De la dynamique moléculaire, via l'homogénéisation, aux modèles macroscopiques de poroélasticité et électrocinétique

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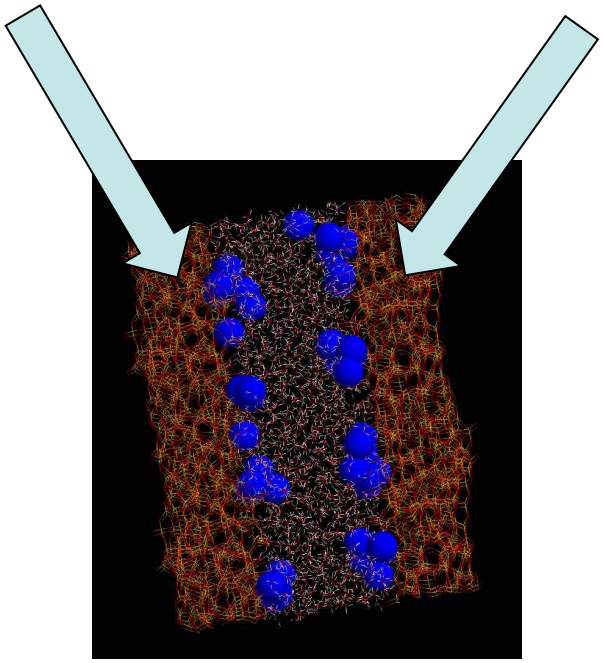
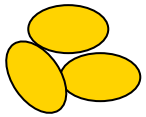
Multi-scale modelling

1 fs

Nuclei and electrons wavefunctions	Atoms, molecules positions	Continuous distributions v(r) C(r) T(r)	Continuous distributions Homogeneous media
Schrödinger equation	Newton's law Liouville's law	Fick Fourier Navier-Stokes equations	Darcy's law Electrokinetics





Homogeneous material

Applications:

Verres poreux (décontamination)

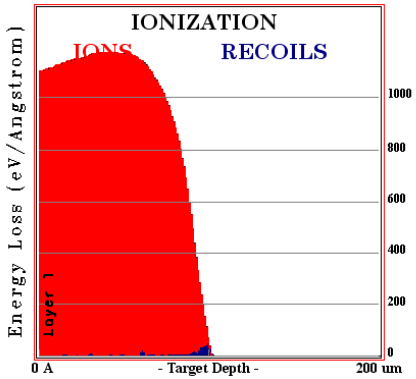
Argiles (stockage déchets)

Porous Glasses for Separation Chemistry (Vycor ®)

Experimental studies of irradiations

irradiation

high energy heavy ions



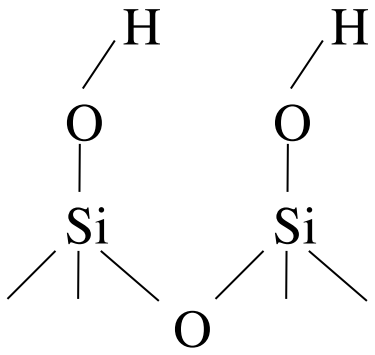
modification of the

surface of the glass

Modification of the surface

No irradiation

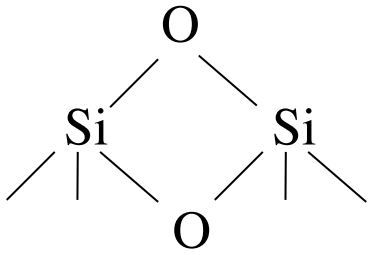
silanol groups



hydrophilic silica (SiO_2)

Irradiation

no silanol groups

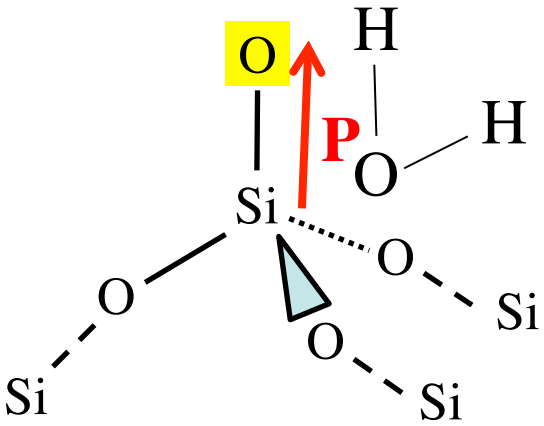


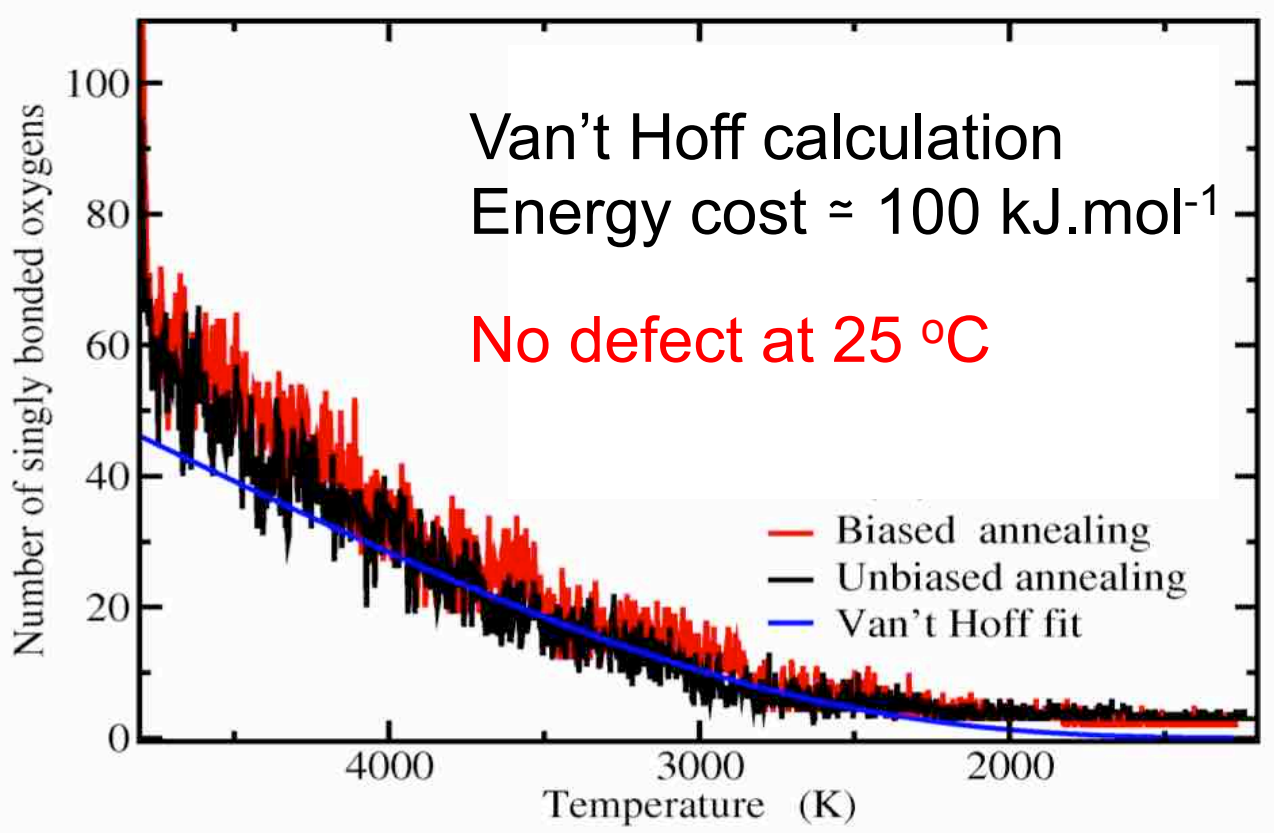
hydrophobic silica (SiO_2)

Building realistic amorphous surfaces

Number of defects (single bonded oxygen) as a function of the temperature) from Monte-Carlo simulations of annealing

Crystal defect
Singly bonded oxygen



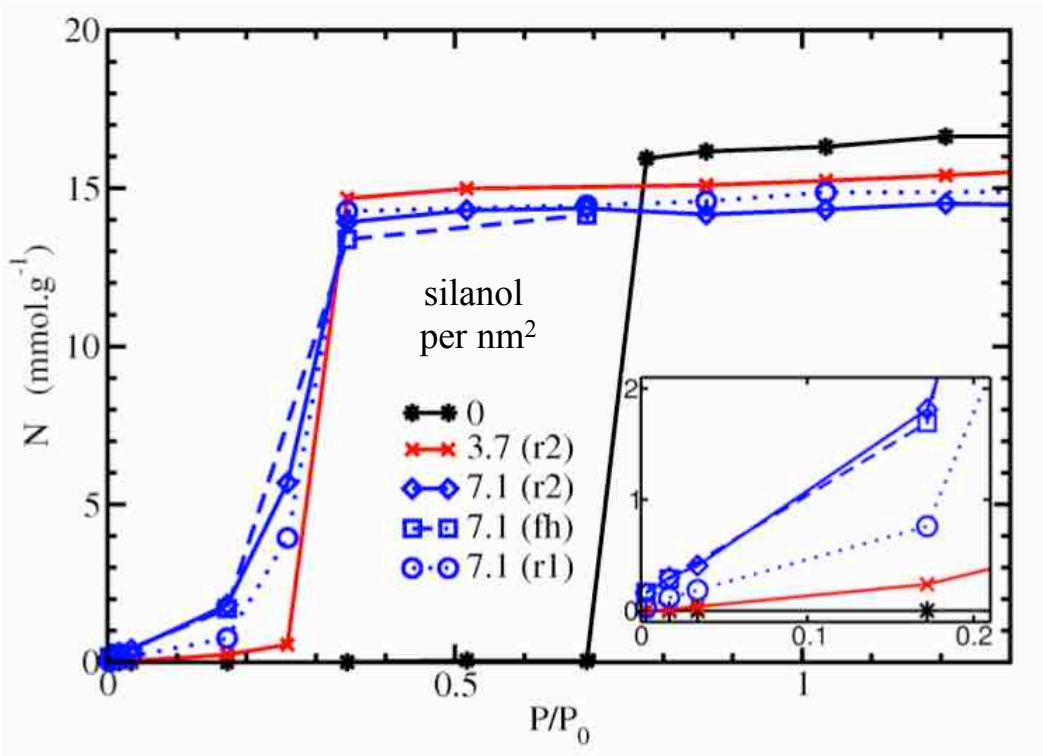


Minimization of F = U – TS

- High temperature: S maximum ☞ Defects
- Low temperature: U minimum ☞No defect

Simulation of silica

Water adsorption isotherms (number of water molecules as a function of the external water pressure)



Journal of Colloid and Interface Science **225**, 411–420 (2000)

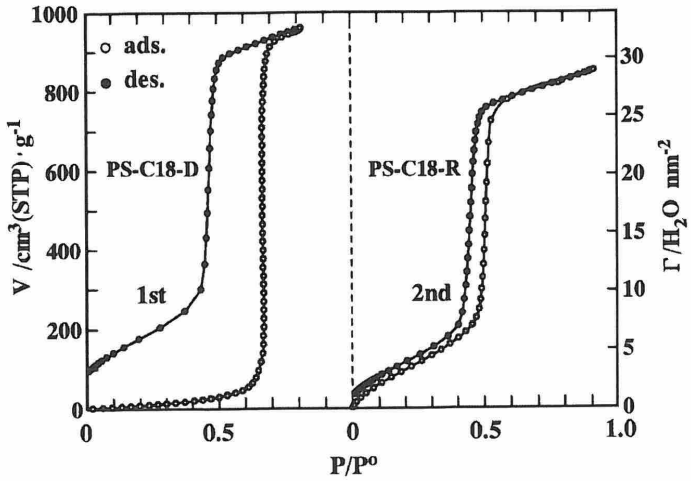


FIG. 9. adsorption–desorption isotherms of water vapor at 298 K for dehydroxylated MCM-41 sample (PS-C18-D) and rehydroxylated MCM- 41 sample (PS-C18-R).

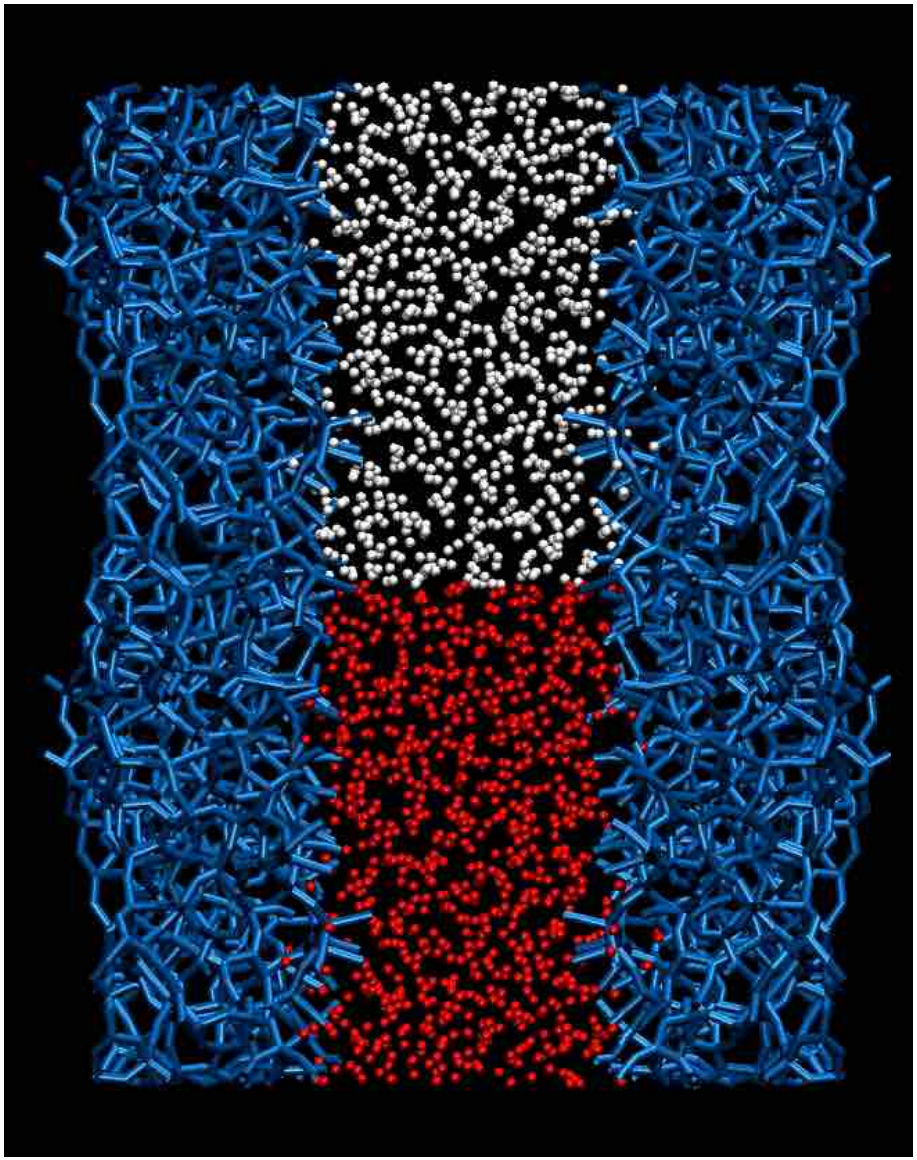
No silanol groups: hydrophobic surface

With silanol groups: hydrophilic surface

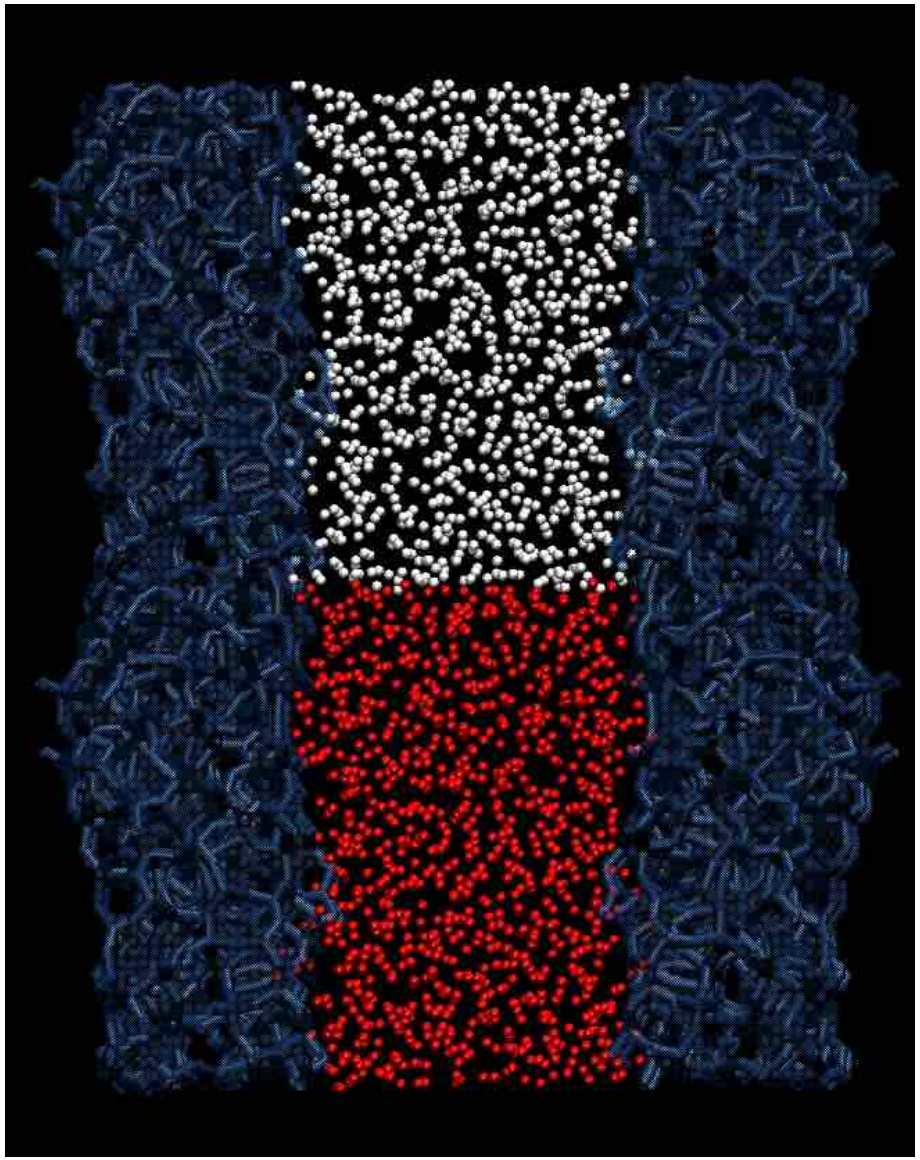
J. Phys. Chem. B **115** 7881 (2011)

Simulation of silica

With silanol : hydrophilic



No silanol : hydrophobic

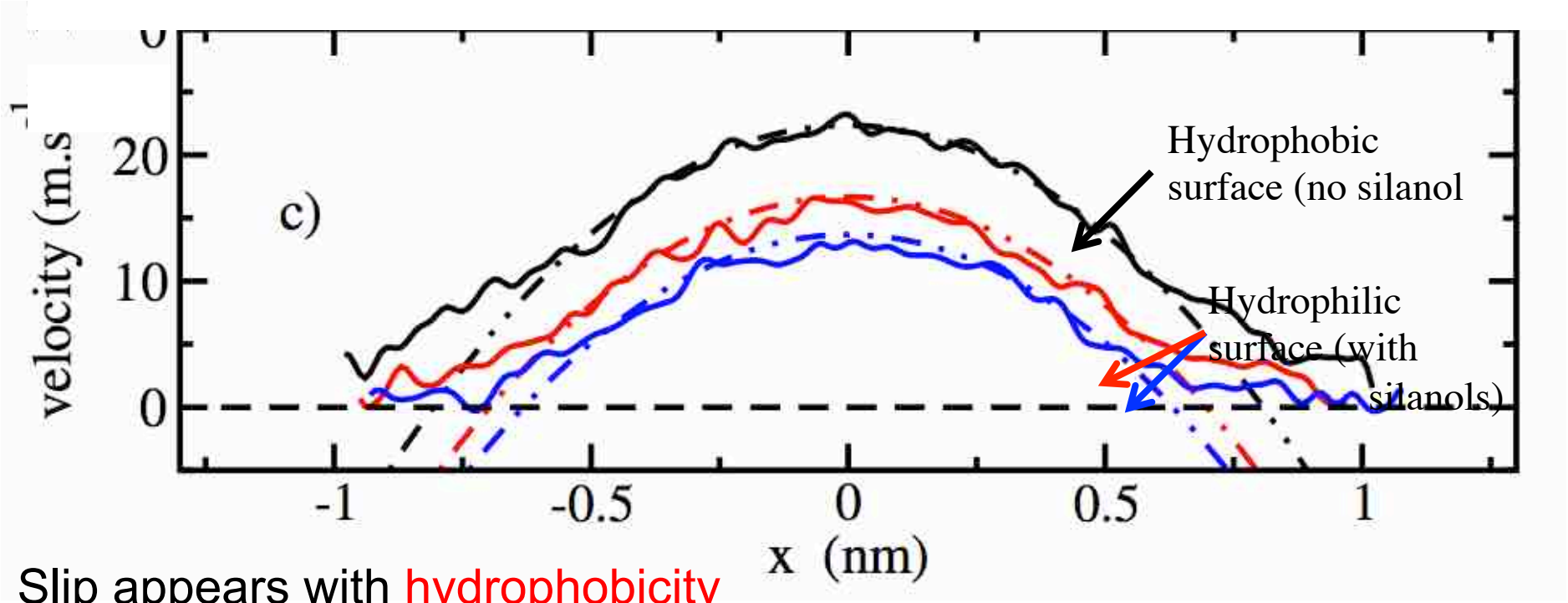


Simulation of silica

J. Phys. Chem. B **115** 7881 (2011)

Hydrodynamic Flux (Poiseuille flow)

NEMD Non equilibrium Molecular Dynamics



Slip appears with hydrophobicity

Slip length δ ≈ 0.4 nm

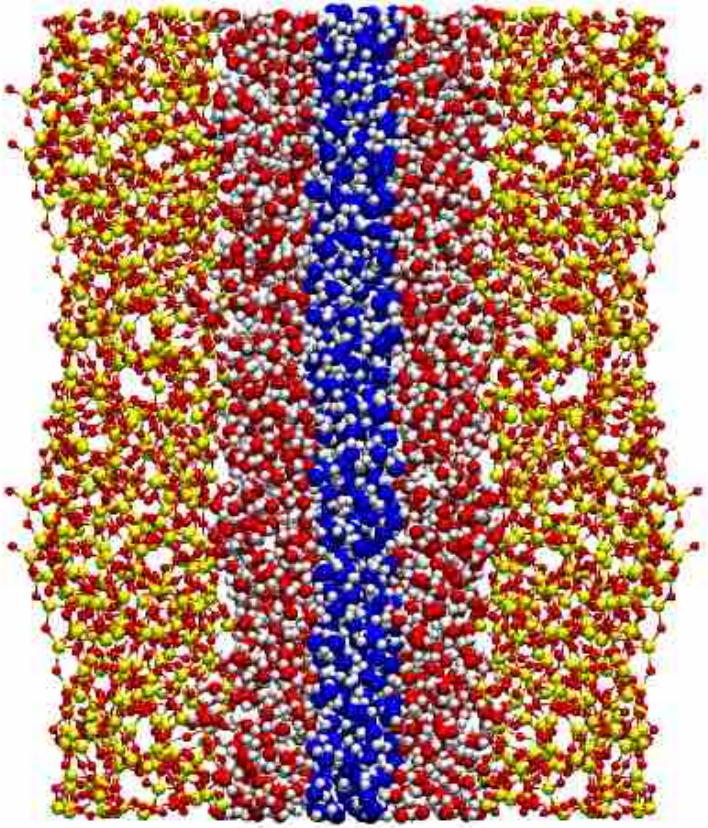
☞ dramatic consequences for the electrokinetic phenomena ?

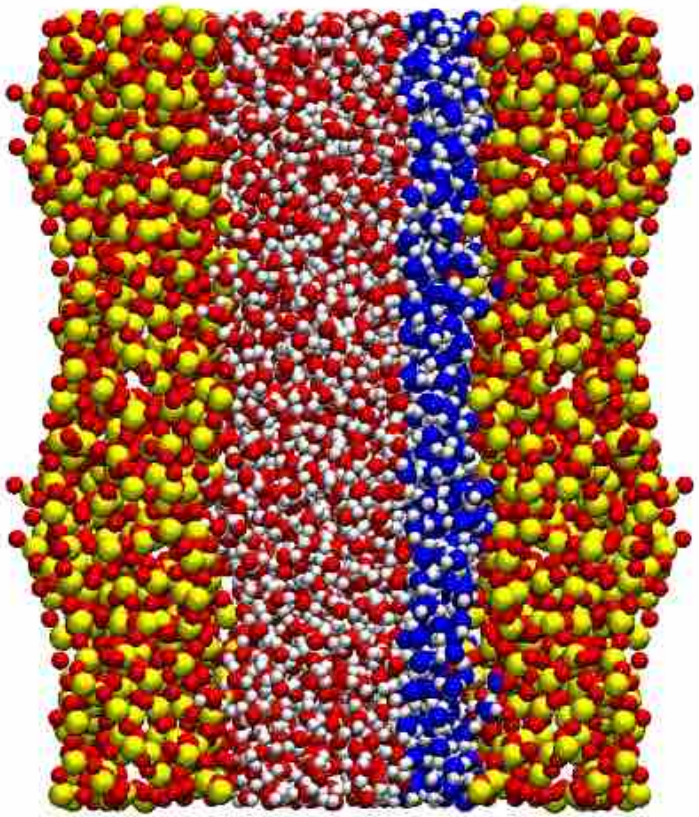
Negligible only if: $\delta << 2\lambda \ln\left(\frac{\Delta}{\lambda}\right)$ λ Gouy length , $\Delta = \min(\kappa^{-1}, L)$

Mol Phys **111** 3410 (2013)

Water diffusion

Parallel and perpendicular diffusion

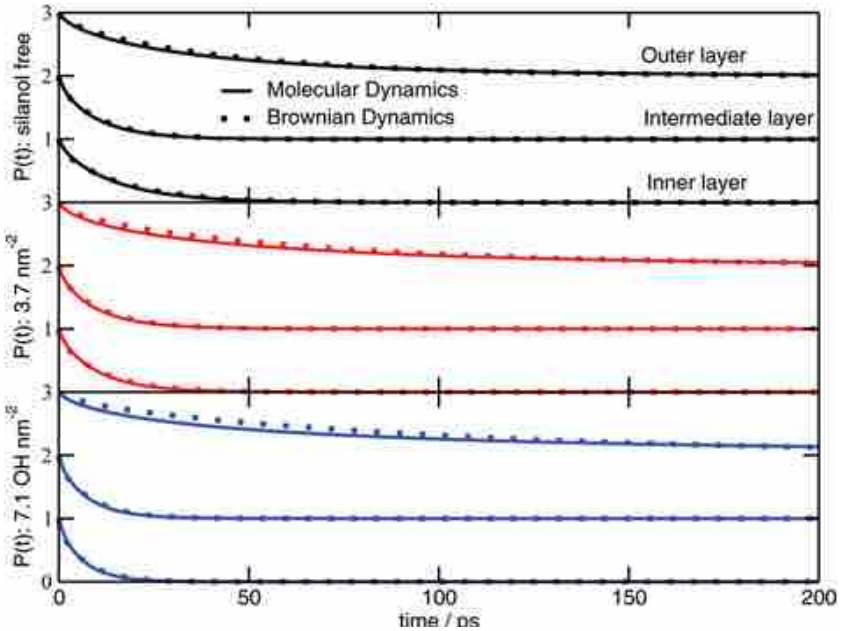




For perpendicular diffusion, *D* calculated from the mean first passage time

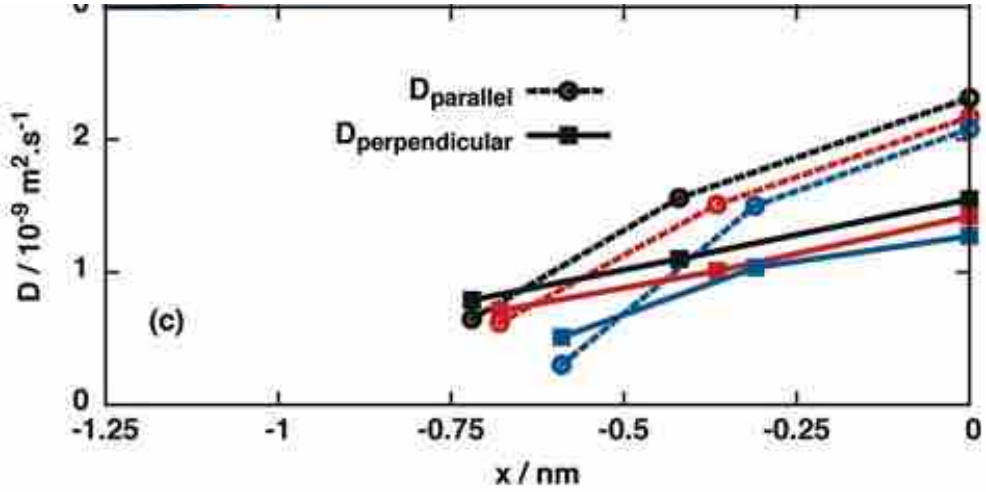
Simulation of silica

persistence probabilities

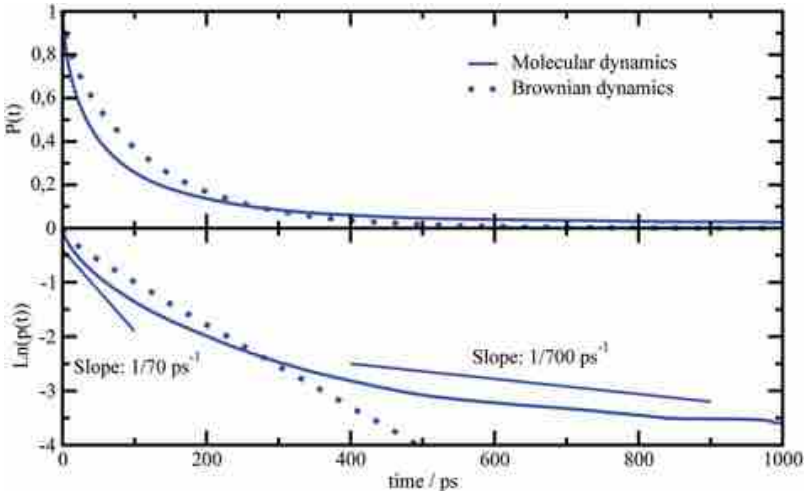


Water diffusion coefficient

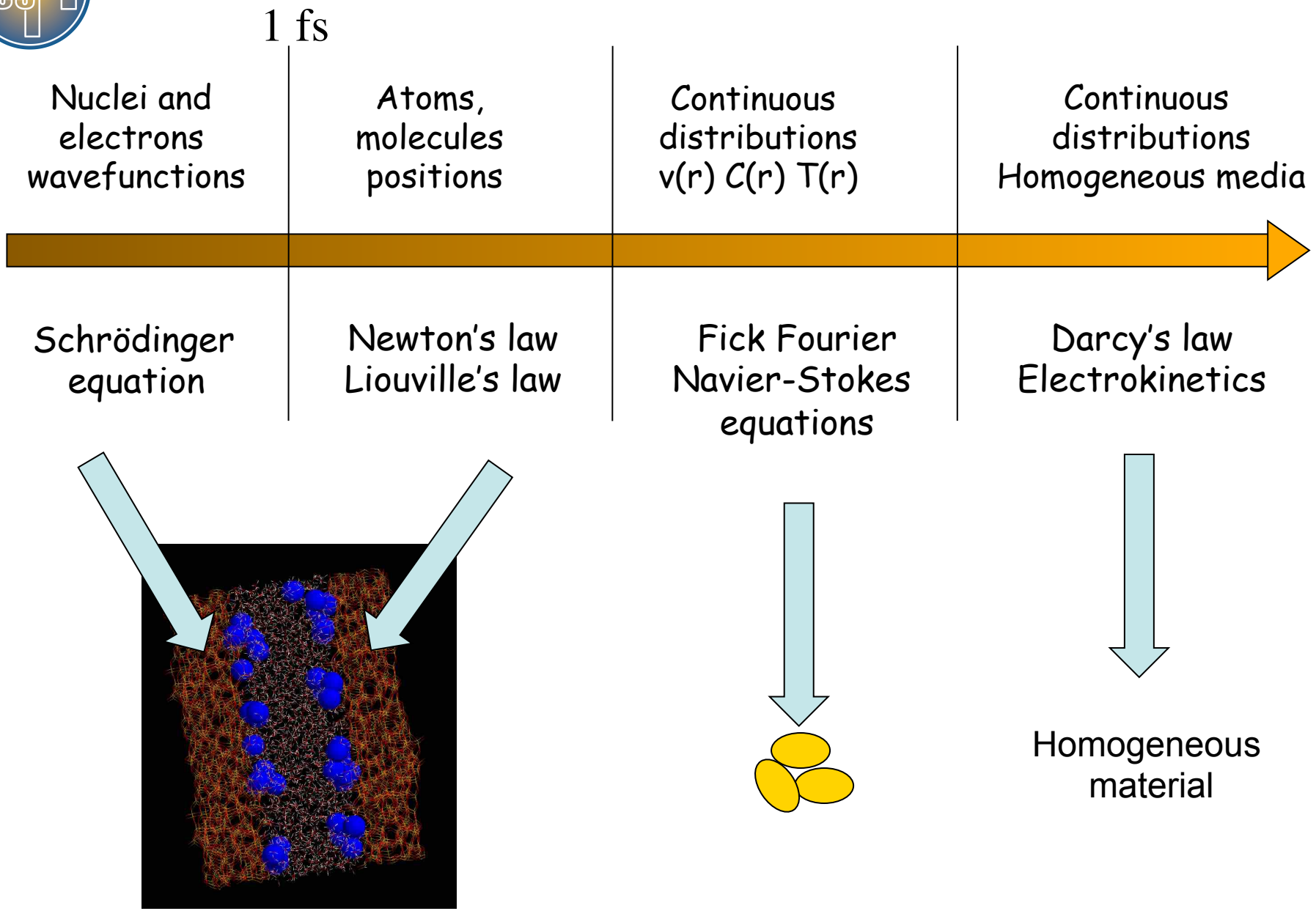
Only the first layers are dynamically different from bulk water



Zoom: outer layer 7.1 OH nm^{-2} 2 populations



Multi-scale modelling



Ideal model

Ideal theory (95 % of models)
Poisson-Nernst-Planck + Stokes equations

Stokes for hydrodynamics

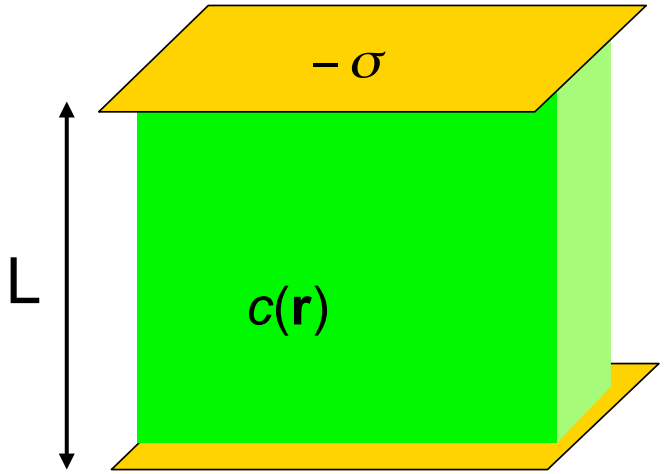
$$\eta\vec{\Delta}\vec{v} + \vec{F}_v - \vec{\nabla}p = 0$$

Fick for ion diffusion

$$\frac{\partial c}{\partial t} + \mathrm{div}\left(\vec{j}_c + \vec{j}_d\right) = 0$$

$$\vec{j}_d = -c\frac{D}{kT}\mathrm{grad}\,\mu + c\frac{D}{kT}\vec{F}_{ext}$$

$$\vec{F}_{ext} = q\vec{E} \qquad ; \qquad \mu = \mu_0 + kT\ln C$$



For equilibrium: correspond to Poisson-Boltzmann

More realistic model

Stokes for hydrodynamics

$$\eta\vec{\Delta}\vec{v} + \vec{F}_v - \vec{\nabla}p = 0$$ + incompressible + conditions aux limites

Fick for ion diffusion

$$\frac{\partial c_i}{\partial t} + \mathrm{div}(\mathbf{j}_i^c + \mathbf{j}_i^d) = 0$$

$$\mathbf{j}_i^d = \sum_j L_{ij}\left(-\mathbf{grad}\mu_j + Z_j e\mathbf{E}\right) \quad + \quad \text{Poisson}$$

- Non-ideal chemical potential
- L_{ij} depend on the concentration

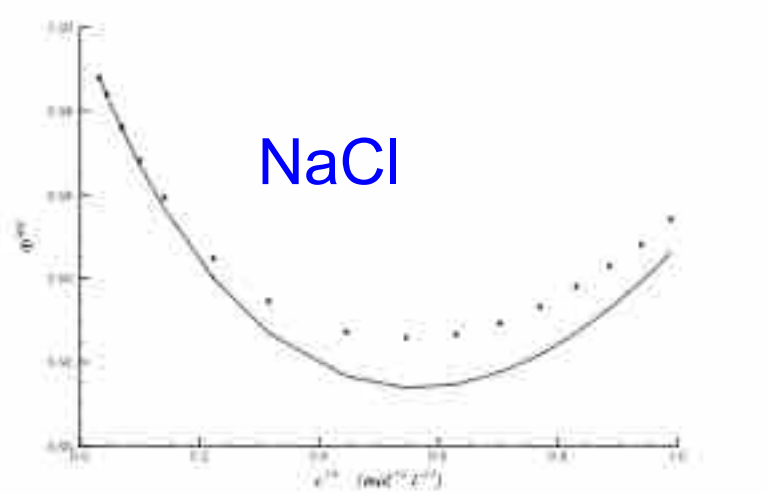
Consequence for modelling ?

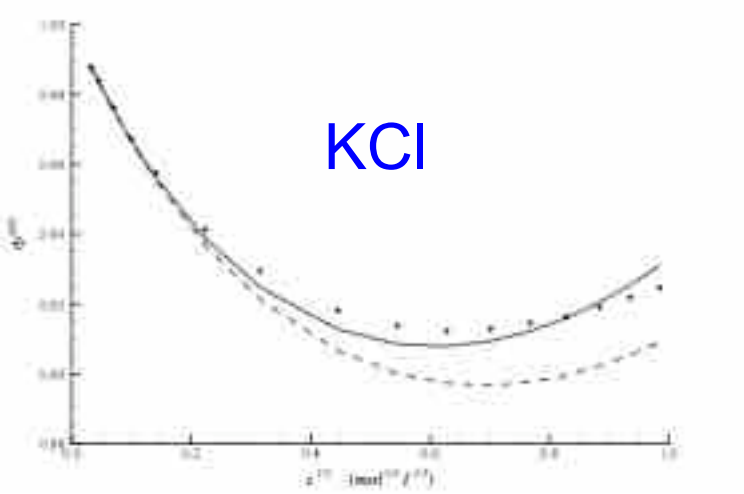
Activity coefficients

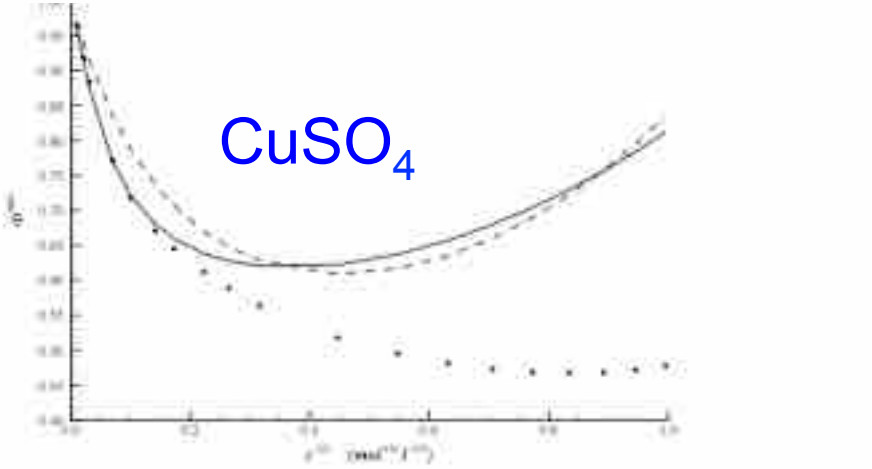
Definition

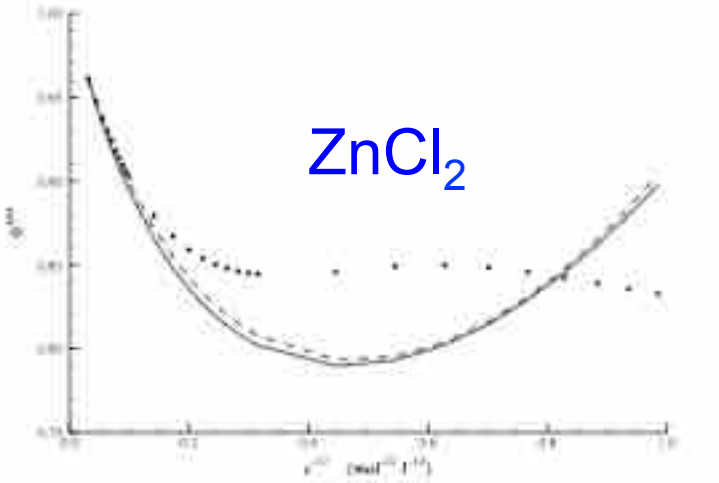
$$\mu = \mu_0 + kT \ln C + kT \ln \gamma$$

γ similar to osmotic coefficient (Gibbs-Duhem)



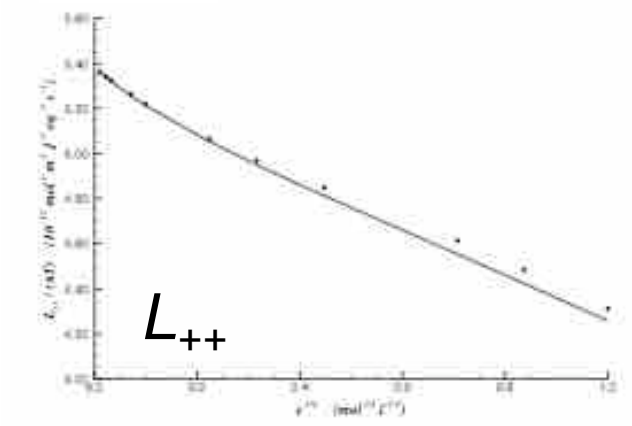


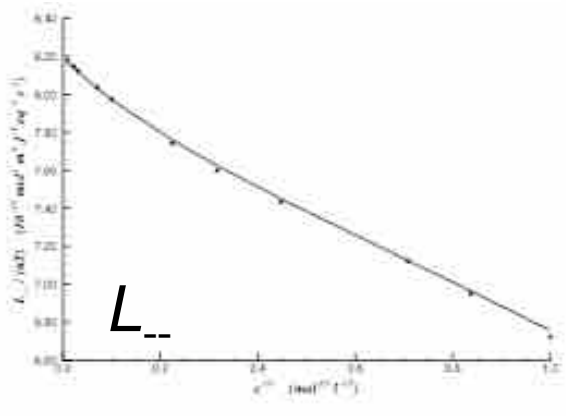


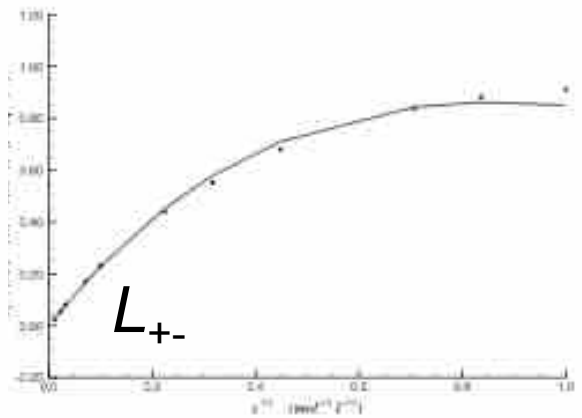


Onsager coefficients

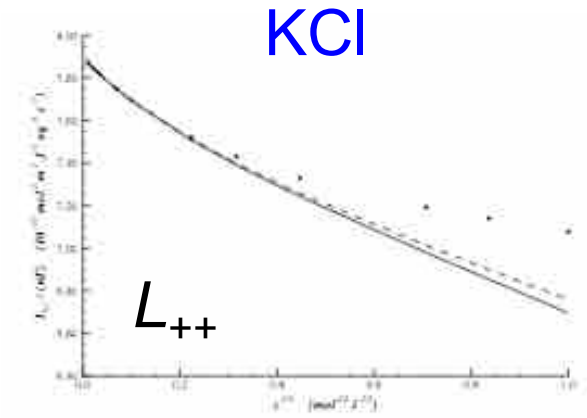
NaCl

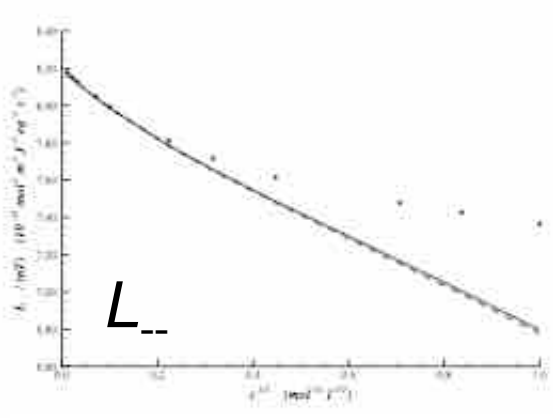


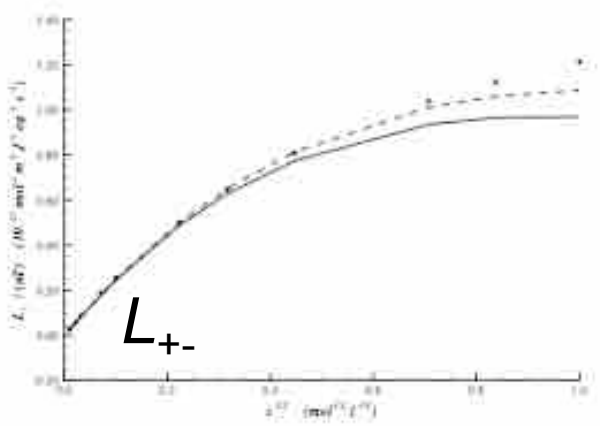




KCl





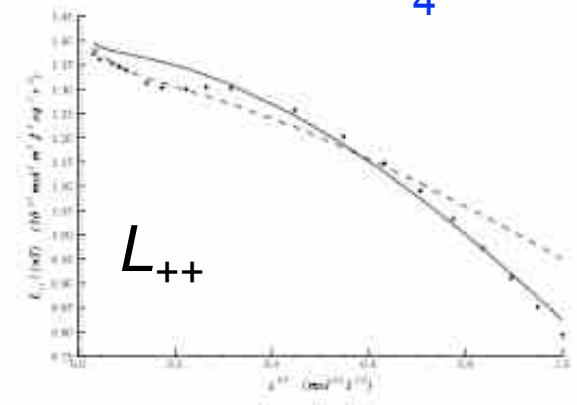


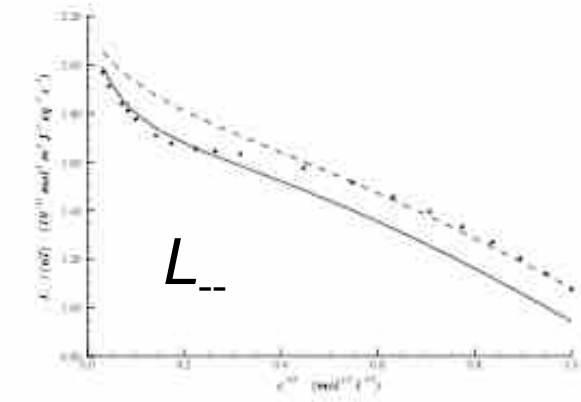
Does not always reduce transport
(Walden wrong)

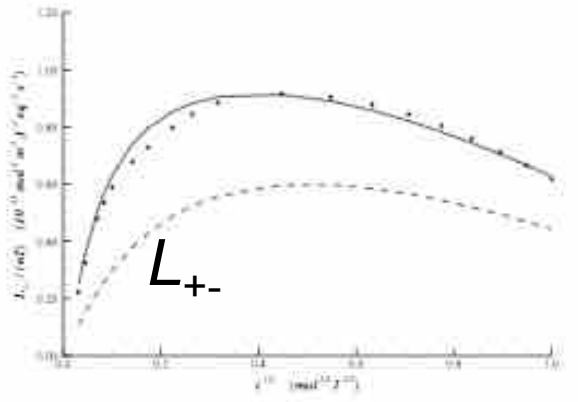
Van Damme et al., *J. Phys. Chem. B* 2006

Onsager coeffcients

$CuSO_4$





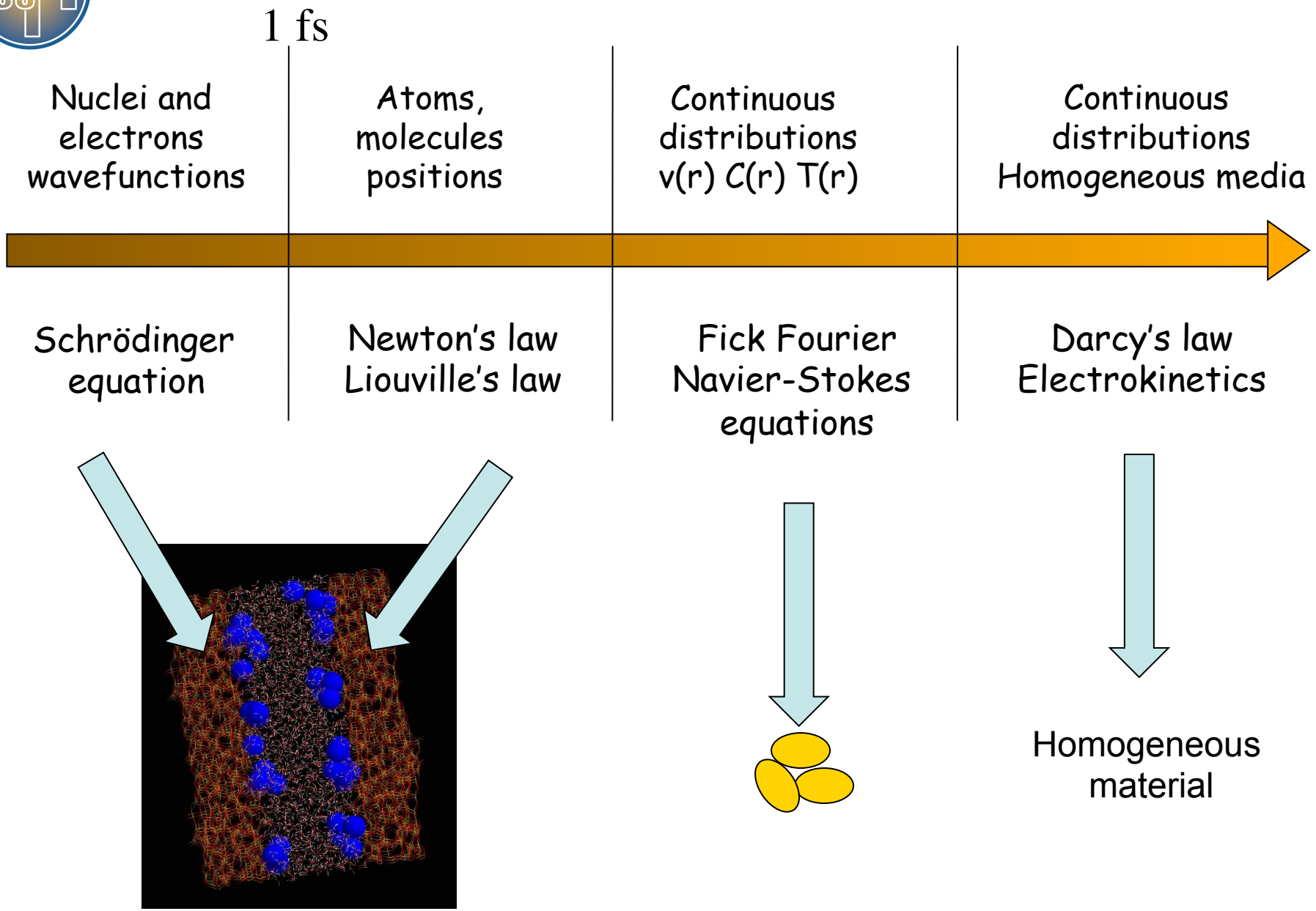


$$\mathbf{j}_i^d = \sum_j L_{ij}\left(-\mathbf{grad}\mu_j + Z_j e\mathbf{E}\right) \qquad + \qquad \text{Poisson}$$

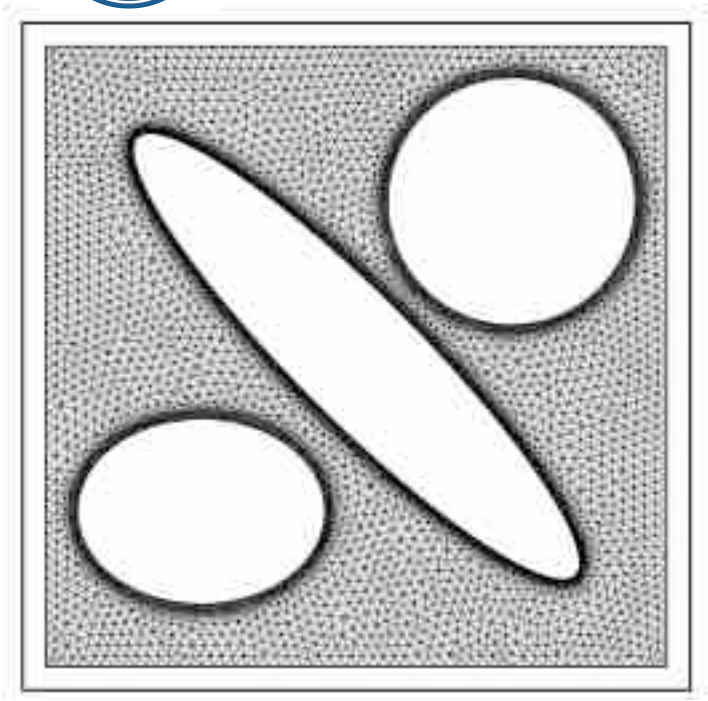
Practical expressions

- Smoluchowski-MSA theory (Ebeling-Turq-Bernard-Dufreche)
- valid up to molar concentrations
- Volume-fixed frame of reference

Multi-scale modelling



Homogenization



Derivation of the macroscopic laws (averaged over the geometry of the system)

→ homogenization

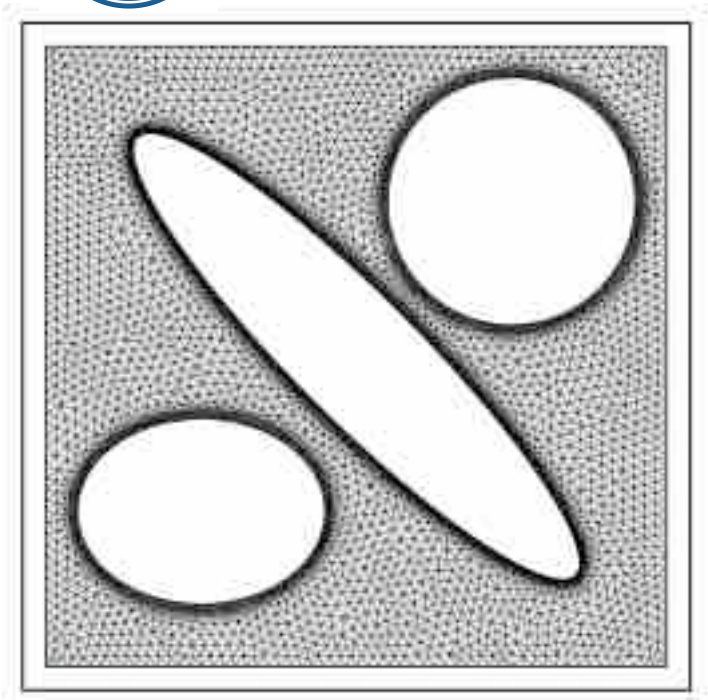
Mathematical procedure proposed by Allaire and Mikelic (*J. Math. Phys.* **51** 123103 (2010))

Periodic homogenization in the linear response regime

General existence theorem

- for not too concentrated solution (molar)
- if the electrolyte charge is not too high (spinodal instabilities → hydrolysis…)
- for ideal and non ideal model

Homogenization



Homogenized law

$$\mathrm{div}_x \mathcal{J} = 0 \quad in \ \ \Omega,$$

$$\mathcal{J} = -\mathcal{M}\mathcal{F} - \mathcal{M}(\mathbf{f}^*, \{0\})$$

$$\begin{pmatrix} \mathbf{u} \\ \mathbf{j}_i \end{pmatrix} \qquad \begin{pmatrix} \nabla_x p^0 \\ \nabla_x \mu_i^0 \end{pmatrix}$$

flux — Homogenized Onsager Coefficients matrix — forces

Hydrolic permeability (Darcy coefficient)

Terms for streaming potential)

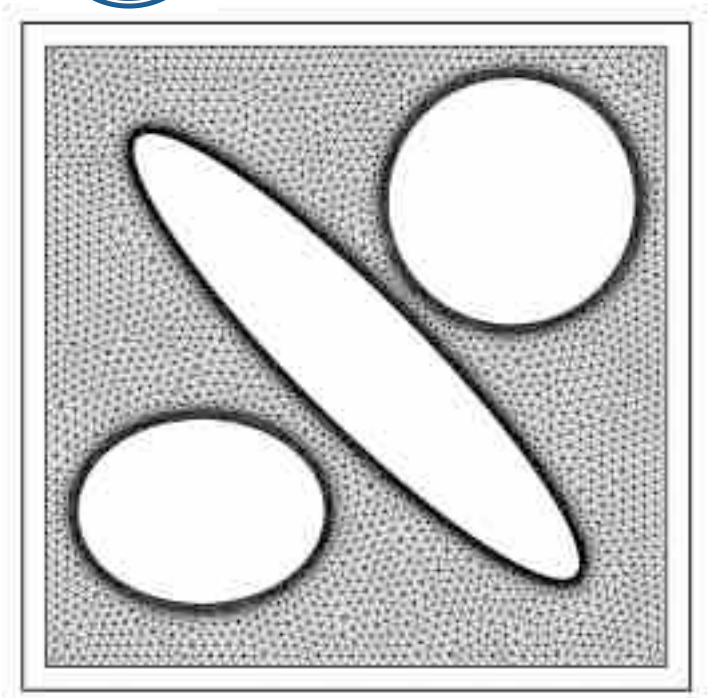
$$\mathcal{M} = \begin{pmatrix} \mathbb{K} & \frac{\mathbb{J}_1}{z_1} & \cdots & \frac{\mathbb{J}_N}{z_N} \\ \mathbb{L}_1 & \frac{\mathbb{D}_{11}}{z_1} & \cdots & \frac{\mathbb{D}_{1N}}{z_N} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbb{L}_N & \frac{\mathbb{D}_{N1}}{z_1} & \cdots & \frac{\mathbb{D}_{NN}}{z_N} \end{pmatrix}$$

Terms for electro-osmosis)

electrodiffusion tensor

Comput. Geosci, **17**, 379 (2013)

Homogenization



Homogenized law

$$\mathrm{div}_x \mathcal{J} = 0 \quad in \ \ \Omega,$$

$$\mathcal{J} = -\mathcal{M}\mathcal{F} - \mathcal{M}(\mathbf{f}^*, \{0\})$$

We show

- the matrix $\mathcal{M}$ is symmetric

(Onsager reciprocal relation) for the ideal and the non ideal model

- the matrix $\mathcal{M}$ is positive definite

$\mathcal{M}$ can be calculated from the solution of a time independent cell problem (integral equation)

Ex:

$$\{\mathbb{K}\}_{lk} = \frac{1}{|Y_F|} \int_{Y_F} \mathbf{v}^{0,k}(y) \cdot \mathbf{e}^l \, dy,$$

$$-\Delta_y \mathbf{v}^{0,k}(y) + \nabla_y \pi^{0,k}(y) = \mathbf{e}^k + \sum_{j=1}^{N} z_j n_j^0(y) \nabla_y \theta_j^{0,k}(y) \ \text{ in } Y_F$$

$$\mathrm{div}_y \mathbf{v}^{0,k}(y) = 0 \quad \text{in } Y_F, \quad \mathbf{v}^{0,k}(y) = 0 \ \text{ on } S,$$

$$-\mathrm{div}_y n_i^0(y) \Big(\sum_{j=1}^{N} K_{ij}(y) z_j \nabla_y \theta_j^{0,k}(y) + \mathrm{Pe}_i \mathbf{v}^{0,k}(y) \Big) = 0 \ \text{ in } Y_F$$

$$\sum_{j=1}^{N} K_{ij}(y) z_j \nabla_y \theta_j^{0,k}(y) \cdot \nu = 0 \ \text{ on } S.$$

Nonlinearity, **26**, 881 (2013)

Numerical results

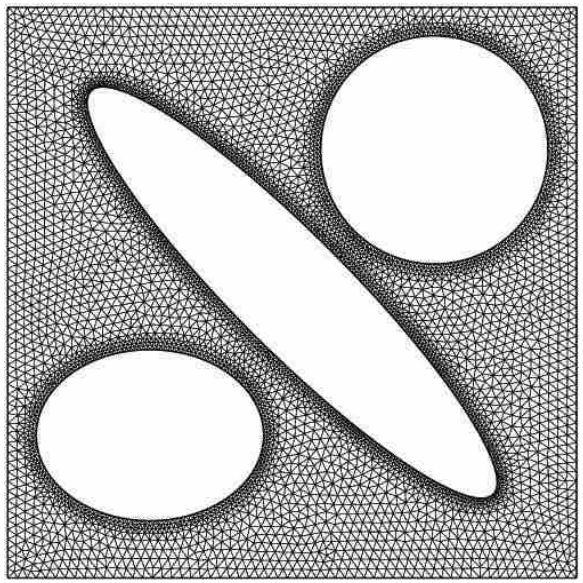
Method

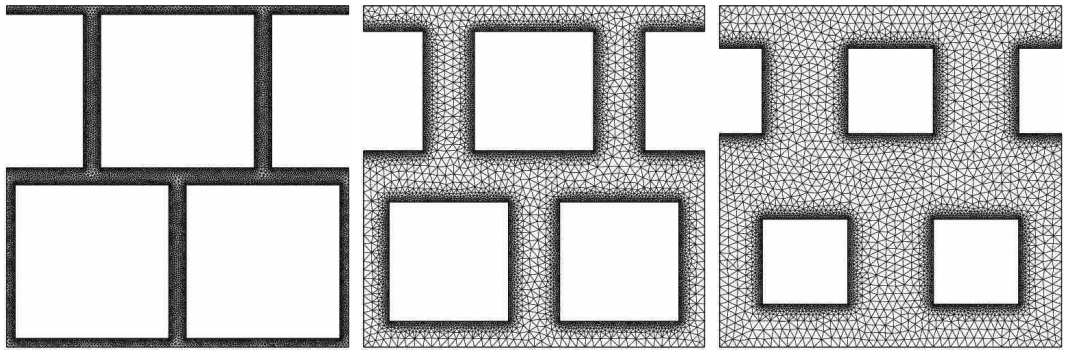
Physica A, accepted

Nonlinearity, **26**, 881 (2013)

Two dimensional systems

FreeFame++ package





Typical values (if not modified)

NaCl electrolyte (D_+ =1.333 10^{-9} , D_- =2.032 10^{-9} m^2s^{-1}

Diameter 3.3 Å) in water at 298 K

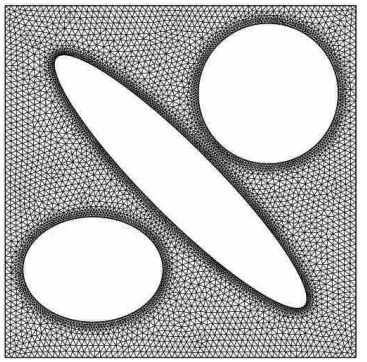
Pore size 3 < l < 50 nm C_{ext} = 0.1 $mol.L^{-1}$

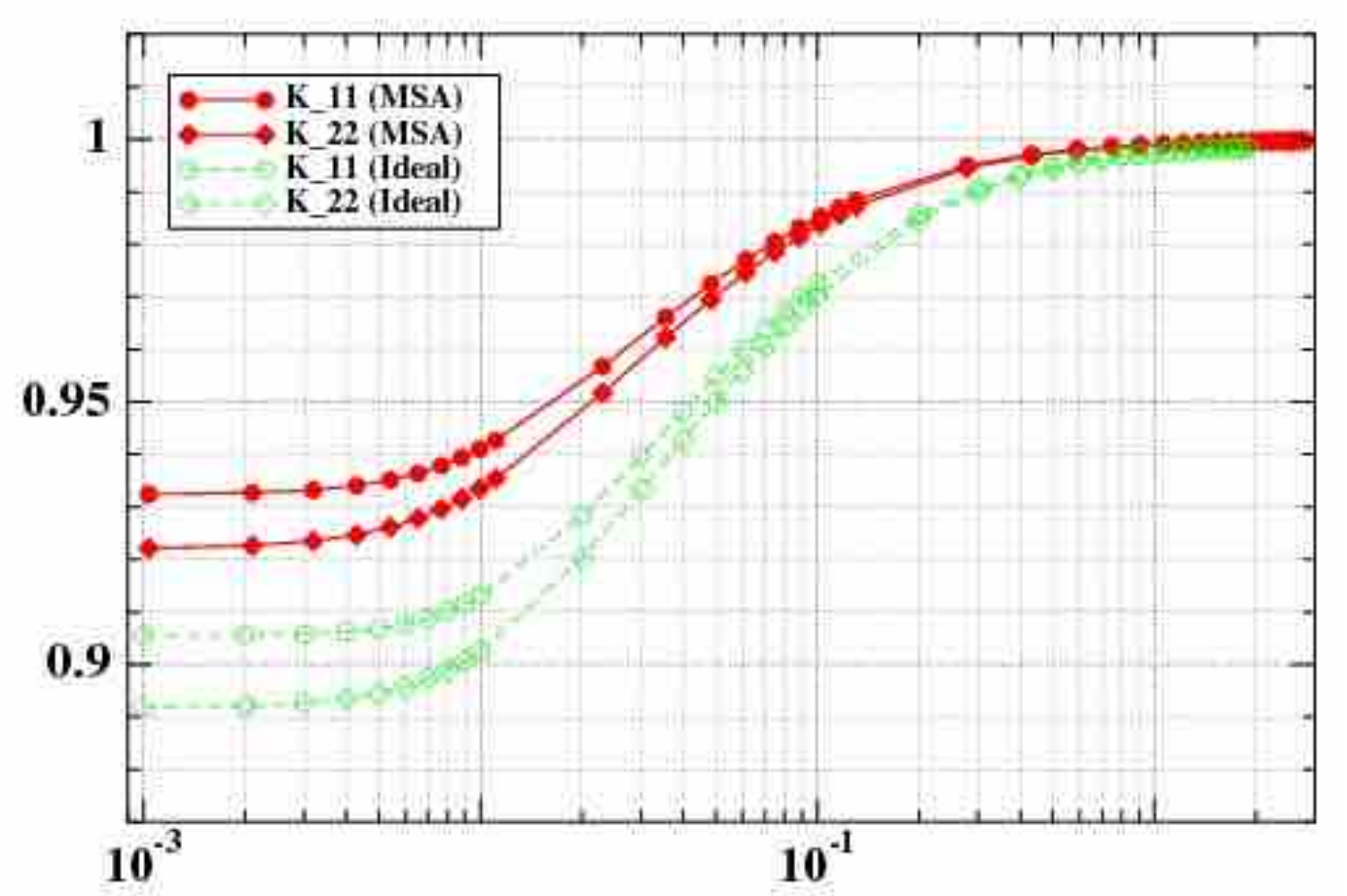
Surface charge: the one of montmorillonite clays

Numerical results

Relative hydraulic permeability (Darcy's law)

(unit: the one of a system with no charges)





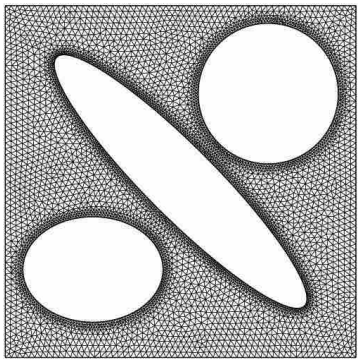
- weak effect of the charge
- role of screening
- Non-ideality can enhance/ reduce screening

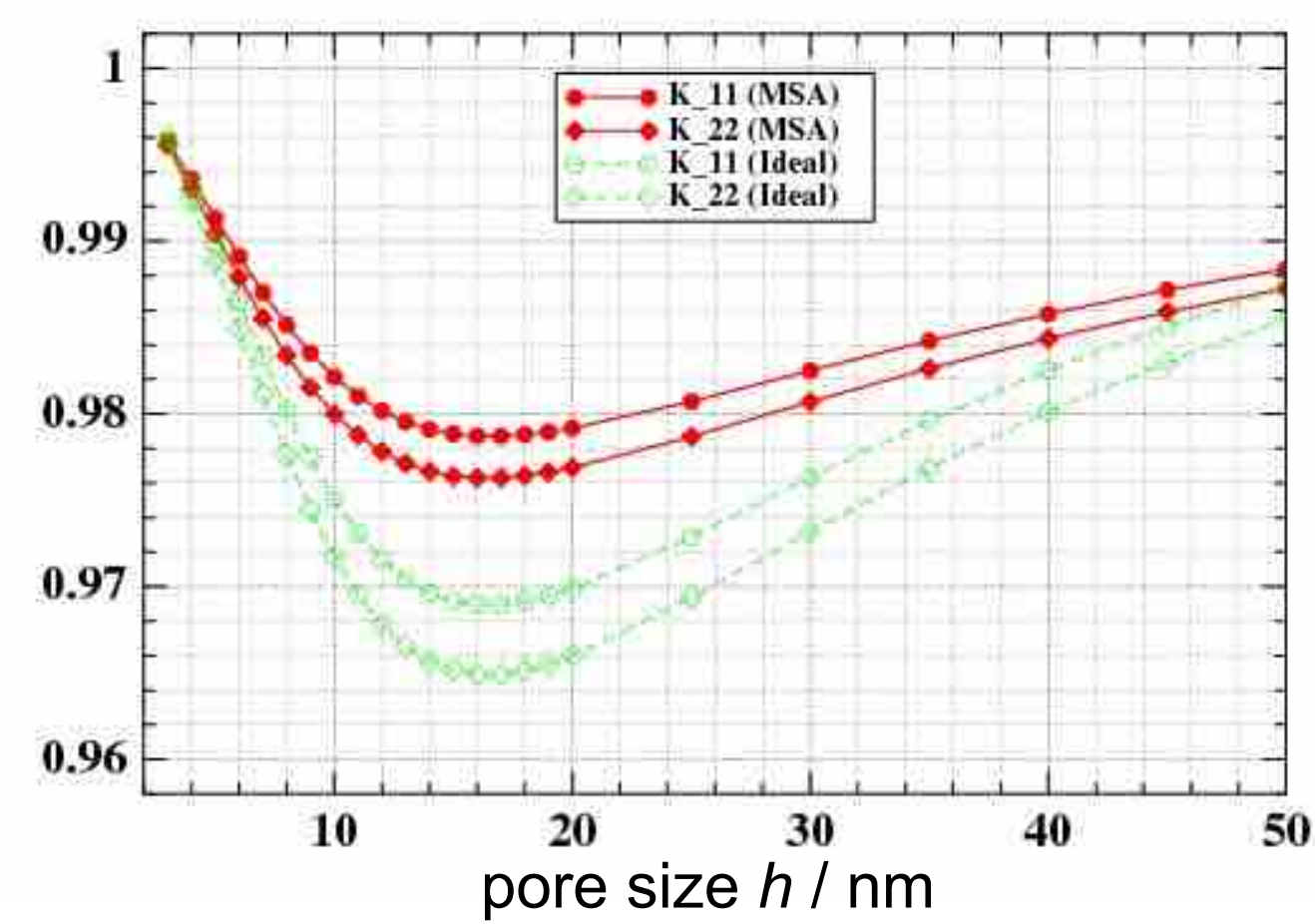
Physica A, accepted

Numerical results

Relative hydraulic permeability (Darcy's law)

(unit: the one of a system with no charges)





Physica A, accepted

If $h \ll \kappa_{Debye}^{-1}$, ion concentration is uniform→ weak effect

If $h \gg \kappa_{Debye}^{-1}$, screening→ weak effect

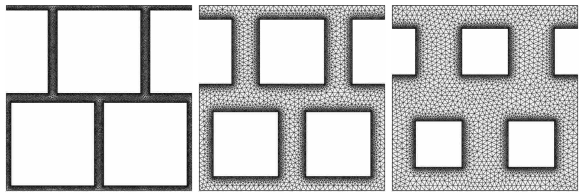
Non-ideality can enhance/reduce screening

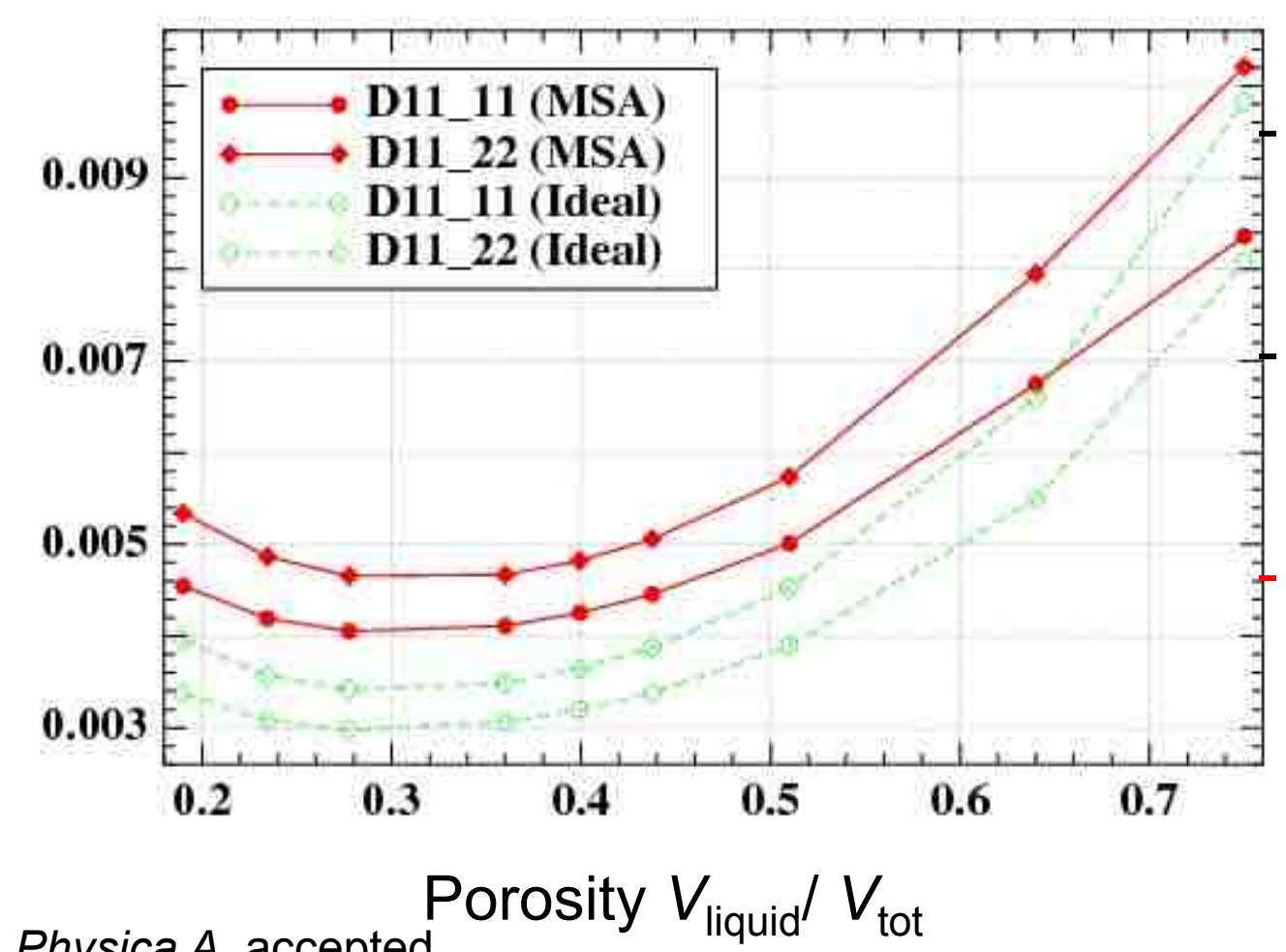
Numerical results

Electrodiffusion tensor

(unit: the one of a system with no charges)

For counterion (Na^+)





- Low porosity: surface diffusion
- High porosity: screening
- Non-ideality can enhance/reduce diffusion

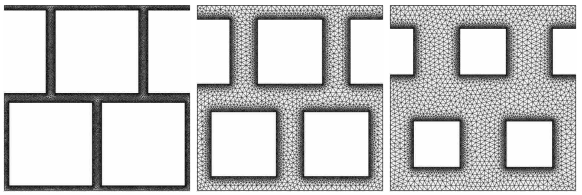
Physica A, accepted

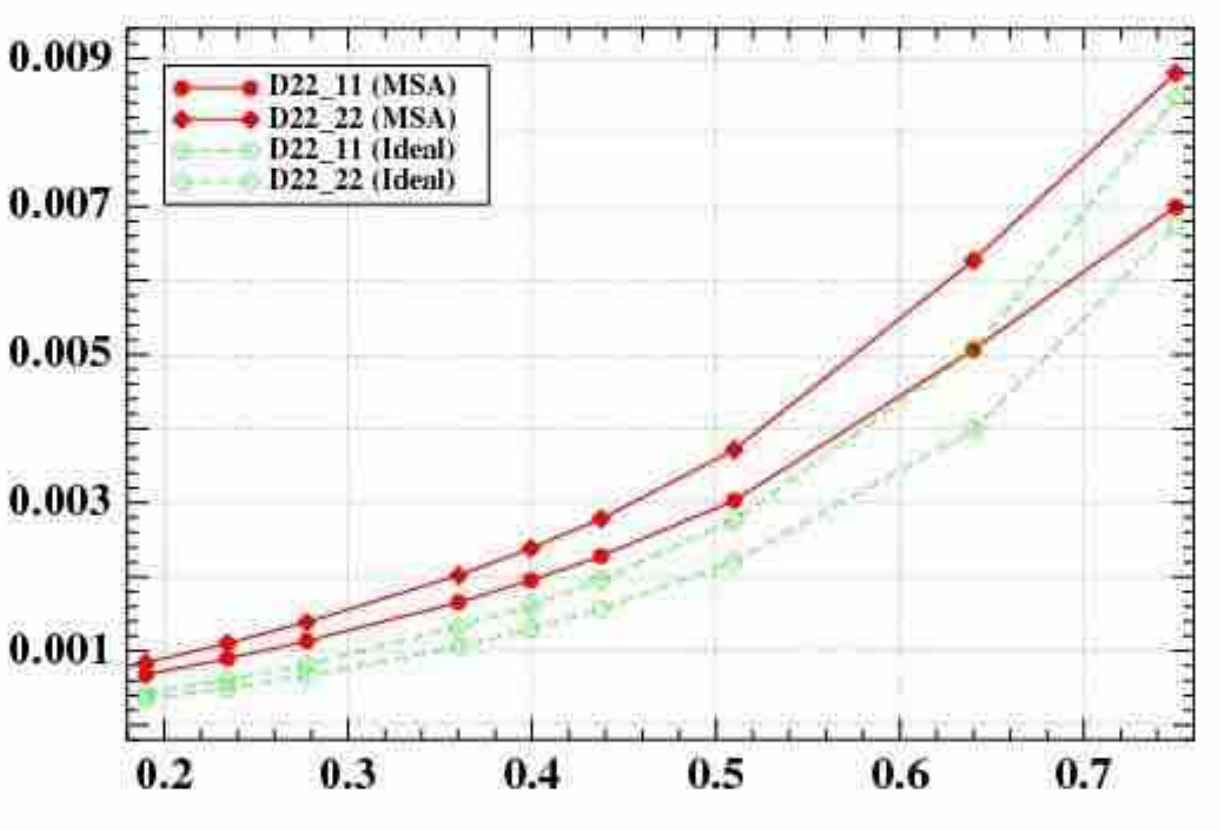
Numerical results

Electrodiffusion tensor

(unit: the one of a system with no charges)

For coion (Cl^-)



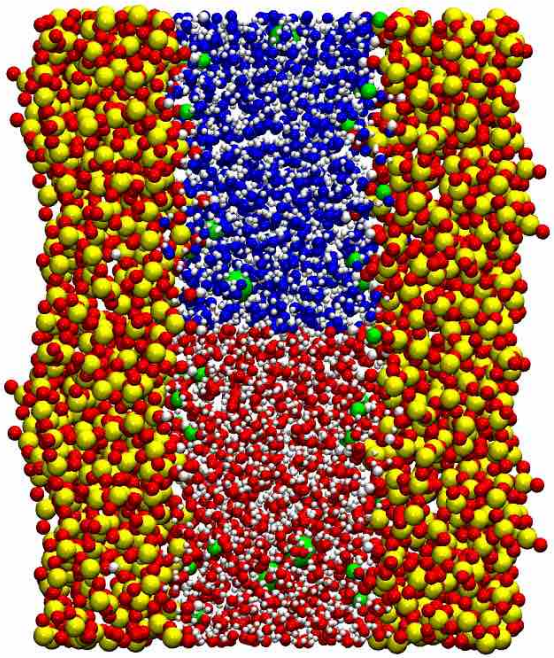


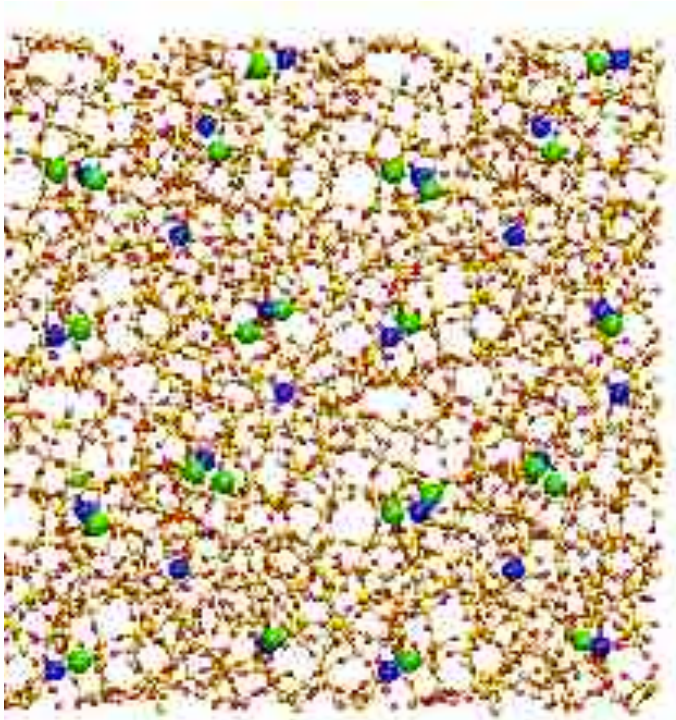
Porosity V_{liquid}/ V_{tot}

- Low porosity: no surface diffusion
- High porosity: screening
- Non-ideality can enhance/reduce diffusion

Physica A, accepted

Conclusion





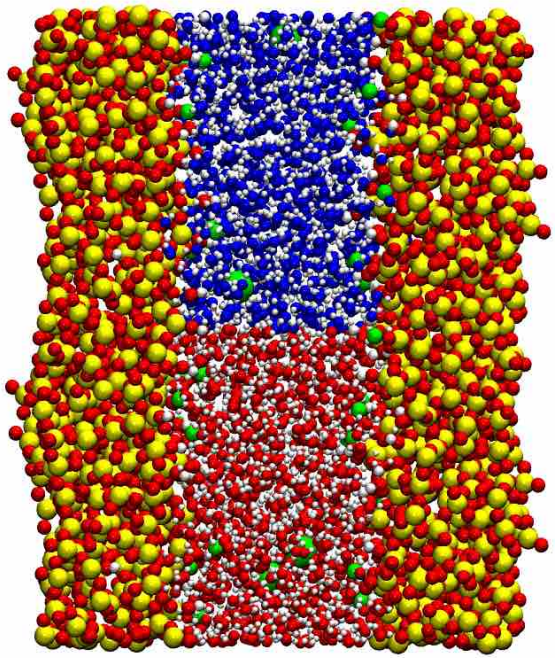
Improving Mesoscopic Models for Electrokinetic Phenomena

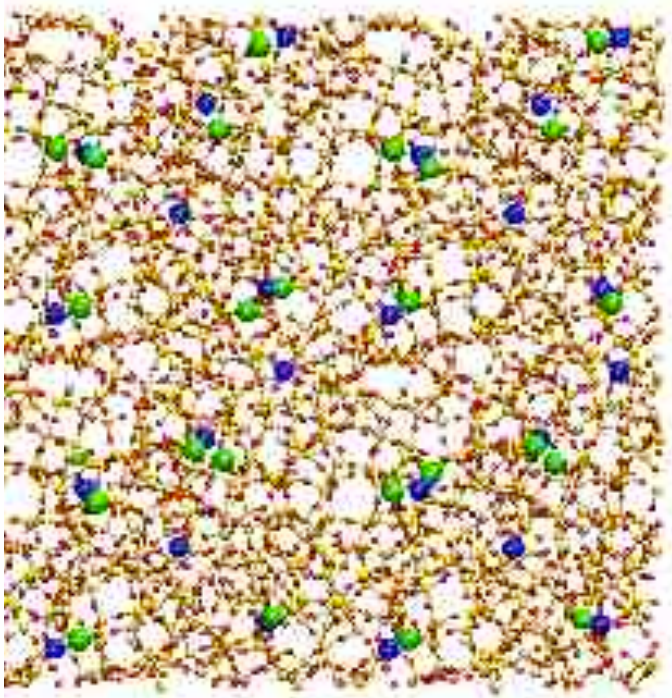
One major effects:

Significance of the ideal models compared to realistic models

Ideal models are qualitatively correct. No quantitative agreement for most of the cases (but order of magnitude)

Conclusion





Improving Mesoscopic Models for Electrokinetic Phenomena

Two major effects:

1 Slipping of the surface

increase the electrokinetic flow / hydrophobic surface

charge from substitution (clays, AgI, etc.) Poisson-Boltzmann OK

2 Specific adsorption

reduced the electrokinetic flow / hydrophilic surface

charge from sites (silica, etc.) Poisson-Boltzmann wrong