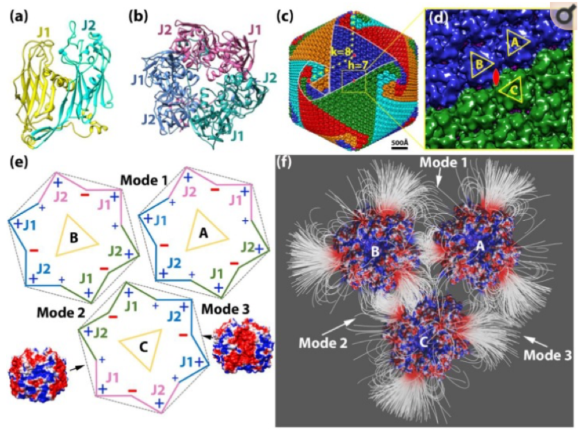
An introduction to electrostatic effects in colloidal dispersions

Yannick Hallez & Christophe Labbez

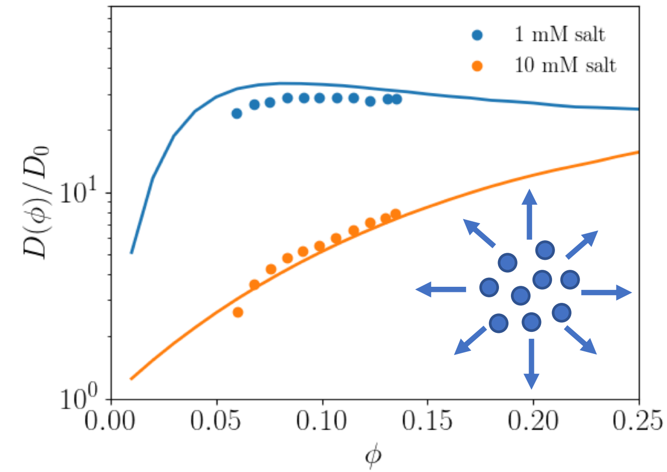
Large scale signature of electrostatic interactions

Biophysics: protein recognition, viral capsid self-assembly...



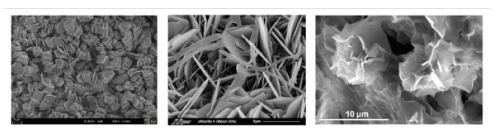
Xian et al., Int. J. Mol. Sci. 2019

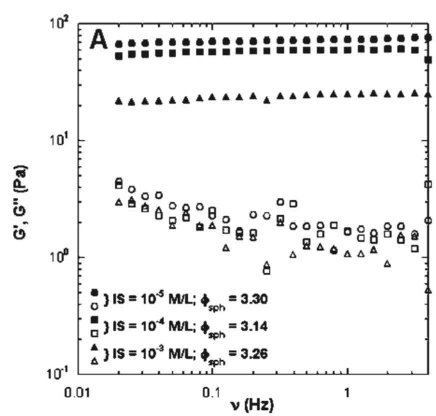
Transport properties: collective diffusion coefficient...

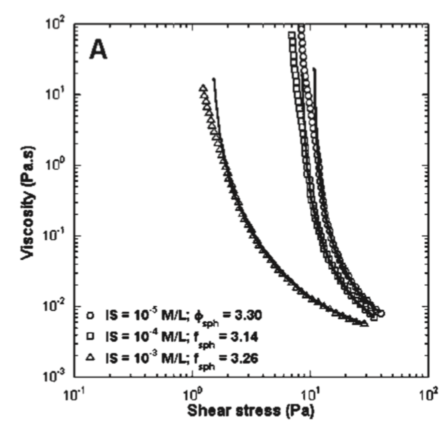


Keita, Salmon (LOF)

Rheology: viscosity, yield stress...

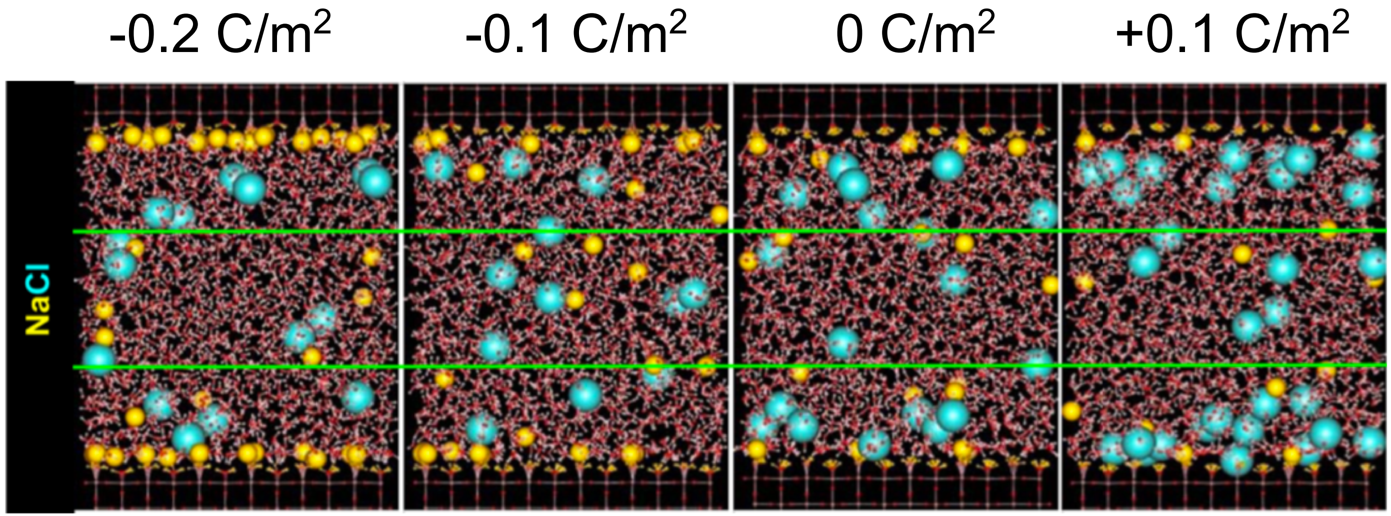






Paineau et al, Langmuir, 2011

The smallest scale: surfaces, solvent, charged species

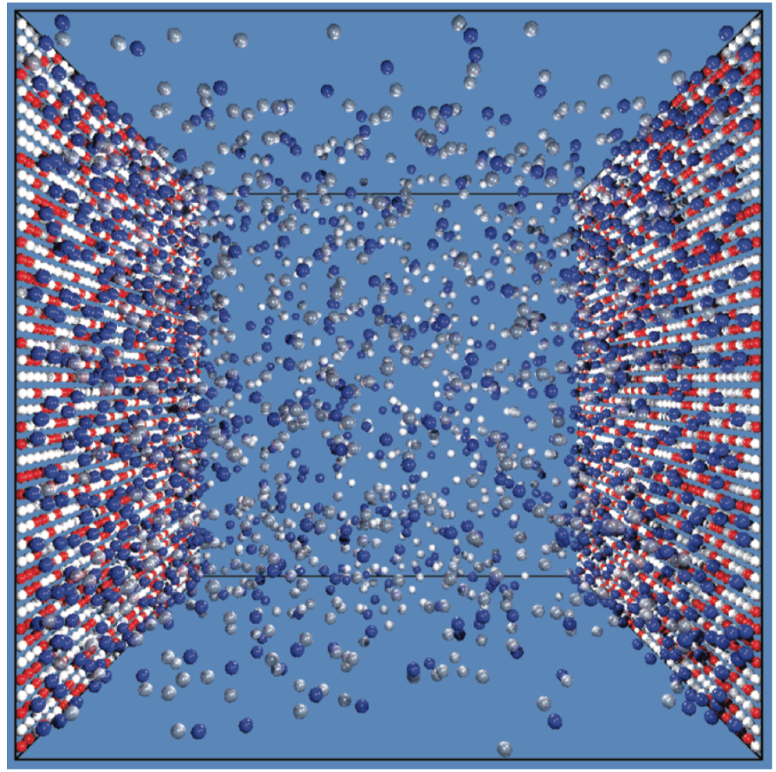


Predota et al., Langmuir, 2016

For all practical purposes, this requires simplification !

The primitive model

The primitive model: get rid of the solvent



Labbez et al., Langmuir, 2009

The primitive model: solvent is a continuous medium with permittivity ε.

Electrostatics in the primitive model

The electric field is given by the Poisson equation:

$$\nabla \cdot (\epsilon \boldsymbol{E}) = \rho_f \longrightarrow \begin{cases} \text{“fixed” surface charges} \\ \text{mobile ions} \end{cases}$$

It derives from a potential:

$$\boldsymbol{E} = -\nabla \Phi$$

$\rho_f(\boldsymbol{x}, t)$

$\Phi(\boldsymbol{x}, t)$

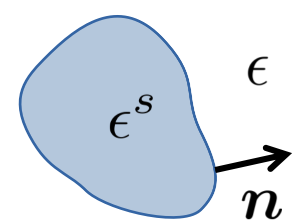
so

$$\nabla \cdot (\epsilon \nabla \Phi) = -\rho_f$$

A priori ε and the charge density can vary in space, be discontinuous...

At an interface between two continuous media:

$$(\epsilon \boldsymbol{E} - \epsilon^s \boldsymbol{E}^s) \cdot \boldsymbol{n} = \sigma$$



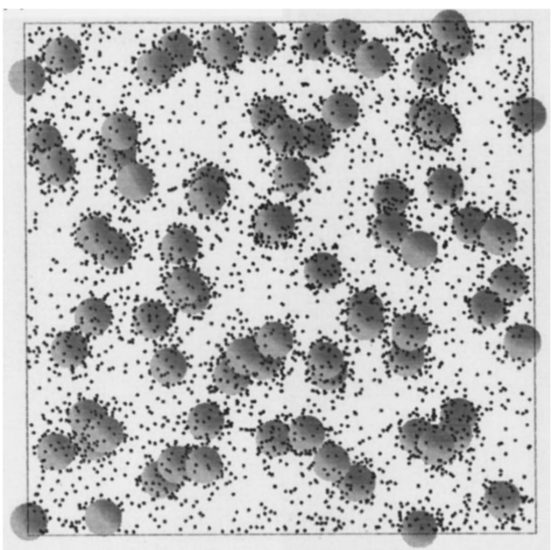
The primitive model in practice

Can we simplify again?

Yes and No

- Well known Coulomb interactions
- Multiple species, so a lot of degrees of freedom

Computer **simulations**



Linse & Lobaskin,
PRL 1999, J. Chem. Phys. 2000

Theory

Statistical physics, multicomponent Ornstein-Zernike equation...

$$Z = \underset{N}{\int_{r_\alpha}^{r_\beta} \cdots} \underset{2N}{\int\int \cdots \int} \exp\left[-\left(\sum_i u_{pi} + \sum_{i>j} u_{ij}\right)\Big/ kT\right] d\mathbf{r}_1 \cdots d\mathbf{r}_N$$

$$h^s_{i,j}(r) = c^s_{i,j}(r) + \sum_{k=1}^{n} c^s_{i,k}(r) * h^s_{k,j}(r)$$

often needs further approximations, not unlikely to end up on a computer

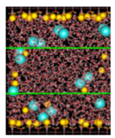
Coarse-graining

Theories / Models

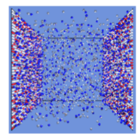
Explicit treatment of ions

QM

MD



PM



Interactions

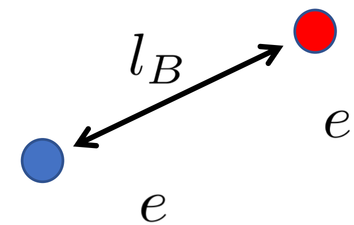
Confidence

Weak or strong electrostatic coupling

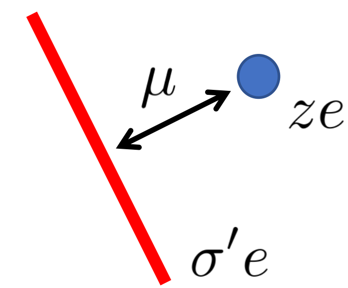
A few length scales

Ions are mobile charges whose trajectories are determined by a balance of electrostatic and thermal effects (a minima).

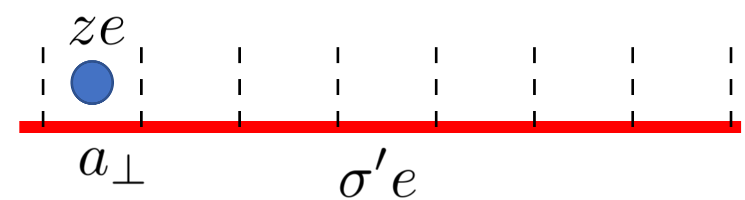
The Bjerrum length: $\frac{e^2}{4\pi\epsilon l_B} = kT \quad \Rightarrow \quad l_B = \frac{e^2}{4\pi\epsilon kT}$



The Gouy-Chapman length $\frac{\sigma' eze\mu}{2\epsilon} = kT \quad \Rightarrow \quad \mu = \frac{1}{2\pi\sigma' z l_B}$



Lateral distance between counterions condensed on the surface $\sigma' \pi a_\perp^2 = z \quad \Rightarrow \quad a_\perp = \sqrt{z/\pi\sigma'}$

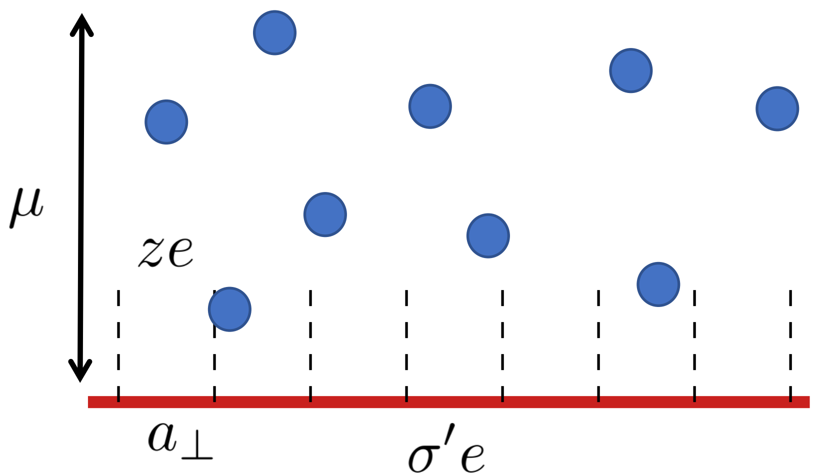


Electrostatic coupling

The (electrostatic) coupling parameter:

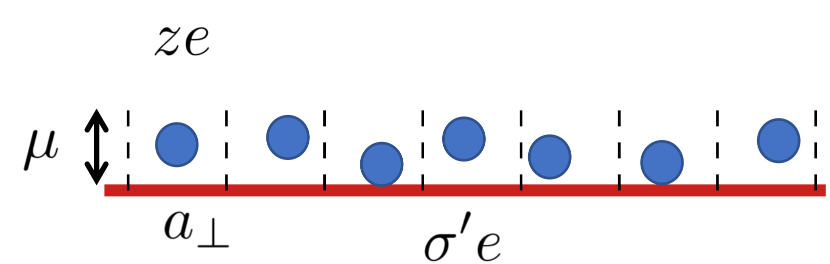
$$\Xi = \frac{1}{2}\left(\frac{a_\perp}{\mu}\right)^2 = 2\pi z^3 l_B^2 \sigma'$$

Weak coupling $\Xi < 1$



Monovalent counterions in water:
Ξ = 1 at σ' ~ 0.3 e/nm^2

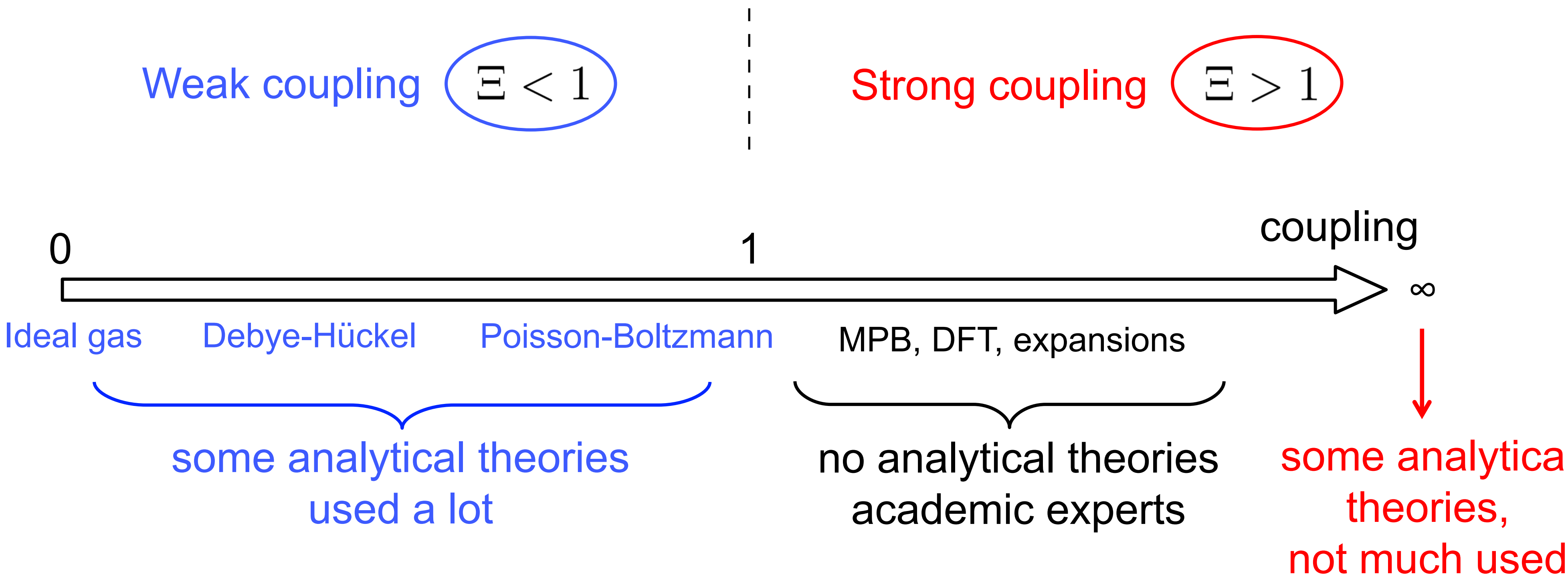
Strong coupling $\Xi > 1$



Multivalent counterions in water:
Ξ >> 1 for any surface charge.

Monovalent counterions in ethanol:
Ξ = 1 at σ' ~ 0.03 e/nm^2

Electrostatic coupling



Mean-field approximation in the weak coupling limit

Electrostatics in the weak coupling limit: the idea

Ions are dilute, so they respond to the **mean electrostatic potential** and not to direct pair interactions

$$\mu^{\pm}(\boldsymbol{x}) = kT \ln n^{\pm}(\boldsymbol{x}) \pm e\Psi(\boldsymbol{x})$$

$$\Psi(\boldsymbol{x}) = \langle \Phi(\boldsymbol{x}, t) \rangle_t$$

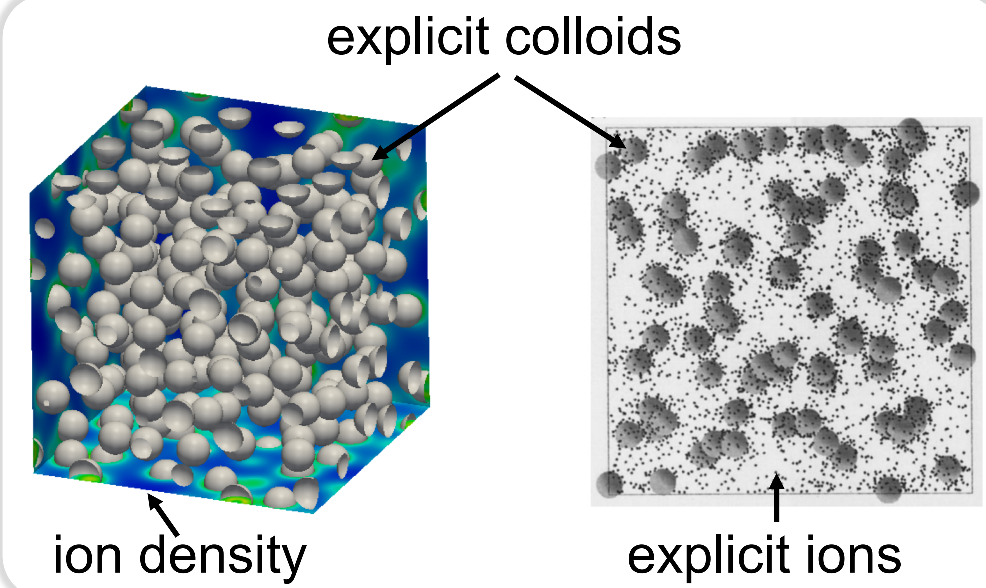
Adiabatic hypothesis: ions are always in thermodynamic equilibrium $\longrightarrow \nabla \mu^{\pm} = \mathbf{0}$

Define some reference ion density as

$$\mu^{\pm} = kT \ln n_0 \pm e \times 0$$

so we get the Boltzmann distribution:

$$n^{\pm} = n_0 e^{\mp \psi} \quad \text{with} \quad \psi = \frac{e\Psi}{kT}$$



The Poisson-Boltzmann theory

Volume charge density in the fluid: $\rho_f = en^+ - en^- = -2n_0 e \sinh \psi$

The Poisson equation becomes the Poisson-Boltzmann (PB) equation:

$$\nabla \cdot (\epsilon \nabla \Psi) = 2n_0 e \sinh \psi$$

Assuming uniform dielectric constant in the fluid…

$$\underline{\nabla} \cdot (\underline{\nabla} \psi) = \underline{\frac{2n_0 e^2}{\epsilon k T}} \sinh \psi$$

Length scale of potential gradients (Debye length): $$\boxed{\lambda_D = \kappa^{-1} = \sqrt{\frac{\epsilon k T}{2n_0 e^2}}}$$

PB equation: $$\boxed{\Delta \psi = \kappa^2 \sinh \psi}$$

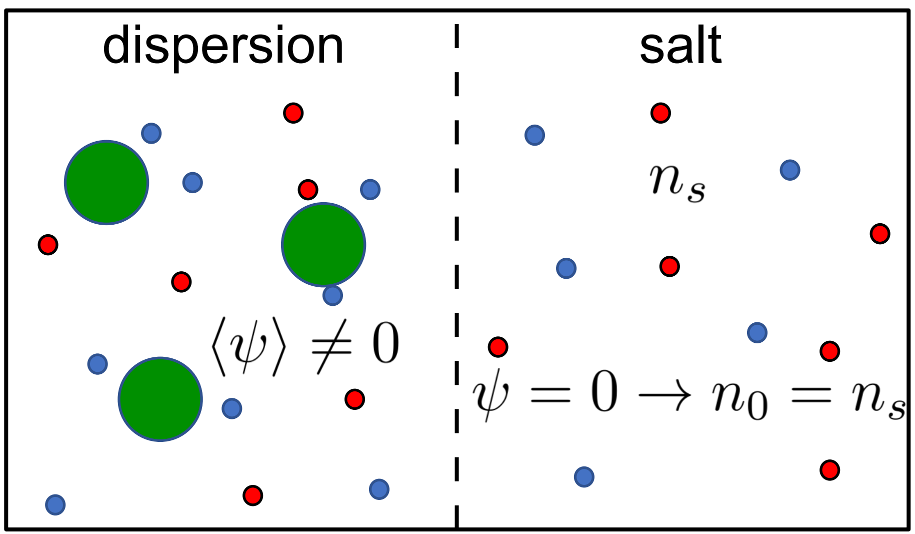
Different expressions for the Debye length?

$$\Delta\psi = \kappa^2 \sinh\psi$$

with

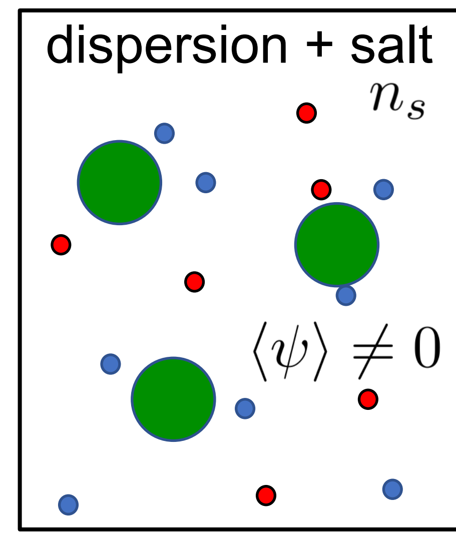
$$\lambda_D = \kappa^{-1} = \sqrt{\frac{\epsilon kT}{2n_0e^2}}$$

Donnan equilibrium



$$\lambda_D = \sqrt{\frac{\epsilon kT}{2n_se^2}}$$

Closed suspension

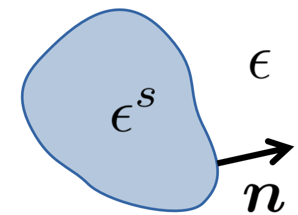


$$\lambda_D = \sqrt{\frac{\epsilon kT(1-\phi)\langle\cosh\psi\rangle_e}{(\rho Z_c + 2n_s)e^2}}$$

Electrostatics in the primitive model

Possible boundary conditions:

$$(\epsilon \boldsymbol{E} - \epsilon^s \boldsymbol{E}^s) \cdot \boldsymbol{n} = \sigma$$



in general $$(\epsilon \nabla \psi - \epsilon^s \nabla \psi^s) \cdot \boldsymbol{n} = \sigma(\psi)$$

Constant Charge (CC)

$\sigma \sim$ const. from weak chemistry-electrostatics coupling.

Constant Potential (CP)

$\sigma(\psi)$ from chemistry-electrostatics coupling such that $\psi \sim$ const. on the surface.

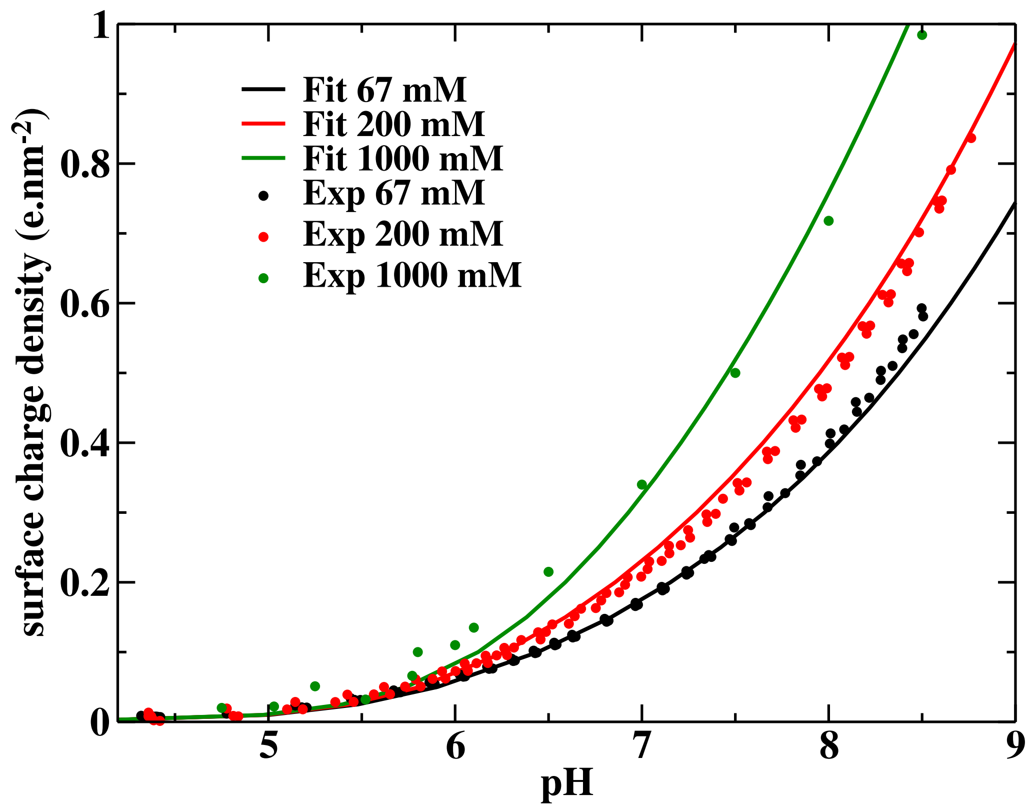
Charge Regulation (CR)

$\sigma(\psi)$ from chemistry-electrostatics coupling

CR: the case of silica

$$\mathrm{Si{-}OH} \xrightleftharpoons{\mathrm{p}K_a} \mathrm{Si{-}O^-} + \mathrm{H^+}$$

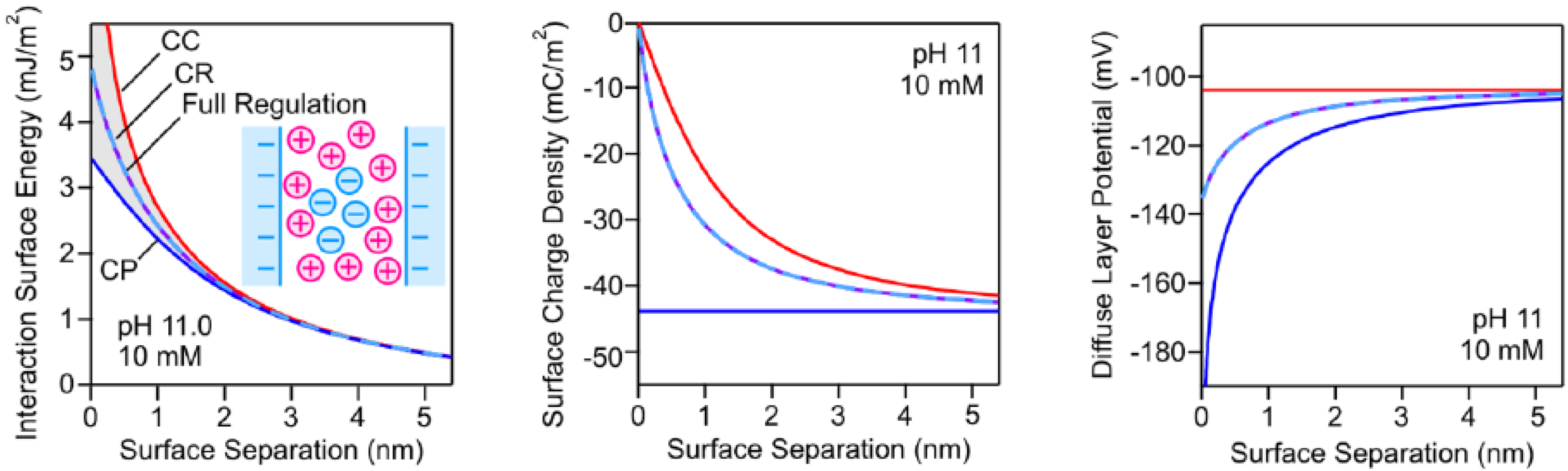
$$\ln\frac{\alpha}{1-\alpha} = kT/\ln(10)(pH - pK_a) - z_{\rm site}e\Psi_0$$



λ_B = 0.7105 nm, pK_a = 7.7, Γ_0 = 5.55 nm^{-2}, λ_{Stern} = 0.107 nm.

The importance of charge regulation

Interaction between two charged plates



CC : constant charge
CP : constant potential
CR : charge regulation

$$\mathrm{Si{-}OH} \xrightleftharpoons{\mathrm{pK}_a} \mathrm{Si{-}O^-} + \mathrm{H}^+$$

$$\ln \frac{\alpha}{1-\alpha} = kT/\ln(10)(pH - pK_a) - z_{\mathrm{site}} e \Psi_0$$

Osmotic pressure between flat plates

The electrostatic double layer contribution to the osmotic pressure between two parallel charged surfaces can be obtained from the contact theorem :

$$\Pi_{DL} = kT\sum_i c_i(0) - \frac{\sigma_0^2}{2\epsilon_r\epsilon_0} = kT\sum_i c_i(\infty)\exp\left(\frac{z_i e\psi_D}{kT}\right) - \frac{\epsilon_r\epsilon_0}{2}\left(\frac{d\psi_D}{dx}\right)^2$$

to which we must substract the bulk osmotic pressure,

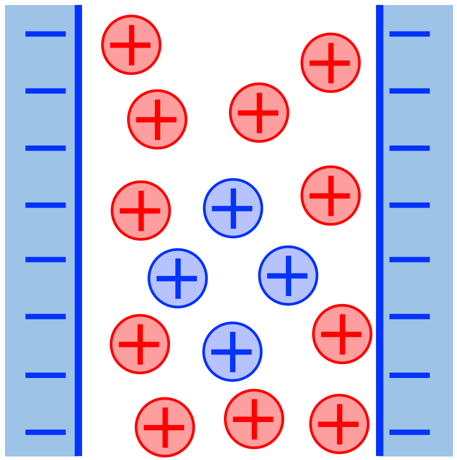
$$\Pi_{bulk} = kT\sum_i c_i(\infty)$$

and add the non-retarded van der Waals forces,

$$F_{vdw}/area = \frac{-H}{6\pi h^3}$$

to get the net DLVO pressure :

$$\Pi_{DLVO}^{net} = \Pi_{DL} - \Pi_{bulk} + F_{vdW}/area$$



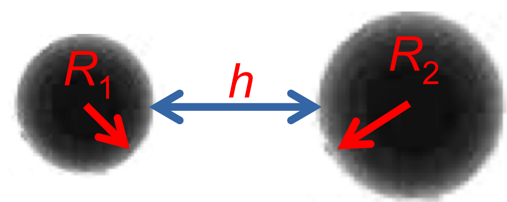
Interaction potential: Derjaguin approximation

The force between two spherical particles can be obtained from the interaction free energy between two flat surfaces (W_{DLVO}) using the Dejarguin approximation as

$$F_{DLVO}(h) = 2\pi R_{eff} W_{DLVO}(h)$$

with

$$R_{eff} = \frac{R_1 R_2}{R_1 + R_2}$$



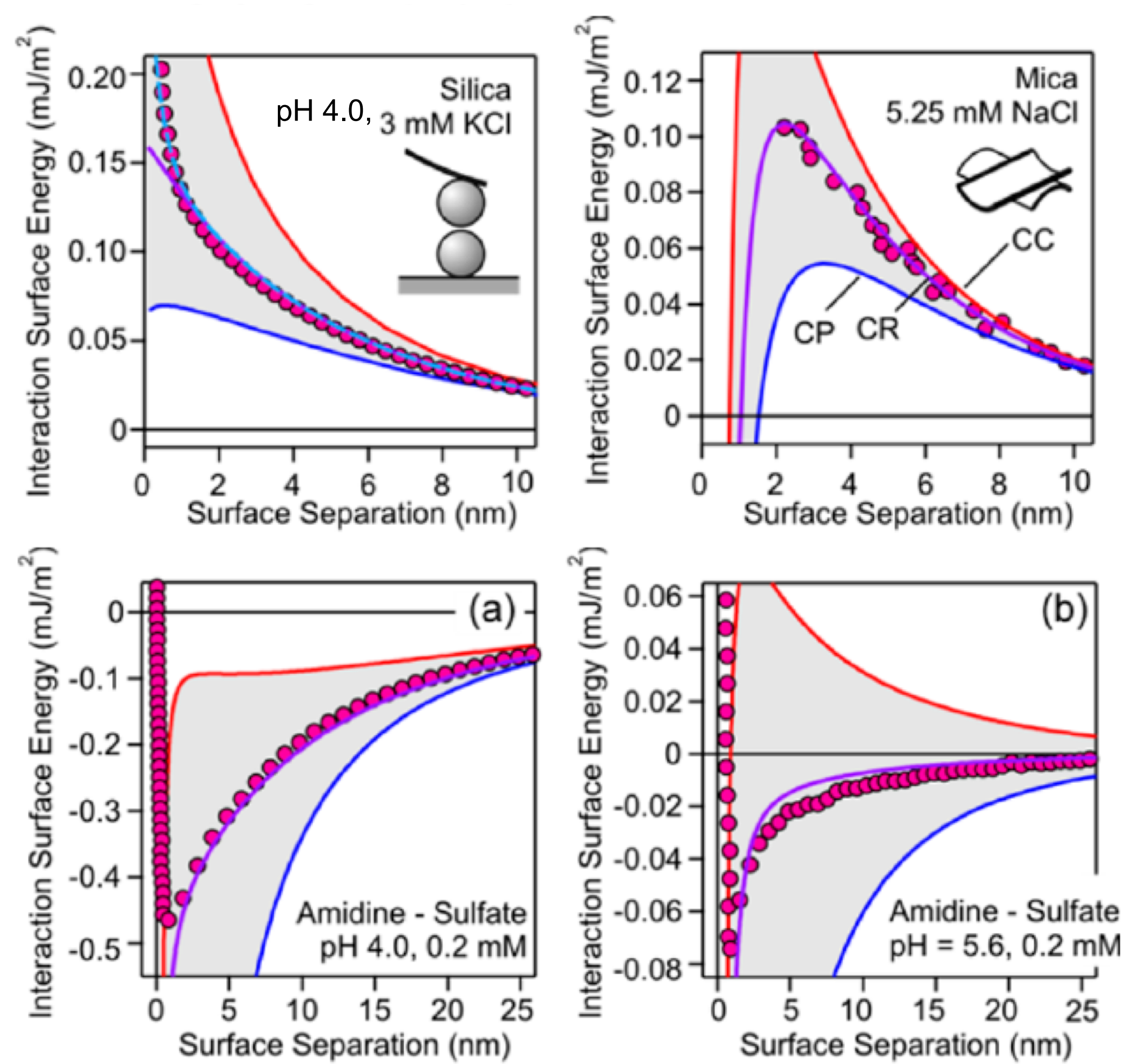
The interaction free energy (W_{DLVO}) is obtained from integrating Π_{DLVO} with respect to the surface separation

$$W_{DLVO}(h) = -\int_h^{\infty} \Pi_{DLVO}^{net}(h')\,dh'$$

Interaction potential: experimental signature of charge regulation

Symmetric systems

Oppositely charged particles



M. Borkovec et al,
Langmuir 2016, 32, 380−400

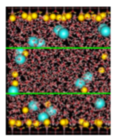
Coarse-graining

Theories / Models

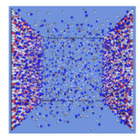
Explicit treatment of ions

QM

MD

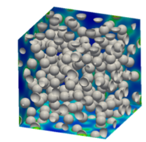


PM



Mean-field treatment of ions

PB



Interactions

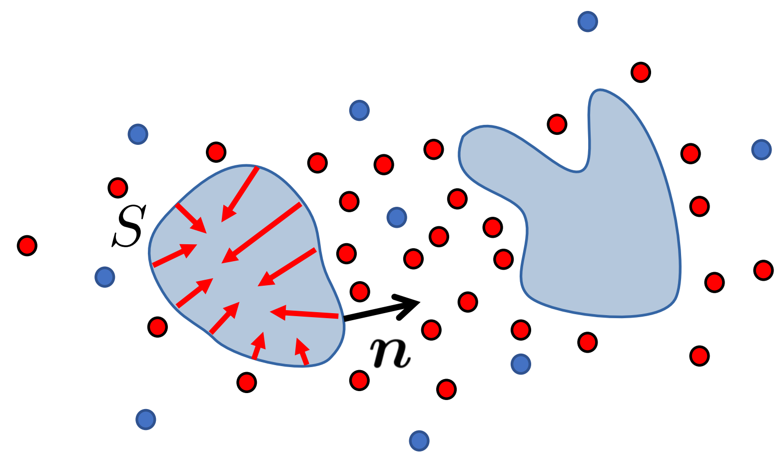
Derjaguin

Confidence

Interaction potential: arbitrary EDL thickness and object shape

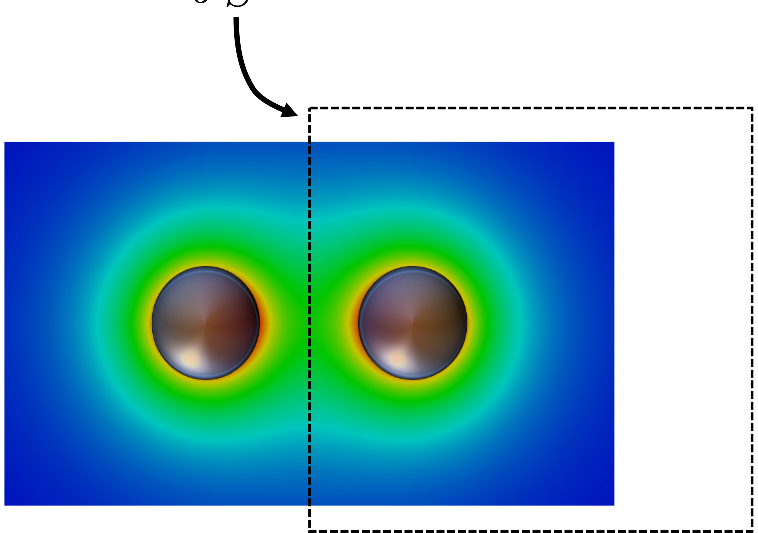
From the excess osmotic stress tensor

$$\tilde{\tau} = -(\cosh\psi - 1)\mathbf{I} + \left[\tilde{\mathbf{E}} \otimes \tilde{\mathbf{E}} - \frac{1}{2}\tilde{\mathbf{E}}^2\mathbf{I}\right]$$



Forces are obtained by integration

$$\tilde{\mathbf{F}} = \int_{\tilde{S}} \tilde{\tau} \cdot \mathbf{n} d\tilde{S}$$



Obtaining ψ analytically is impossible with PB

If we linearize PB, we can get the DLVO model **at large distance**:

$$\beta u(r) \simeq Z^2 l_B \left(\frac{e^{-\kappa a}}{1+\kappa a}\right)^2 \frac{e^{-\kappa r}}{r}$$

The Debye-Hückel theory

$$\Delta\psi = \kappa^2 \sinh\psi$$

$$\lambda_D = \kappa^{-1} = \sqrt{\frac{\epsilon k T}{2 n_0 e^2}}$$

Debye and Hückel proceeded to linearize this equation. Technically, linearization is only valid if $\psi \ll 1$, however, being practically minded Debye and Hückel linearized first and worried about the consequences later.

Yan Levin, in Braz. J. Phys. 2004

At low potentials... $\sinh\psi \simeq \psi + \ldots$

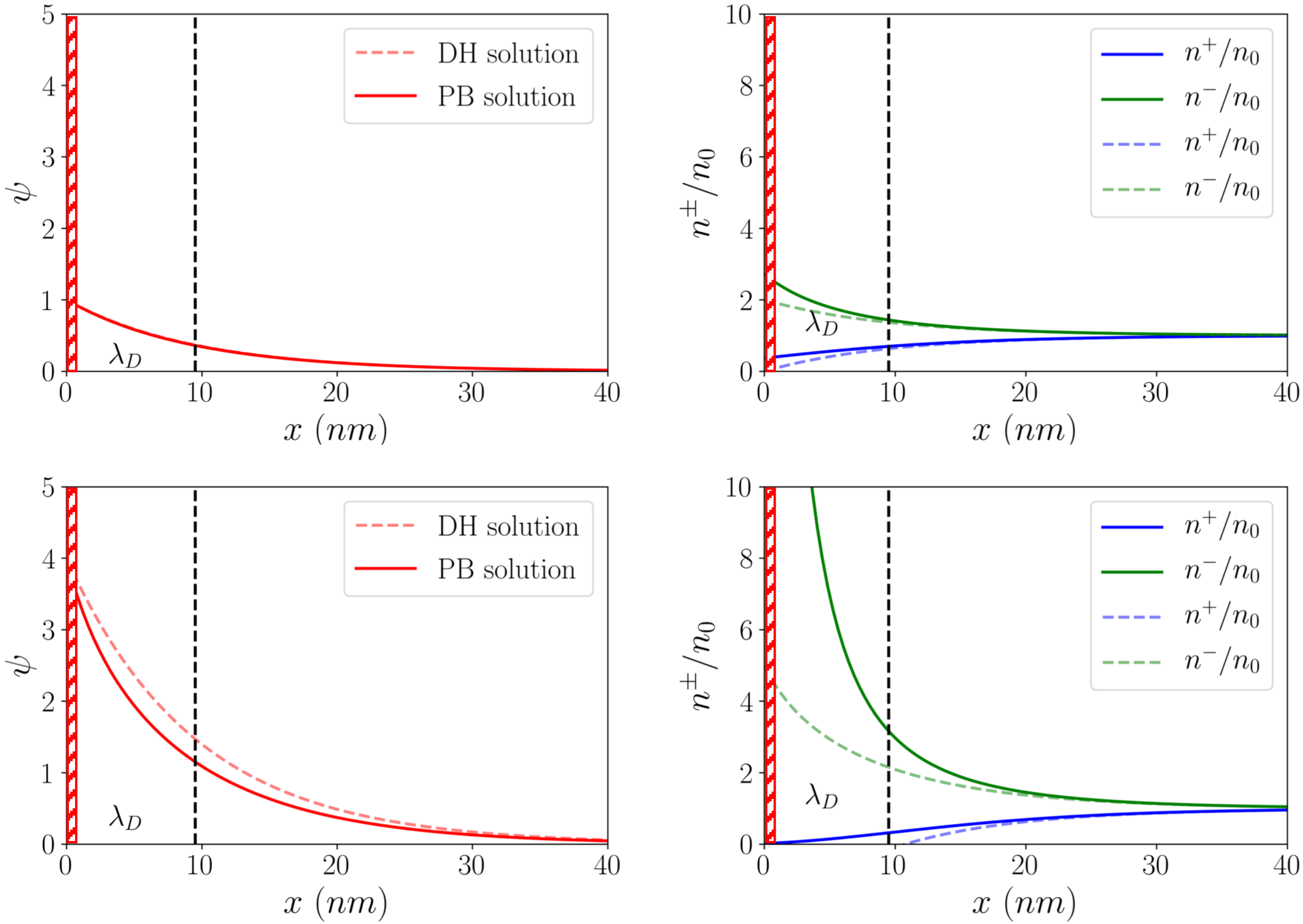
The Debye-Hückel (DH) equation: $\Delta\psi = \kappa^2\psi$

$$n^{\pm} \simeq n_0(1 \mp \psi)$$

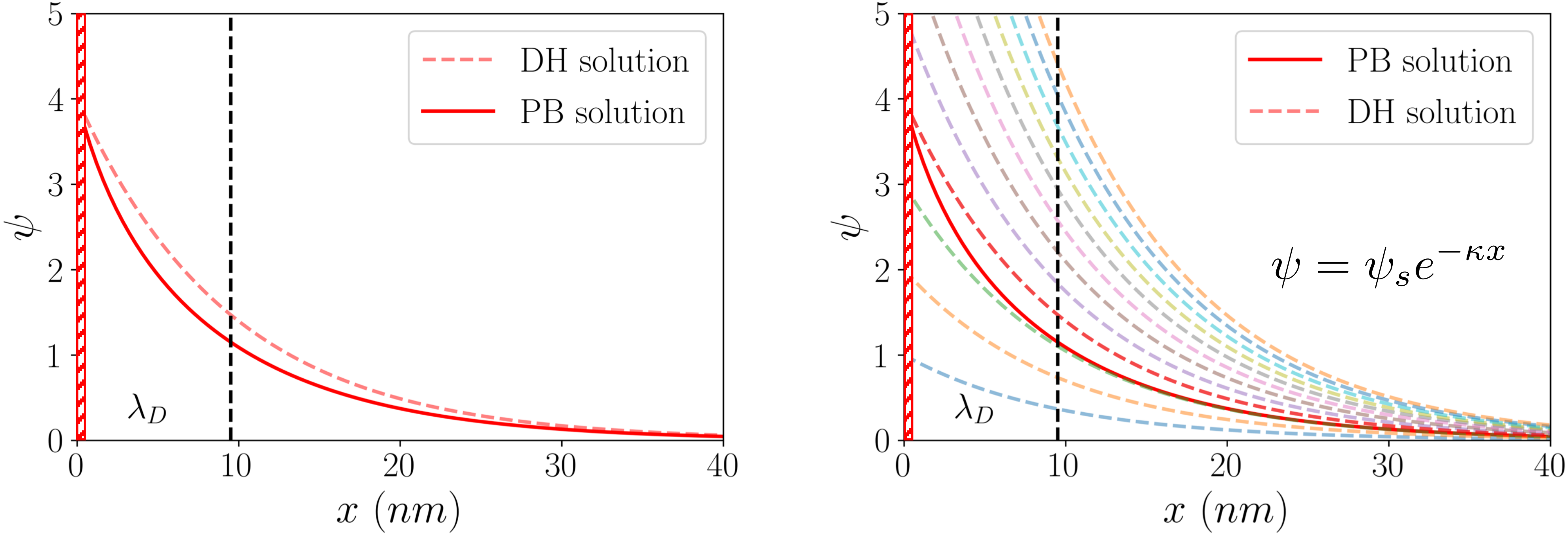
Poisson-Boltzmann theory Vs. Debye-Hückel theory

$$\Psi_s = 25\,mV$$

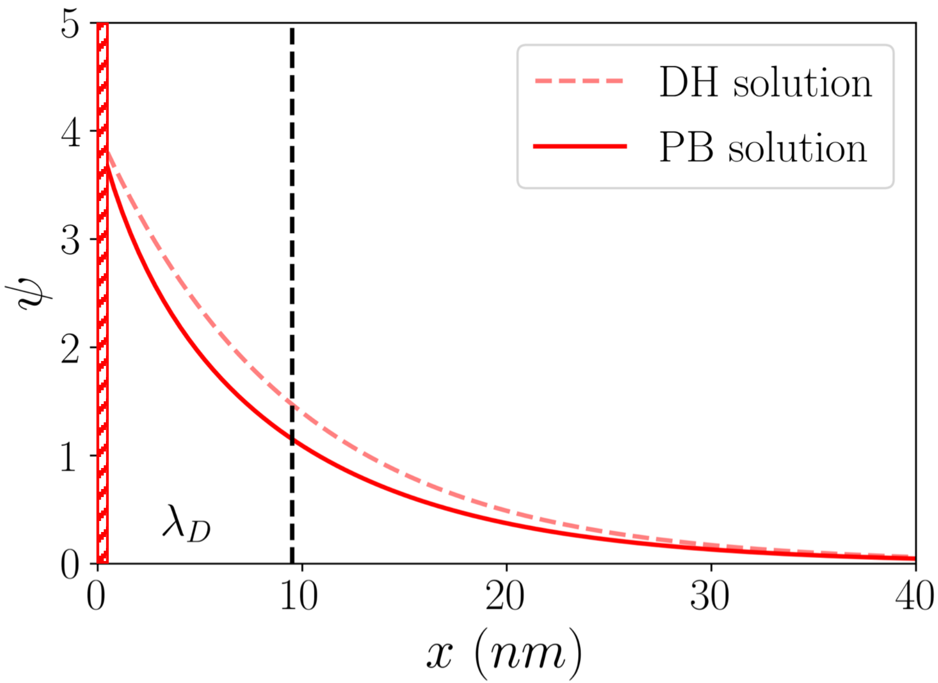
$$\Psi_s = 100\,mV$$

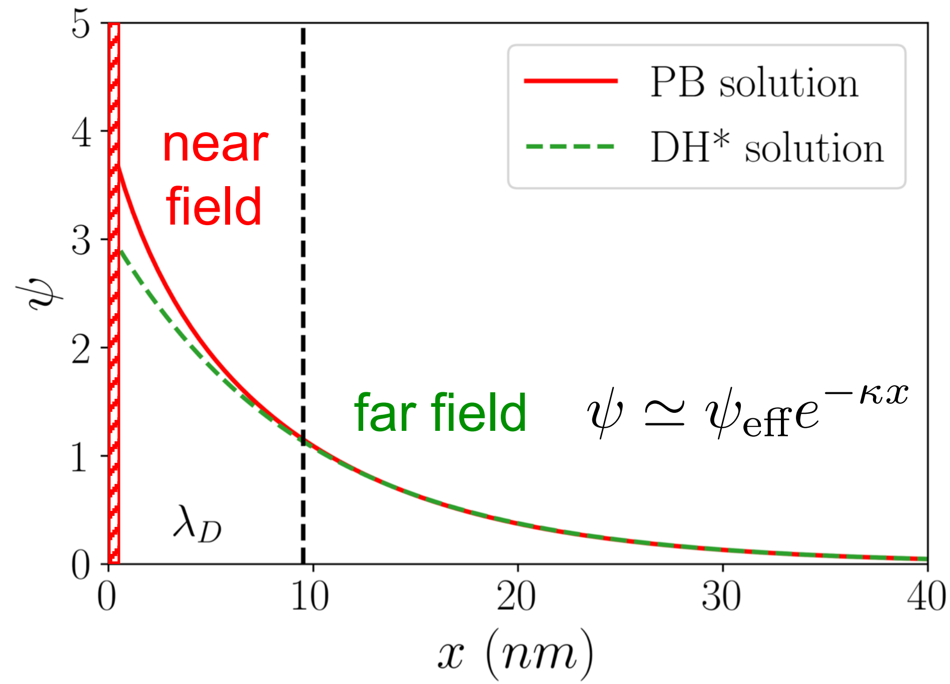


Renormalization and effective charges or potentials



Renormalization and effective charges or potentials





Renormalization: PB ⟶ DH* mapping

→ Redefine boundary conditions:
Effective surface charge/potential

→ Redefine screening length if $\langle \psi \rangle \neq 0$:
Effective screening length

Example: pressure between 2 flat plates at distance $h \gg \lambda_D$:

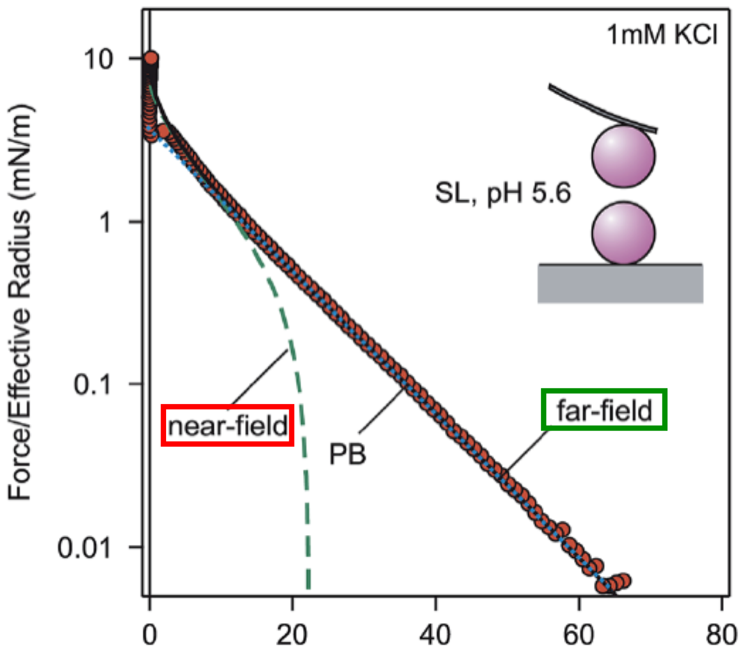
$$\psi(h/2) \simeq 2\psi_{\text{eff}} e^{-\kappa h/2}$$

$$\Pi \simeq 4 n_0 k T \psi_{\text{eff}}^2 e^{-\kappa h}$$

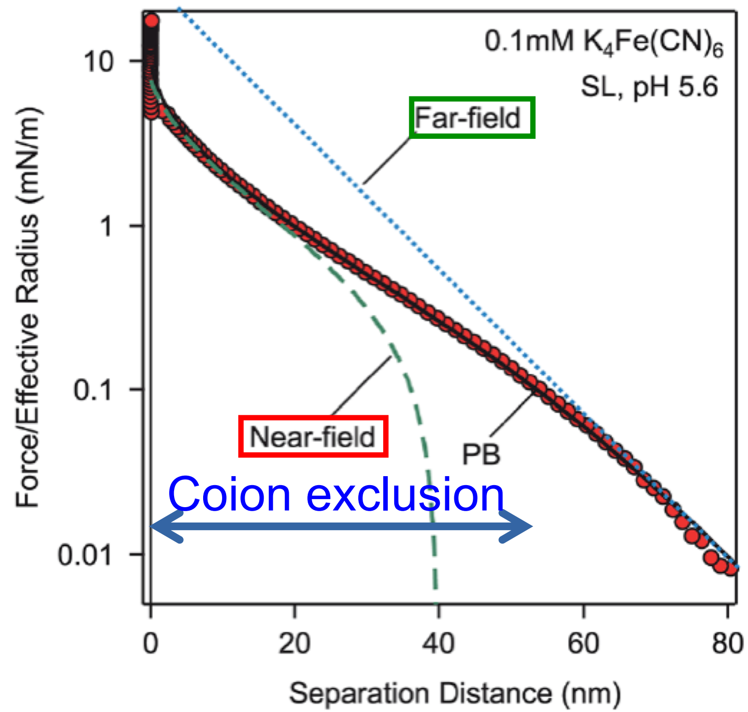
} from DH theory

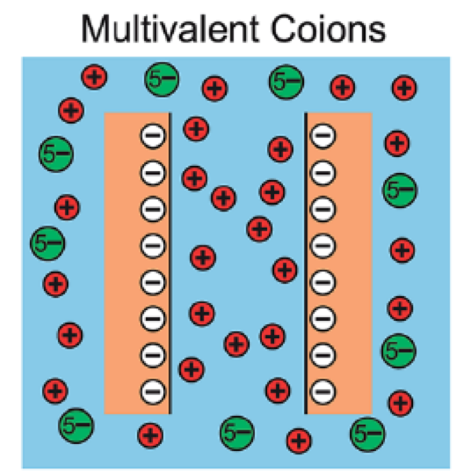
Interaction potentials at arbitrary charge (PB): renormalization

1:1 electrolyte



1:6 electrolyte





Far field, weak overlap (DH*)

$$\Pi \simeq 4 n_0 k T \psi_{\text{eff}}^2 e^{-\kappa h}$$

$$\psi_{\text{eff}} = \begin{cases} \psi_s & for \quad \psi_s \ll 1 \\ \alpha & for \quad \psi_s \gg 1 \end{cases}$$

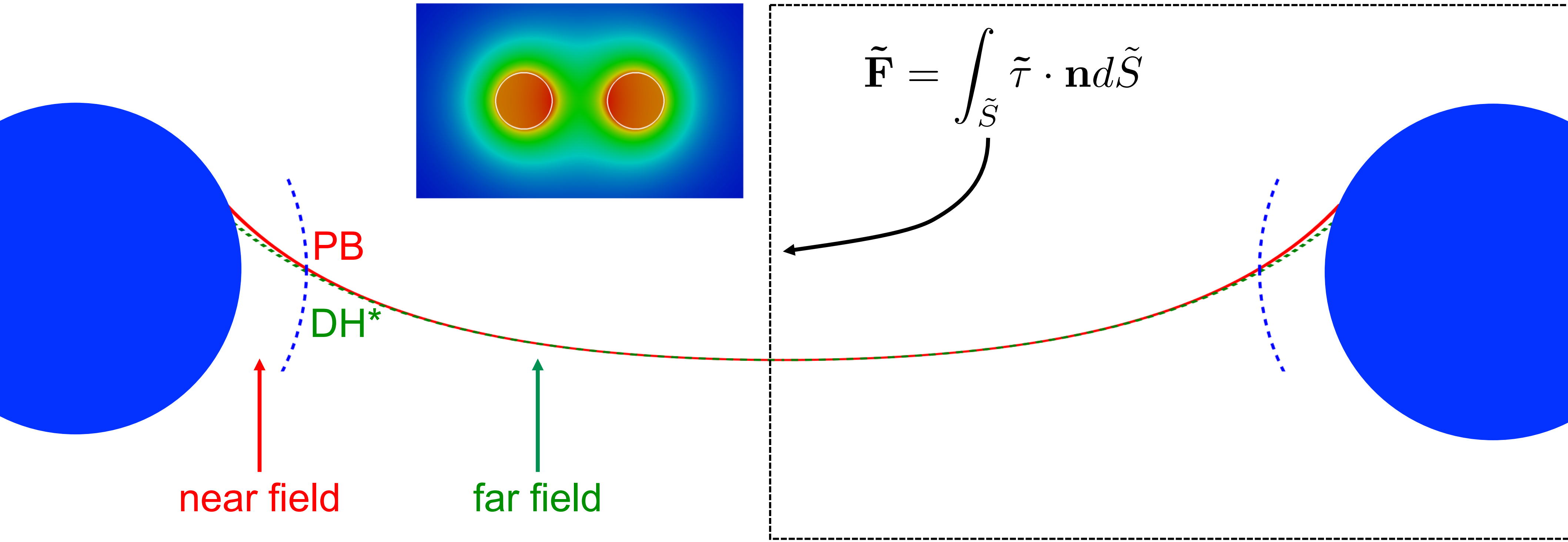
Near field, salt free behavior (PB)

$$\Pi \simeq \frac{2\pi^2 \epsilon}{\beta^2 e^2} \frac{1}{h^2}$$

(at high charge and large separation)

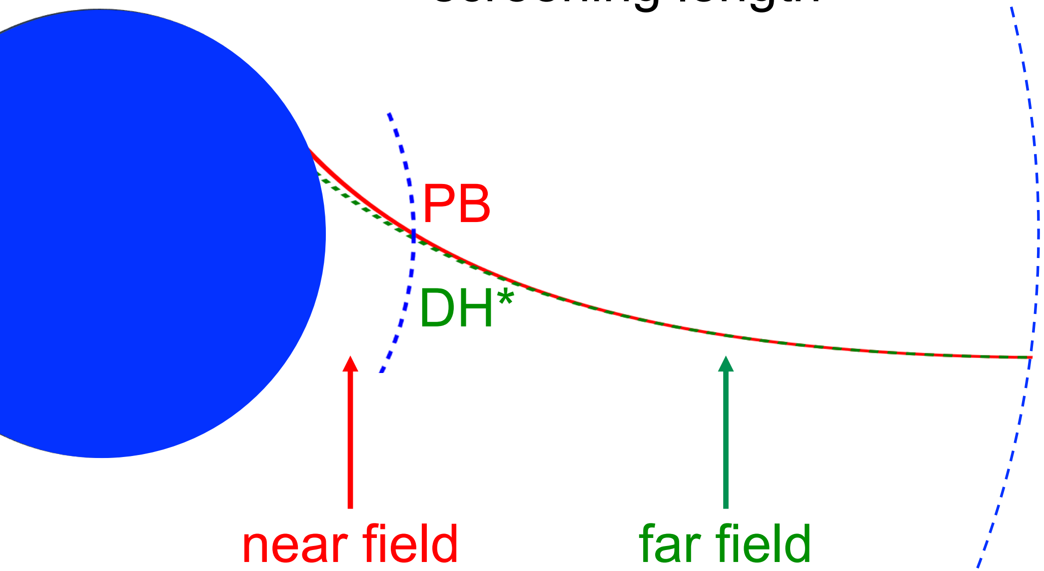
Ruiz-Cabello et al., Soft Matter 2015

Interaction potentials at arbitrary charge (PB): renormalization



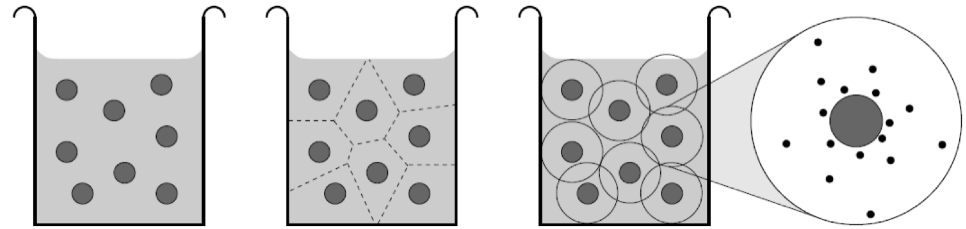
Interaction potentials at arbitrary charge (PB): renormalization

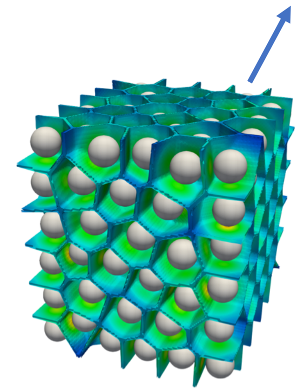
Use cell model to get renormalized charge and screening length



$$\beta u(r) \simeq Z_{\text{eff}}^2 l_B \left(\frac{e^{-\kappa_{\text{eff}} a}}{1 + \kappa_{\text{eff}} a} \right)^2 \frac{e^{-\kappa_{\text{eff}} r}}{r}$$

The cell model





In primitive model, DFT, PB...

Python 2.7 code available in SI of Hallez & Meireles, Langmuir 2017

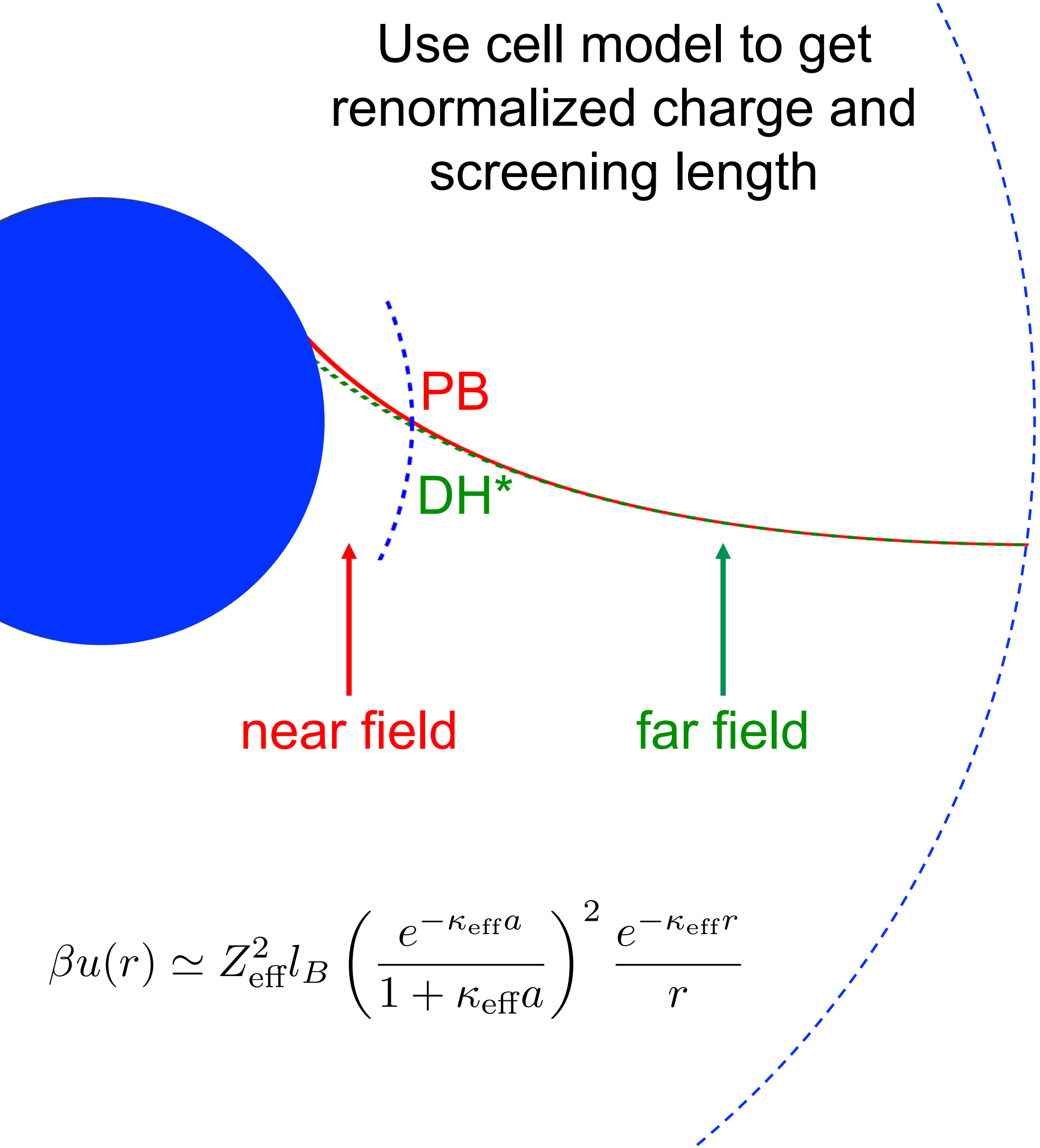
```
sim.SetParameters( a=10, I=0.001, phi=0.1, sigma=0.5 )
sim.renormalize()
print( sim.Z, sim.Zeff )

628.3185307179587 164.84684836304274
```

Alexander et al., J. Chem. Phys., 1984
Trizac et al., Langmuir, 2003
Deserno & Holm, in Electrostatic Effects in Soft Matter and Biophysics, 2000

Interaction potentials at arbitrary charge (PB): renormalization

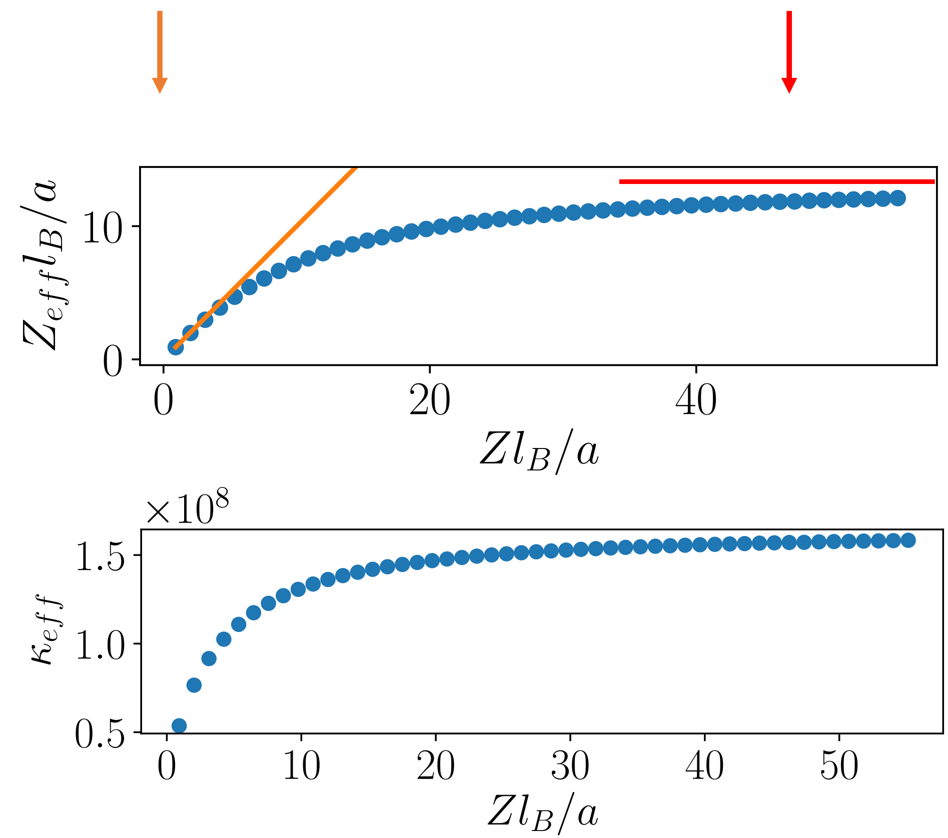
Use cell model to get renormalized charge and screening length



$$\beta u(r) \simeq Z_{\text{eff}}^2 l_B \left(\frac{e^{-\kappa_{\text{eff}} a}}{1+\kappa_{\text{eff}} a} \right)^2 \frac{e^{-\kappa_{\text{eff}} r}}{r}$$

$Z_{\text{eff}} \simeq Z$ at low charge

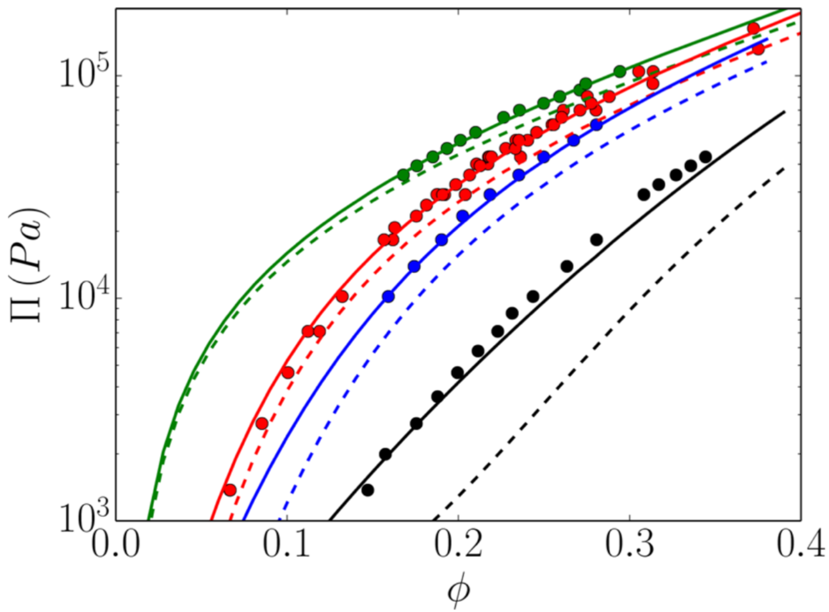
$Z_{\text{eff}} \simeq Z_{\text{eff}}^{\text{sat}}$ at very large charge



Interaction potentials at arbitrary charge (PB): renormalization

Osmotic compression of silica Ludox HS40 in water

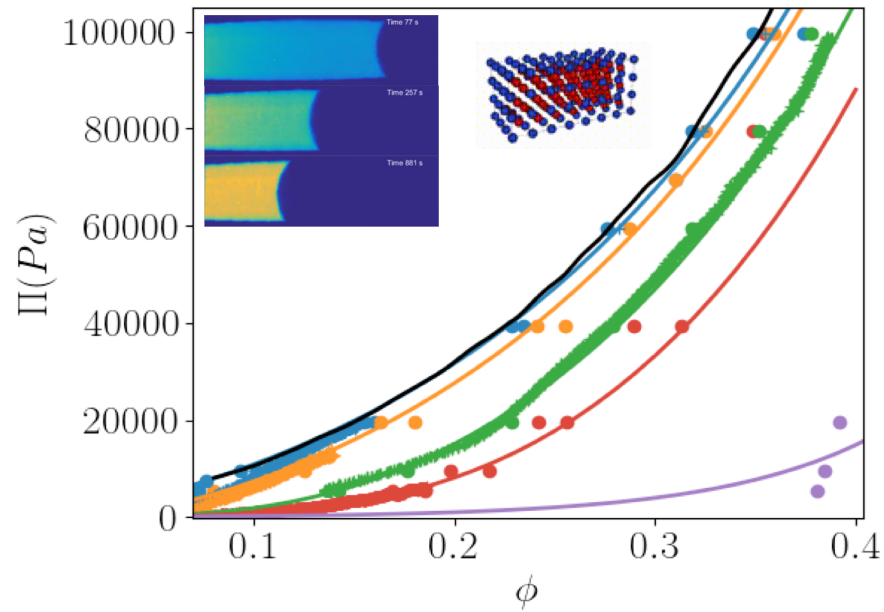
a = 8 nm, σ = 0.5 e/nm^2,
I = 0.5 to 50 mM.



Goehring et al., Philos. Trans. R. Soc. A, 2017
Hallez et al., Langmuir, 2017

Microfluidic compression of sulfate latex in water

a = 10 nm, σ = 0.36 e/nm^2,
I = 0.1 to 100 mM.



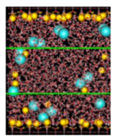
Keita & Salmon, LOF

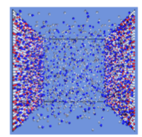
Coarse-graining

Theories / Models

Explicit treatment of ions

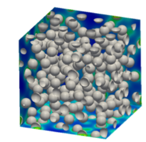
QM

MD 

PM 

Mean-field treatment of ions

PB



DH

Interactions

Derjaguin

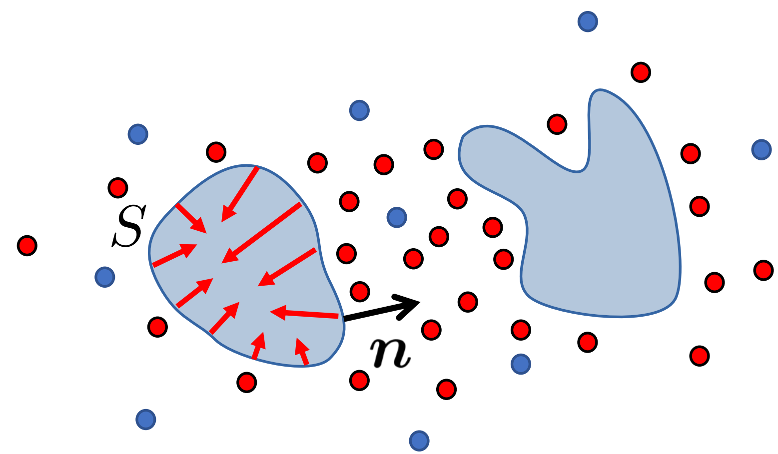
Renormalized potential

Confidence

Interaction potential: arbitrary EDL thickness and object shape

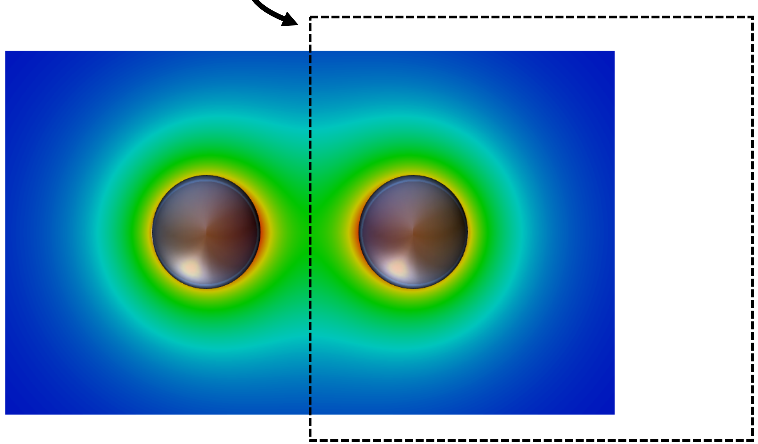
From the linearized excess osmotic stress tensor

$$\tilde{\tau} = -\frac{\psi^2}{2}\mathbf{I} + \left[\tilde{\mathbf{E}} \otimes \tilde{\mathbf{E}} - \frac{1}{2}\tilde{\mathbf{E}}^2\mathbf{I}\right]$$



Forces are obtained by integration

$$\tilde{\mathbf{F}} = \int_{\tilde{S}} \tilde{\tau} \cdot \mathbf{n} d\tilde{S}$$



Exact DH solution for 2 spheres

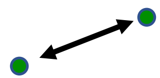
$$\begin{aligned}
V(R) = {} & 4\pi\varepsilon_{rs}\varepsilon_o\Psi_{o1}\Psi_{o2}a_1a_2 \frac{\exp[-\kappa(R - a_1 - a_2)]}{R} + 2\pi\varepsilon_{rs}\varepsilon_o\Psi_{o1}^2 a_1^2 \frac{\exp(2\kappa a_1)}{R} \sum_{n=0}^{\infty} (2n + 1)H_n(2)K_{n+1/2}^2(\kappa R) \\
& + 2\pi\varepsilon_{rs}\varepsilon_o\Psi_{o2}^2 a_2^2 \frac{\exp(2\kappa a_2)}{R} \sum_{n=0}^{\infty} (2n + 1)H_n(1)K_{n+1/2}^2(\kappa R) + 4\pi\varepsilon_{rs}\varepsilon_o\Psi_{o1}\Psi_{o2}a_1a_2 \frac{\exp[\kappa(a_1 + a_2)]}{R} \\
& \times \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} (2n + 1)(2m + 1)B_{nm} \times H_n(2)H_m(1)K_{n+1/2}(\kappa R)K_{m+1/2}(\kappa R) + \cdots \\
& + 2\pi\varepsilon_{rs}\varepsilon_o\Psi_{o1}\Psi_{o2}a_1a_2 \frac{\exp[\kappa(a_1 + a_2)]}{R} \times \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_{2\nu}=0}^{\infty} [M_{12}(n_1, n_2, \ldots, n_{2\nu}) + M_{21}(n_1, n_2, \ldots, n_{2\nu})] \\
& \times K_{n_1+1/2}(\kappa R)K_{n_{2\nu}+1/2}(\kappa R) + 2\pi\varepsilon_{rs}\varepsilon_o \sum_{n_1=0}^{\infty}\cdots\sum_{n_{2\nu-1}=0}^{\infty} (2n_{2\nu-1} + 1)B_{n_{2\nu-2}n_{2\nu-1}} \times [\Psi_{o1}^2 a_1^2 \frac{\exp(2\kappa a_1)}{R} \\
& \times M_{21}(n_1, n_2, \ldots, n_{2\nu-2})H_{n_{2\nu-1}}(2) + \Psi_{o2}^2 a_2^2 \frac{\exp(2\kappa a_2)}{R} M_{12}(n_1, n_2, \ldots, n_{2\nu-2})H_{n_{2\nu-1}}(1)] \\
& \times K_{n_1+1/2}(\kappa R)K_{n_{2\nu-1}+1/2}(\kappa R) + \cdots . \quad [2]
\end{aligned}$$

Glendinning & Russel, JCIS 1982,
Carnie & Chan, JCIS 1993, Ohshima, JCIS 1995

Interaction potentials at low charge (DH)

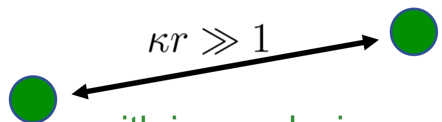
Yukawa 2-body:

$$\beta u(r) = Z^2 l_B \frac{e^{-\kappa r}}{r}$$



DLVO 2-body:

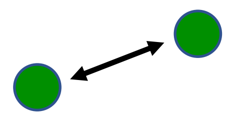
$$\beta u(r) = Z^2 l_B \left(\frac{e^{-\kappa a}}{1+\kappa a}\right)^2 \frac{e^{-\kappa r}}{r}$$



with ion exclusion

Exact 2-body DH:

$$\beta u(r) = Z^2 l_B \left(\frac{e^{-\kappa a}}{1+\kappa a}\right)^2 \frac{e^{-\kappa r}}{r} + \mathcal{O}\left(f\left(\frac{\epsilon_s}{\epsilon}\right)\frac{e^{-2\kappa r}}{r}\right)$$



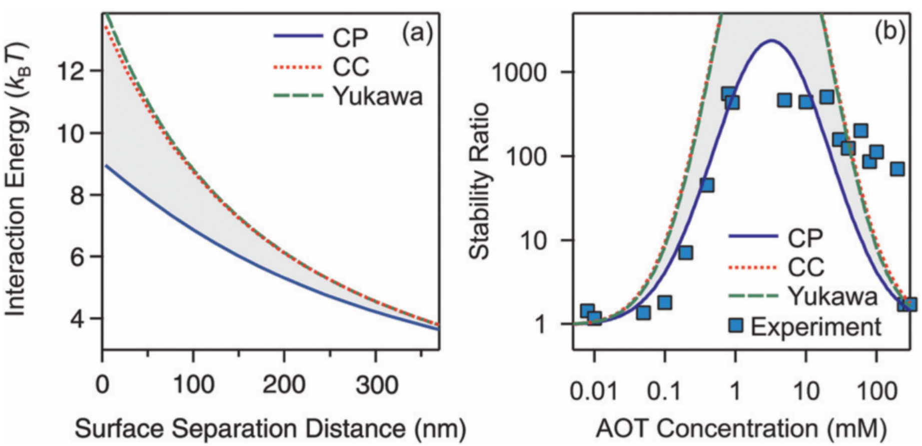
with ion exclusion
and image interactions

Glendinning & Russel, JCIS 1982
Carnie & Chan, JCIS, 1993
Ohshima, JCIS, 1995

Interaction potentials at low charge (DH)

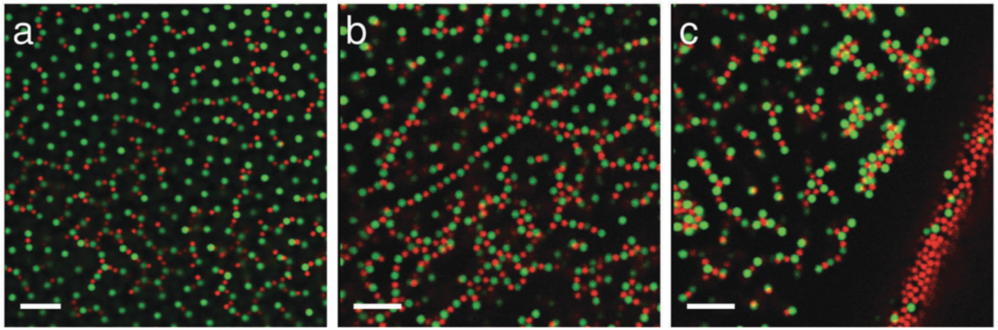
Image interactions at play

Silica + AOT in decane

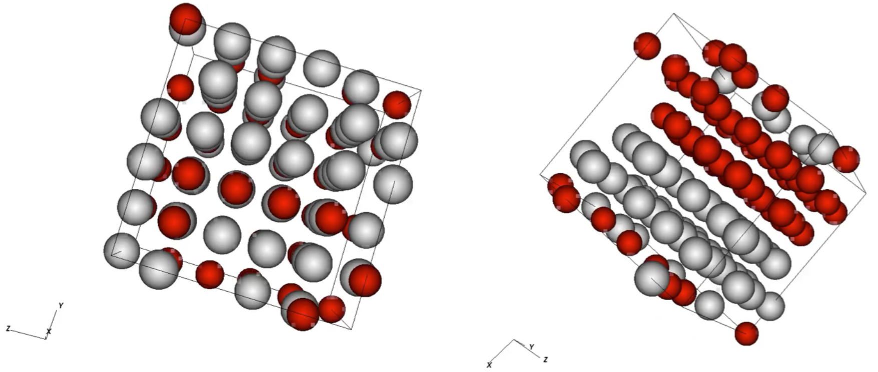


Farrokhbin et al, PCCP, 2019

PMMA+PHSA in CHB



Everts et al., Soft Matter, 2016



Interaction potentials at low charge (DH)

Yukawa 2-body:

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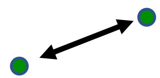
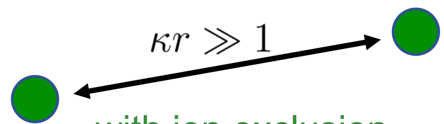


DLVO 2-body:

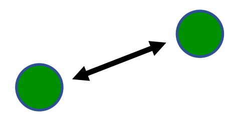
$$\beta u(r) = Z^2 l_B \left(\frac{e^{-\kappa a}}{1+\kappa a}\right)^2 \frac{e^{-\kappa r}}{r}$$



with ion exclusion

Exact 2-body DH:

$$\beta u(r) = Z^2 l_B \left(\frac{e^{-\kappa a}}{1+\kappa a}\right)^2 \frac{e^{-\kappa r}}{r} + \mathcal{O}\left(f\left(\frac{\epsilon_s}{\epsilon}\right)\frac{e^{-2\kappa r}}{r}\right)$$



with ion exclusion
and image interactions

Glendinning & Russel, JCIS 1982
Carnie & Chan, JCIS, 1993
Ohshima, JCIS, 1995

Interaction potentials at low charge (DH)

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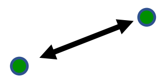
$$\beta u(r) = Z^2 l_B \frac{e^{-\kappa r}}{r}$$



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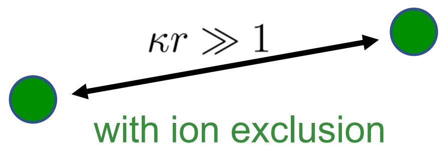

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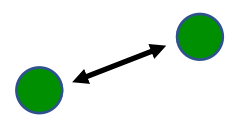
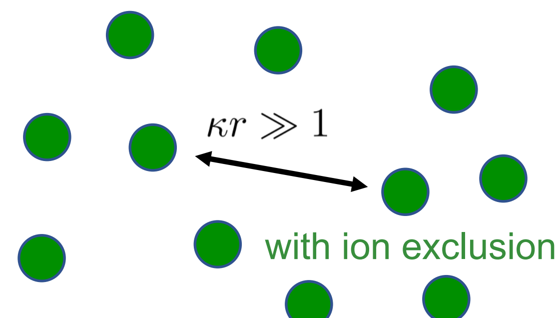


with ion exclusion
and image interactions

Glendinning & Russel, JCIS 1982
Carnie & Chan, JCIS, 1993
Ohshima, JCIS, 1995

Dense DH:

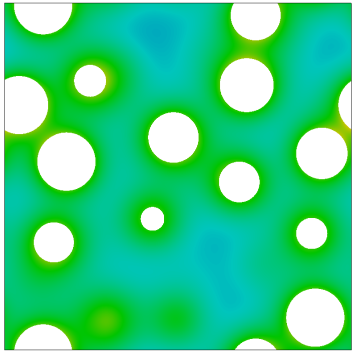
$$\beta u(r) = Z^2 l_B \left[\frac{e^{\bar{\kappa} a}}{1+\bar{\kappa} a + \alpha \rho_c \int_0^\infty g(r) \frac{e^{-\bar{\kappa}(r-2a)}}{\bar{\kappa} r} dr} \right]^2 \frac{e^{-\bar{\kappa} r}}{r}$$

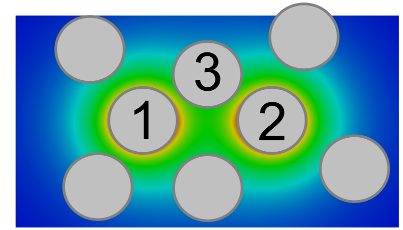


Khan et al., Phys. Rev. A, 1987

Interaction potentials at low charge (DH)

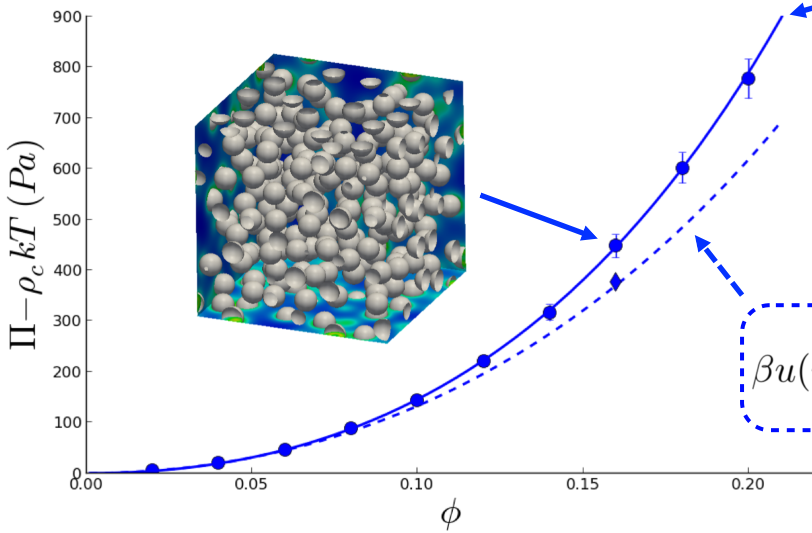
Many-body effects





$$\beta u(r) = Z^2 l_B \left[\frac{e^{\bar{\kappa} a}}{1 + \bar{\kappa} a + \alpha \rho_c \int_0^\infty g(r) \frac{e^{-\bar{\kappa}(r-2a)}}{\bar{\kappa} r} dr} \right]^2 \frac{e^{-\bar{\kappa} r}}{r}$$

Khan et al., Phys. Rev. A, 1987
Belloni, J. Chem. Phys., 1986



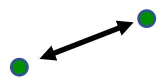
$$\beta u(r) = Z^2 l_B \left(\frac{e^{-\kappa a}}{1 + \kappa a} \right)^2 \frac{e^{-\kappa r}}{r}$$

Hallez & Meireles, Langmuir, 2016

Interaction potentials at low charge (DH)

Yukawa 2-body:

$$\beta u(r) = Z^2 l_B \frac{e^{-\kappa r}}{r}$$



DLVO 2-body:

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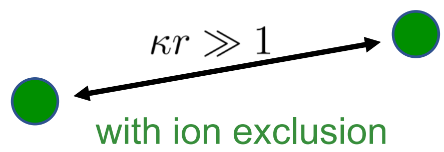

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Carnie & Chan, JCIS, 1993
Ohshima, JCIS, 1995

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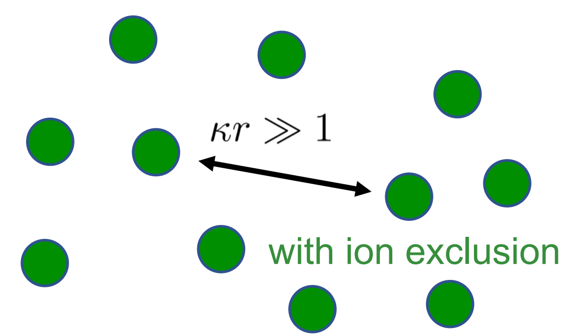

Khan et al., Phys. Rev. A, 1987

Interaction potentials at low charge (DH)

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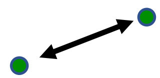

DLVO 2-body:

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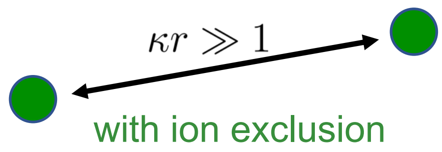

Exact 2-body DH:

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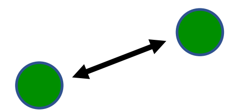

with ion exclusion
and image interactions

Glendinning & Russel, JCIS 1982
Carnie & Chan, JCIS, 1993
Ohshima, JCIS, 1995

Dense DH:

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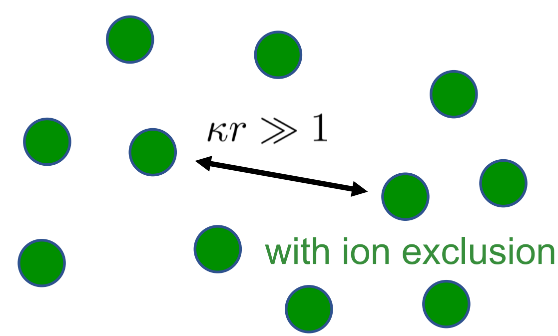


Khan et al., Phys. Rev. A, 1987

Effective interaction potential

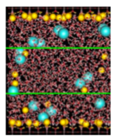
$$\beta u(r) = Z_e^2 l_B \frac{e^{-\kappa_e r}}{r}$$

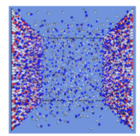
Coarse-graining

Theories / Models

Explicit treatment of ions

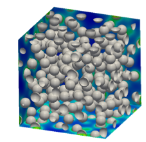
QM

MD 

PM 

Mean-field treatment of ions

PB
MPB
DFT



DH

Interactions

Derjaguin

Renormalized potential

Dilute: DLVO
Exact DH

Dense: Effective Yukawa

Confidence

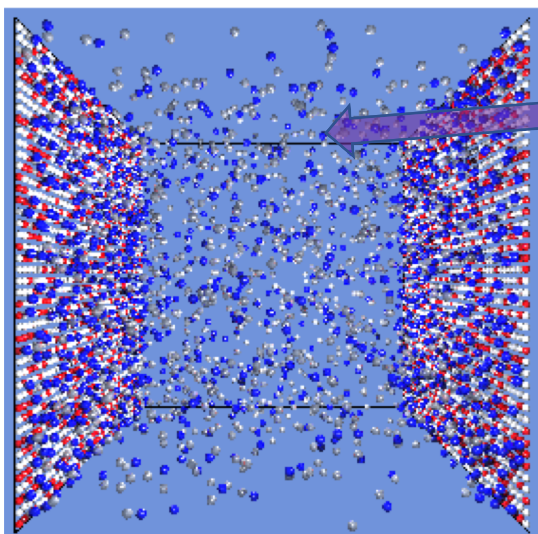
How good is the Poisson-Boltzmann theory?

Summary of the PB model

$$\Delta\psi = \kappa^2 \sinh\psi$$

If ion-ion core exclusion and ion-ion correlation effects are small compared to the effect of the mean electrostatic field.

Benchmark against Primitive Model Monte Carlo simulations



Bulk solution
pH, $\mu_i, \ldots, \mu_N$

Electrolyte solution: primitive model

$$\begin{cases} u(\boldsymbol{r_i}, \boldsymbol{r_j}) = \dfrac{z_i z_j e^2}{4\pi\epsilon|\boldsymbol{r_i} - \boldsymbol{r_j}|} & \text{when} \quad |\boldsymbol{r_i} - \boldsymbol{r_j}| < \dfrac{\sigma_i + \sigma_j}{2} \\ u(\boldsymbol{r_i}, \boldsymbol{r_j}) = \infty & \text{otherwise} \end{cases}$$

A comparison of mean-field and exact solutions of the PM

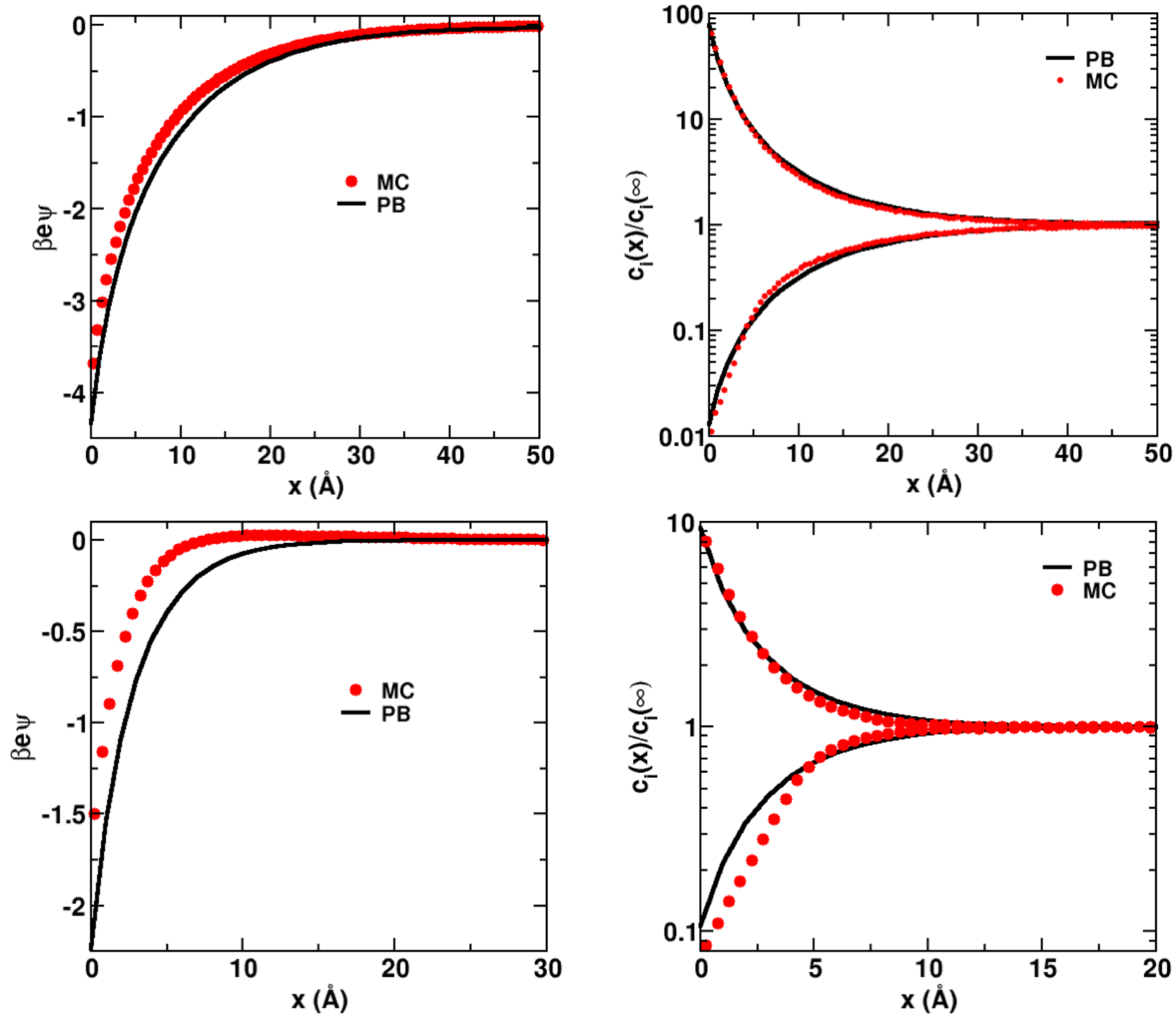
1:1 salt
σ = - 0.16 C/m^2 = 1 e/nm^2
Ξ = 3.35

The PB equation only gives an exact solution of the EDL for low enough c_{salt} and σ otherwise it overestimates ψ and c_i (in absolute terms)

potential | ion density

0.1 M

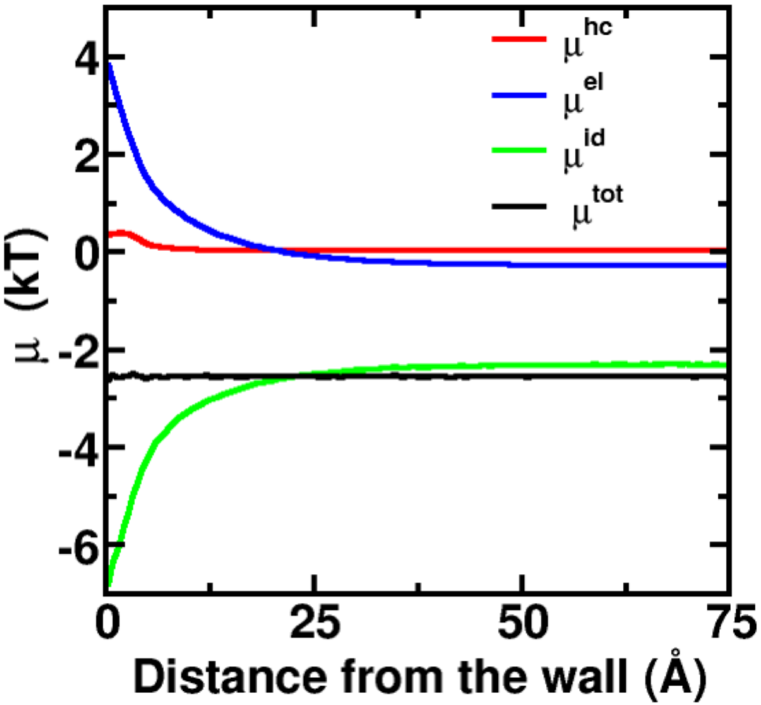
1 M



A comparison of mean-field and exact solutions of the PM

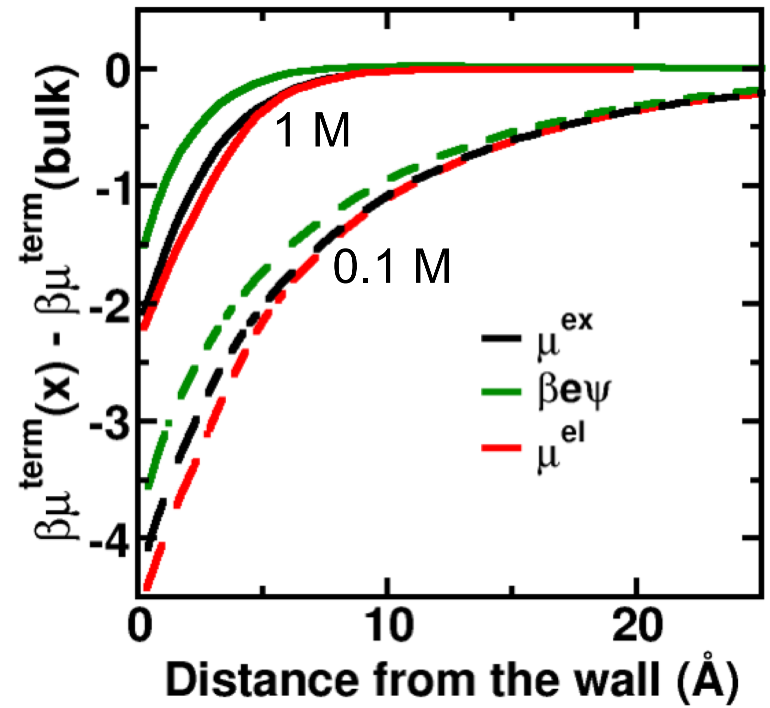
Chemical potential

anion; σ = -0.16 C/m^2; 0.1 M



Potential of mean force (PMF)

cation; σ = -0.16 C/m^2



$$\mu_i^{tot} = \mu_i^{id} + \mu_i^{hc} + \mu_i^{el} = \mu_i^{id} + \mu_i^{ex}$$

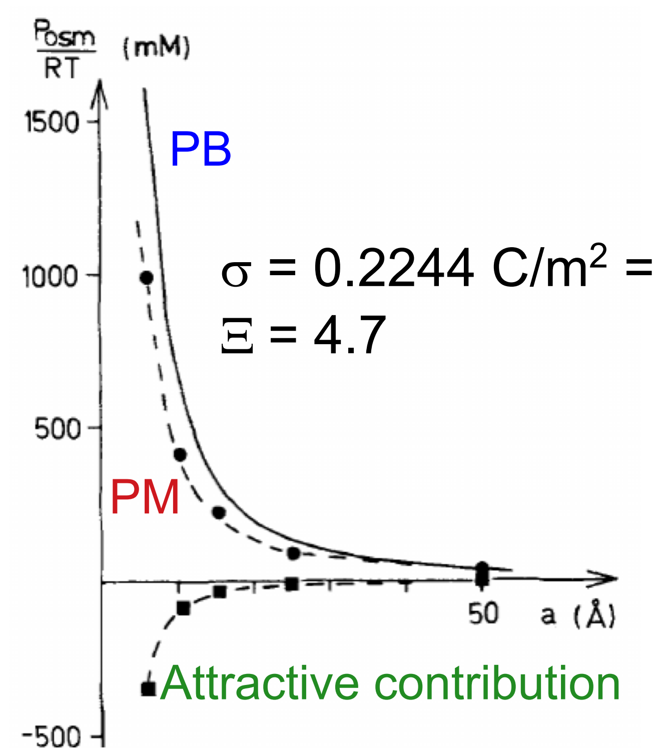
$$\Delta\mu_i^{ex} \neq z_i e\psi \qquad \Delta\mu_i^{el} \neq z_i e\psi$$

The chemical potential and the PMF of the ions are NOT a function of the **mean** $\Psi = \langle \Phi \rangle_t$

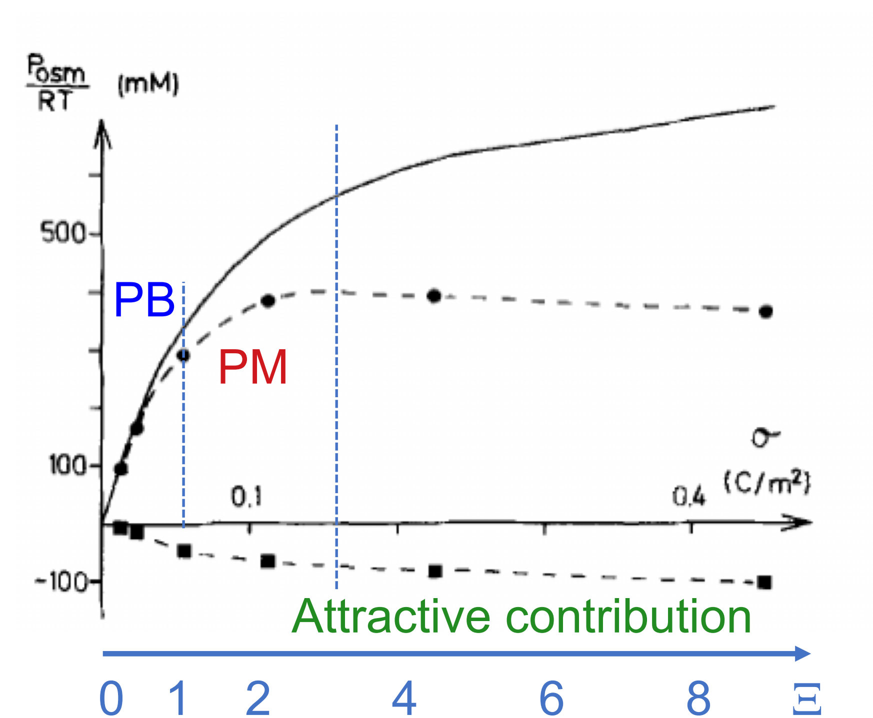
A comparison of mean-field and exact solutions of the PM

Osmotic pressure (salt free case)

The PB equation overestimates P_{osm}. It is all the more so as σ is increased.



Fixed wall separation (2a = 21 Å)



Guldbrand et al, J. Chem. Phys. 1984

Modified Poisson-Boltzmann (MPB) or Density Functional Theories

Additional effects can be introduced in the chemical potential

$$\mu^{\pm} = kT\ln(\gamma n^{\pm}) \pm e\Psi = kT\ln(\gamma_0 n_0) \longrightarrow n^{\pm}(\boldsymbol{x}) = n_0 \frac{\gamma_0}{\gamma(\boldsymbol{x})} e^{\mp\psi(\boldsymbol{x})}$$

or in the thermodynamic potential.

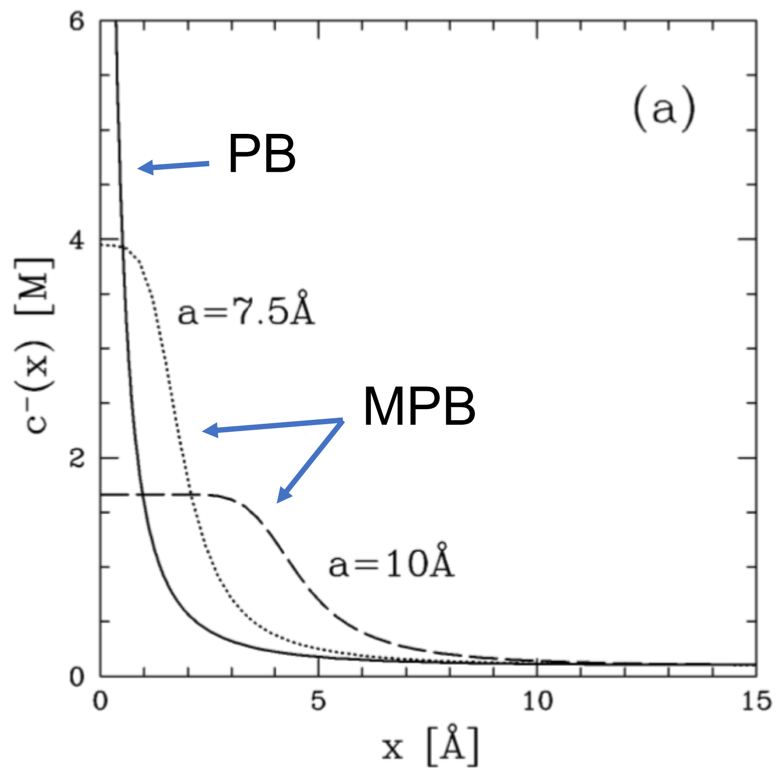
Example of MPB model:

$$\tilde{\Delta}\psi = \frac{\sinh\psi}{1 - \phi_0 + \phi_0 \cosh\psi}$$

where ϕ_0 is the bulk volume fraction of ions.

Various MPB models exist for:

- Finite size of ions
- Hydration (or other short-range) interactions
- Potential fluctuations



Borukhov et al., PRL 1997

The weak coupling regime, a summary

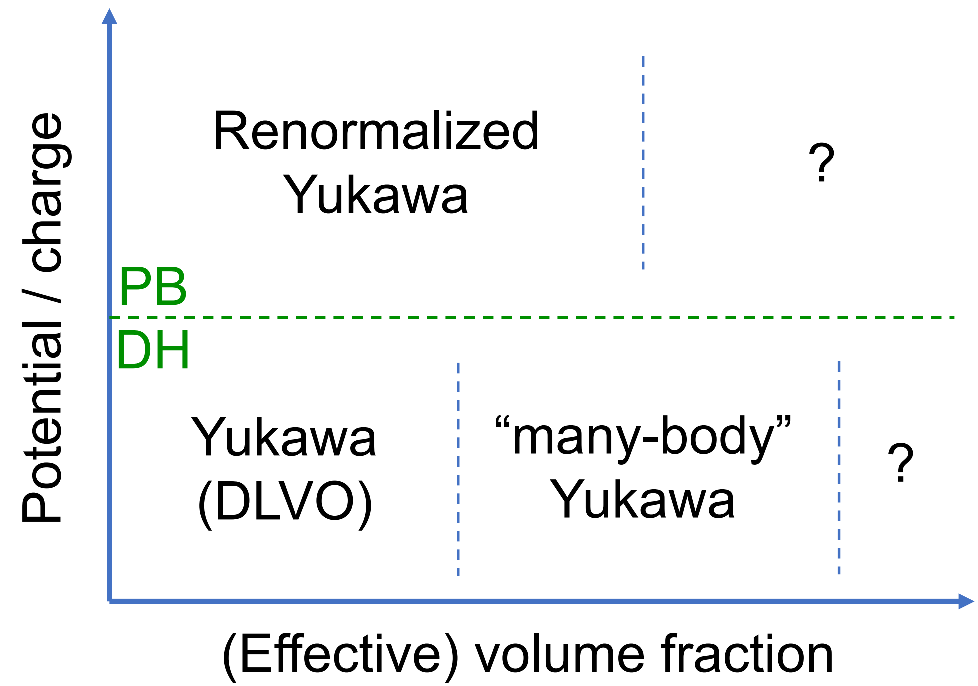
$$\Xi = 2\pi z^3 l_B^2 \sigma' < 1$$

As a rule of thumb:
- monovalent counterions in water
- ion concentration < 0.1M

Higher ion concentrations can be considered with MPB (e.g. biophysics).

The weak coupling realm (PB) is way broader than that of the DLVO theory.

Going beyond DLVO is possible in practice in the weak coupling limit.



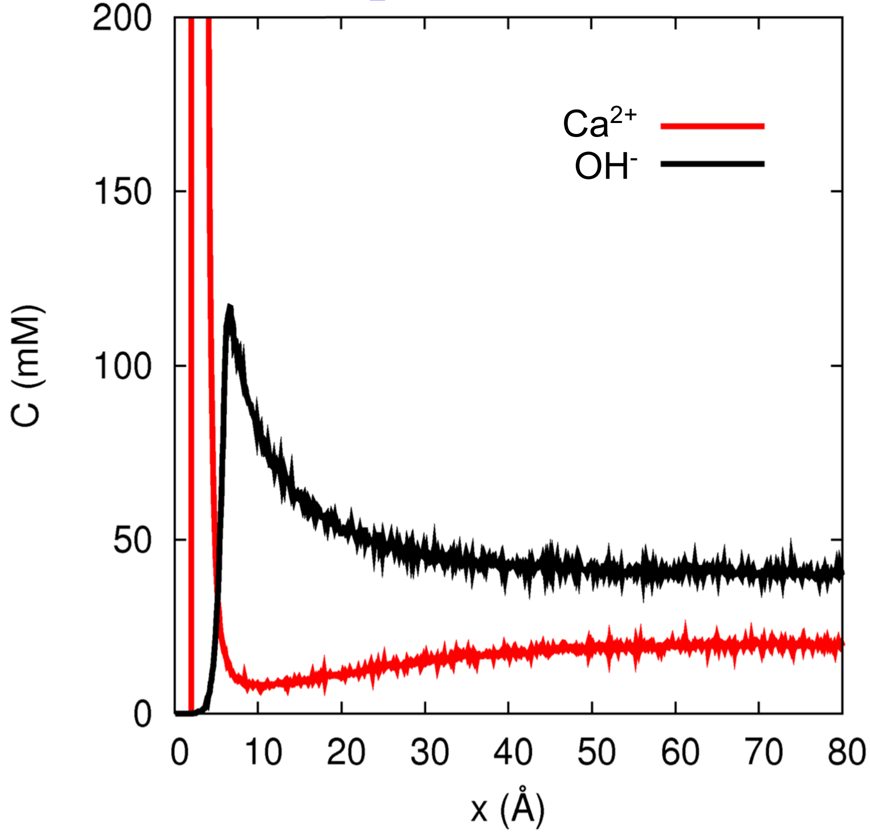
To be continued with strong coupling effects...

Effects of strong coupling

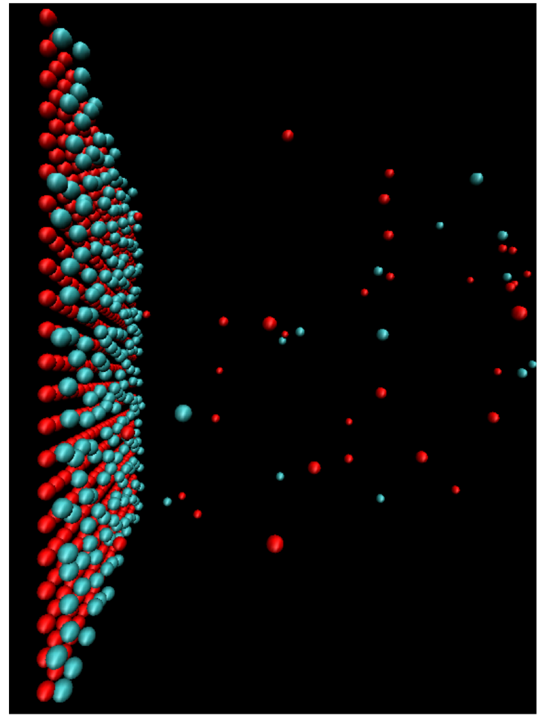
Electrostatics in the strong coupling regime

Ion concentration profiles

20 mM $Ca(OH)_2$ (pH 12.5 ; σ = -0.74 C/m^2)



Γ_{SiOH} = 4.8 / nm², pK_a = 9.8

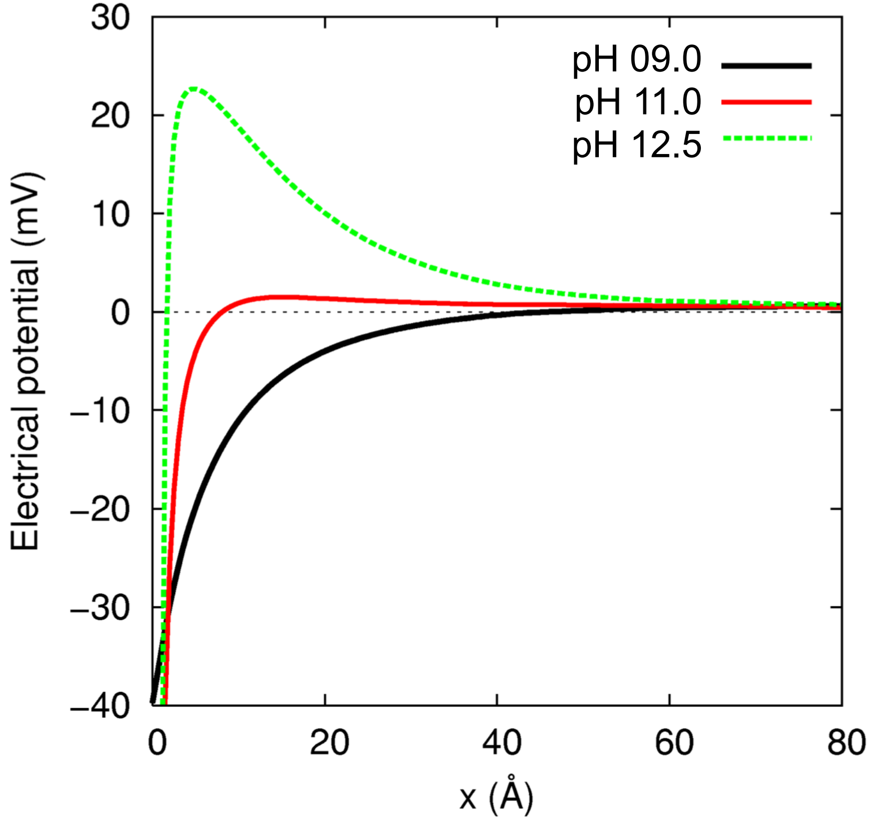


The multivalent counterions more than simply compensate the surface charge !

Electrostatics in the strong coupling regime

Profile of mean electrostatic potential

pH set by $Ca(OH)_2$ concentration
(Γ_{SiOH} = 4.8 / nm², pK_a = 9.8)

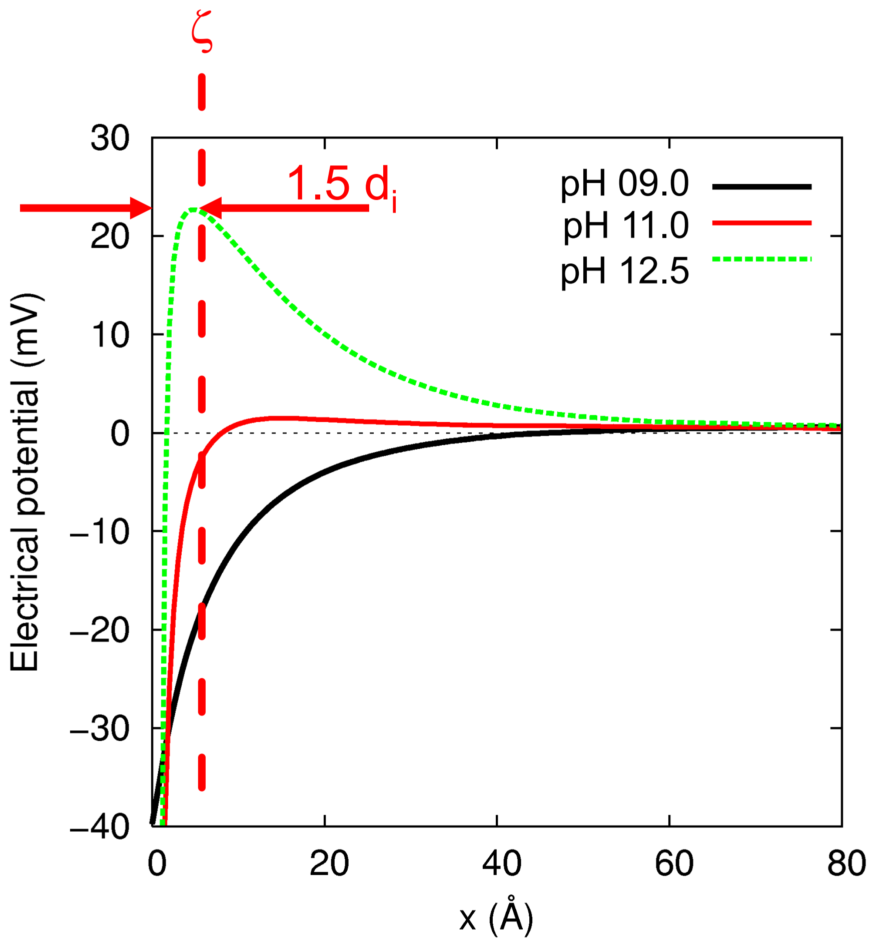


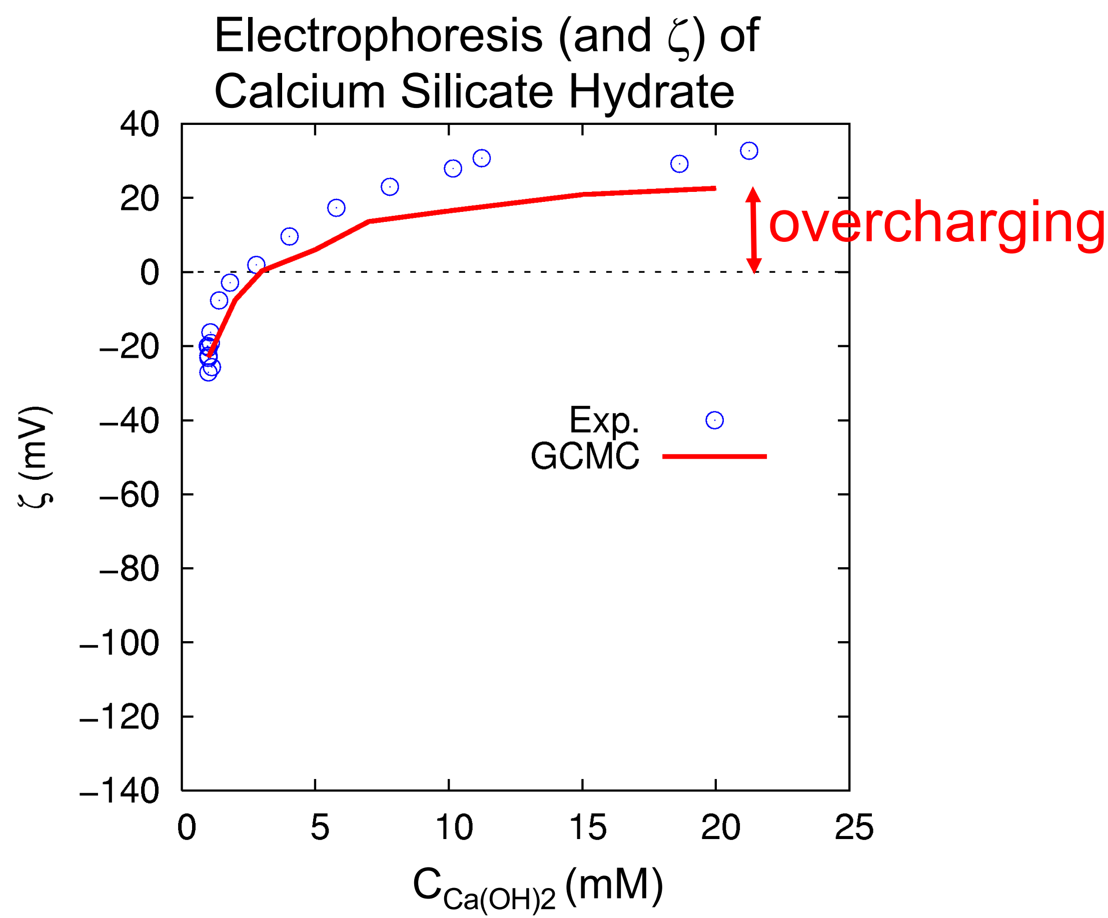
As the concentration of $Ca(OH)_2$ and pH are increased, the charge is progressively overcompensated by Ca^{2+}

This leads to non monotonic profiles of the mean electrostatic potential (ψ)

Electrostatics in the strong coupling regime

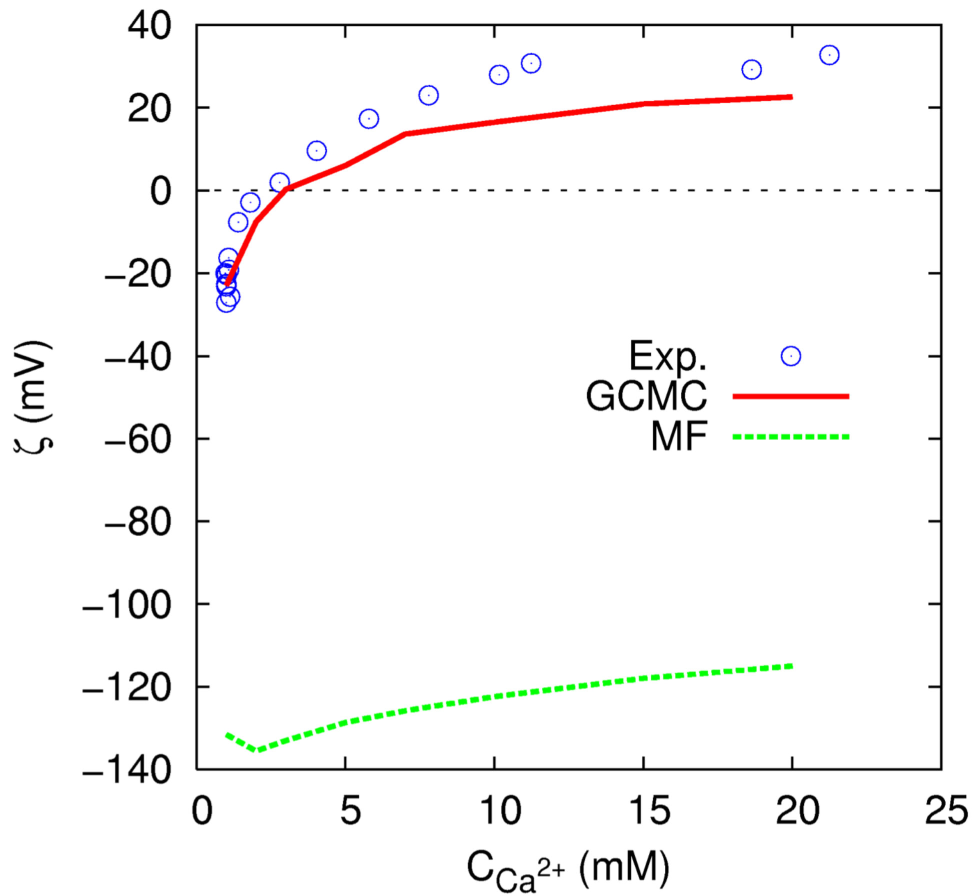
The overcharging of the bare σ leads to a sign reversal of the electrokinetic potential ζ





Electrostatics in the strong coupling regime

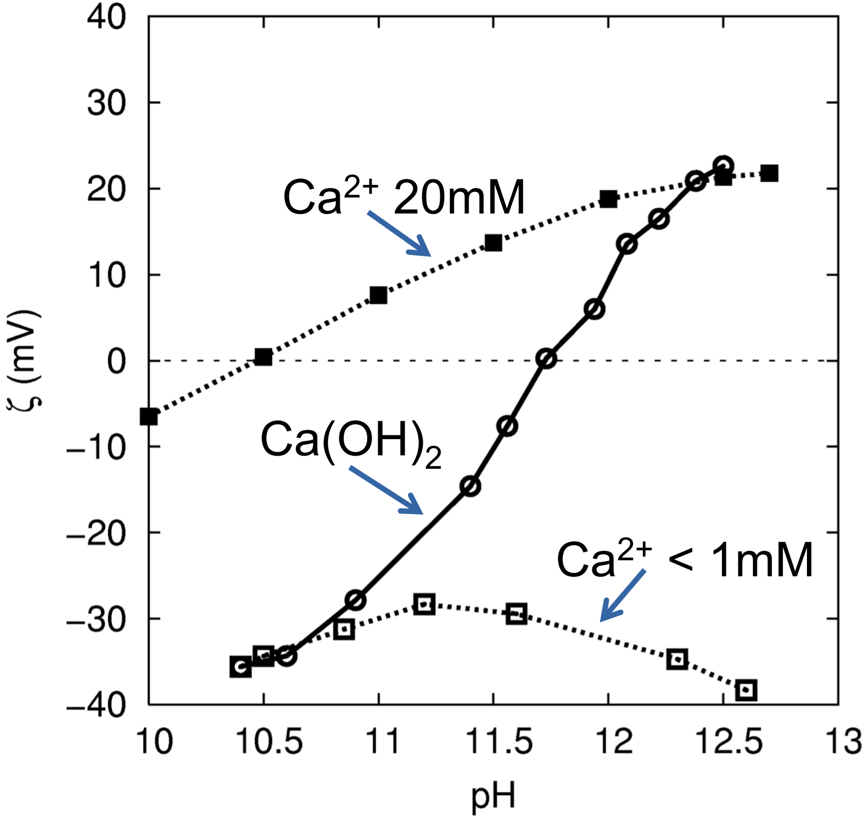
The mean field theory (MF) fails to predict the overcharging



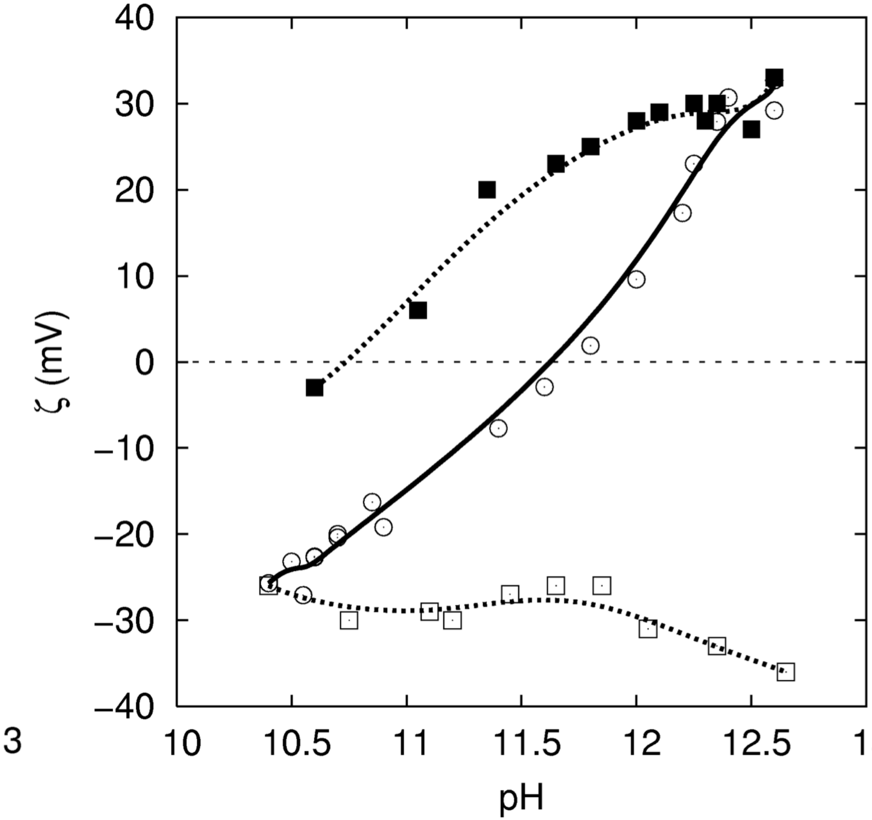
Electrostatics in the strong coupling regime

Charge reversal example

Exact solution of the PM

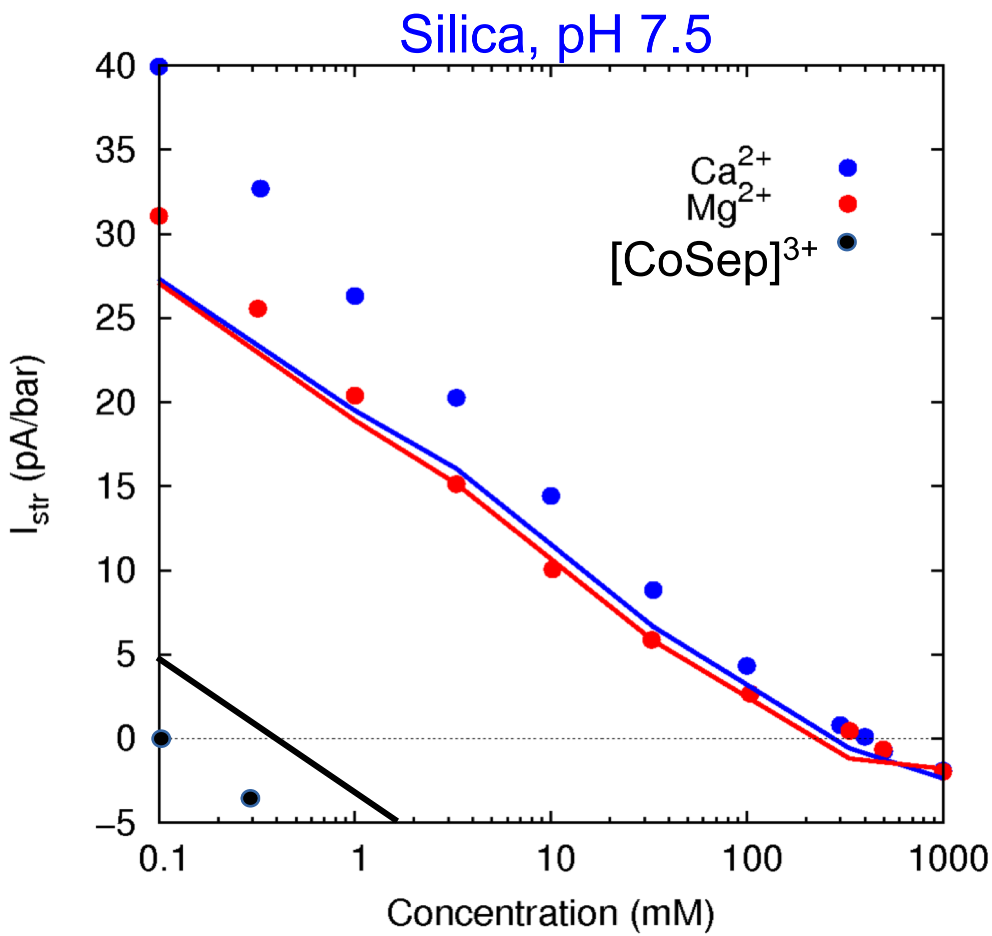


ζ from electrophoretic mobility of C-S-H



Labbez, C. et al J. Phys. Chem. B 2006, 110, 9219

Electrostatics in the strong coupling regime



$$I_{str} = S\int_{-h/2}^{h/2} \rho\,(x)u(x).\,dx$$

Exp. data: van der Heyden et al, PRL, 2005

Charge reversal

The titration of surface sites has a prominent role in the generation of CR

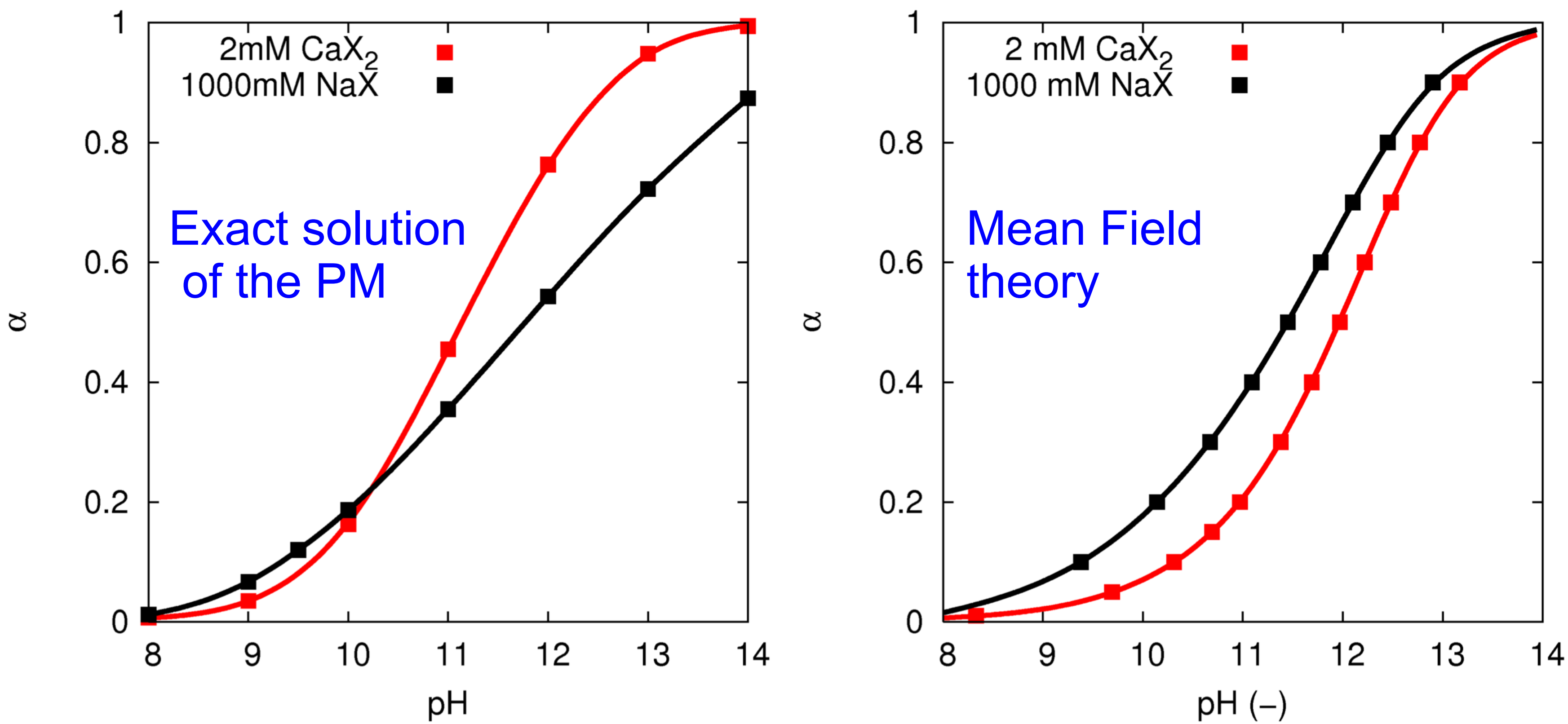
Labbez, C. et al Langmuir 2009, 25, 7209

Electrostatics in the strong coupling regime

Charge formation

$$\mathrm{Si{-}OH} \overset{\mathrm{pK}_a}{\rightleftharpoons} \mathrm{Si{-}O^-} + \mathrm{H^+}$$

Γ_{SiOH} = 4.8 / nm², pK_a = 9.8



↳ The ion correlations, here promoted by Ca^{2+}, facilitate surface ionisation

Electrostatics in the strong coupling regime

Potentiometric titration of silica in Na and Ca salts

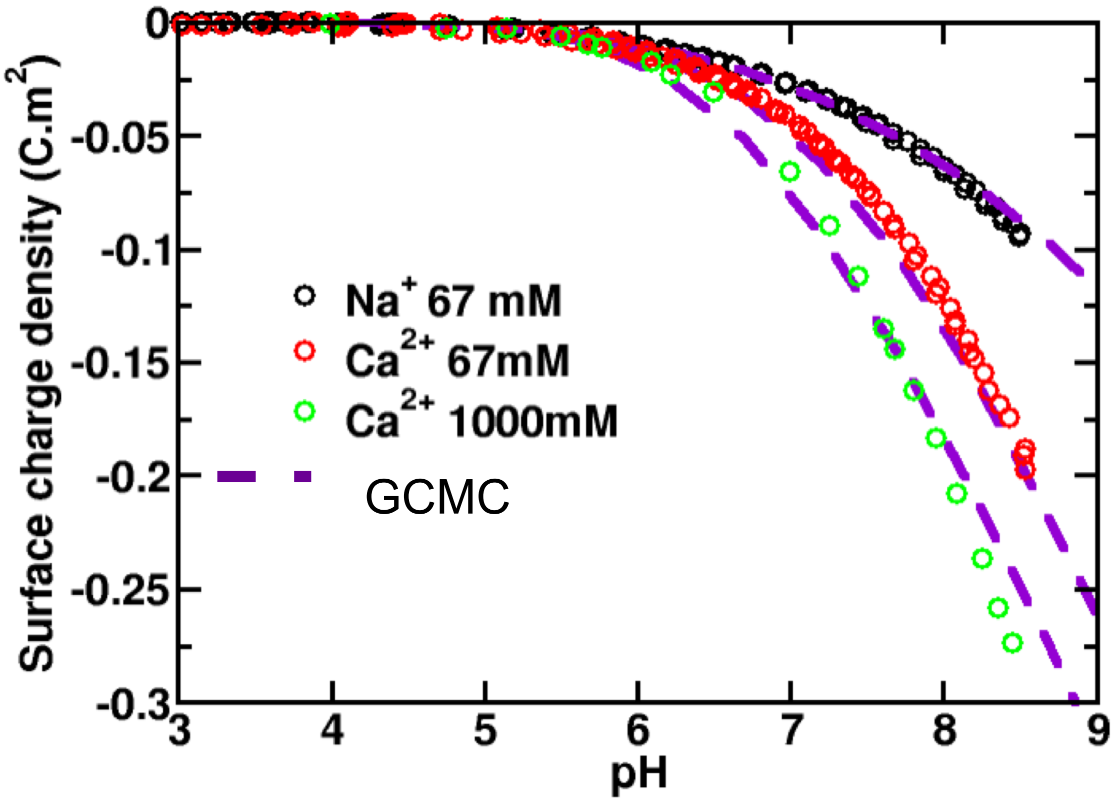
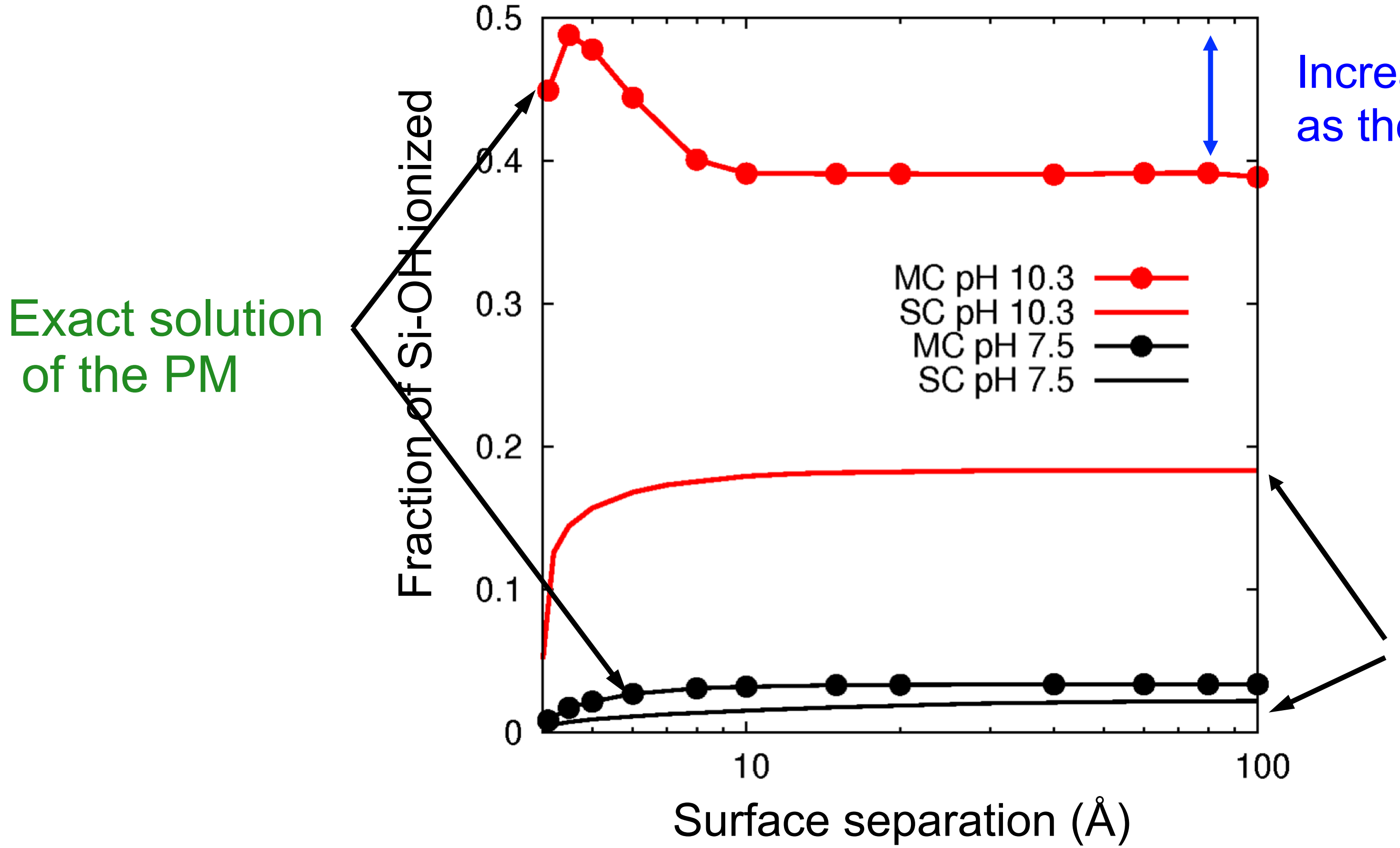


Figure: Experimental (exp) and simulated (GCMC) surface charge density of silica particles dispersed in 67 mM sodium salt and 67mM and 1000mM calcium salt.

GCMC: ρ_s=4.8 sites/nm^2
pK_a=7.7
Exp. data: Dove *et al*

Electrostatics in the strong coupling regime

Charge regulation of silica surfaces in a calcium salt (0.2 mM)



ρ_s=4.8 sites/nm^2
pK_a=7.7

Labbez, C. et al Langmuir 2009, 25, 7209

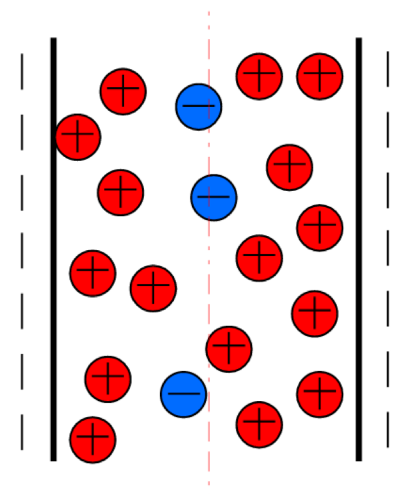
Electrostatics in the strong coupling regime

Osmotic pressure in the **mean field approximation**

- The osmotic pressure of the confined solution between two equally charged surfaces can be shown, with the contact theorem, to be a simple function of the ion concentrations at the mid plane:

$$P_{osm}^{DL} = kT \sum_i c_i(\text{mid plane})$$

$\Rightarrow$ In the MF approximation P_{osm}^{DL} is of purely entropic origin



- The net osmotic pressure is then given by

$$P_{osm}^{net} = P_{osm}^{DL} - P_{osm}^{bulk} = kT \sum_i c_i(\text{mid plane}) - c_i(\text{bulk})$$

$\Rightarrow P_{osm}^{net}$ *always* > 0

Electrostatics in the strong coupling regime

Osmotic pressure in the **full primitive model**

- The osmotic pressure of the confined solution can be written as:

$$P_{osm}^{DL} = \underbrace{P_{ideal}^{mp} + P_{hardcore}^{mp}}_{\text{Entropic} > 0} + \underbrace{P_{correlations}^{mp}}_{\text{Energetic} < 0}$$

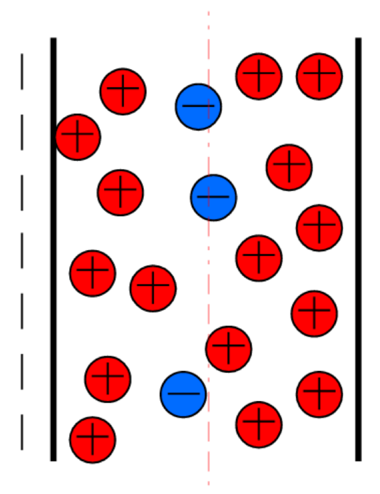
Entropic **> 0** Energetic **< 0**

with $P_{ideal}^{mp} = k_B T \sum c_i(mid\,plane) = mean\ field\ P_{osm}^{DL}$

- The net osmotic pressure is also obtained by substracting that of the bulk

$$P_{osm}^{net} = P_{osm}^{DL} - P_{osm}^{bulk}$$

⇒ Two charged surfaces can attract each others when the ion-ion correlations are strong enough (high σ or multivalent counterions)

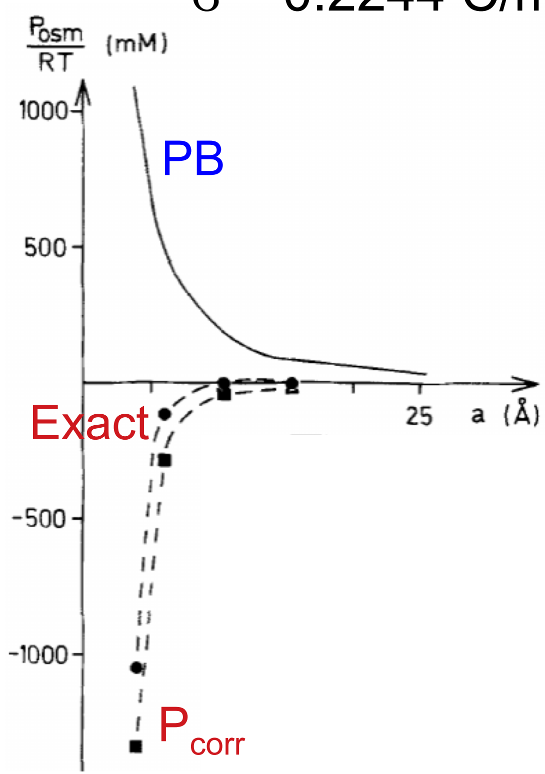


Electrostatics in the strong coupling regime

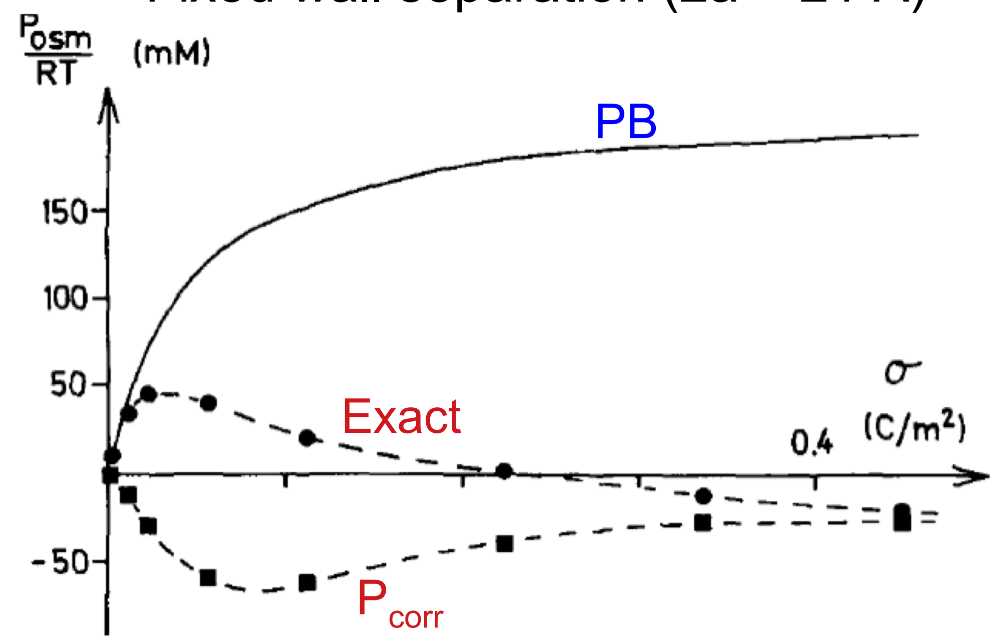
Osmotic pressure (divalent counterions, salt free)

In presence of multivalent counterions and at sufficiently high σ, the ion correlations dominate over entropic contributions to P_{osm} which results in an overall attraction

$\sigma = 0.2244\ C/m^2$



Fixed wall separation (2a = 21 Å)

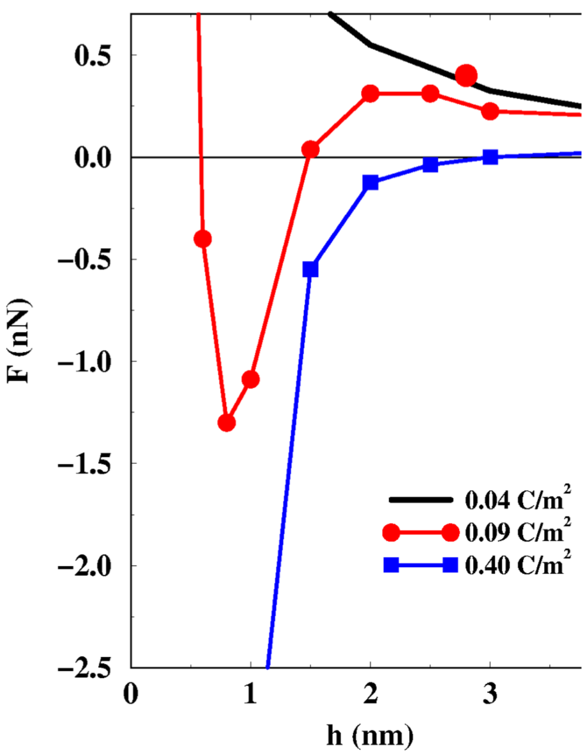


Guldbrand et al, J. Chem. Phys. 1984

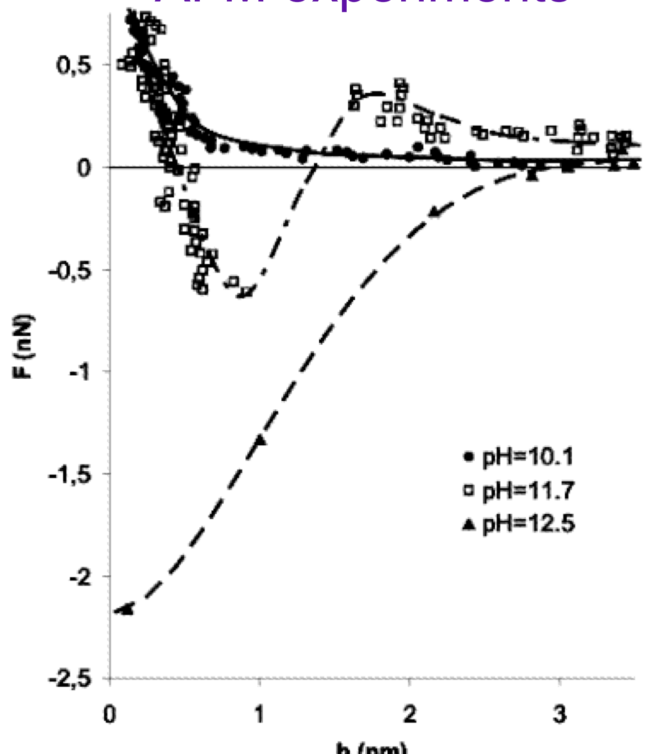
Electrostatics in the strong coupling regime

Ion correlation attraction between homo-particles, example

Simulations



AFM experiments



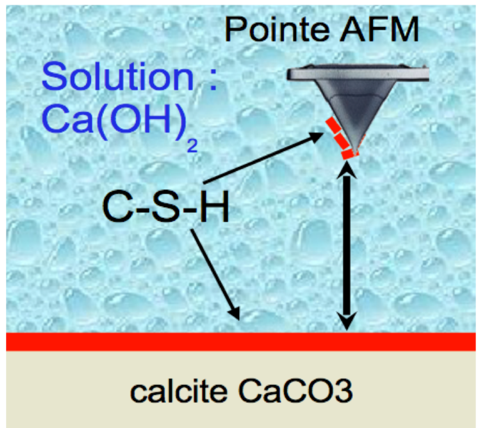


Figure: Calculated force as a function of separation (h) corresponding to the different AFM experiments for varying $Ca(OH)_2$ concentration (pH).

Jönsson et al, Langmuir 2004, 20, 6702

Electrostatics in the strong coupling regime

Ion correlation attraction between homo-particles, example

Sulphate latex in presence of tetravalent cations

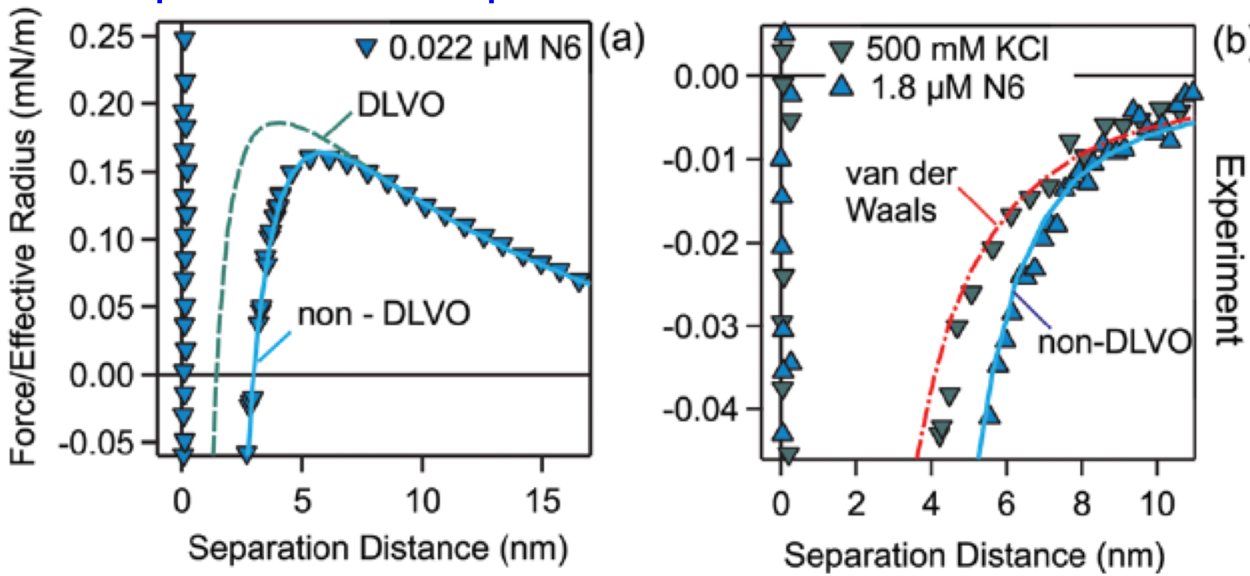


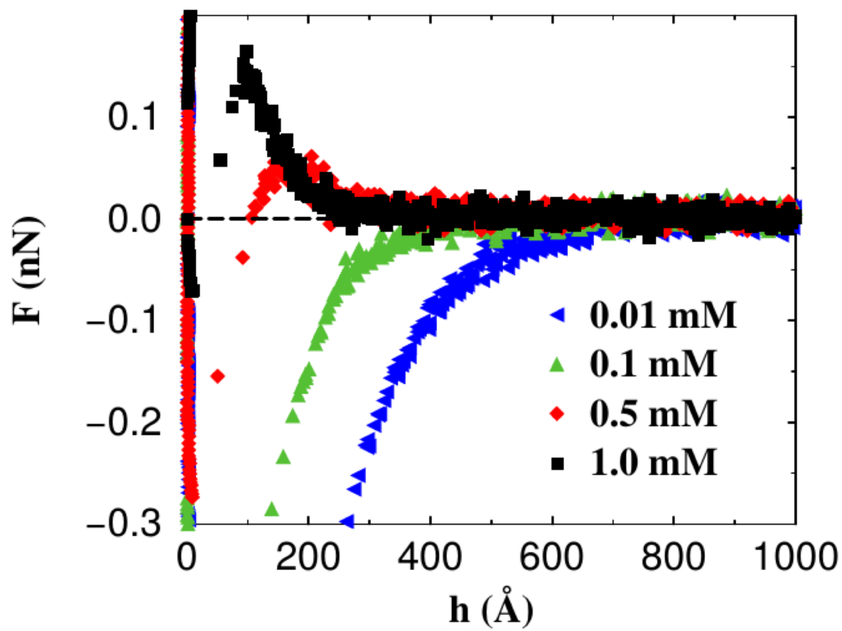
Fig. (a and b) Experimentally measured forces between two SL particles in the presence of tetravalent cation. Forces at lower counterion concentration (left) and at apparent charge neutralization (right) are shown. well. The parameters σ = -24 mC.m^{-2} and H = 3.5 10^{-21} J, the latter determined at 1M concentration of KCl.

Borkovec et al, PCCP, 2017, 19, 10069

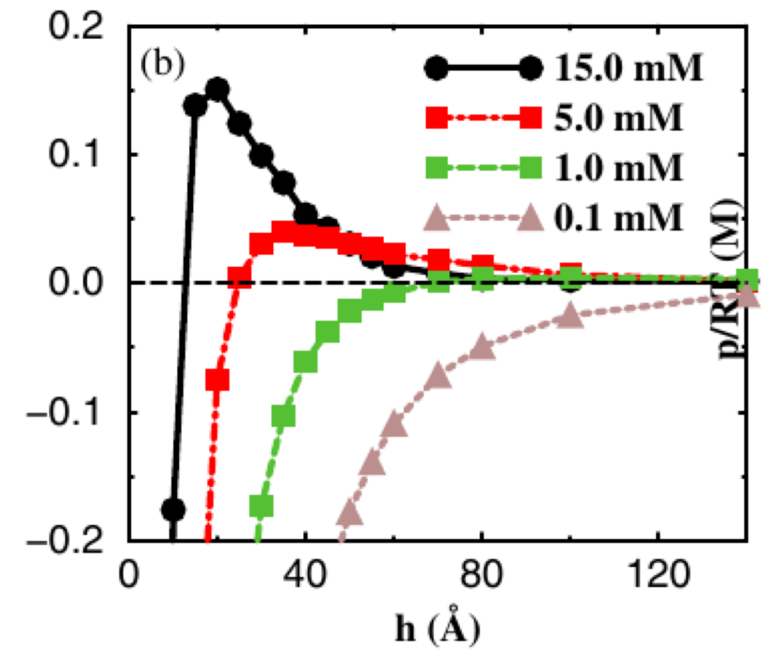
Electrostatics in the strong coupling regime

Repulsion between oppositely charged surfaces in 3:1 salt solution

Amine latex/silica bathing in La^{3+} salt solution



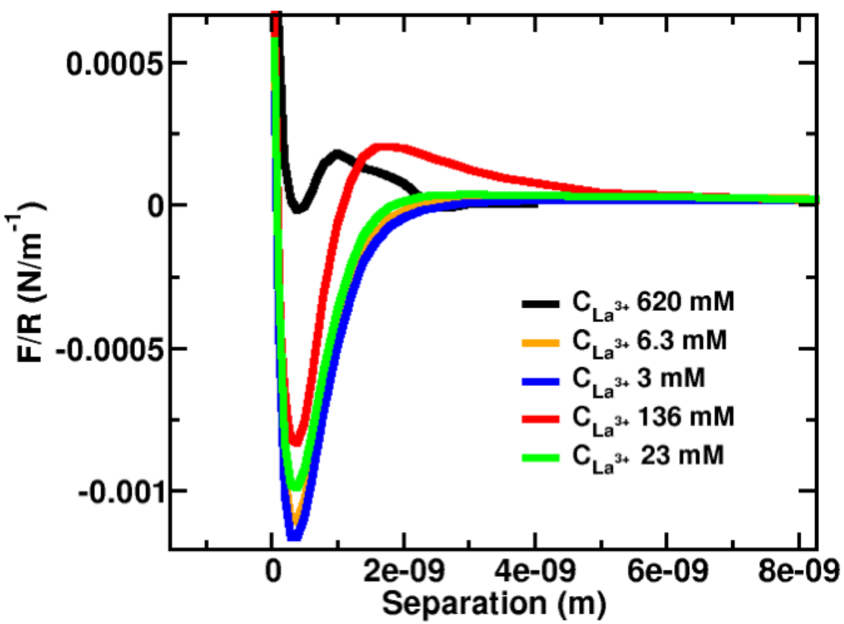
Simulations



Trulesson et al, PRL, 2006

Electrostatics in the strong coupling regime

Simulated interaction free energy of silica particles bathing in increasing concentration of 3:1 salt solution at pH 4 (σ = 80 mC/m^2)



Van der Waals interactions are not included

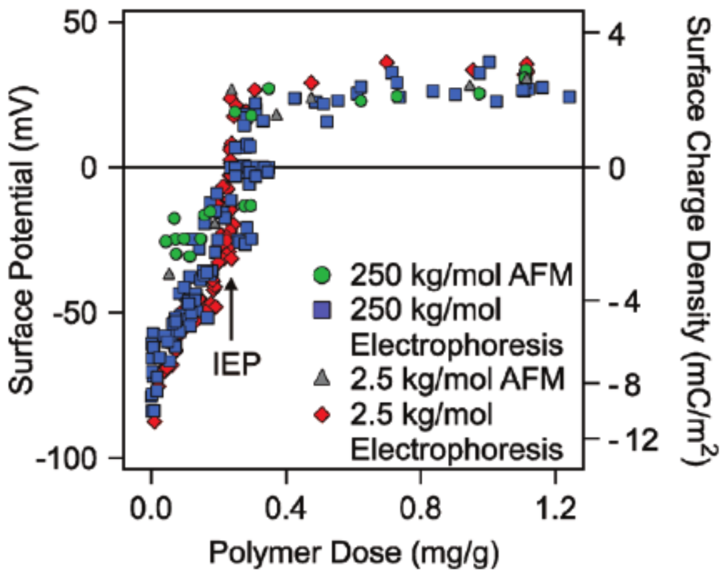
Electrostatics in the strong coupling regime

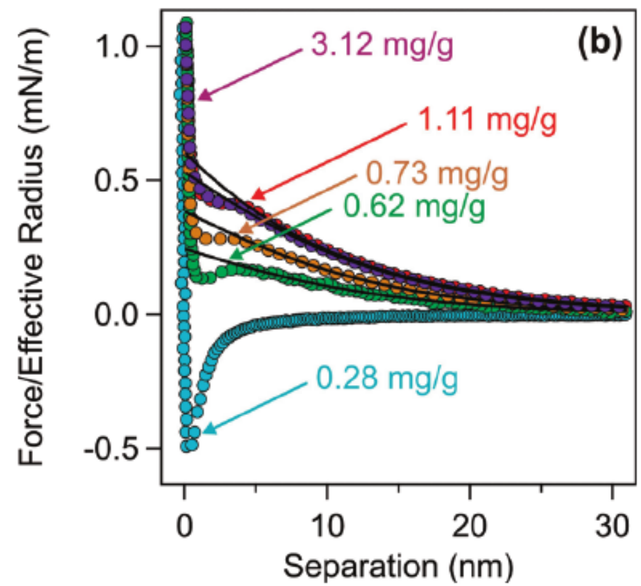
At large surface separation the interaction free energy can still be described with a DH like interaction potential but with renormalized parameters

$$w_{IJ}(R) \sim \frac{2\sigma_I^* \sigma_J^*}{\kappa E} e^{-\kappa R}, \qquad R \to \infty .$$

R. Kjellander, 'Dressed ion theory'

Sulphate latex in presence of poly(ethylene imine)



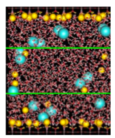


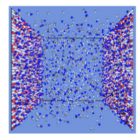
Coarse-graining →

Theories / Models

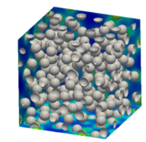
Explicit treatment of ions | Mean-field treatment of ions

QM

MD 

PM 

PB
MPB
DFT



DH

←

Interactions

?

Effective Yukawa ?

Dilute and dense (?):

Renormalized Yukawa

Dilute: Yukawa (DLVO)

Multipole solution

Dense: Effective Yukawa

← Confidence

Conclusions on the strong coupling regime

In this regime, charge fluctuations, also called ion-ion correlations, are important and lead to non classical electrostatic phenomena

- Multivalent counterions can more than simply compensate the bare charge of the colloids → overcharging (sign reversal of ζ)
- Overcharging increases with the magnitude of the bare charge of the colloids (σ) and the valence of the counterions (ν_i)
- Surface site ionization is facilitated → synergy between charge formation and overcharging

Conclusions on the strong coupling regime

In this regime, charge fluctuations, also called ion-ion correlations, are important and lead to non classical electrostatic phenomena

- Two equally charged colloids can attract each others due to correlation attraction
- The correlation attraction is short range ($\sim 1/r^6$) and increases with σ and ν_i
- In the far field, the mean electrostatic potential and colloidal interactions can still be described with a “renormalized” DH theory