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## Simulation at the service of liquid solid interfaces: insight from molecular dynamics

Jean-François Dufrêche, Magali Duvail, Bertrand Siboulet, Mario Špadina,  
Wang, Kunyu

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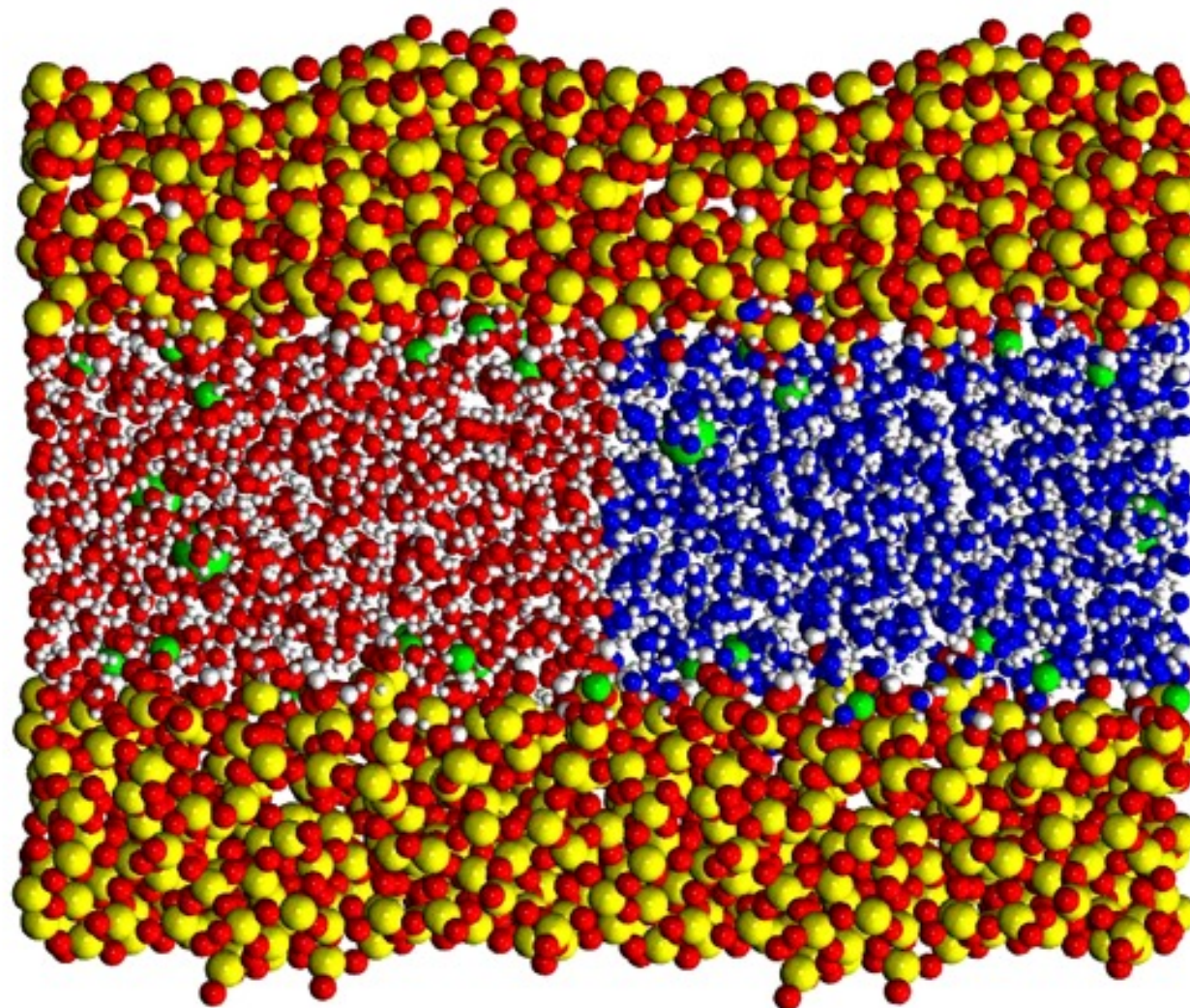


# Simulation at the service of liquid solid interfaces: insight from molecular dynamics



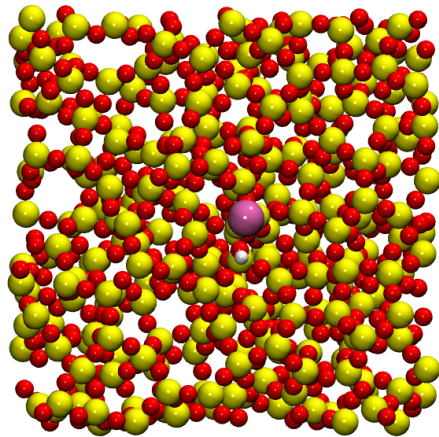
**Laboratoire Modélisation Mésoscopique et Chimie Théorique  
Institut de Chimie Séparative de Marcoule (LMCT/ICSM):  
Jean-François DUFRECHE, Magali DUVAIL, Bertrand SIBOULET,  
Mario SPADINA, Kunyu WANG**

# Liquid solid interfaces

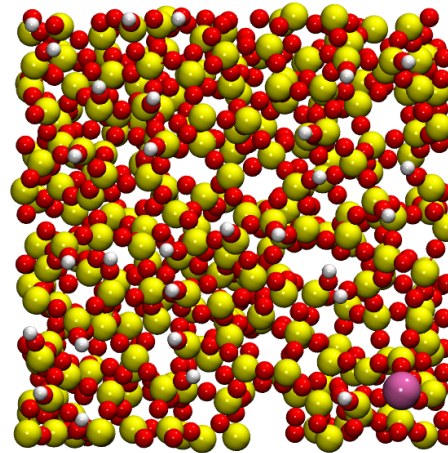


## Varying hydrophicity (Monte-Carlo)

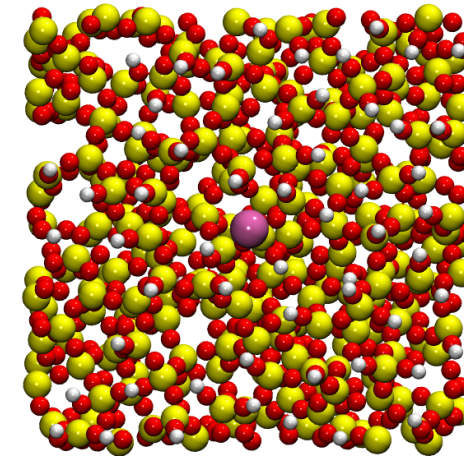
●  
charge ( $O_c$ )



1 OH



29 OH



57 OH

- Silica surfaces : various protonation-hydrophilicity
- Surface charge : pH dependent
- Punctual surface charges

# Surface ion interaction



Li<sup>+</sup>

$r_+ = 0,60 \text{ \AA}$

Na<sup>+</sup>

$r_+ = 0,95 \text{ \AA}$

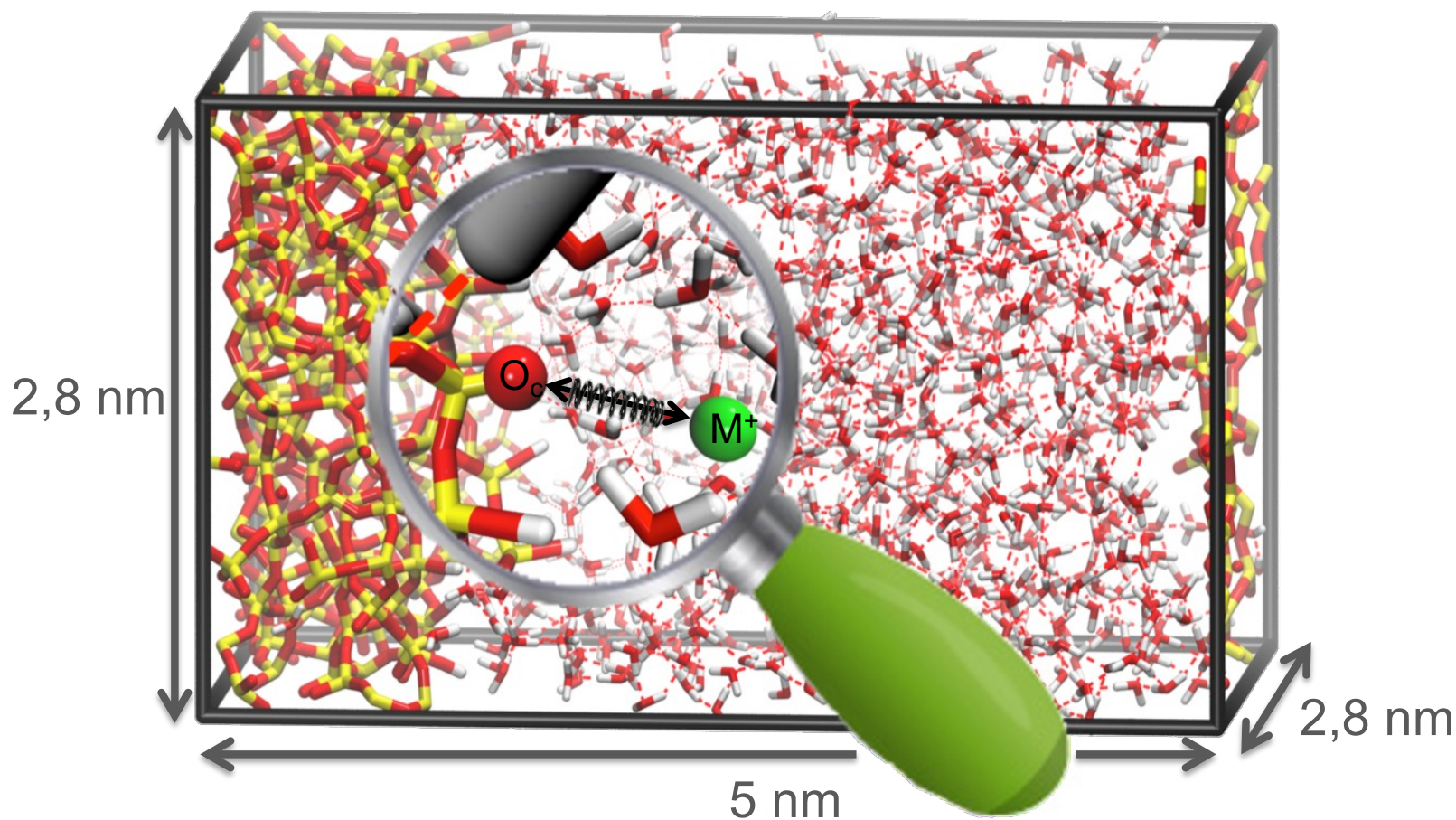
K<sup>+</sup>

$r_+ = 1,33 \text{ \AA}$

Cs<sup>+</sup>

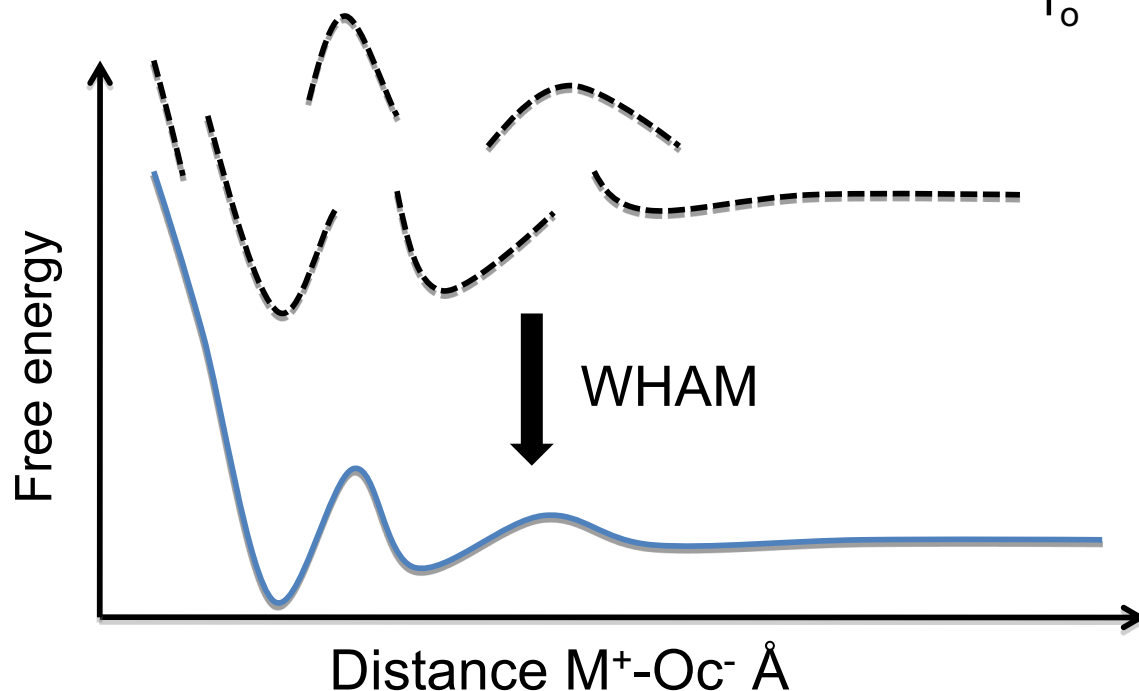
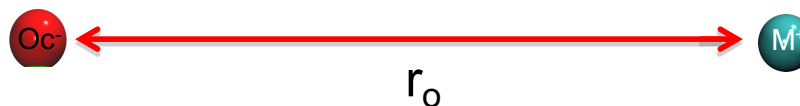
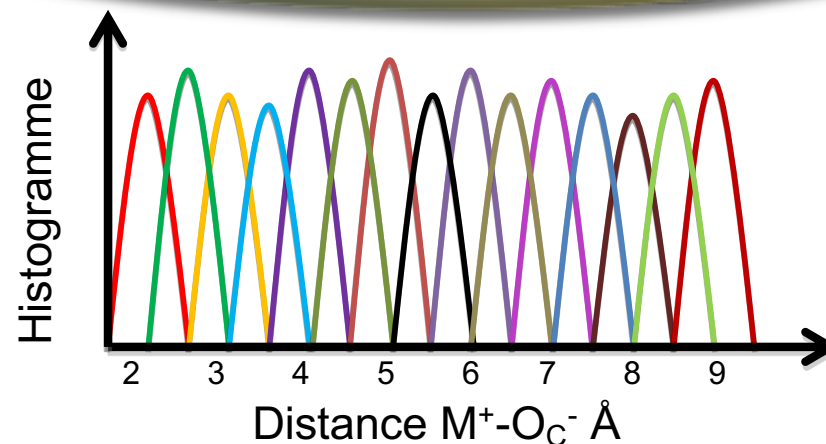
$r_+ = 1,69 \text{ \AA}$

Simulation box for bonding properties analysis



$M^+ = \text{Li}^+ / \text{Na}^+ / \text{K}^+ \text{ ou } \text{Cs}^+$

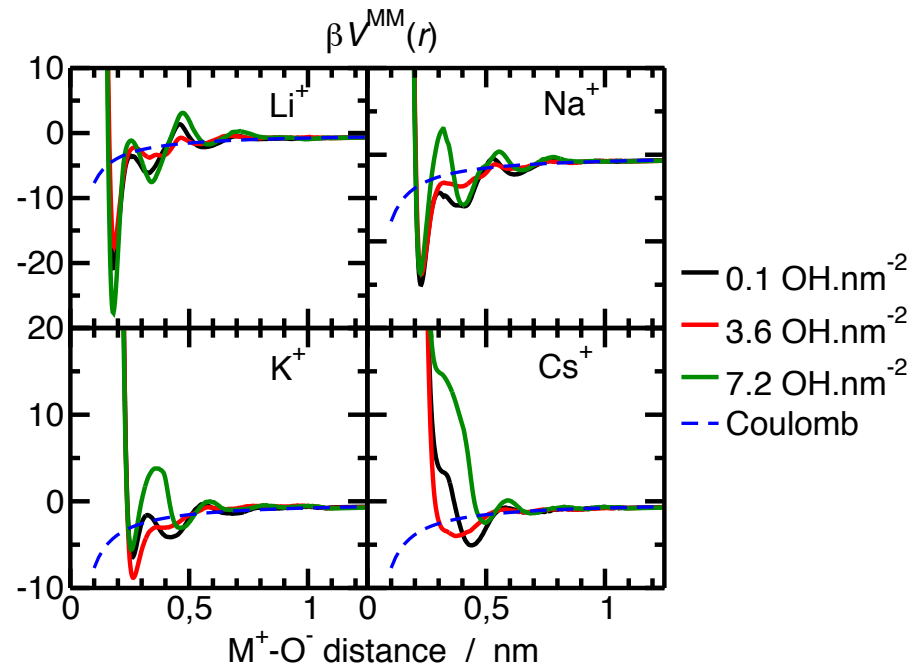
# Umbrella sampling



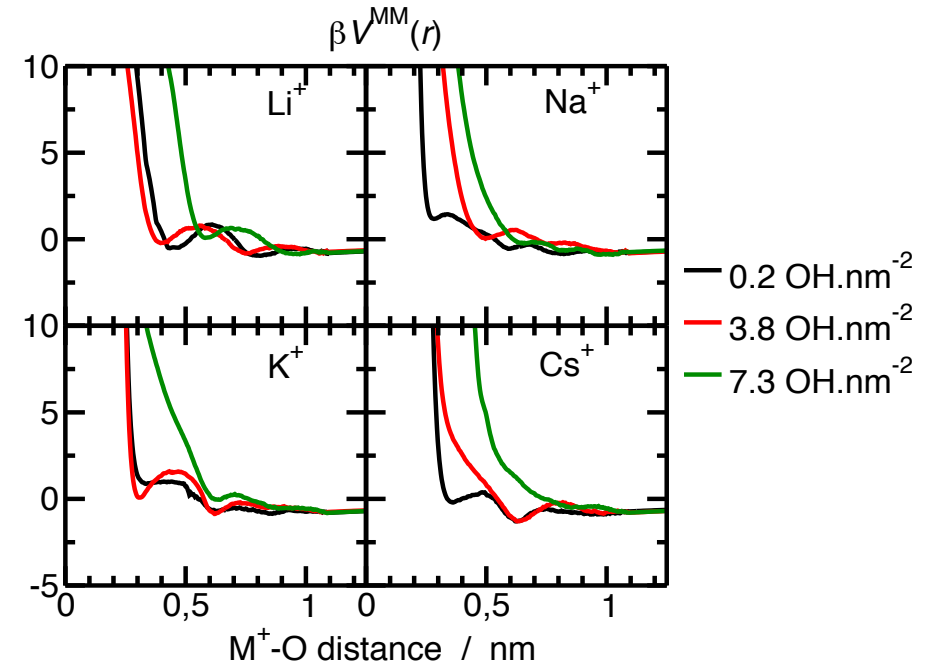
**PMF :**  
**Potential of Mean Force**

Biased simulations  
WHAM <sup>[1]</sup> (Weighted Histogram  
Analysis Method)  
A. Grossfield, « Implementation  
of WHAM : the Weighted  
Histogram Analysis Method »

## Silanolate : charged

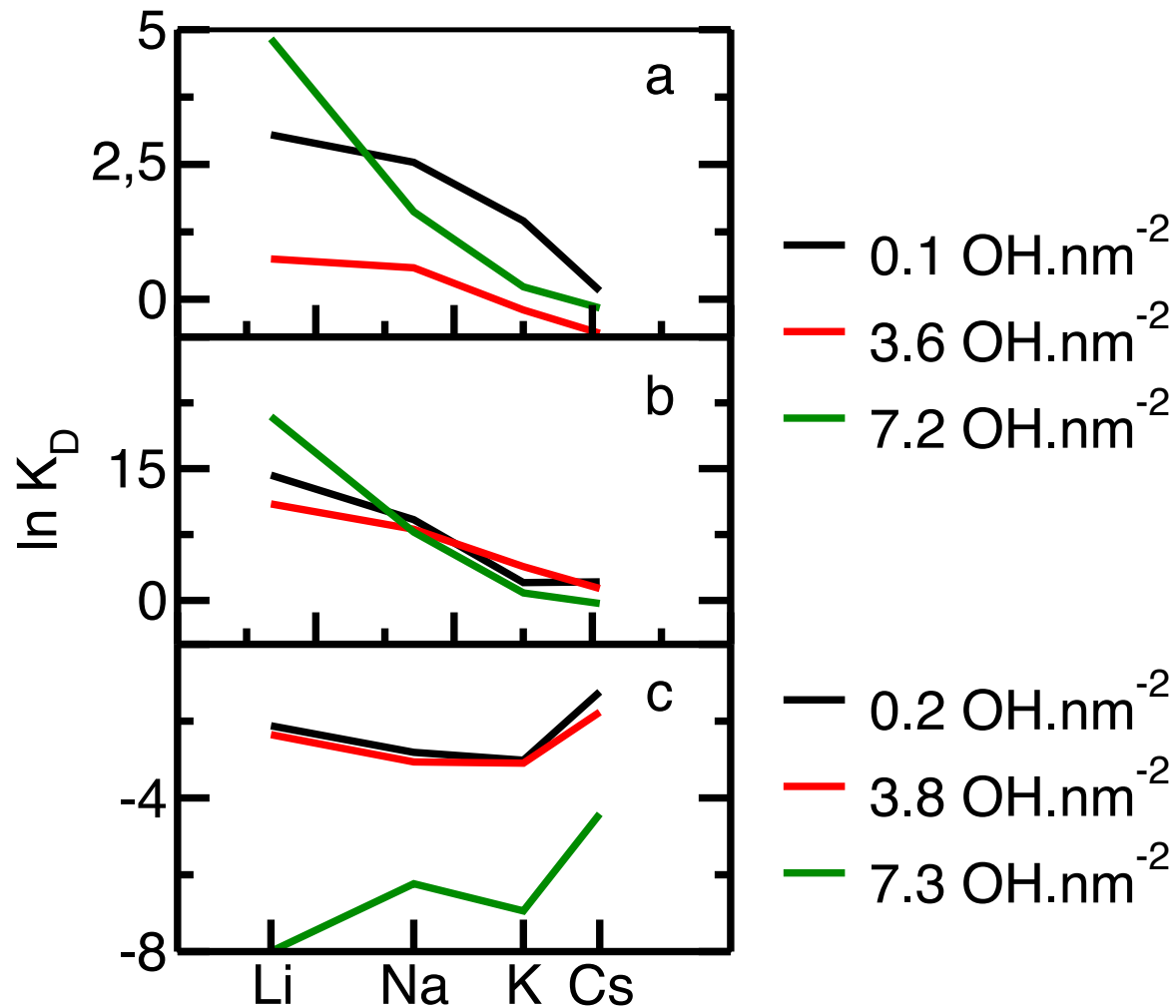


## Siloxane : neutral



- The punctual charge on the surface favors small cations adsorption
- In contrast, big cation bind to neutral surface
- We need association constants (next slide)

# Association constants: reversal of selectivity with pH



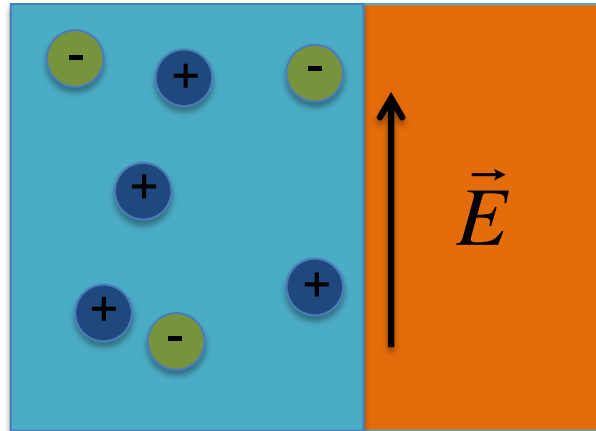
Experimental data :

Morag, J.; Dishon, M.; Sivan, U. Langmuir 2013, 29, 6317–6322.



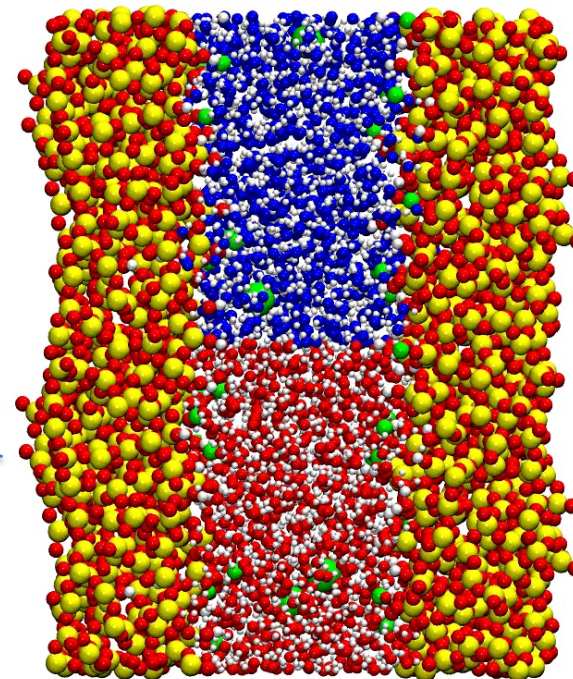
To perform Electrokinetics, you need :

**Solvent with electrolytes**



**Solid**

Today: electroosmosis:  
source is electric field  
effect is fluid velocity



Water and ions confined in a silica slot  
under an electric field.

What would we like to know ?



## MEASUREMENT AND INTERPRETATION OF ELECTROKINETIC PHENOMENA

### (IUPAC Technical Report)

*Prepared for publication by*

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University, Wageningen, The Netherlands*

*With contributions from (in alphabetical order):* S. Alkafeef, College of Technological Studies, Hadyia, Kuwait; E. Chibowski, Maria Curie Sklodowska University, Lublin, Poland; C. Grosse, Universidad Nacional de Tucumán, Tucumán, Argentina; A. S. Dukhin, Dispersion Technology, Inc., New York, USA; S. S. Dukhin, Institute of Water Chemistry, National Academy of Science, Kiev, Ukraine; K. Furusawa, University of Tsukuba, Tsukuba, Japan; R. Jack, Malvern Instruments, Ltd., Worcestershire, UK; N. Kallay, University of Zagreb, Zagreb, Croatia; M. Kaszuba, Malvern Instruments, Ltd., Worcestershire, UK; M. Kosmulski, Technical University of Lublin, Lublin, Poland; R. Nöremberg, BASF AG, Ludwigshafen, Germany; R. W. O'Brien, Colloidal Dynamics, Inc., Sydney, Australia; V. Ribitsch, University of Graz, Graz, Austria; V. N. Shilov, Institute of Biocolloid Chemistry, National Academy of Science, Kiev, Ukraine; F. Simon, Institut für Polymerforschung, Dresden, Germany; C. Werner, Institut für Polymerforschung, Dresden, Germany; A. Zhukov, University of St. Petersburg, Russia; R. Zimmermann, Institut für Polymerforschung, Dresden, Germany





Some Differential Equations for EK :

$$\Delta v = \frac{\rho(z) E}{\eta}$$

Navier-Stokes

$$U_C = \frac{1}{4 \pi \epsilon \epsilon_0} \frac{q q'}{r}$$

Coulomb

$$\vec{E} = -\vec{\nabla} U_C$$

Poisson

$$\Delta \psi(z) = -\frac{\rho(z)}{\epsilon \epsilon_0}$$

Boltzmann

$$C_i(z) = C_0 \exp\left(-\frac{q_i \psi(z)}{k_B T}\right)$$



Boltzmann

Gouy-Chapman

$$\psi_{GC}(z) = \frac{4k_B T}{q} \tanh^{-1} \left( \tanh \left( \frac{q\zeta}{4k_B T} \right) \exp(-\kappa z) \right)$$

Poisson

Smoluchowski

$$v_{fluid}(z) = -\frac{\epsilon_0 \epsilon_r}{\eta} (\zeta - \psi(z)) E$$

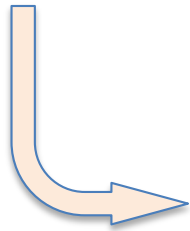
Navier-Stokes

$$v_{eo} = -\frac{\epsilon_0 \epsilon_r \zeta}{\eta} E$$

# Bikerman : excess surface conductivity of the free layer



Migration



Gouy-Chapman  
Smoluchowski

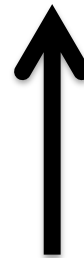
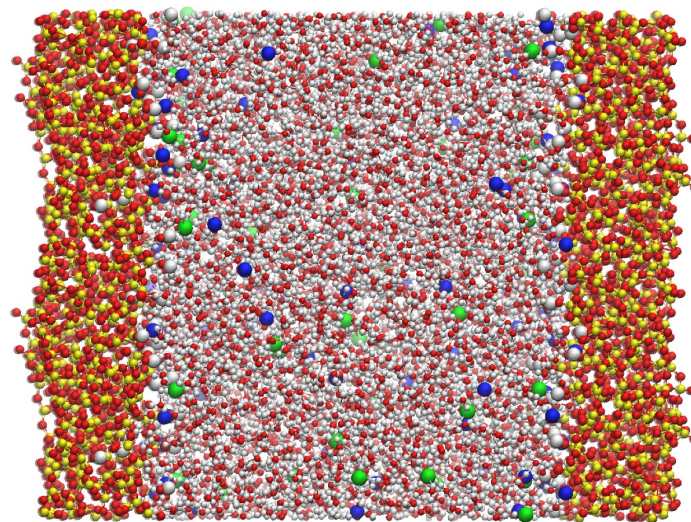


Bikerman

Convection



$$K_{\sigma} = \frac{2 C_0}{\kappa} \left( \frac{q^2}{kT} (D_+ (\exp(\frac{-q_+ \zeta}{2k_B T}) - 1) + D_- (\exp(\frac{-q_- \zeta}{2k_B T}) - 1)) + \frac{2 \epsilon \epsilon_0 kT}{\eta} ((\exp(\frac{-q_+ \zeta}{2k_B T}) - 1) + (\exp(\frac{-q_- \zeta}{2k_B T}) - 1)) \right)$$



$\vec{E}$

## Silica surface built from:

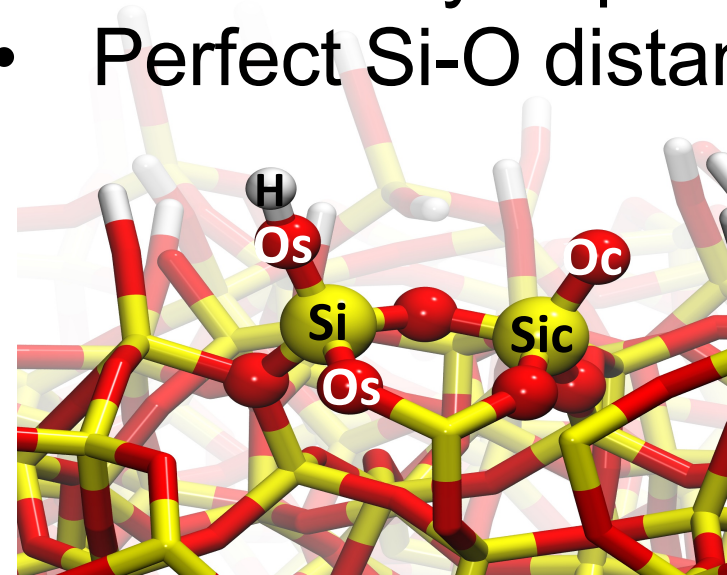
- Monte Carlo process,
- BKS potential
- Addition of silanols

## Result:

- Defect Free surface
- Tunable hydrophilicity
- Perfect Si-O distances

## Effective charges

Atoms	Hs	Os	Si	Oc	Sic
Potential					
0	+0.5	-1	+2	-1.5	+2
1	+0.5	-1	+2	-1	+2

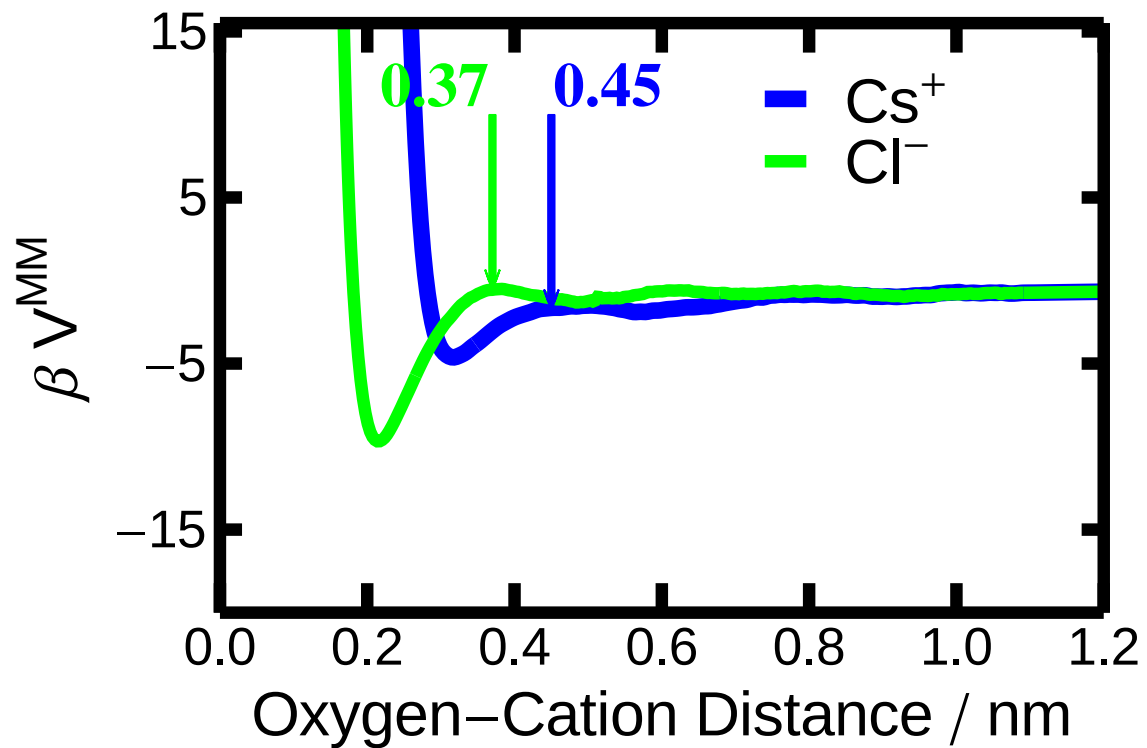


## How Ion Condensation Occurs at a Charged Surface: A Molecular Dynamics Investigation of the Stern Layer for Water–Silica Interfaces

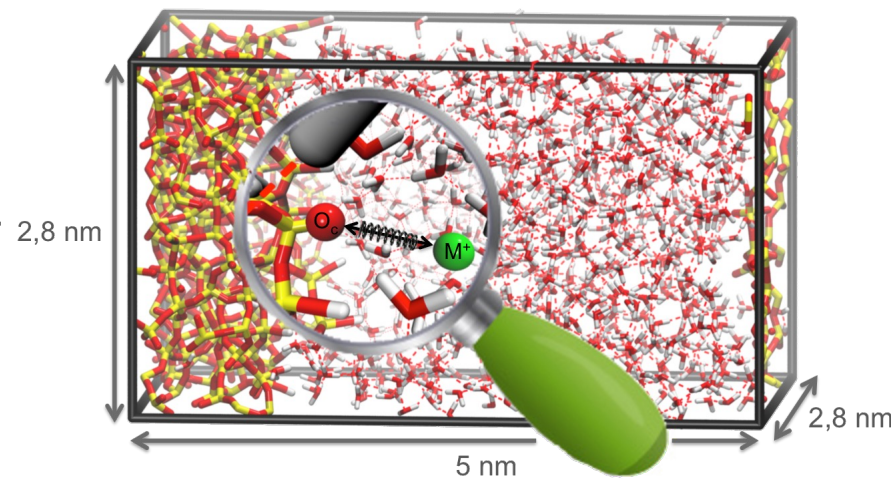
Sarah Hocine,<sup>†</sup> Remco Hartkamp,<sup>‡,§,||</sup> Bertrand Siboulet,<sup>\*,†</sup> Magali Duvail,<sup>†</sup> Benoit Coasne,<sup>‡,§,||</sup> Pierre Turq,<sup>#</sup> and Jean-François Dufreche<sup>\*,†</sup>

*J. Phys. Chem. C* 2016, 120, 963–973

# Potential of Mean Force



$$P(z) \propto \exp(-\beta V^{MM})$$



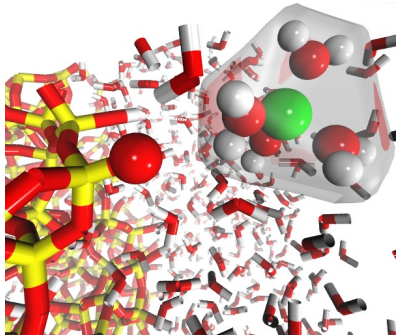


# Defining Free Ions and Surface Bonded Ions (FI and SBI)



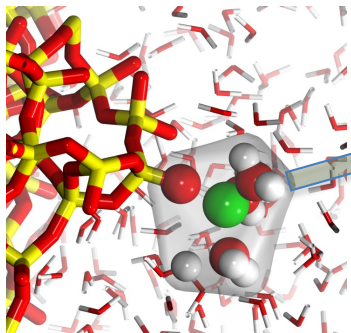
Solvent Separated Ion Pair (SSIP)

? FI or SBI ?

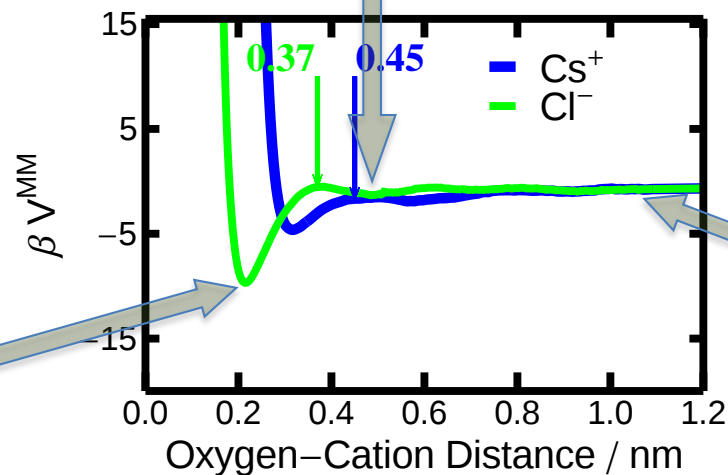


Contact Ion Pair (CIP)

Surface Bonded Ions (SBI)

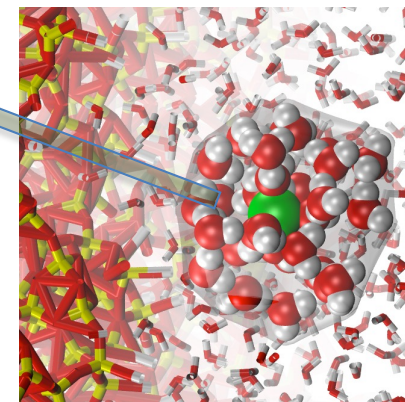


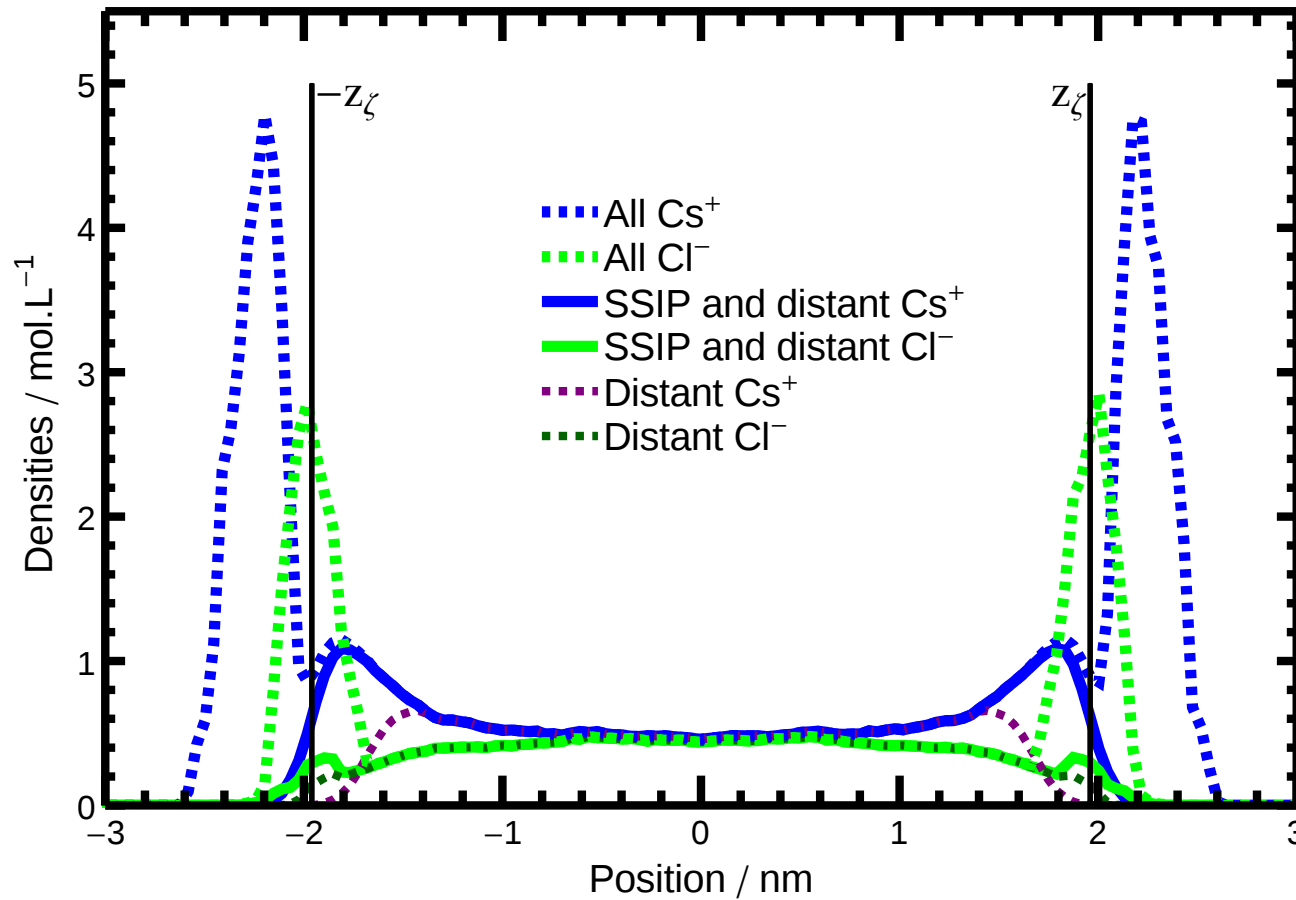
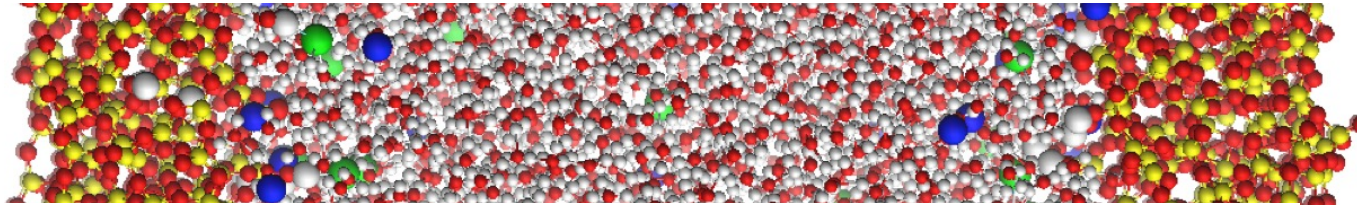
PMF:  
Simple definition of bonds



Distant ions

Free Ions (FI)



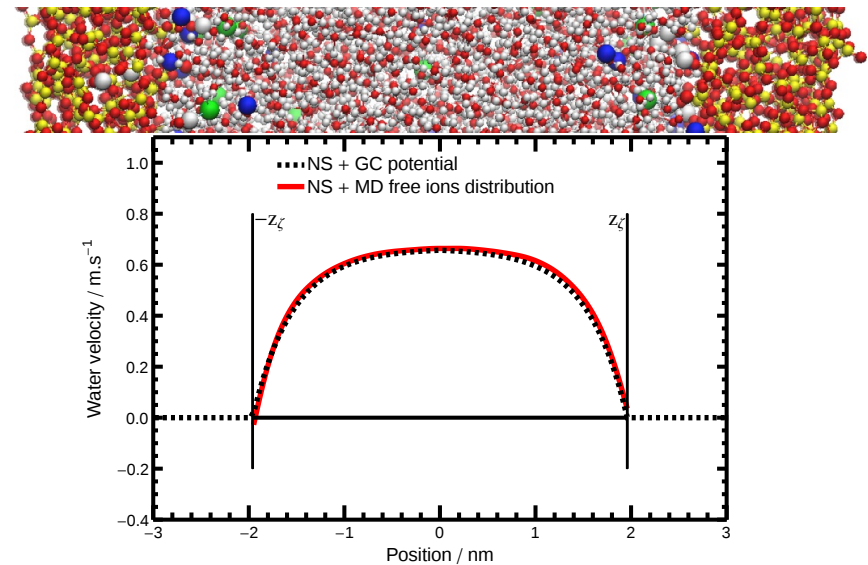
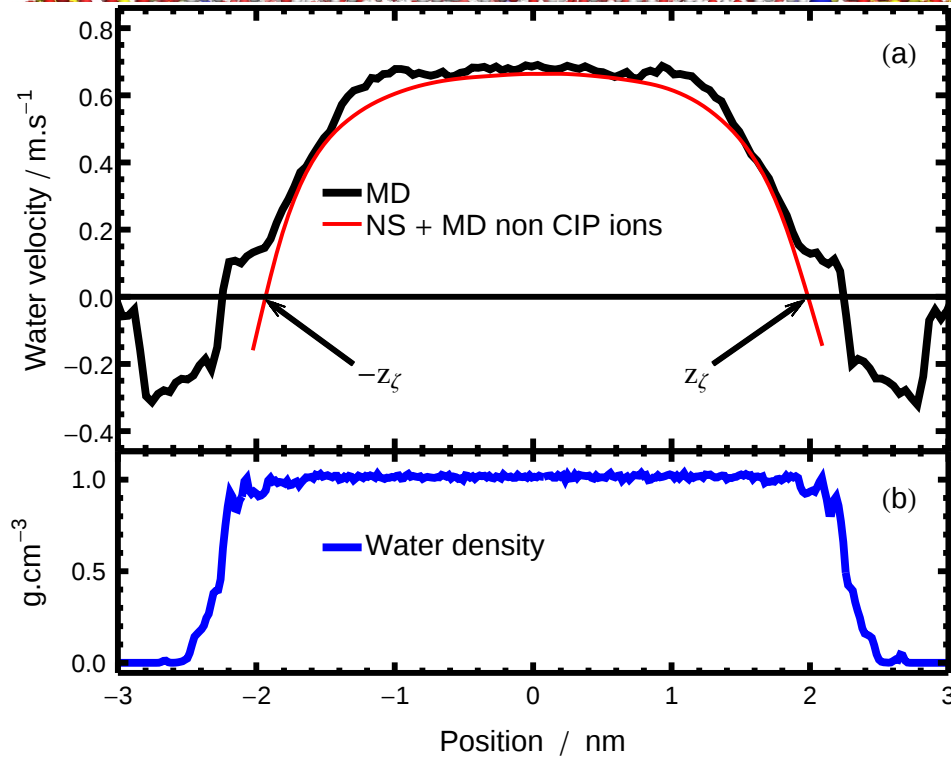
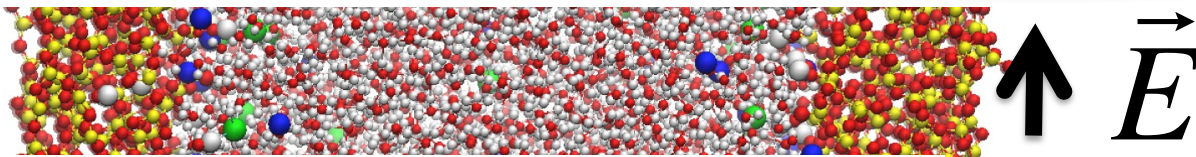


Distance criteria: very selective . Is it operative for:

- 1) Electroosmosis ?
- 2) Surface conduction ?

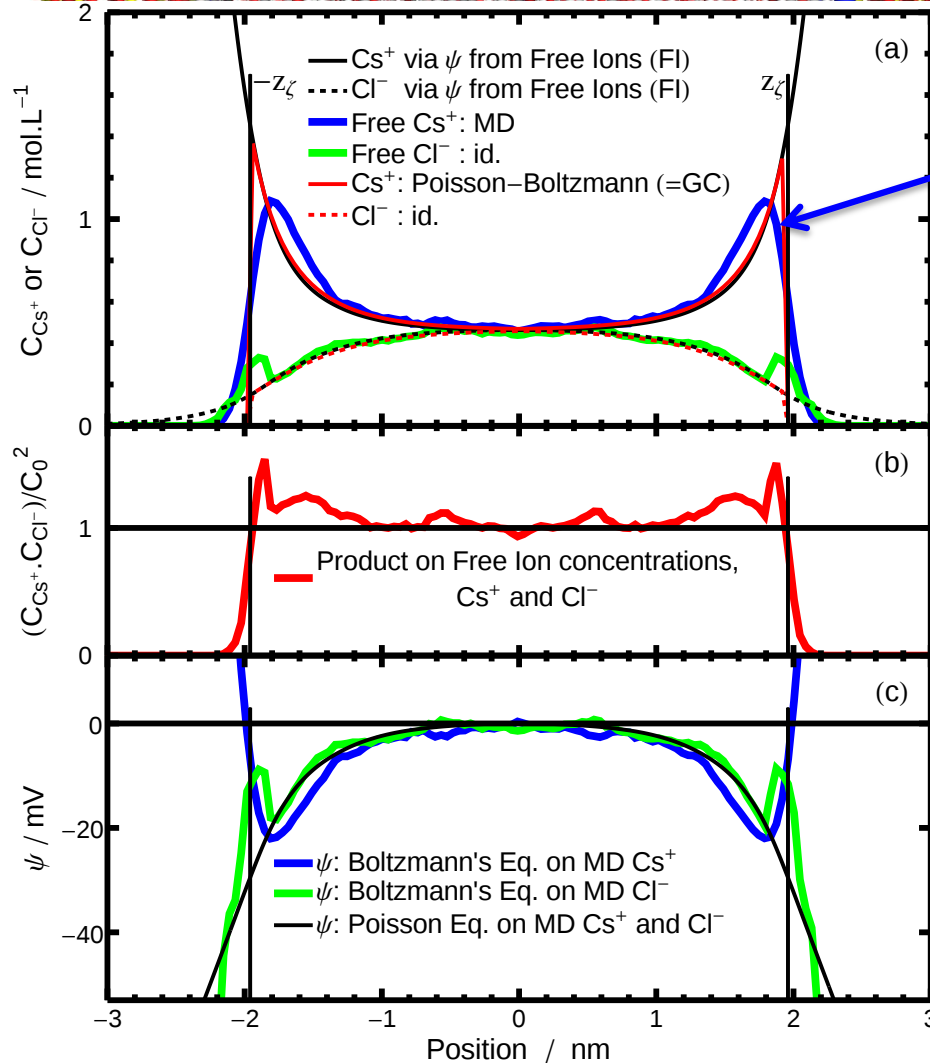
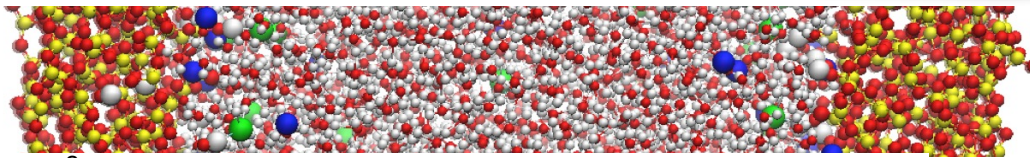
## Ion densities with surface distance criteria

# Is there a shear plane ? What is the $\zeta$ -potential ?



- No shear plane in solvent
- $\zeta$ -potential from MD on FI or from Gouy-Chapman
- No space dependent viscosity or permittivity
- OHP does not appear: included in FI

# «Boltzmann »'s continuous description valid ?



Smoothing from roughness

$$C_i(z) = C_0 \exp\left(-\frac{q_i \psi(z)}{k_B T}\right)$$

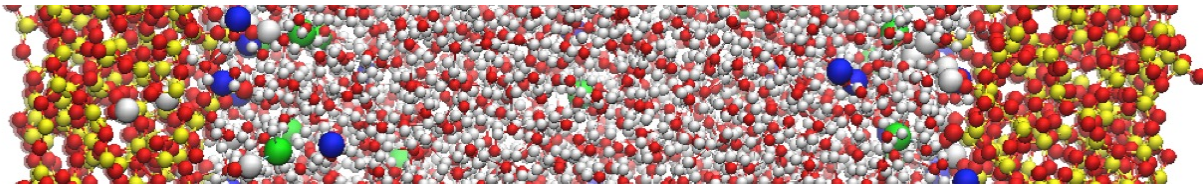
$$C_{Cs^+}(z) C_{Cl^-}(z)$$

$$= C_0 \exp\left(-\frac{q \psi(z)}{k_B T}\right) C_0 \exp\left(+\frac{q \psi(z)}{k_B T}\right)$$

$$= C_0^2 \quad \text{if Boltzmann's law is met}$$

$$\psi(z) = -\frac{k_B T}{q_i} \ln\left(\frac{C_i(z)}{C_0}\right)$$

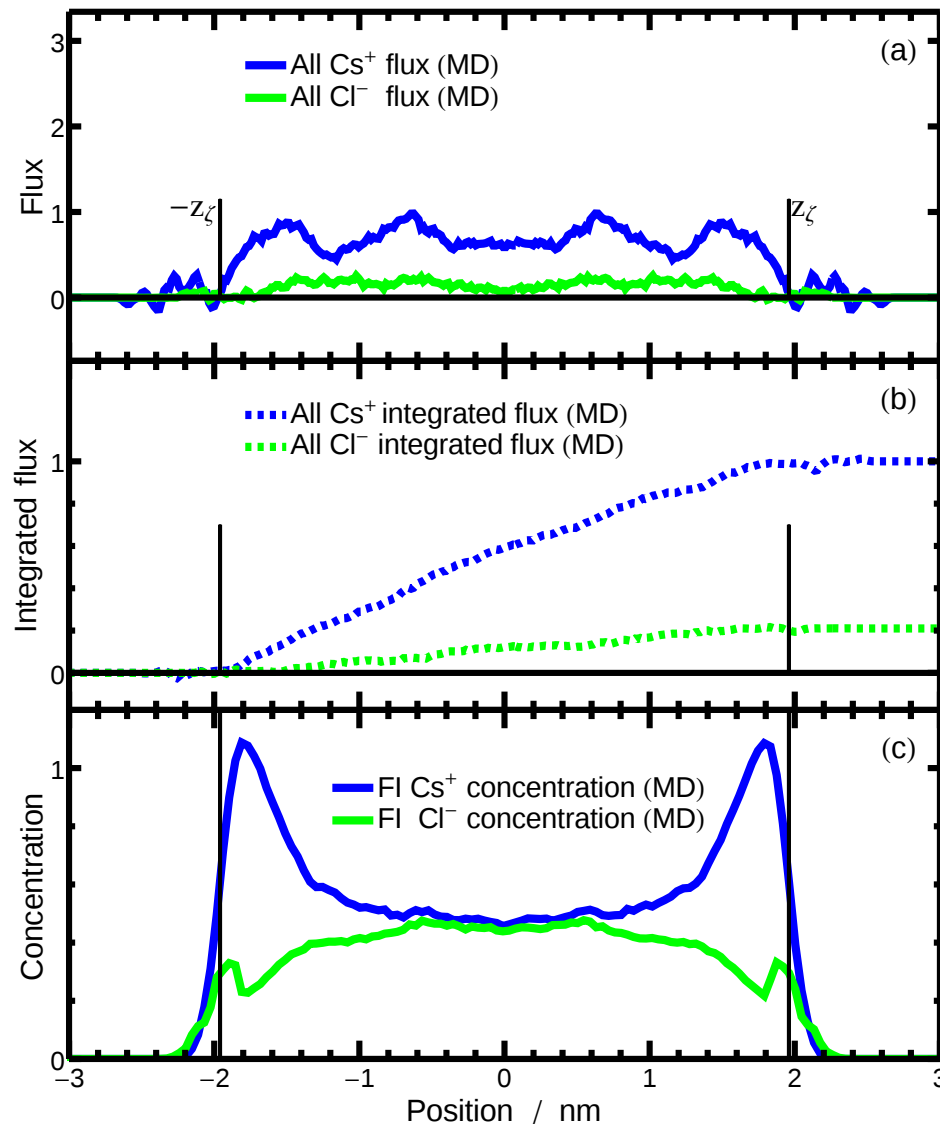
# Is there conduction in the Stern Layer ? (1)



Conductivity:  
charges moving

$$J^{\pm}(z) = C^{\pm}(z) v^{\pm}(z)$$

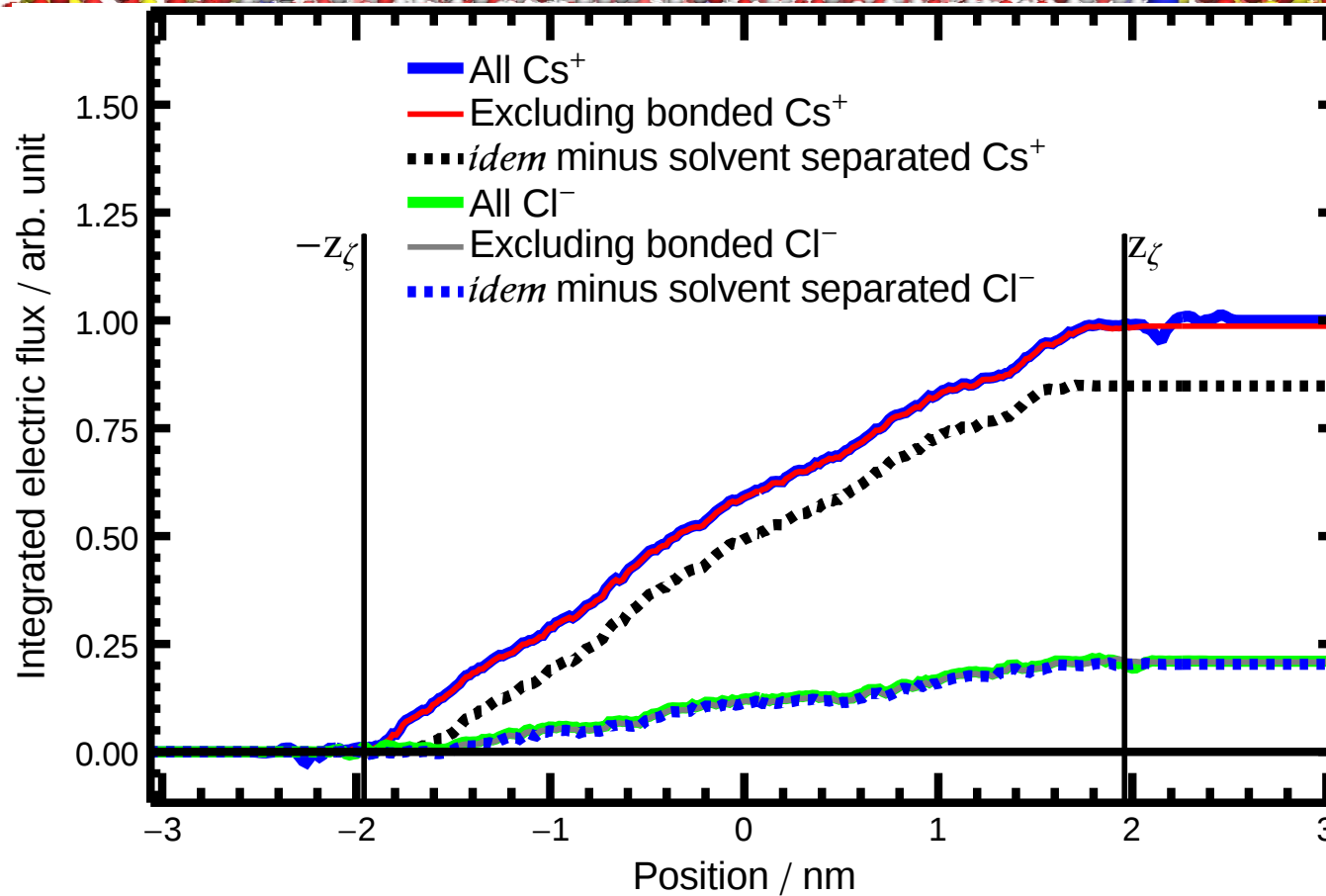
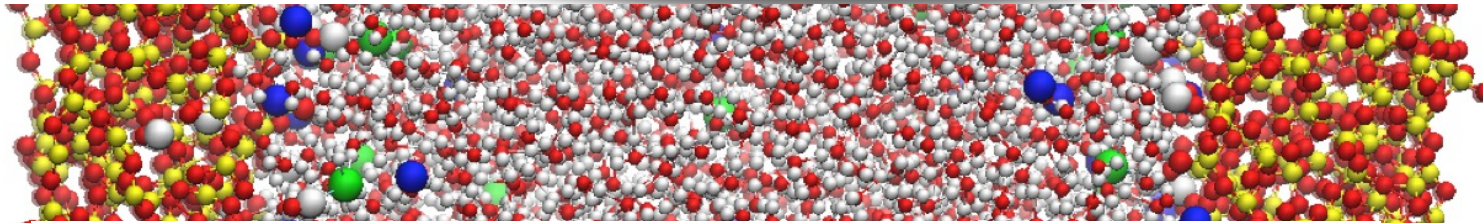
FI contribution  
very small here



$$K_{\sigma} = \frac{1}{E} \int_{\text{left}}^{\text{right}} (J^{+}(z) + J^{-}(z)) dz$$

**Which ions  
need to  
be included  
for conductivity  
?**

# Is there conduction in the Stern Layer ? (2)



Free Ions contribute / Bonded ions do not  
OHP included in FI (again)



Surface conductivity an excess term:  
 the **observed** conductivity  
 minus  
 the **bulk** conductivity for the same width

$K_{\sigma} \leftarrow$  MD : -3.0 nS  
 Bikerman's is always  
 positive

Hypothesis:  
 constant permittivity  
 constant viscosity  
 constant mobility

$$K_{\sigma} = \frac{2C_0}{\kappa} \left( \frac{q^2}{kT} (D_+ (\exp(\frac{-ve\zeta}{2k_B T}) - 1) + D_- (\exp(\frac{ve\zeta}{2k_B T}) - 1)) \right) + \frac{2\epsilon\epsilon_0 kT}{\eta} \left( (\exp(\frac{-ve\zeta}{2k_B T}) - 1) + (\exp(\frac{ve\zeta}{2k_B T}) - 1) \right)$$

# Hydrodynamic reduction of mobility ?(1)



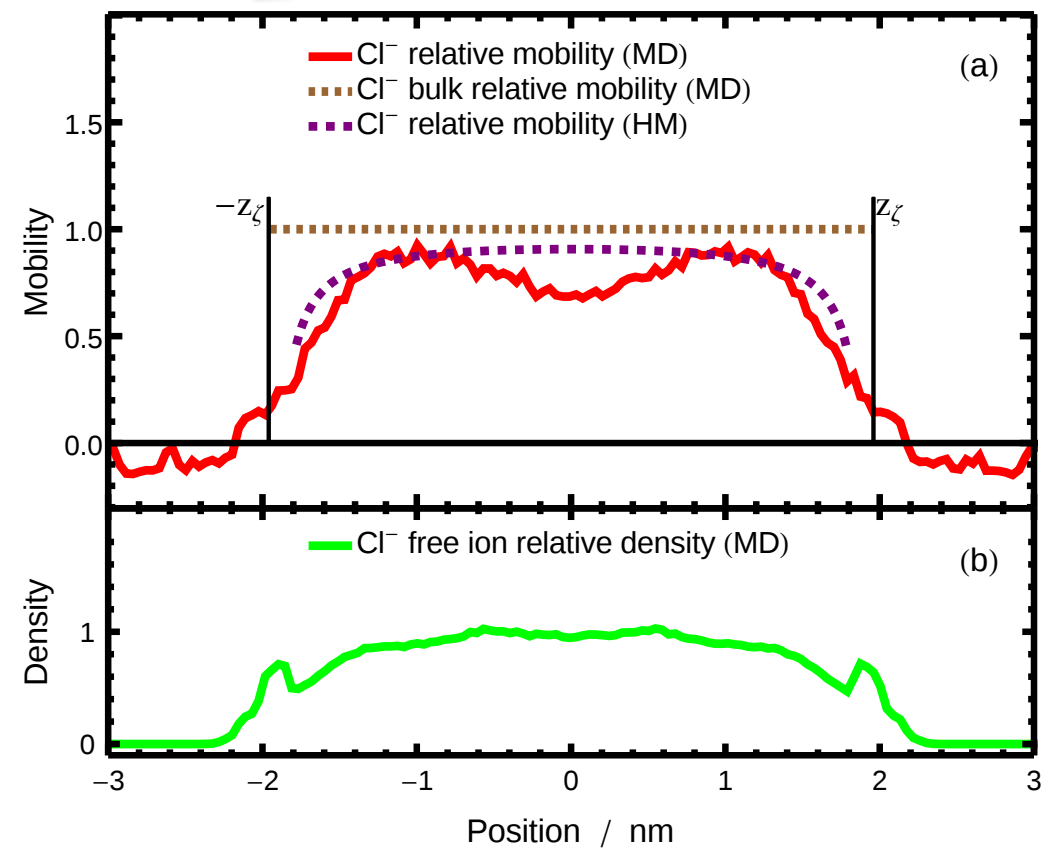
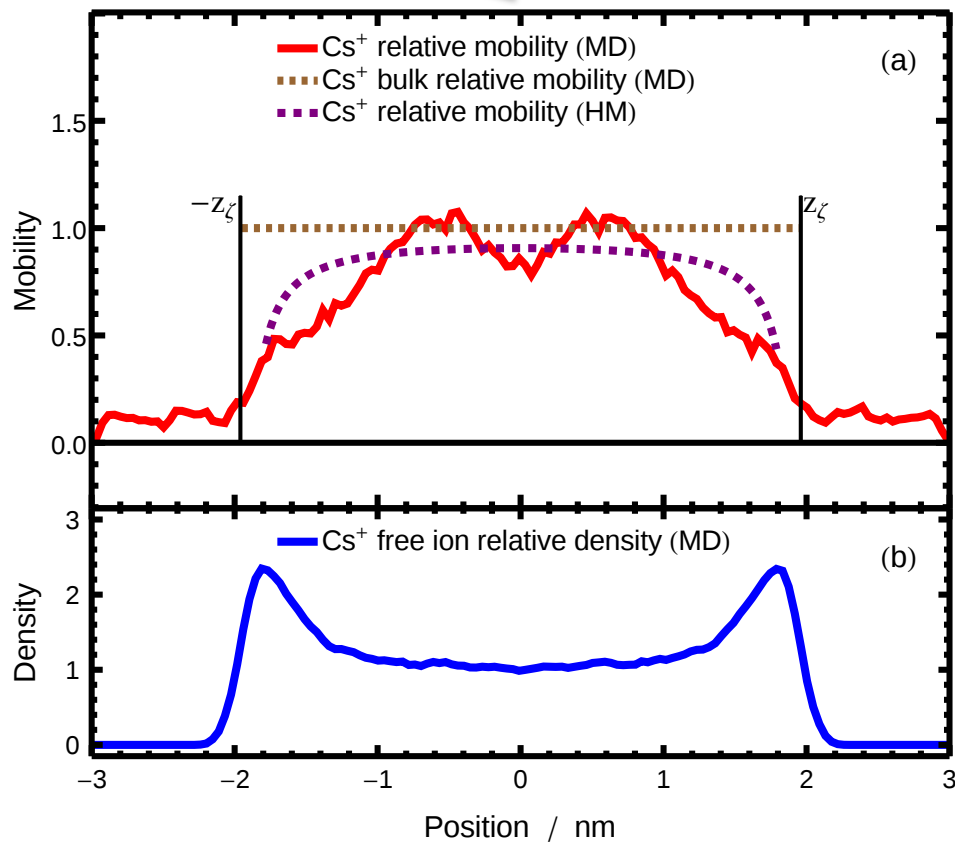
## Diffusion in pores and its dependence on boundary conditions

J. Phys.: Condens. Matter **17** (2005) S4075–S4090

A Saugey<sup>1</sup>, L Joly<sup>2</sup>, C Ybert<sup>2</sup>, J L Barrat<sup>2</sup> and L Bocquet<sup>2</sup>

$$\mu(z) = \frac{v_{ion}(z) - v_{el-osm}(z)}{e E}$$

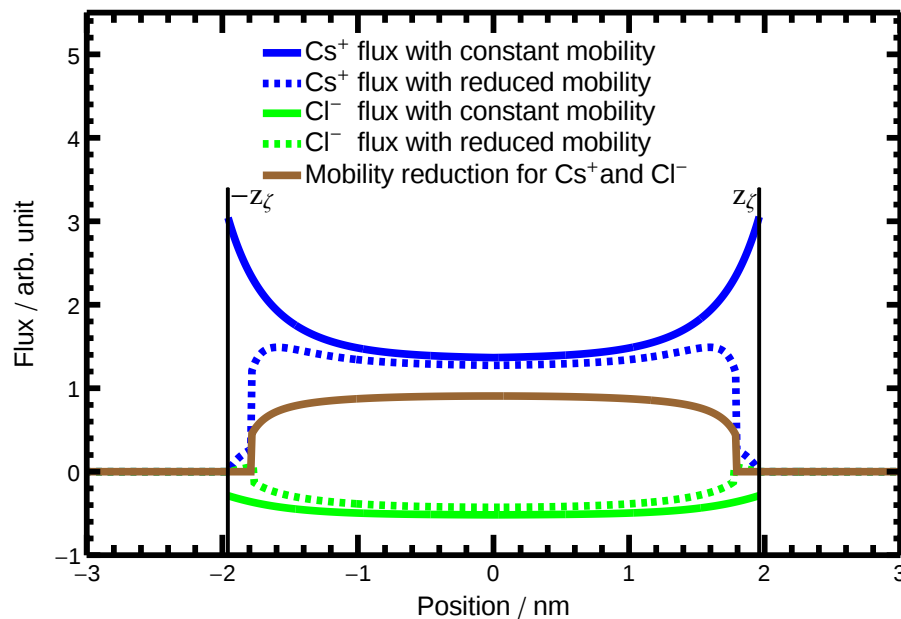
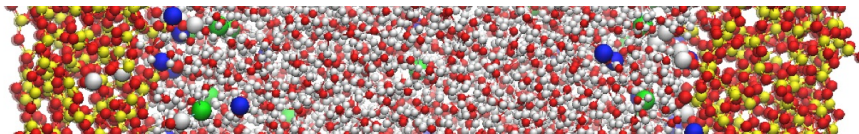
$\mu(\text{MD}), \mu(\text{HD})$



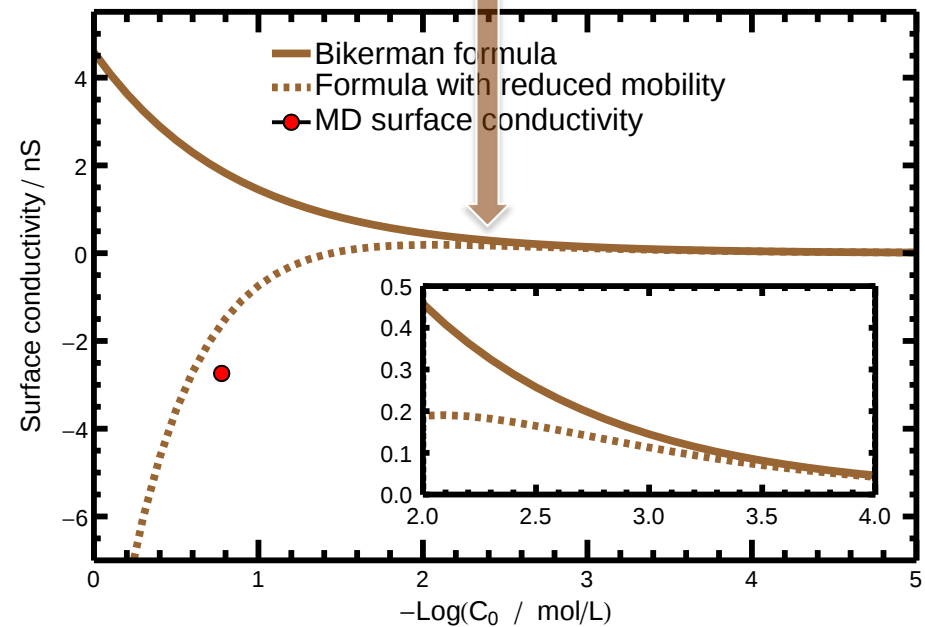


Estimating the impact of mobility reduction:  
Adding a numerical reduction on Bikerman's formula

Limit of Bikerman's  
formula validity



No Dynamic Stern Layer





Where is the non Bikerman missing conductivity ?

$$K_{slip} = \frac{\delta \sigma^2}{\eta}$$

$\sigma = -0.05 \text{C.m}^{-1}$  and  $\delta = 0.1 \text{ nm}$   $\rightarrow K_{slip} = 0.34 \text{ nS}$

Typical                      Minimal                      Experimental  
slip length

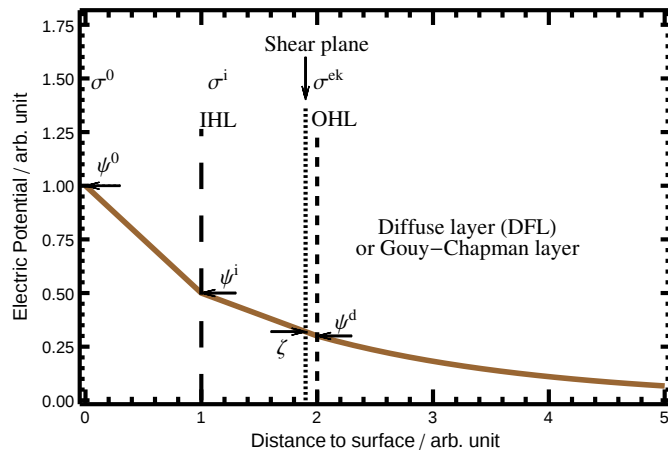
Streaming Potentials and Conductivities of Latex Plugs  
in Indifferent Electrolytes

Marcel Minor,<sup>1</sup> Ab J. van der Linde, and Johannes Lyklema

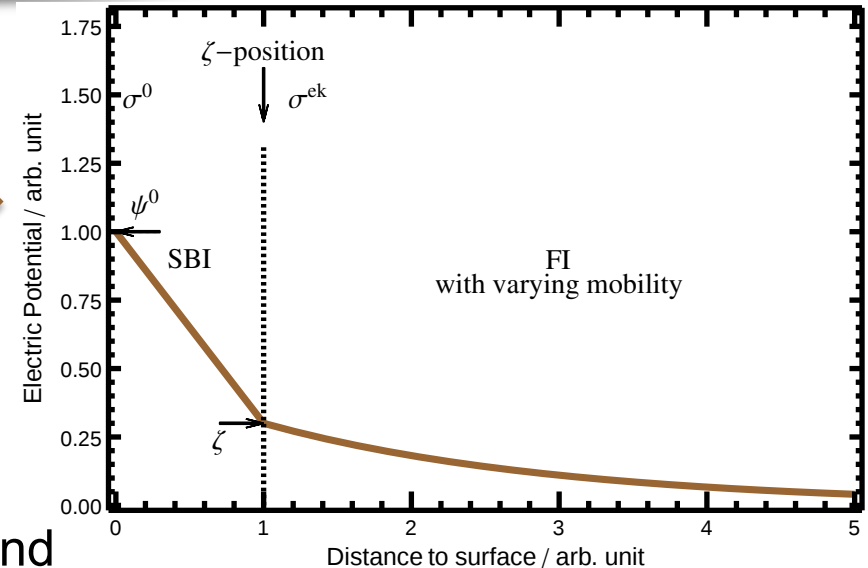
Department of Physical and Colloid Chemistry, Wageningen Agricultural University, Dreijenplein 6, 6703 HB Wageningen, The Netherlands



# Conclusions



Simpler description



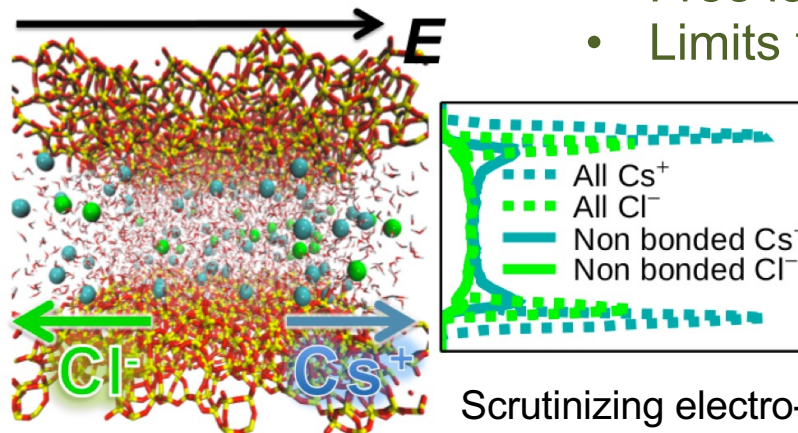
Simple description:

Classical profiles can be met with

- NO VARYING PERMITTIVITY
- NO VARYING VISCOSITY
- VARYING MOBILITY

We find

- No stagnant layer
- No Dynamic Stern Layer
- No OHP
- Free ions conduct, SBI do not
- Limits to Bikerman's



Scrutinizing electro-osmosis and surface conductivity with MD, Siboulet, Hocine, Hartkamp, Dufreche, JPCC 2017

# Thanks



Thank you to everyone in the audience for his attention,  
And many thanks to Magali and Diane.

Thank you to my colleagues for their contributions

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- Hartkamp Remco

Delft University of Technology, The Netherlands

- Wang Kunyu

ICSM

- Spadina Mario

ICSM (From Croatia)

Université  
Joseph Fourier   
GRENOBLE

  
TU Delft

