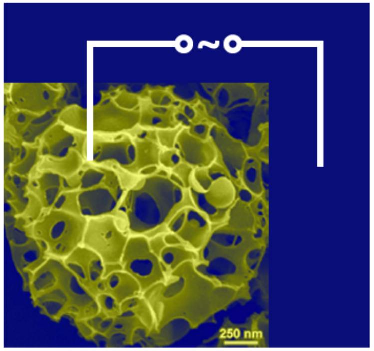
Ions at aqueous interfaces

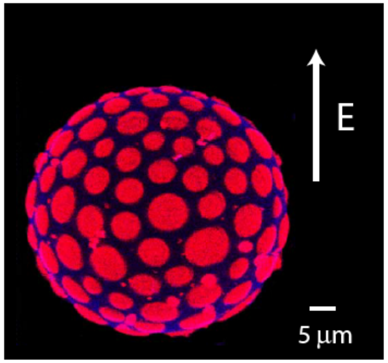
Douwe Jan Bonthuis

Ions adsorb at or desorb from surfaces

Double layer capacitance



Electrophoretic mobility
& conductivity

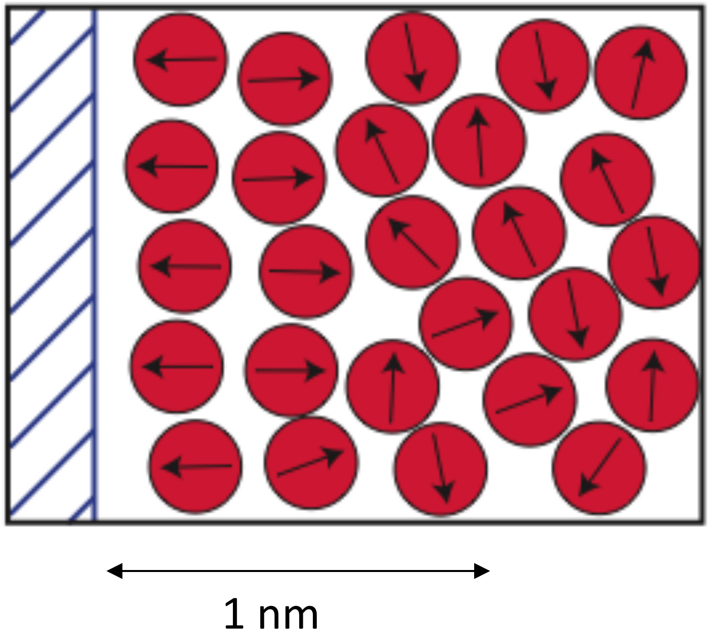


Colloidal stability
Gel electrophoresis
Vesicular transport in cells

Gouy-Chapman, DLVO do not reproduce experimental results

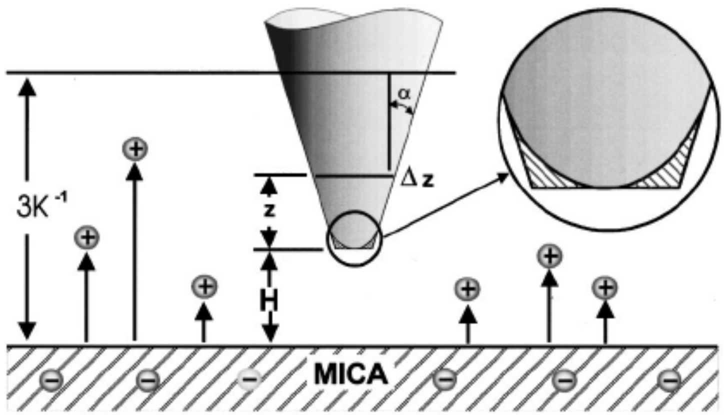
Interfacial Water Layers

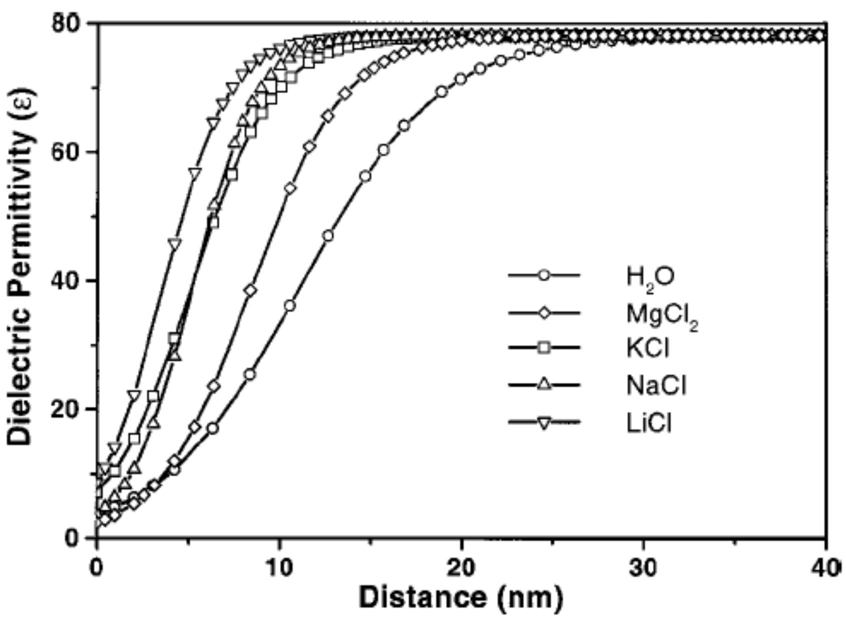
Bulk



Orientation

Structure

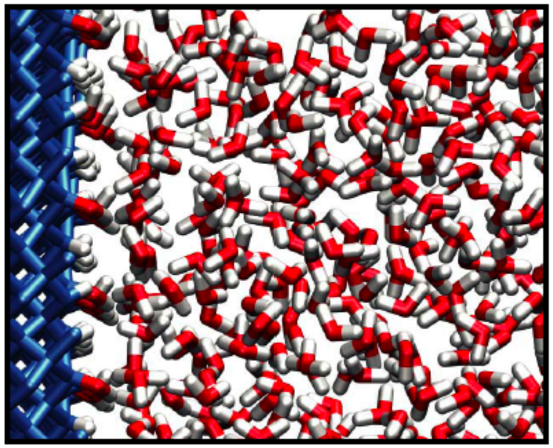




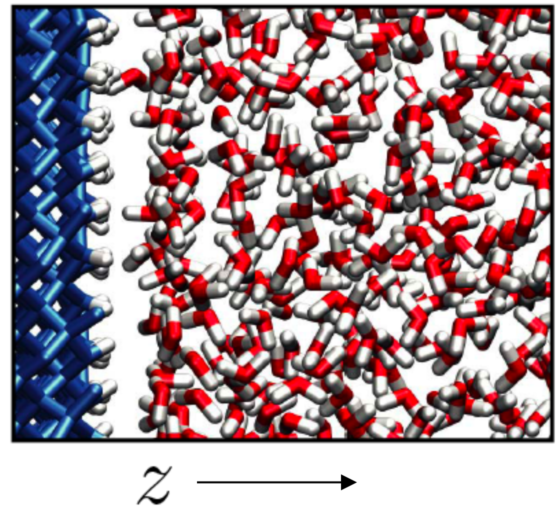
Teschke et al., PRE 64, 011605 (2001)

Molecular dynamics simulations at planar solid interfaces

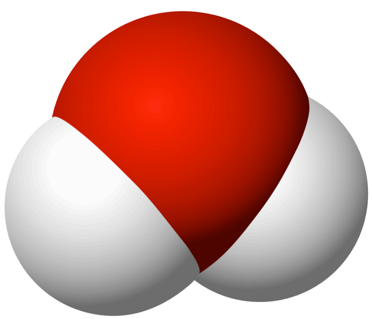
Hydrophilic



Hydrophobic



SPC/E:



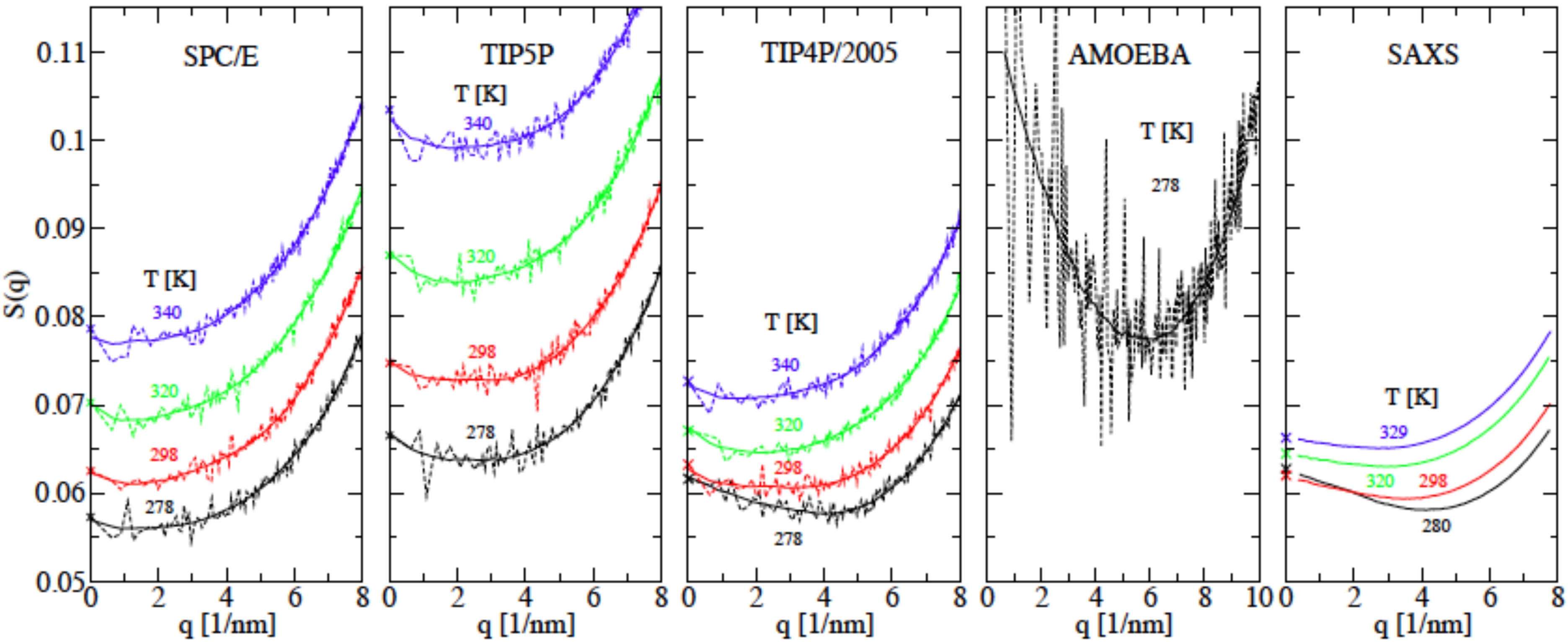
Rigid, non-polarizable

Permanent partial charge distribution

Spherically symmetric Lennard-Jones potential

SPC/E water (bulk)

Structure factor

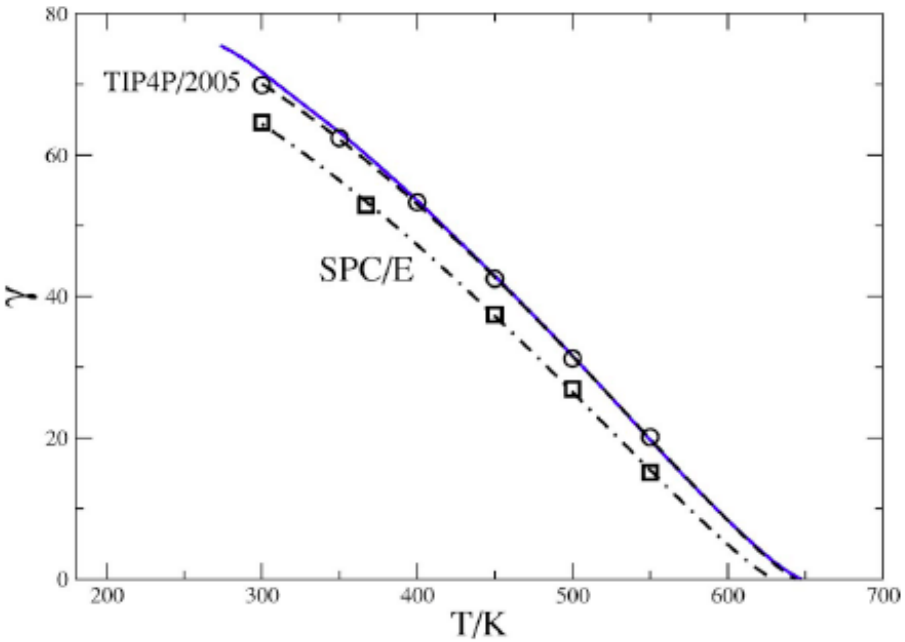


F. Sedlmeier et al., JACS 133, 1391 (2011)

SPC/E water (interfaces)

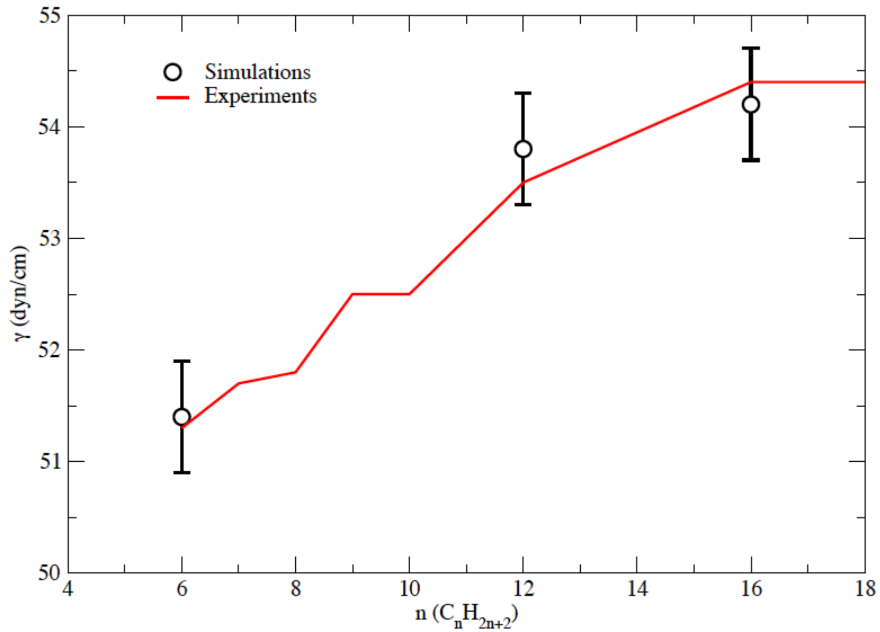
Surface tension

Air/water



Temperature

Oil/water



Chain length

Vega & De Miguel,
J. Chem. Phys. ***126***, 154707 (2007)

Dielectric tensor

$$\Delta \boldsymbol{D}(\boldsymbol{r}) = \int \varepsilon_0 \varepsilon_{nl}(\boldsymbol{r}, \boldsymbol{r}') \cdot \Delta \boldsymbol{E}(\boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}'$$

$$\Delta \boldsymbol{E}(\boldsymbol{r}) = \int \varepsilon_0^{-1} \varepsilon_{nl}^{-1}(\boldsymbol{r}, \boldsymbol{r}') \cdot \Delta \boldsymbol{D}(\boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}'$$

Local dielectric tensor at planar surfaces:

$$\varepsilon_{\|}(z) = \int \varepsilon_{nl}(z)\, \mathrm{d}z$$

$$\varepsilon_{\perp}^{-1}(z) = \int \varepsilon_{nl}^{-1}(z)\, \mathrm{d}z$$

Dielectric tensor

Excess polarization for a constant field F

$$\Delta \boldsymbol{m} = \langle \boldsymbol{m} \rangle_{\mathbf{F}} - \langle \boldsymbol{m} \rangle_0$$

$$= \frac{\int (\boldsymbol{m} - \langle \boldsymbol{m} \rangle_0) \exp[-\beta(U - \mathbf{M}\cdot\mathbf{F})] \, \mathrm{d}X}{\int \exp[-\beta(U - \mathbf{M}\cdot\mathbf{F})] \, \mathrm{d}X}$$

$$\Delta \boldsymbol{m} \approx \frac{\int (\boldsymbol{m} - \langle \boldsymbol{m} \rangle_0)(1 + \beta \mathbf{M}\cdot\mathbf{F}) \exp[-\beta U] \, \mathrm{d}X}{\int \exp[-\beta U] \, \mathrm{d}X}$$

Parallel (constant E)

$$\varepsilon_{\|}(z) \approx 1 + \varepsilon_0^{-1} \beta \left[\langle m_{\|}(z) M_{\|} \rangle_0 - \langle m_{\|}(z) \rangle_0 \langle M_{\|} \rangle_0 \right]$$

Perpendicular (constant D)

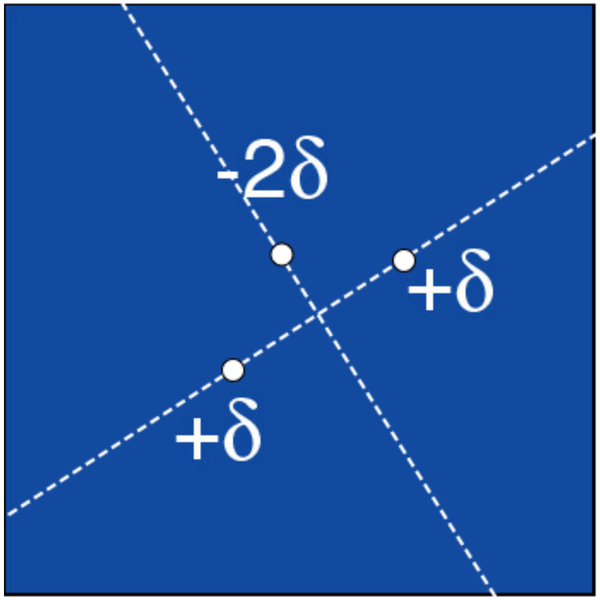
$$\varepsilon_{\perp}^{-1}(z) \approx 1 - \varepsilon_0^{-1} \beta \left[\langle m_{\perp}(z) M_{\perp} \rangle_0 - \langle m_{\perp}(z) \rangle_0 \langle M_{\perp} \rangle_0 \right]$$

Expansion of the electric field

Directly from the charge density

$$m_{\perp}(z) = -\int_{0}^{z} \rho(z')\, \mathrm{d}z'$$

$$m_{\parallel}(z) = \mp \int_{\mathcal{V}} P_0(x, z)\, \mathrm{d}x$$



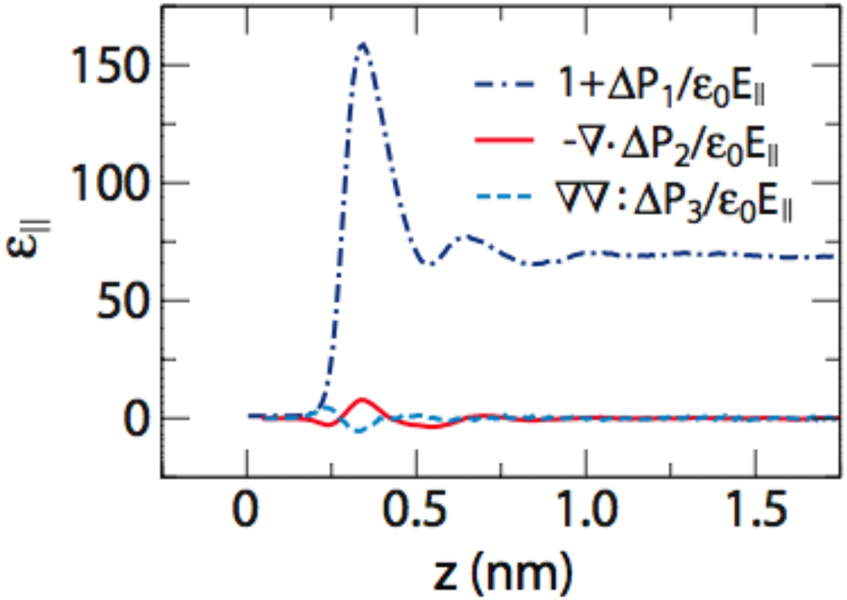
Expanding the polarization

$$\boldsymbol{m}(\boldsymbol{r}) = \boldsymbol{P}_1(\boldsymbol{r}) - \nabla \cdot \mathsf{P}_2(\boldsymbol{r}) + \nabla\nabla : \mathsf{P}_3(\boldsymbol{r}) - \ldots$$

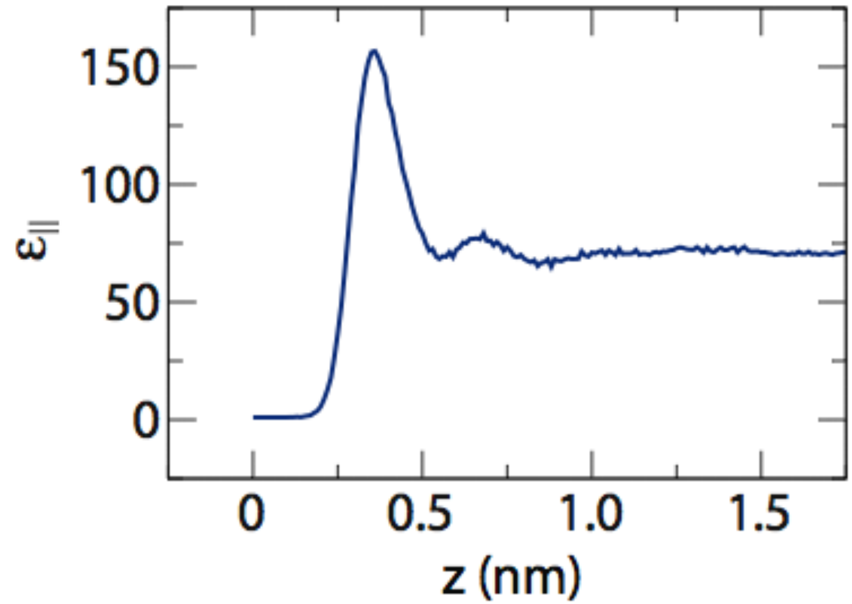
dipole quadrupole octupole

Parallel response

components



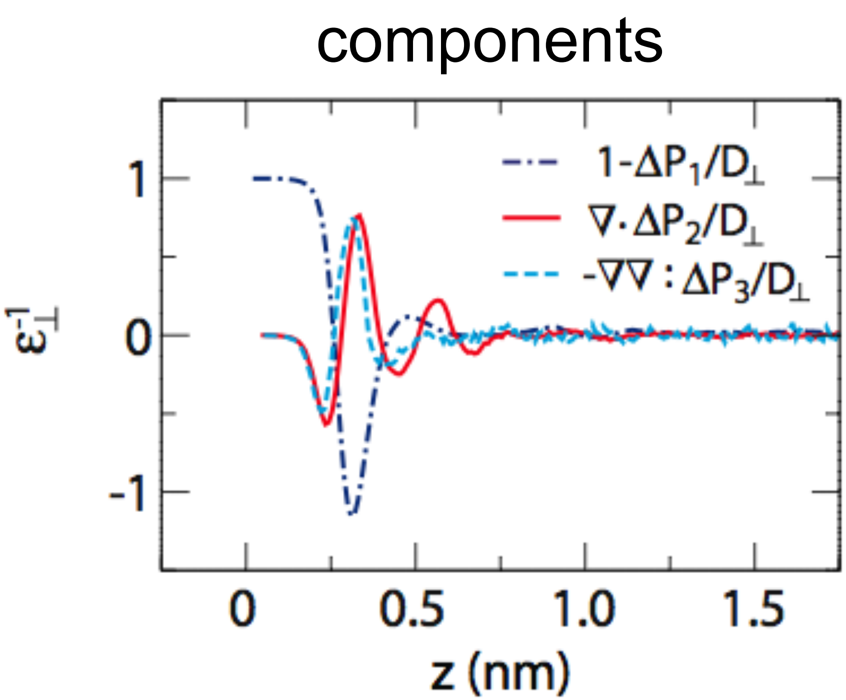
total

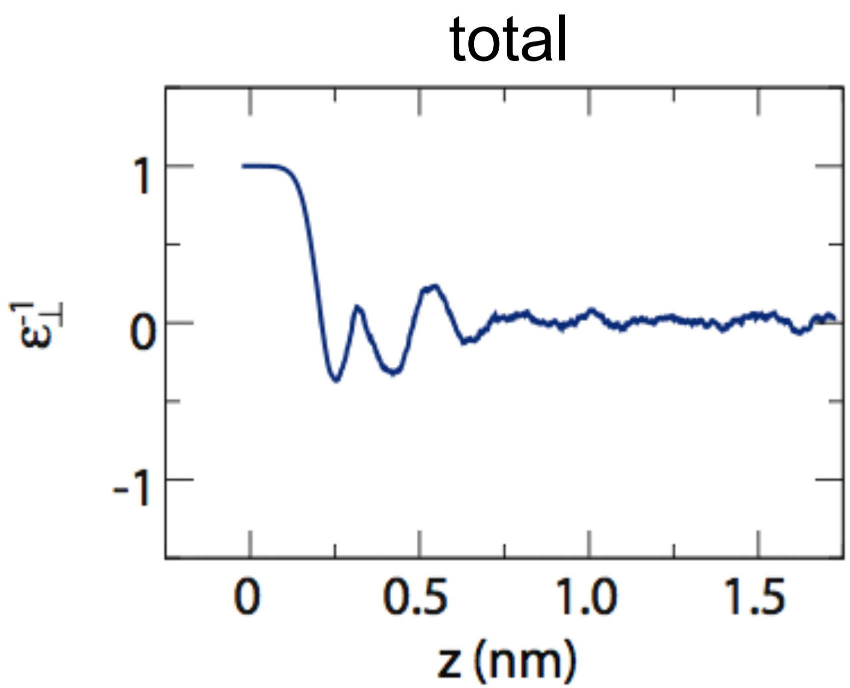


The dipole dominates the parallel response

Roughly proportional to the density

Perpendicular response





Significant contribution from higher order moments

$\varepsilon_{\perp}^{-1} < 0$: overscreening

Extended Poisson-Boltzmann

$$\varepsilon_0 E_\perp(z) = \varepsilon_\perp^{-1}(z) D_\perp(z)$$

Dielectric effects

$$\varepsilon_0 \nabla^2 \psi(z) = -\varepsilon_\perp^{-1}(z) P_0(z) - D_\perp(z) \nabla \varepsilon_\perp^{-1}(z)$$

$$D_\perp(z) = \int_0^z P_0(z')\, \mathrm{d}z'$$

Surface charges

$$P_0(z) = e(c_+(z) - c_-(z))$$

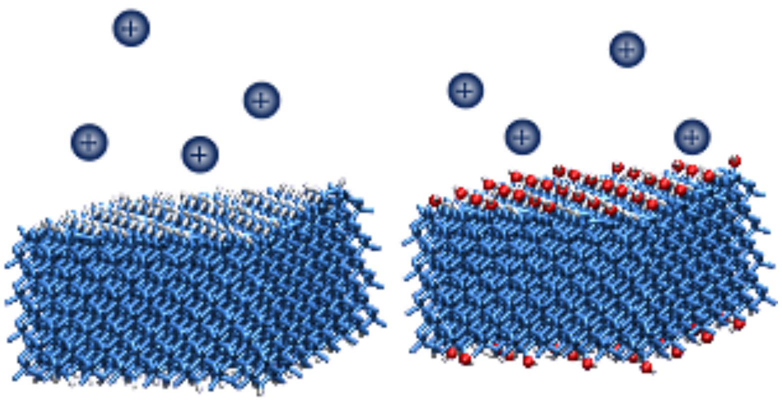
Steric effects

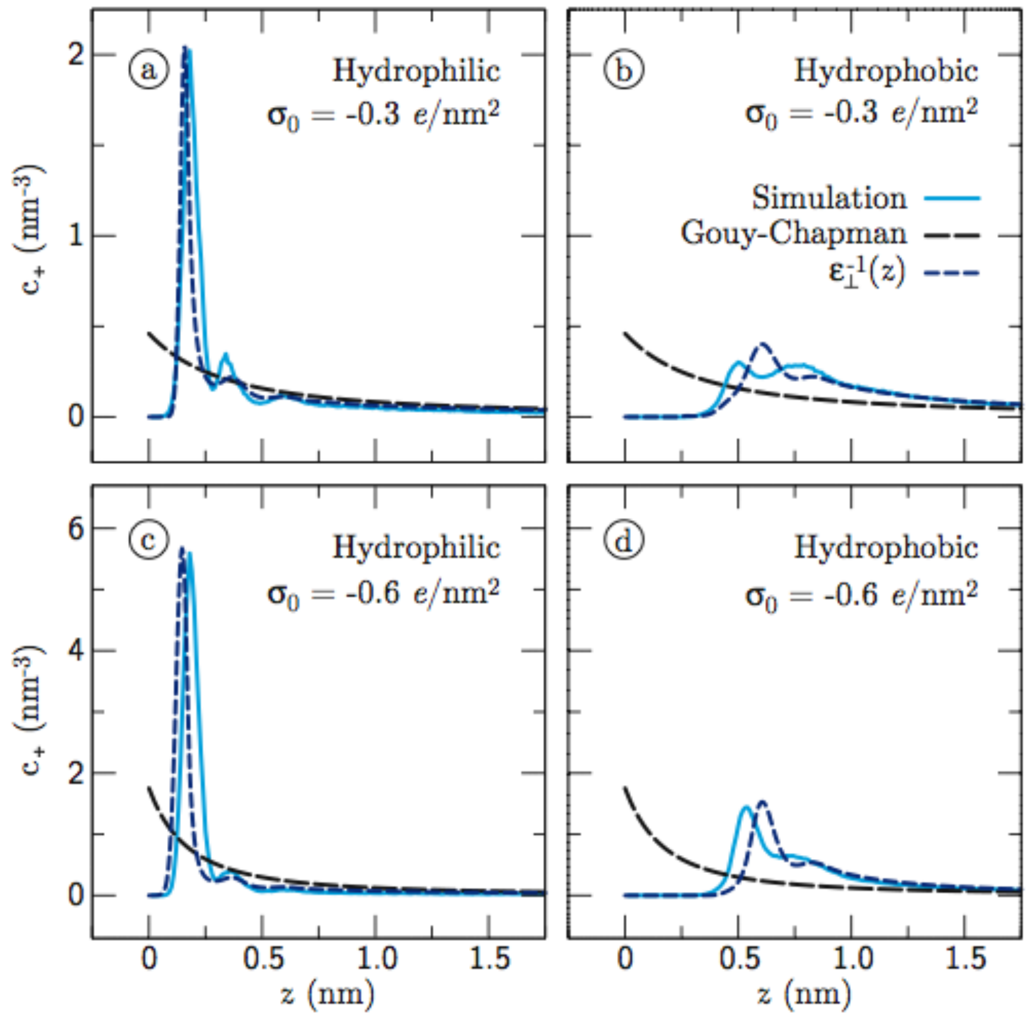
$$c_\pm(z) = \frac{\sqrt{2}\,\tilde{c}_\pm(z)}{\sqrt{2} + \lambda_+^3(\tilde{c}_+(z) - c_0) + \lambda_-^3(\tilde{c}_-(z) - c_0)}$$

$$\tilde{c}_\pm(z) = c_0 \exp(-\mu_\pm(z) \mp \beta e \psi(z))$$

Other nonelectrostatic contributions

Sodium ion density



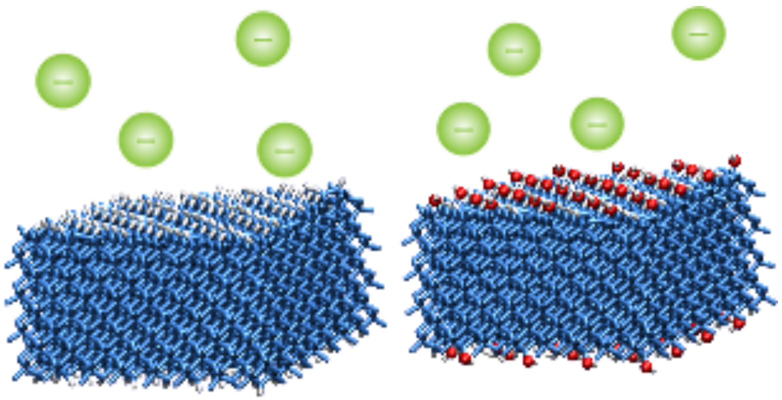


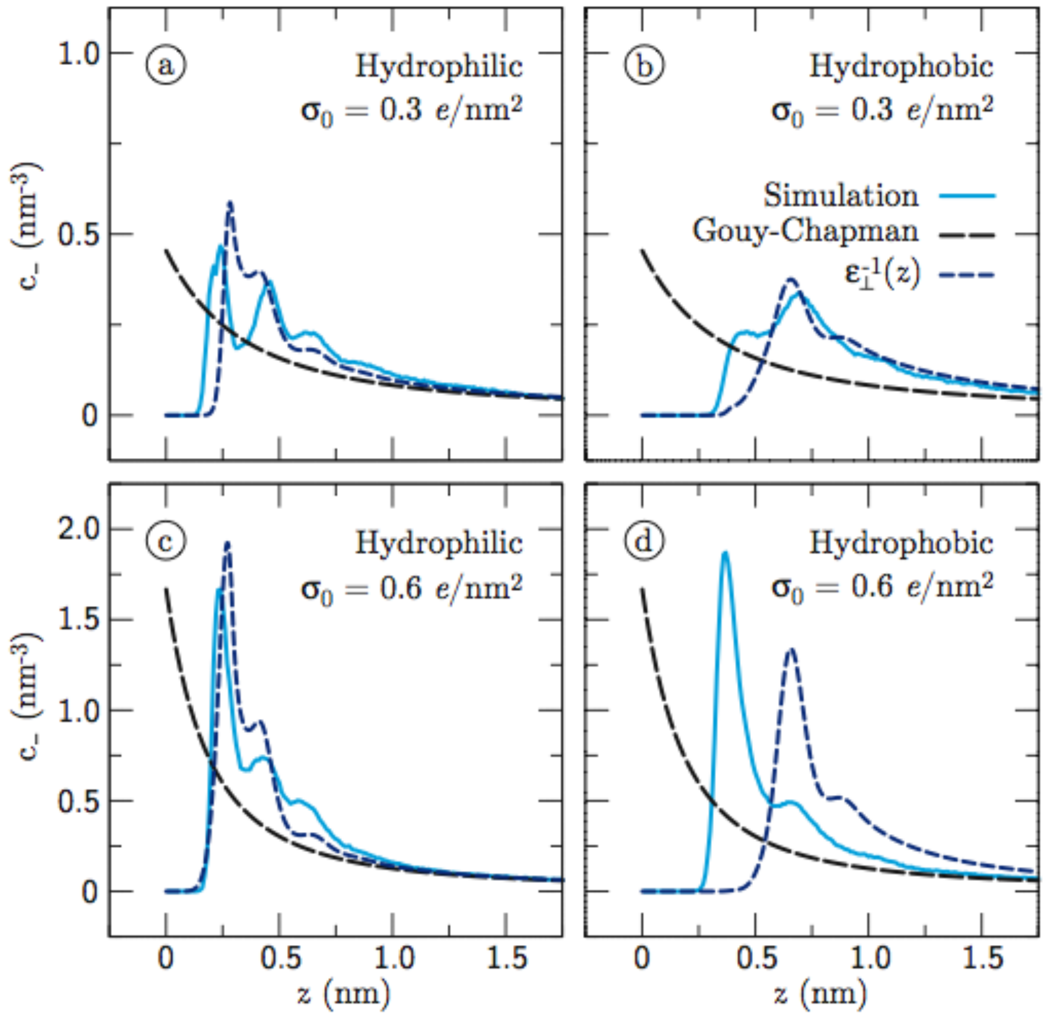
Non-electrostatic interaction

$\mu_{\pm}(z)$

soft wall repulsion

Chloride ion density

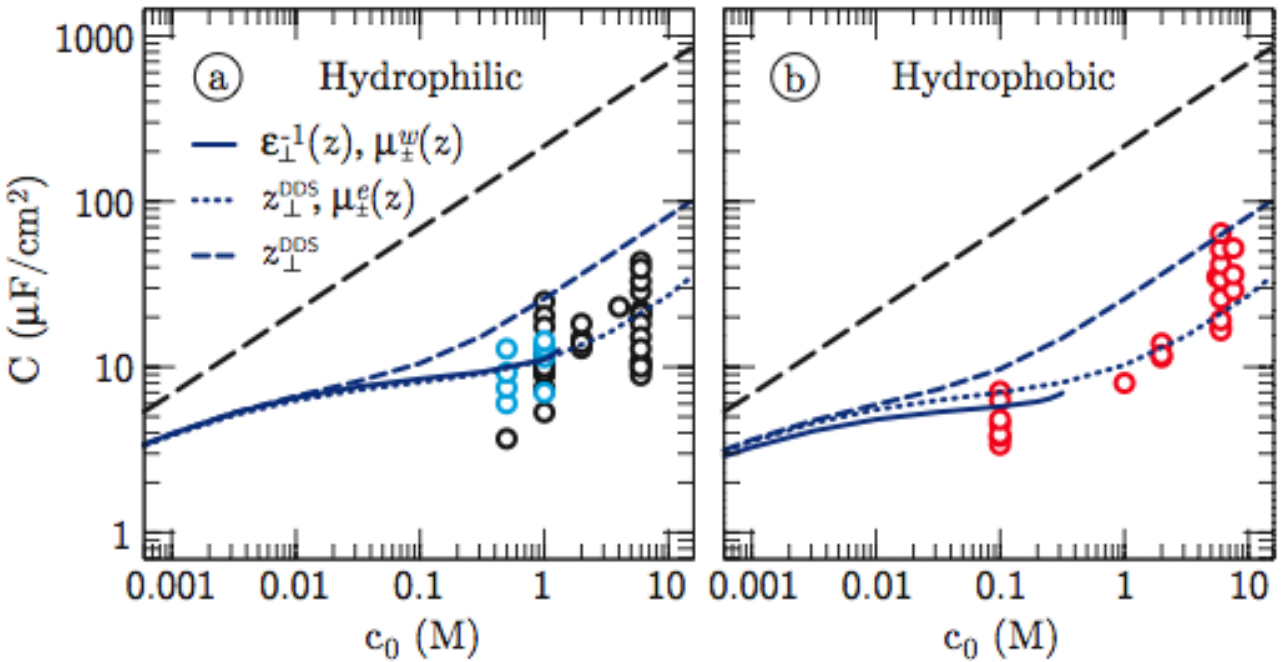




Dielectric profile & soft wall reproduce ion density profiles

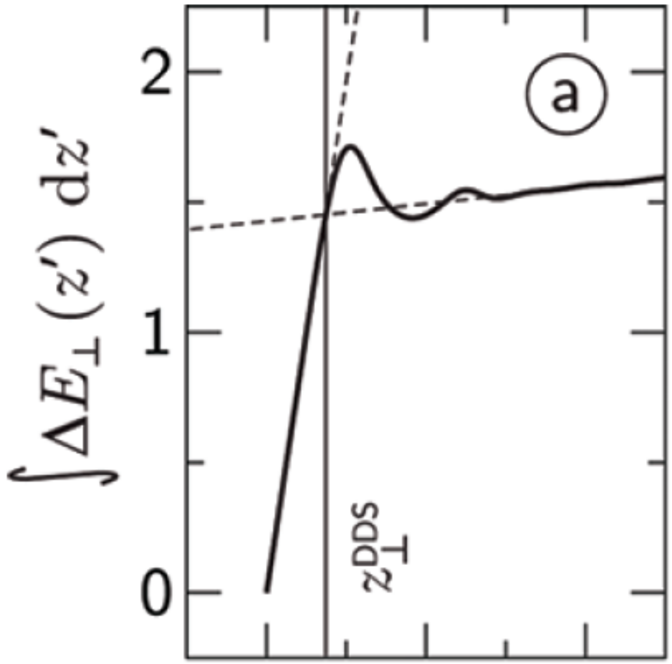
Except for big ions at hydrophobic surfaces

Double-layer capacitance



$$\mu_{\pm}^{e}(z) = \alpha \exp\left[1 - 2z/\lambda_{\pm}\right]$$

Analytical approximation



$$\varepsilon_\perp^{-1}(z) = \begin{cases} 1 & \text{if } z < z_\perp^{\mathrm{DDS}} \\ \varepsilon_{bulk}^{-1} & \text{otherwise,} \end{cases}$$

Debye-Hückel:

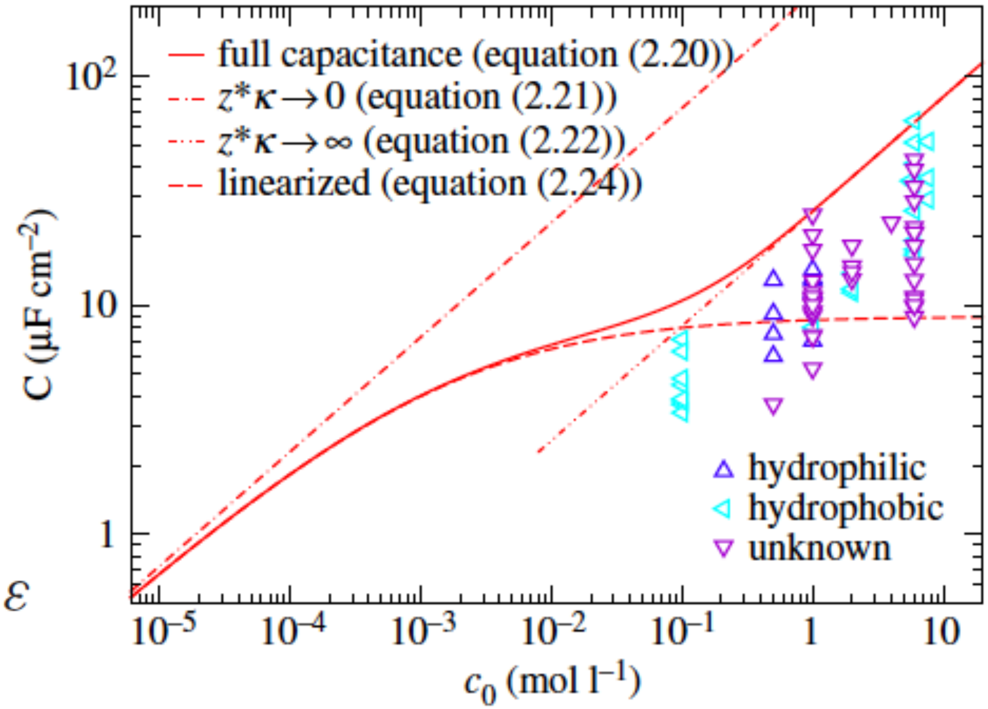
$$\nabla^2\psi(z) = \begin{cases} \varepsilon\kappa^2\psi(z), & \text{for } z < z^* \\ \kappa^2\psi(z), & \text{for } z > z^* \end{cases}$$

$$C = \left(\frac{d\psi(z=0)}{d\sigma_0}\right)^{-1}$$

Capacitance

$$C = \varepsilon_0 \kappa \sqrt{\varepsilon}\, \frac{1 + \mathrm{e}^{-2z^*\kappa\sqrt{\varepsilon}}(\sqrt{\varepsilon}-1)/(\sqrt{\varepsilon}+1)}{1 - \mathrm{e}^{-2z^*\kappa\sqrt{\varepsilon}}(\sqrt{\varepsilon}-1)/(\sqrt{\varepsilon}+1)}$$

$$C \simeq \varepsilon_0 \kappa \sqrt{\varepsilon}$$



$$C \simeq \varepsilon_0 \kappa \varepsilon$$

To linear order in z*k

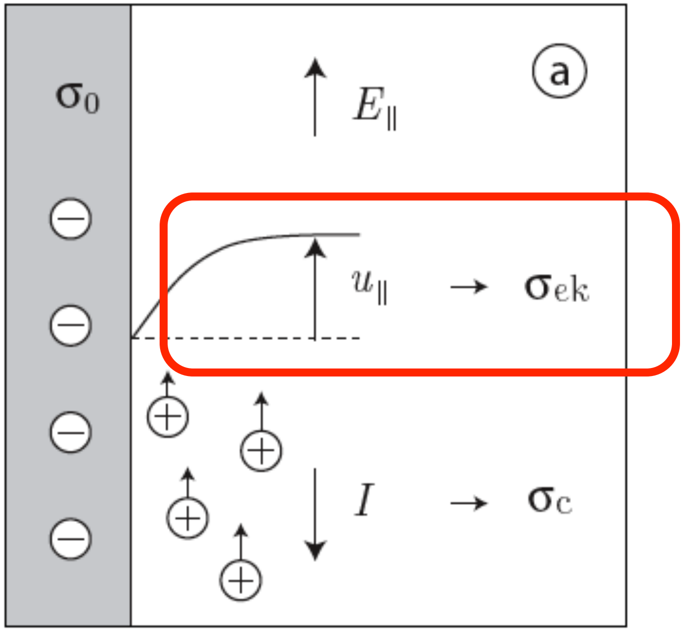
$$C \simeq \left(\frac{\kappa^{-1} - z^*}{\varepsilon_0 \varepsilon} + \frac{z^*}{\varepsilon_0} \right)^{-1}$$

2 capacitors in series!

Electrokinetics

Electroosmotic mobility

$$\lim_{z\to\infty} \frac{u_{\parallel}(z)}{E_{\parallel}} = -\frac{\varepsilon_0 \varepsilon_{bulk}}{\eta_{bulk}} \zeta$$



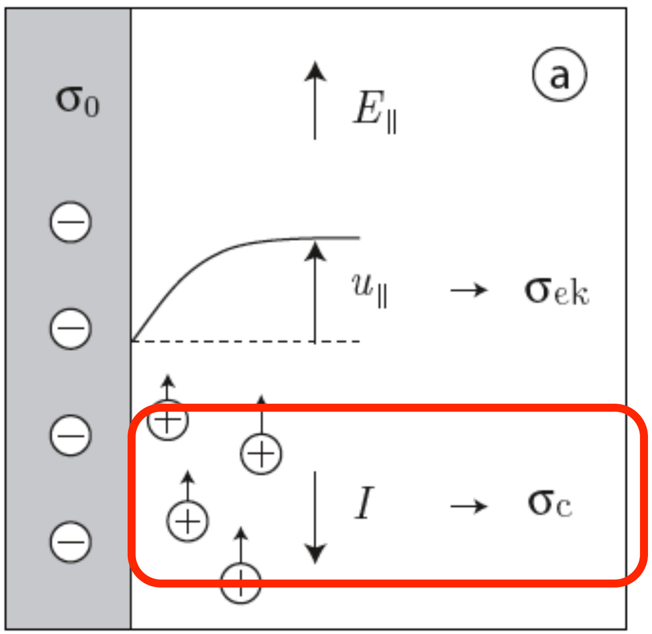
Electrokinetic surface charge density:

$$\sigma_{ek} = \sqrt{\frac{8 c_0 \varepsilon_0 \varepsilon_{bulk}}{\beta}} \sinh\left[\frac{\beta e \zeta}{2}\right]$$

Electrokinetics

Surface conductivity

$$\frac{I}{E_\parallel} = \int_0^\infty e\left[c_+(z) - c_-(z)\right]\left[u_\parallel(z)/E_\parallel\right]\mathrm{d}z + \int_0^\infty e\left[\nu_+(c_+(z) - c_0) + \nu_-(c_-(z) - c_0)\right]\mathrm{d}z$$

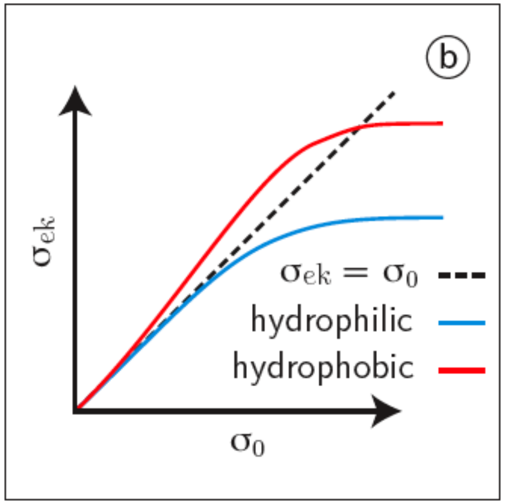


Conductive surface charge density:

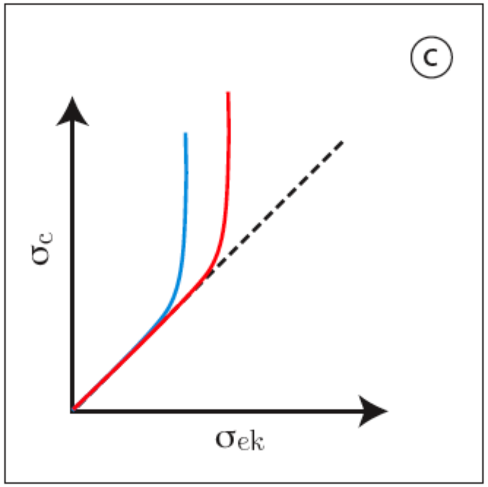
$$\sigma_c = \frac{\eta\kappa^2}{4ec_0 + \eta\nu\kappa^2}\sqrt{\frac{I}{E_\parallel}}\sqrt{\frac{I}{E_\parallel} + \frac{32e^2c_0^2}{\eta\kappa^3} + \frac{8ec_0\nu}{\kappa}}$$

Experimental inconsistencies

1. mobility

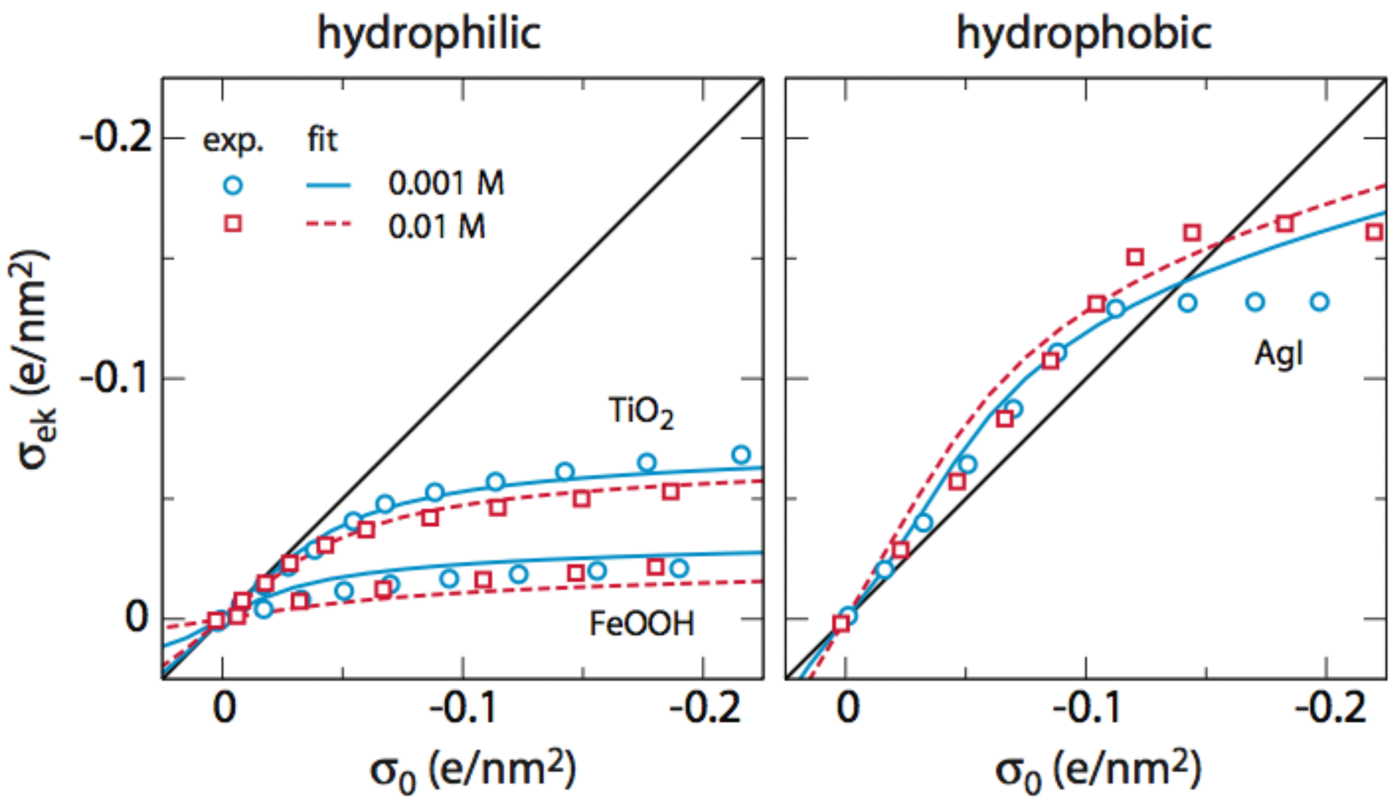


2. conductivity

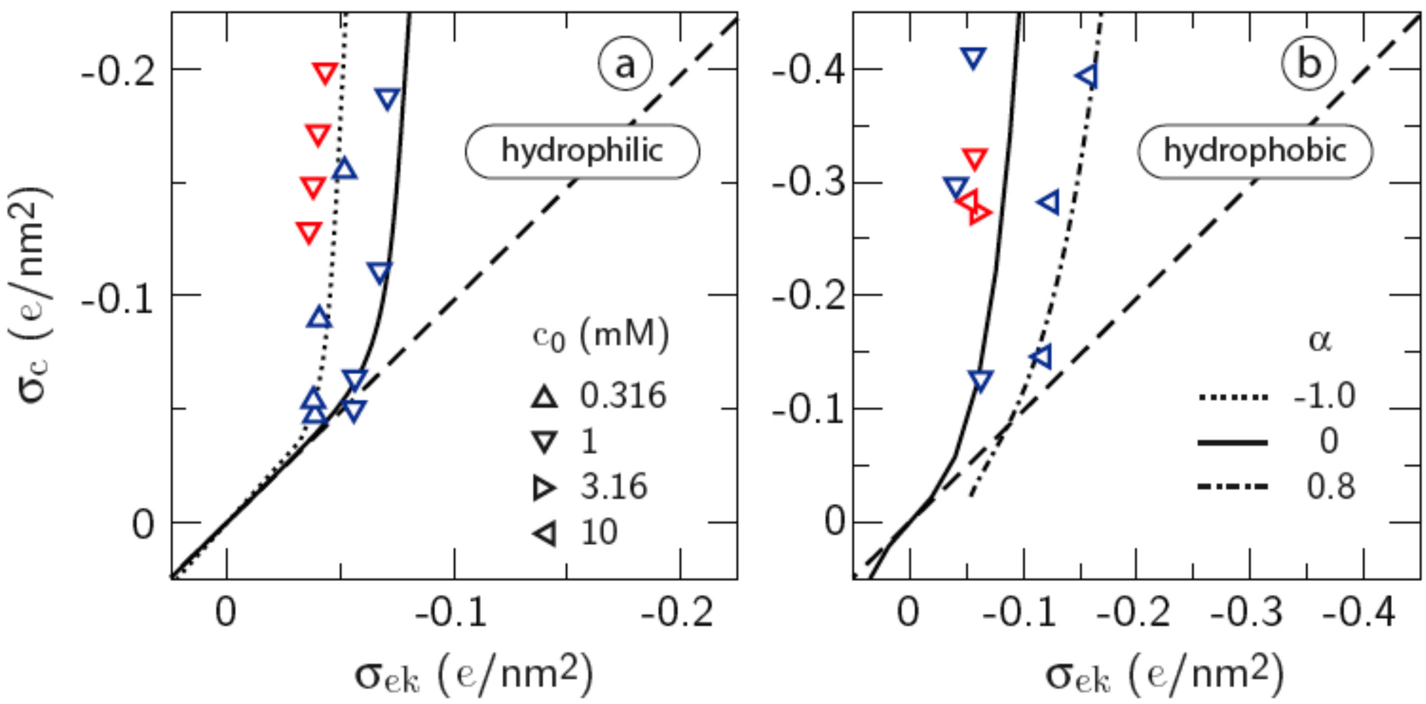


Electrophoretic mobility

Fit parameter: $$\mu(z) = \alpha \exp\left[1 - z/\lambda\right]$$



Excess conductivity



Water ions

Auto-ionization

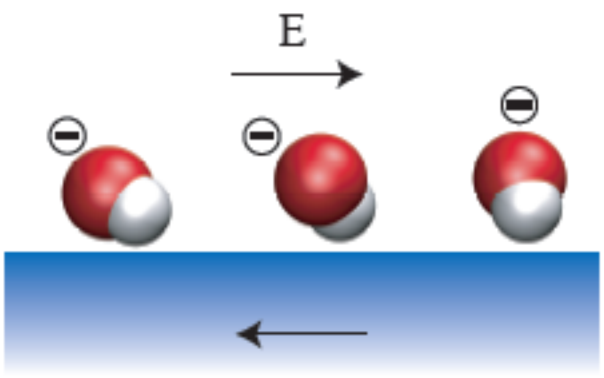
$$2H_2O \leftrightarrow OH^- + H_3O^+$$

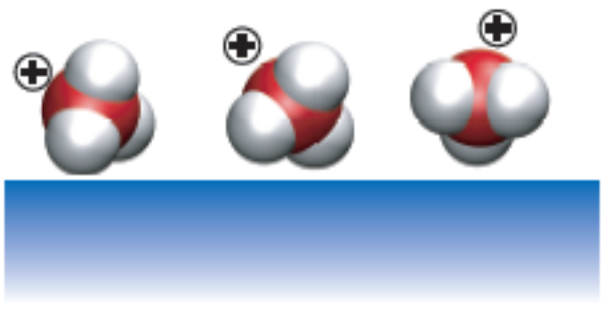
Always present, typically at very low concentration

Experiments on bubbles and oil droplets

Electrophoresis
Beattie's sonication experiment

Spectroscopy
Second harmonics generation
Surface tension

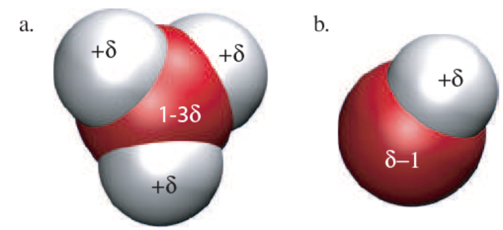




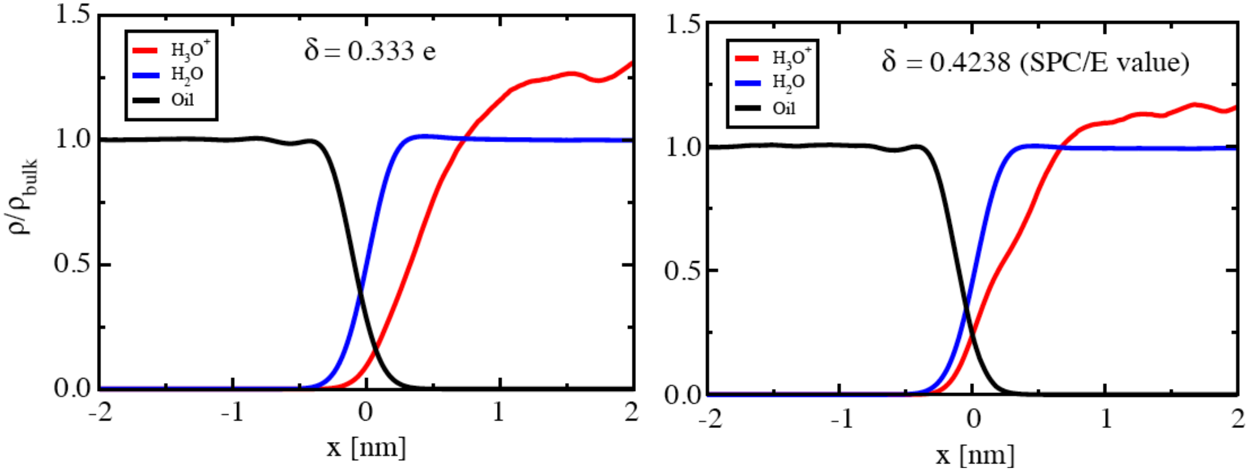
Negative effective surface charge

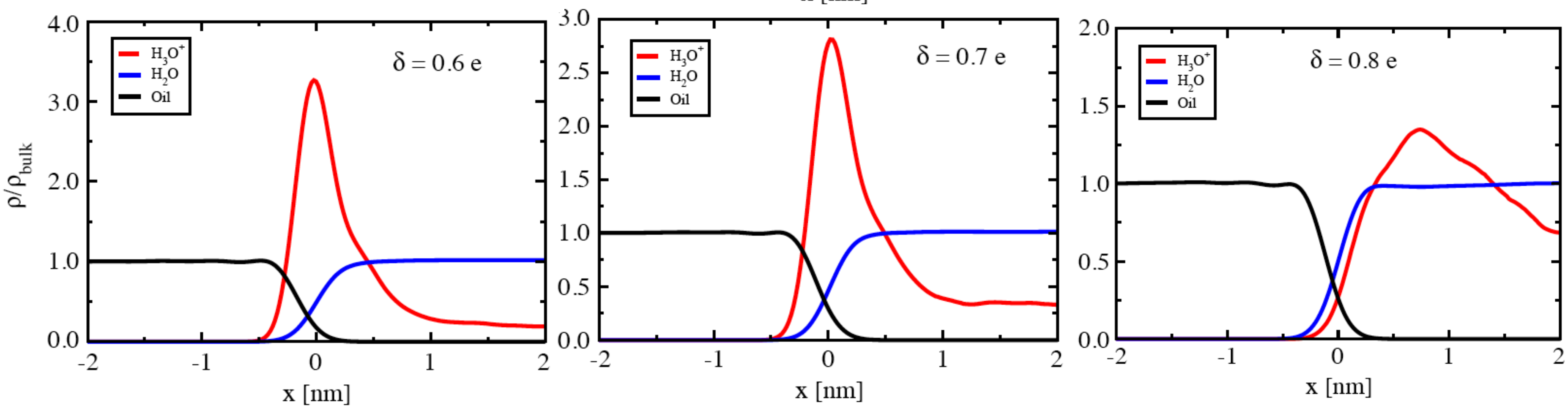
Positive effective surface charge

Effect of the charge distribution

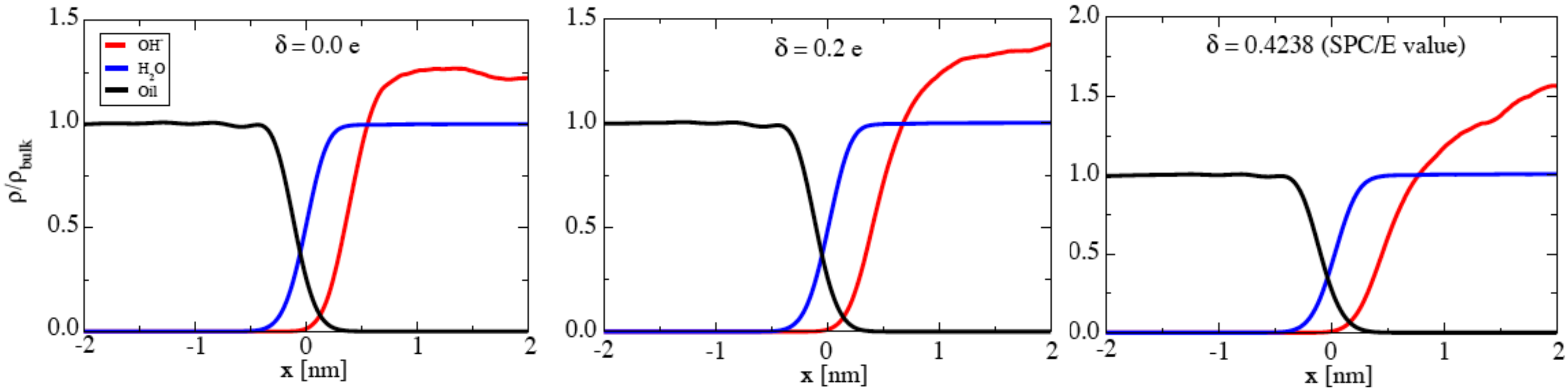


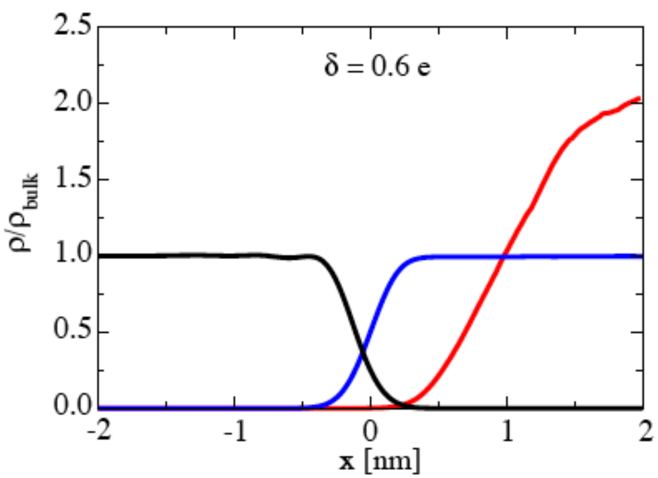
The same Lennard-Jones parameters as SPC/E water





Effect of the charge distribution

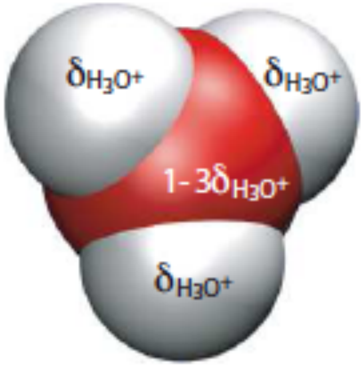




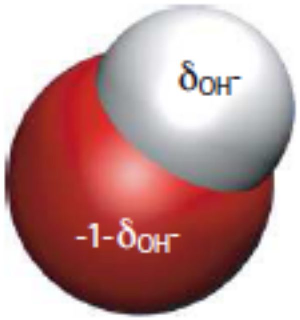
For both H3O+ and OH-, the partial charges have a strong influence on the adsorption

Force fields

a)



b)



Like the water:
No atomic polarizability
No molecular polarizability

Parameters:

1. Lennard-Jones of the oxygen
2. Partial charge on the hydrogen
3. Combination rules

Observables:

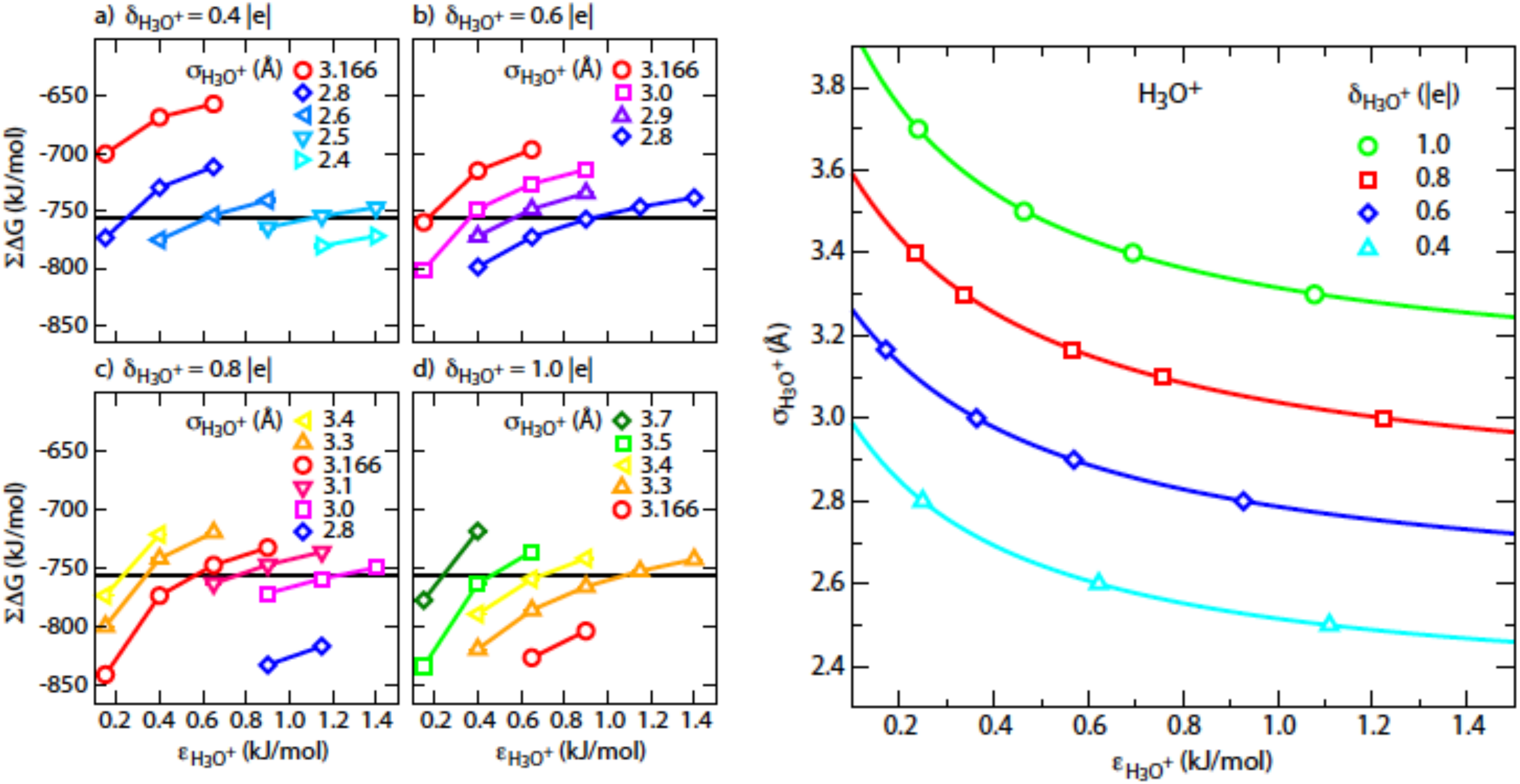
1. Ion-water interaction: solvation free energy
2. Ion-ion interaction: activity coefficient

$$\gamma_i(x_i)x_i = e^{-\beta(\mu-\mu_0)}$$

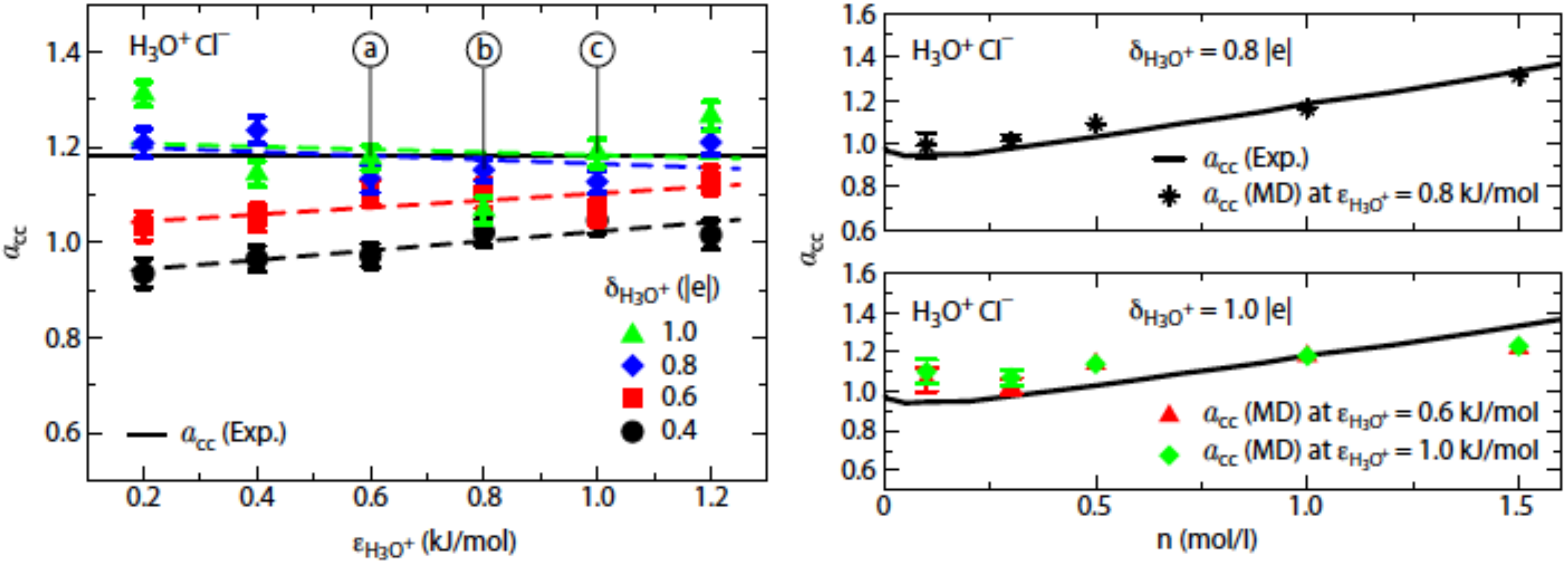
$$1 + \frac{\partial \ln \gamma}{\partial \ln n} = \frac{G^{\infty}_{+-} - G^{\infty}_{++}}{2\left(G^{\infty}_{+-} - G^{\infty}_{+s}\right)}$$

$$G^{R}_{\alpha\beta}(R) = \frac{1}{v(R)} \int_{v(R)} \int_{v(R)} \left[g_{\alpha\beta}\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right) - 1\right] \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2$$

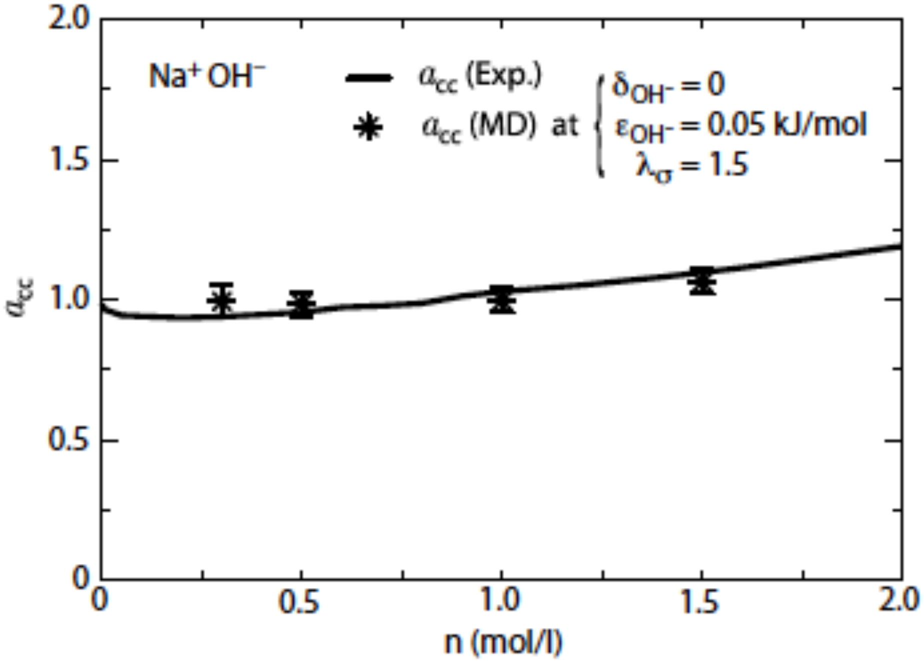
Free energy optimization



Activity optimization HCl

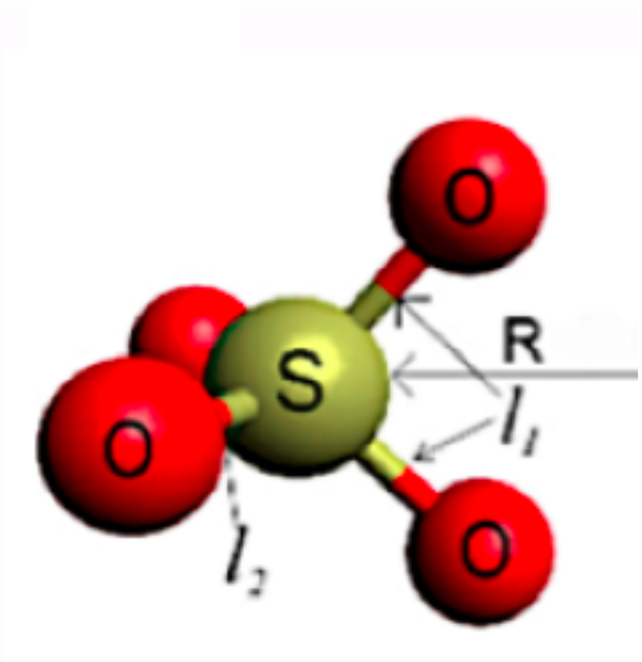


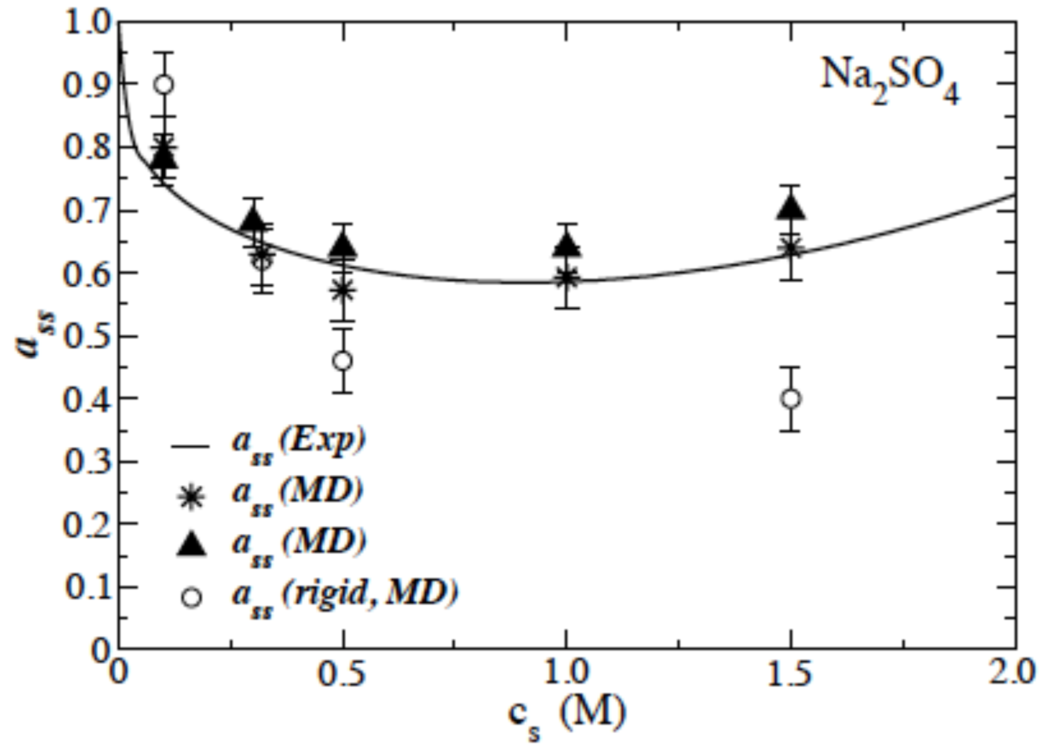
Activity optimization NaOH



$$\sigma_{+-} = \lambda_\sigma \sqrt{\sigma_+ \sigma_-}$$

Suphate





Slightly different procedure:

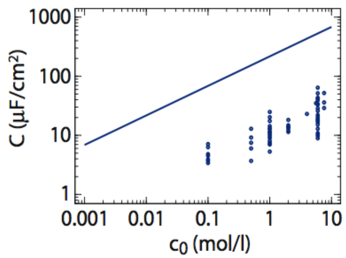
- Fix the partial charge
- Allow for some flexibility

Extra parameters:

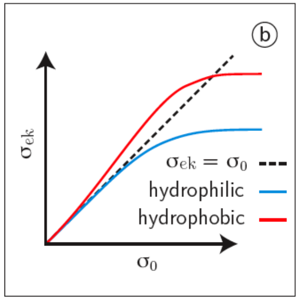
- Bonds
- Angles
- Intramolecular interactions

Conclusions

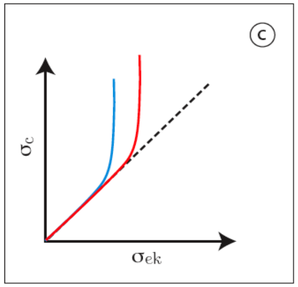
1. capacitance



2. mobility



3. conductivity



4. Optimization of thermodynamically consistent ion force fields

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Stephan Gekle

Glasstone Fellowship

Linacre College

DFG

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