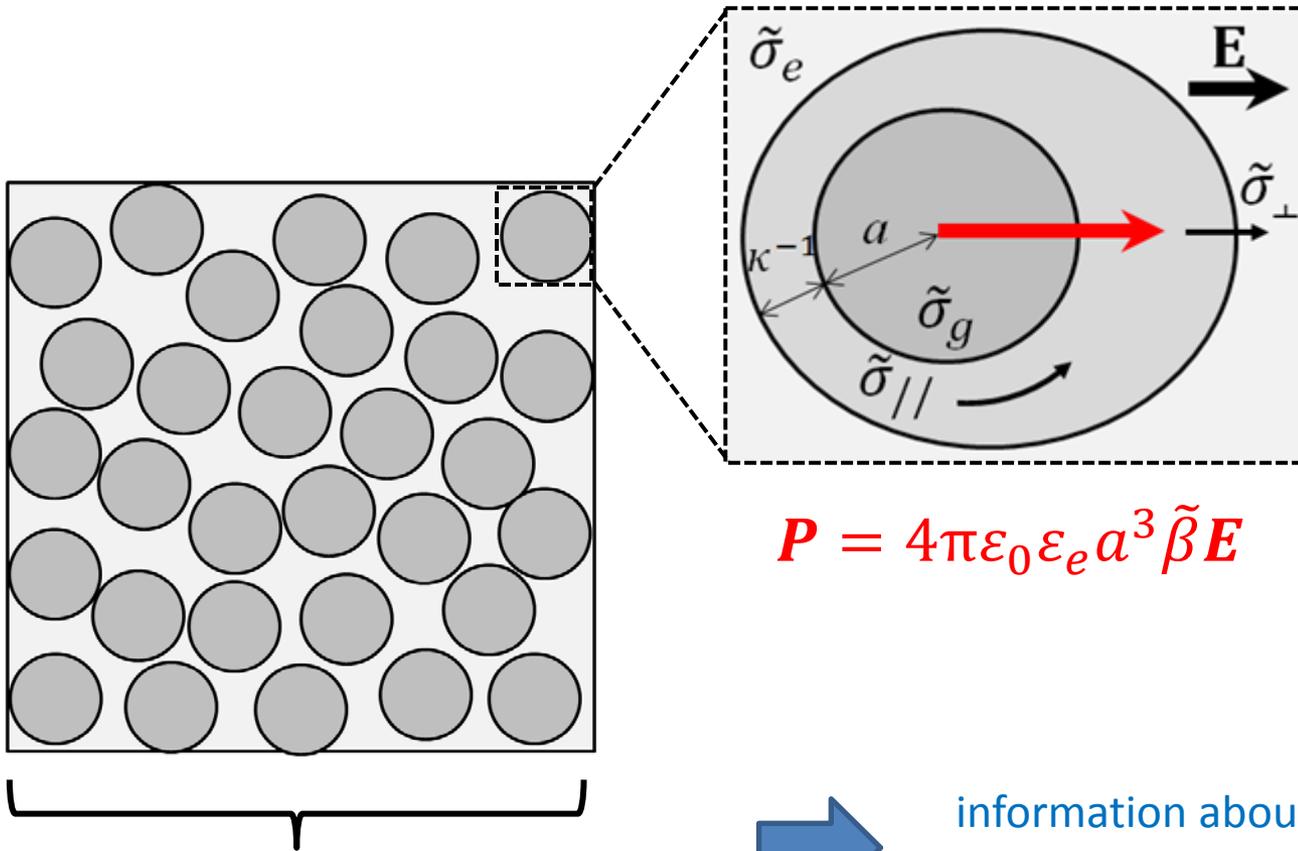
$$\tilde{\sigma}_m \left(\frac{\partial \tilde{\Psi}_{in}}{\partial r} \right)_{r=R} = \tilde{\sigma}_e \left(\frac{\partial \tilde{\Psi}_{out}}{\partial r} \right)_{r=R}$$

$$\Delta \tilde{\Psi}_{in}(r < R) = 0$$

$$\tilde{\Psi}_{in}(R) = \tilde{\Psi}_{out}(R)$$

$$\tilde{\beta}_m = \frac{\tilde{\sigma}_m - \tilde{\sigma}_e}{\tilde{\sigma}_m + 2\tilde{\sigma}_e}$$

How to correlate β to relevant system parameters



$$P = 4\pi\epsilon_0\epsilon_e a^3 \tilde{\beta} E$$



information about :
particle charge, size, Stern layer,
porosity, ionic strength, temperature

$$\tilde{\sigma}_m = \sigma_m + i\omega\epsilon_0\epsilon_r$$

Maxwell-Wagner-Clausius-Mossotti

$$\tilde{\sigma}_m(\omega) = \tilde{\sigma}_e(\omega) \frac{1 + 2\phi_s \tilde{\beta}(\omega)}{1 - \phi_s \tilde{\beta}(\omega)}$$

Maxwell-Wagner

Uncharged sphere



$$\tilde{\beta} = \frac{\tilde{\sigma}_g - \tilde{\sigma}_e}{\tilde{\sigma}_g + 2\tilde{\sigma}_e}$$



$$\frac{\tilde{\sigma}_m - \tilde{\sigma}_e}{\tilde{\sigma}_m + 2\tilde{\sigma}_e} = \phi_s \frac{\tilde{\sigma}_g - \tilde{\sigma}_e}{\tilde{\sigma}_g + 2\tilde{\sigma}_e}$$

Charged sphere



$$\tilde{\beta} = \frac{\tilde{\sigma}_g - \tilde{\sigma}_e + \tilde{\sigma}_{//} + \tilde{\sigma}_{\perp}}{\tilde{\sigma}_g + 2\tilde{\sigma}_e + \tilde{\sigma}_{//} - 2\tilde{\sigma}_{\perp}}$$



new expression

$$\tilde{\sigma}_{//} = \sigma_{//} = 2 \frac{\sigma_e}{\kappa a} \left[\exp\left(\frac{e|\zeta|}{2kT}\right) - 1 \right]$$

$$\tilde{\sigma}_{\perp} = -\frac{J_1}{J_2} \sigma_{//}$$

$$J_1 = 1 + a\sqrt{i\omega/D}$$

$$J_2 = 1 + (1 + a\sqrt{i\omega/D})^2$$

$$\tilde{\sigma}_m = \tilde{\sigma}_e \frac{[\tilde{\sigma}_g + 2\tilde{\sigma}_e + \sigma_{//} (1 + 2J_1/J_2)] + 2\phi_s [\tilde{\sigma}_g - \tilde{\sigma}_e + \sigma_{//} (1 - J_1/J_2)]}{[\tilde{\sigma}_g + 2\tilde{\sigma}_e + \sigma_{//} (1 + 2J_1/J_2)] - \phi_s [\tilde{\sigma}_g - \tilde{\sigma}_e + \sigma_{//} (1 - J_1/J_2)]}$$

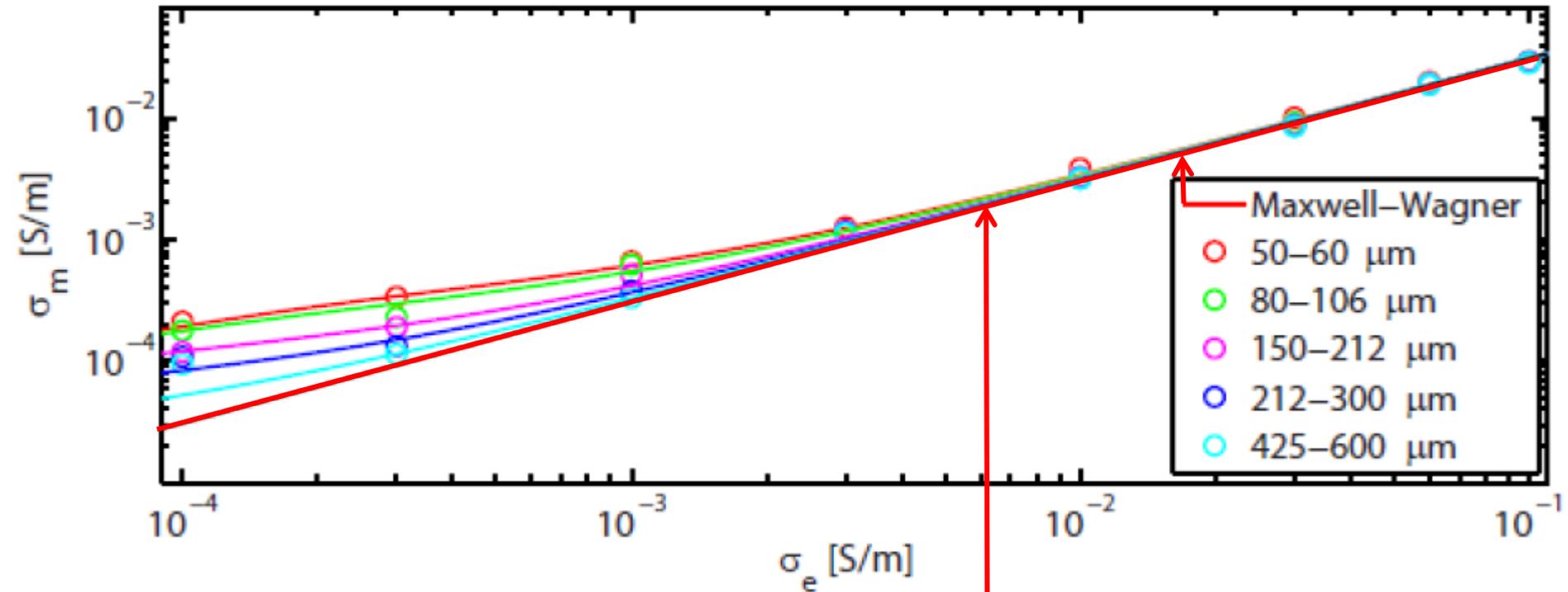
Comparison with other theories

models based on Schwartz (1962)	full theory
considers only the movement of counterions parallel to the sphere: $\tilde{\sigma}_{\perp} = 0$	all movements of ions are considered
$\sigma_{\parallel, Schwartz} = \sigma_{\parallel} \left(\frac{i\omega\tau_k}{1 + i\omega\tau_k} \right); \tau_k = a^2/(2D)$	
<p>for $\omega \gg \omega_a = D/a^2$: the theories give the same (complex) conductivity</p> $\sigma_{\parallel, Schwartz} = \sigma_{\parallel}$ $\tilde{\sigma}_{\perp} = 0$	
$\tilde{\sigma}_m = \sigma + \tilde{\sigma}_{surf} + \tilde{\sigma}_{hf}$ <p style="text-align: center;">↑ Archie ↓</p> $\sigma = \phi^m \sigma_e$ $m \equiv \ln \left[\frac{\phi}{3/2 - \phi/2} \right] / \ln [\phi] \simeq 3/2$	$\sigma \equiv \frac{1 - \phi_s}{1 + \phi_s/2} \sigma_e$ $\tilde{\sigma}_{surf} \equiv \frac{3\phi_s x \tilde{\sigma}_e}{1 + \phi_s(1-x) + \phi_s^2(1/2-x)/2}$ $\tilde{\sigma}_{hf} \equiv \frac{1 - \phi_s}{1 + \phi_s/2} i\omega\epsilon_0\epsilon_e$ $x = \frac{3(\tilde{\sigma}_g + \sigma_{//})}{2[\tilde{\sigma}_g + 2\tilde{\sigma}_e + \sigma_{//}(1 + 2J_1/J_2)]}$

Revil, André, and Magnus Skold. "Salinity dependence of spectral induced polarization in sands and sandstones." *Geophysical Journal International* 187.2 (2011): 813-824.

Vinegar, H. J. & Waxman, M. H., 1984. Induced polarization of shaly sands, *Geophysics*, 49(8), 1267–1287.

Charged glass beads ($q = 6.2 \text{ mC/m}^2$) at $\omega \rightarrow 0$

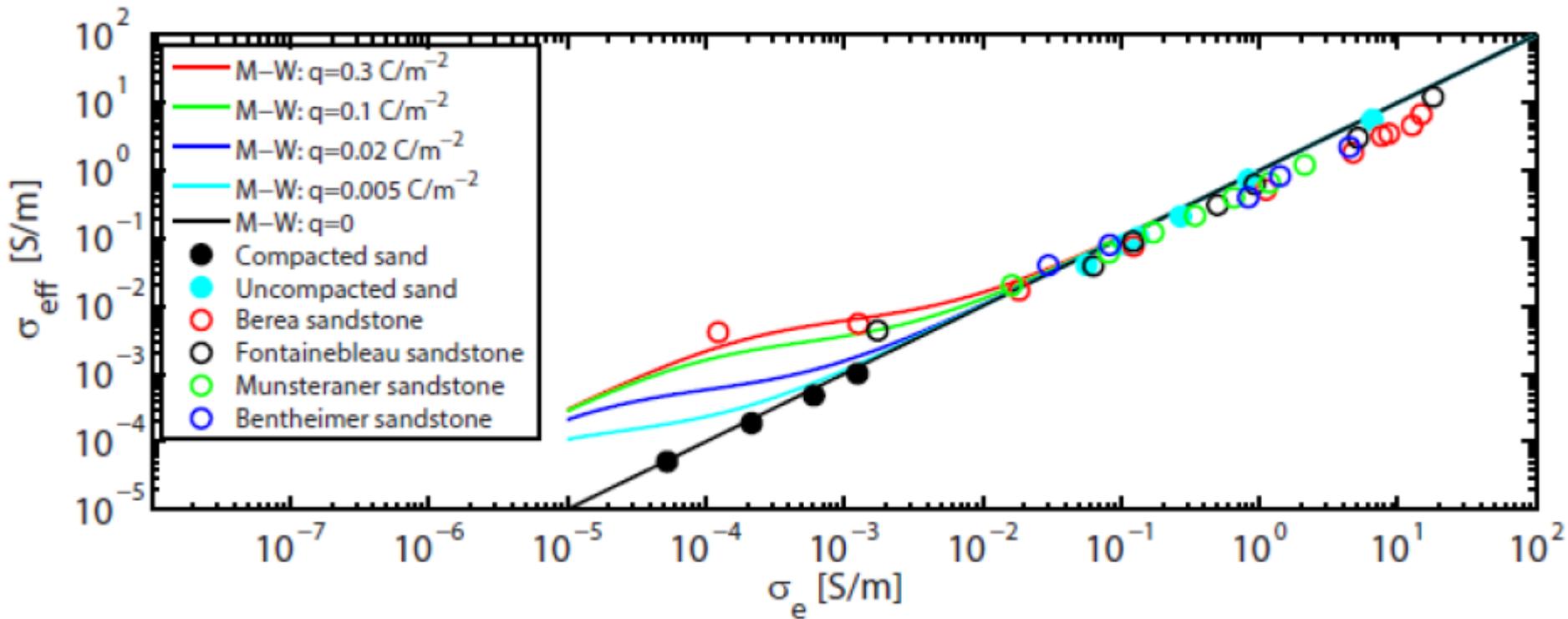


$$Du = \frac{\sigma_{//}}{\sigma_e} = \frac{2}{\kappa a} \left[\exp\left(\frac{e|\zeta|}{2kT}\right) - 1 \right]$$



$$\sigma_m^{Du=0} = \sigma_e \frac{1 - \phi_s}{1 + \phi_s/2}$$

Sands and sandstones at $\omega \rightarrow 0$



$$\sigma_{eff} = \sigma_m / \sigma_m^{Du=0}$$

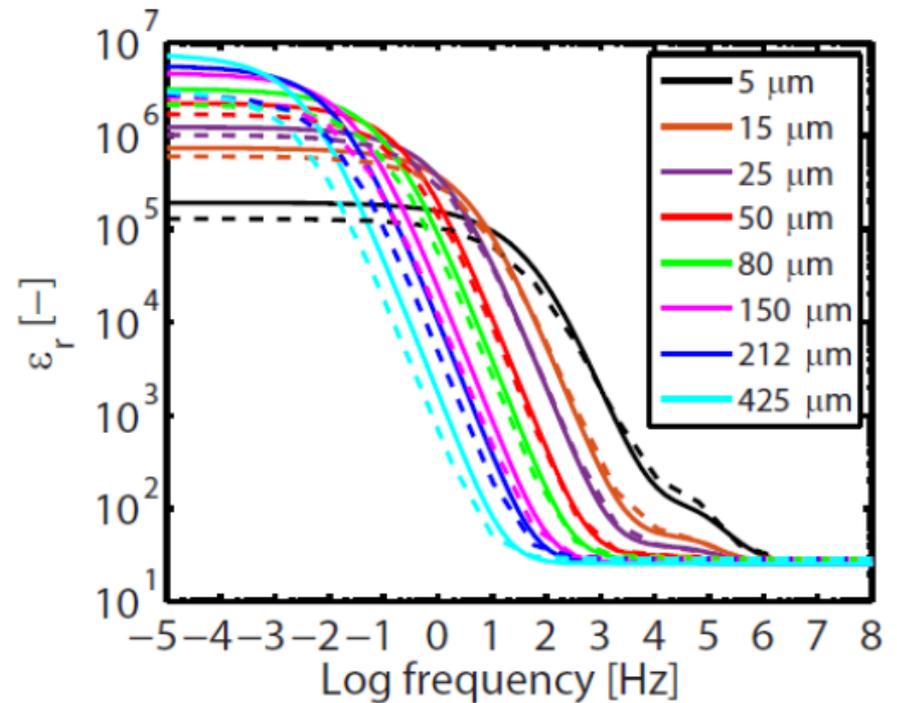
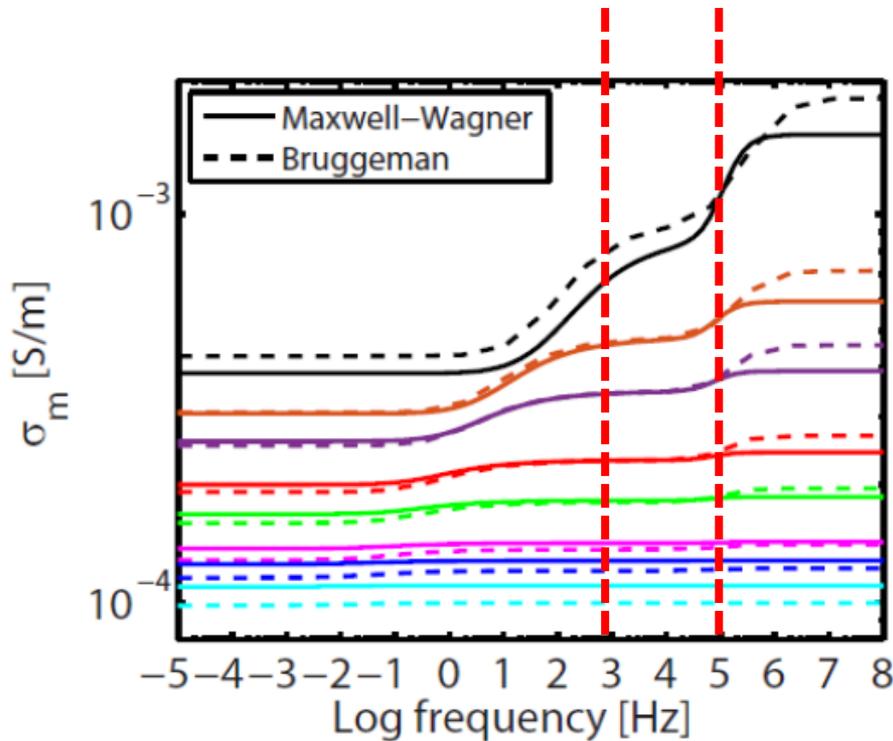
with $\sigma_m^{Du=0} = \sigma_e \frac{1 - \phi_s}{1 + \phi_s/2}$

Kirichek, A., C. Chassagne, and R. Ghose. "Dielectric spectroscopy of granular material in an electrolyte solution of any ionic strength." Colloids and Surfaces A: Physicochemical and Engineering Aspects (2017).

Frequency dependence

$$\tilde{\sigma}_m = \sigma_m + i\omega\epsilon_0\epsilon_r$$

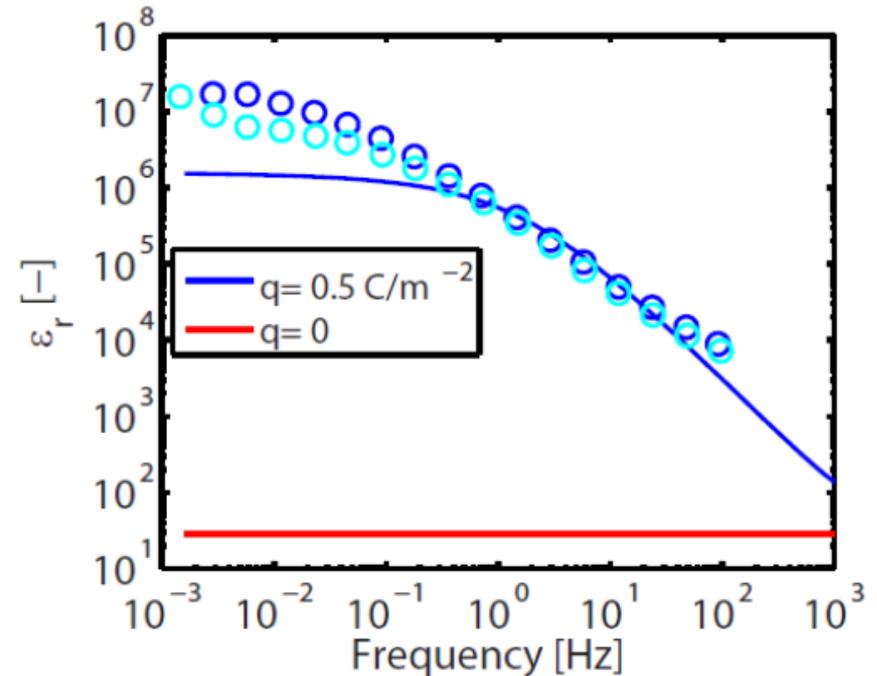
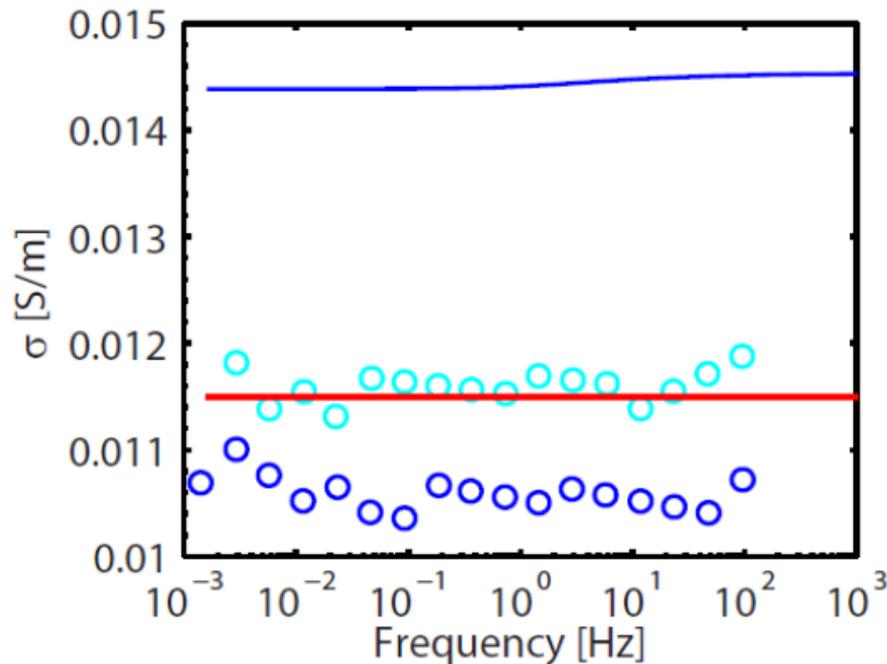
$$\omega_a \simeq D/a^2 \quad \omega_0 \simeq D\kappa^2$$



Frequency dependence

$$\tilde{\sigma}_m = \sigma_m + i\omega\varepsilon_0\varepsilon_r$$

accuracy is extremely important
(should be less than 10% error !)



Discussion and conclusion

- better conductivity measurements are needed (accuracy)
- the models work provided that double layers do not interact significantly (i.e. for large particles the major contribution comes from the dielectric core)
- clogging was not considered
- the models can be adapted easily for spheroidal particles
- in case the particles are polydisperse, the dominant contribution comes from the particles having the largest $\phi_s Du$. For small Du one can show that:

$$\sigma_m = \frac{1 - \phi_s}{1 + \phi_s/2} \sigma_e + \frac{9 (\phi_s^1 Du_1 + \phi_s^2 Du_2) \sigma_e}{4 [1 + \phi_s - \frac{3}{4} (\phi_s^1 Du_1 + \phi_s^2 Du_2)]}$$

uncharged spheres

$$Du = \frac{\sigma_{//}}{\sigma_e} = \frac{2}{\kappa a} \left[\exp \left(\frac{e|\zeta|}{2kT} \right) - 1 \right]$$

For shaley sands/ sandstones the dominant contribution could therefore come from the clayey part.

This work has been done in collaboration with:

- Dick Bedeaux (NTNU)
- Simon Gourdin (UPMC)
- Olivier Bernard (UPMC)
- Marie Jardat (UPMC)
- Emmanuelle Dubois (UPMC)
- Alex Kirichuk (TUD)



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