Electrostatic Interactions in Confinement

Simulating soft matter across scales

TUHH
Technische
Universität
Hamburg

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CECAM Flagship School
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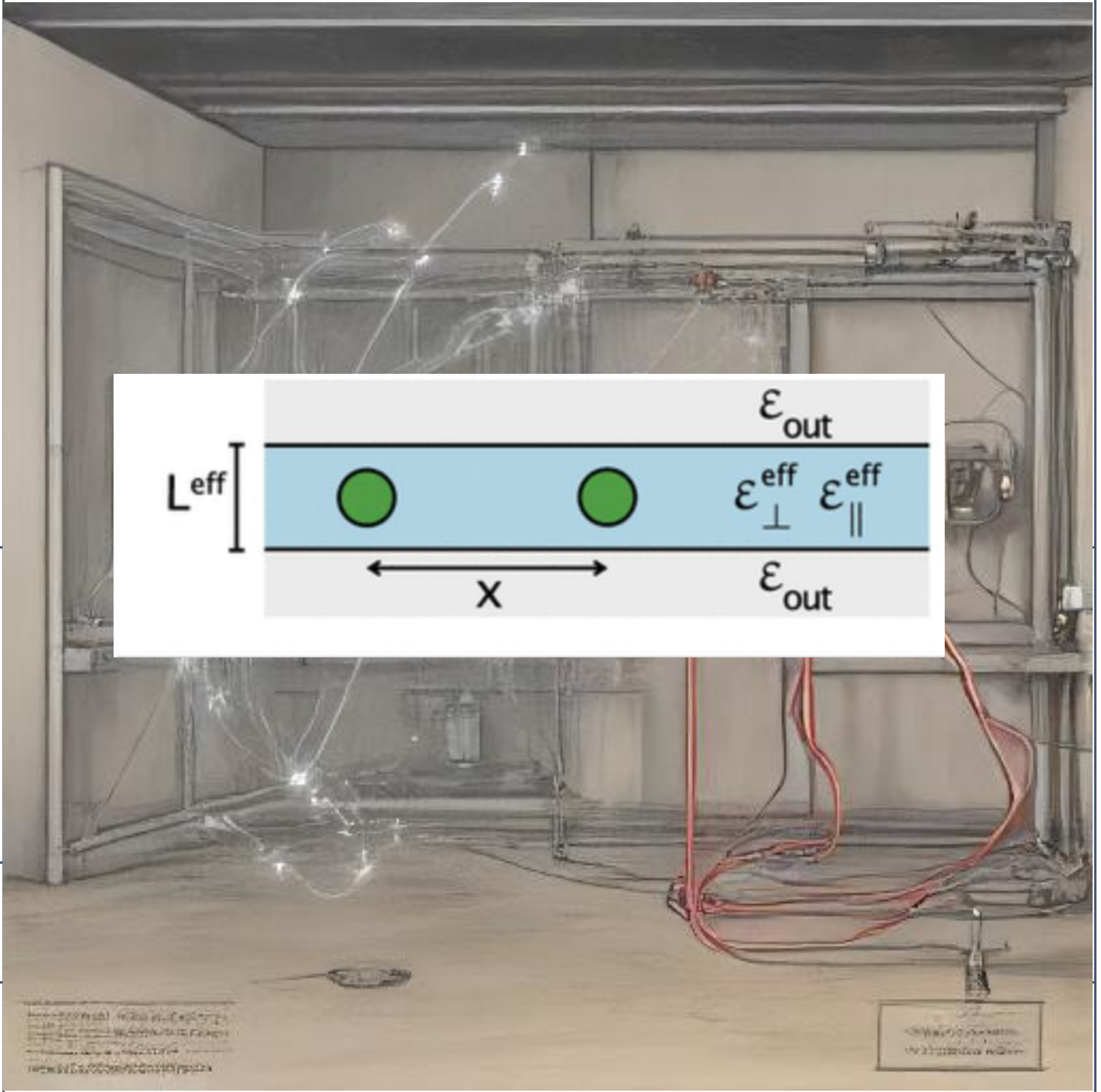
Institute for Atomistic Modeling of Materials in Aqueous Media

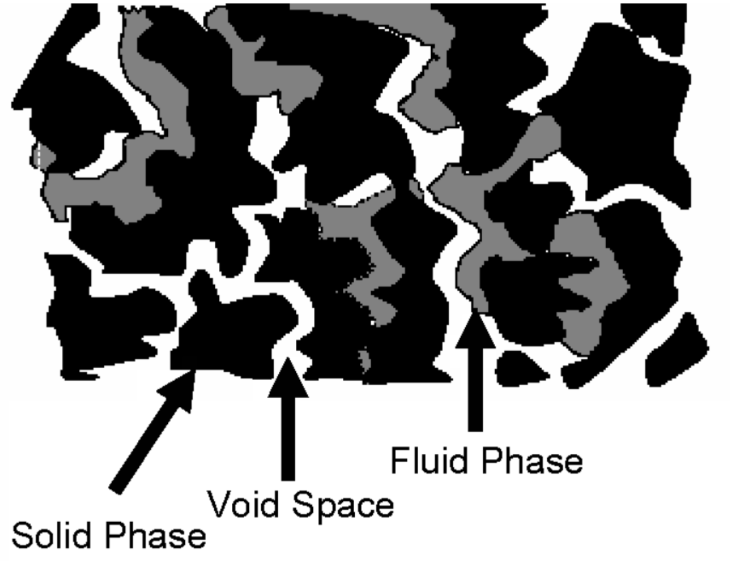
Alexander Schlaich



Confined Systems

A porous medium is a solid which contains an interconnected void space which is filled with one or more fluids. (Bear, 1990; Nield and Bejan, 1999)

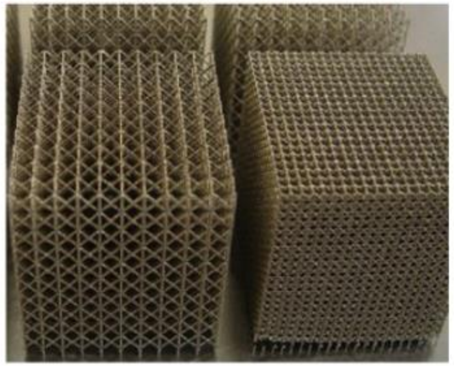
Naturally occurring porous media typically exhibit irregular geometry

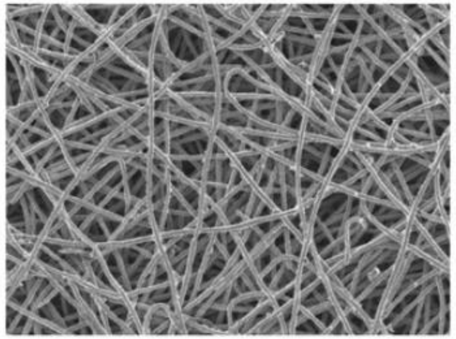



(a) porous sand


(b) honeycomb


(c) rocks with oil

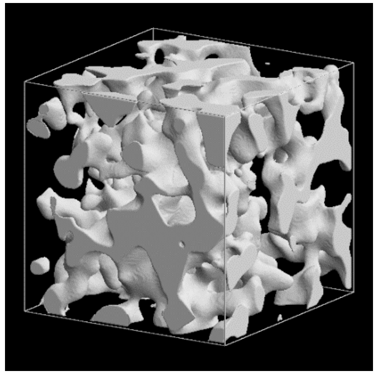

(d) lattice frame material


(e) metallic fiber


(f) metal foam

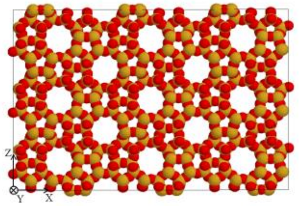
Porous materials

… a material that consists of solid domains and pore voids

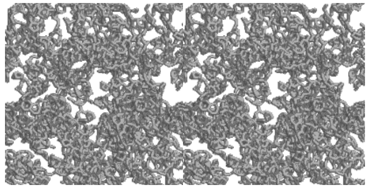


Courtesy of P. Levitz, reconstruction of Vycor

- **Large surface areas** (ex. ashes ~m^2/g) but much larger surfaces can be reached with zeolithes, activated carbon ~1000 m^2/g

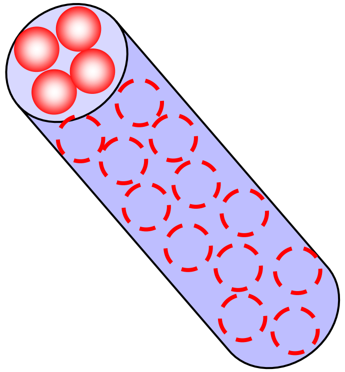


zeolite: aluminosilicate nanoporous crystal

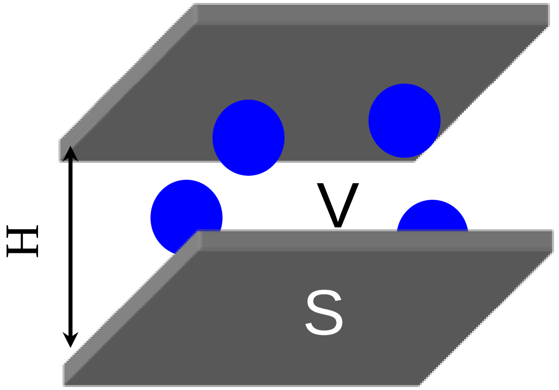


Activated carbon: a disordered porous carbon

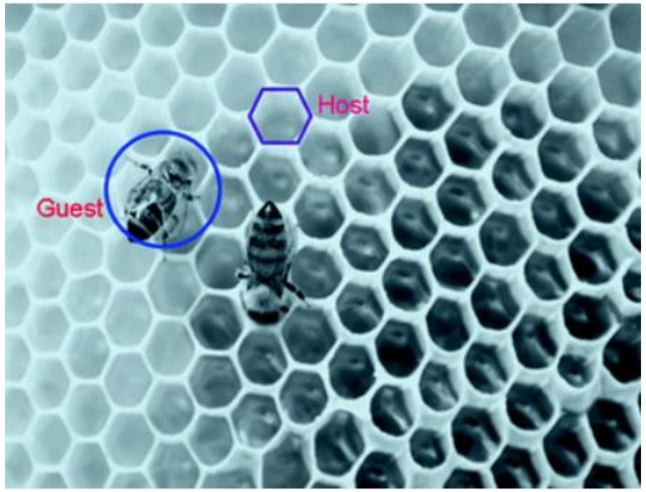
- **Confinement**
  - Both thermodynamics and dynamics of nanoconfined fluids are modified with respect to their bulk counterpart
  - New phenomena such as phase transitions driven by surface or confinement (ex: Kelvin equation)

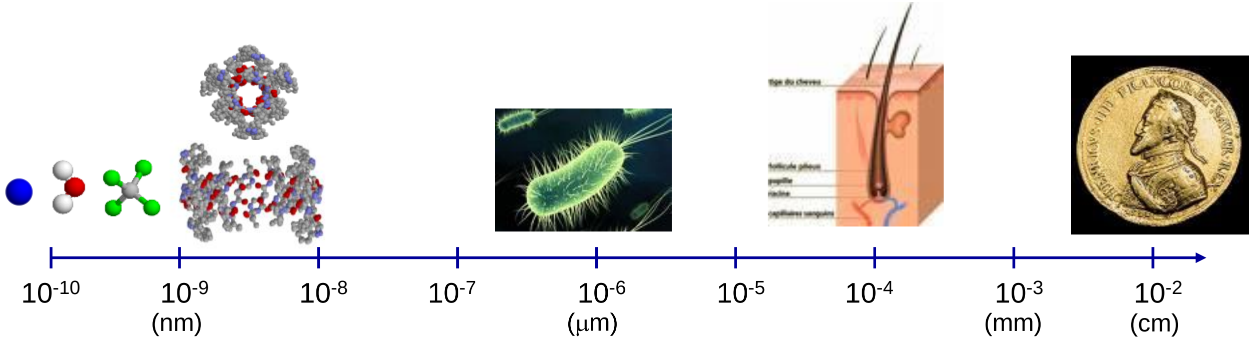


Length scales



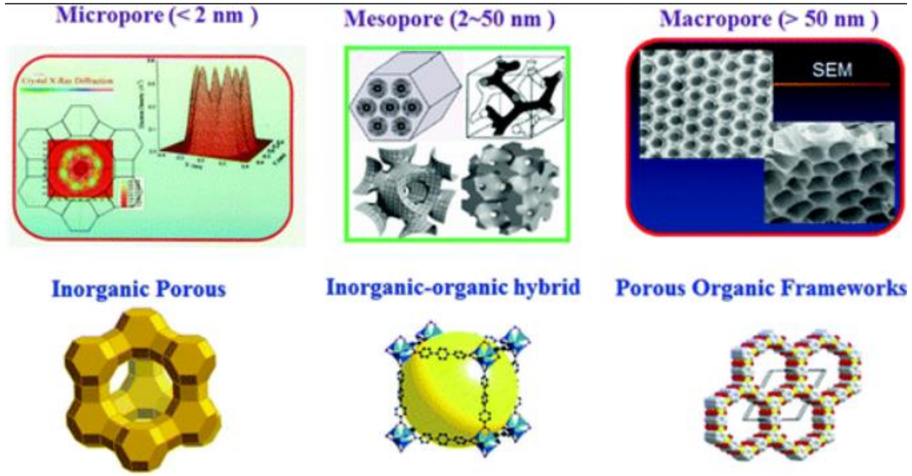
Independently of the pore morphology, decreasing the pore size H increases the surface to volume ratio S/V ~ 1/H





Nanoporous solids
(with one dimension ~ *nm*)
are of particular interest because D ~ ξ

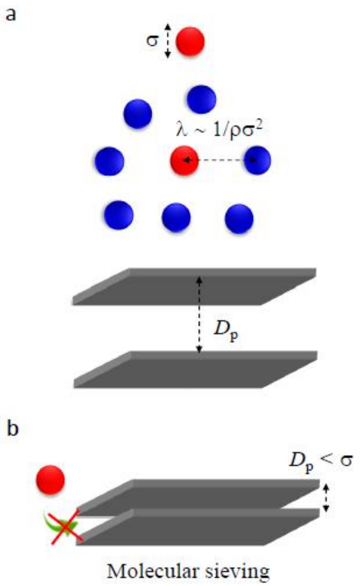
International Union of Pure and Applied Chemistry (IUPAC) classification



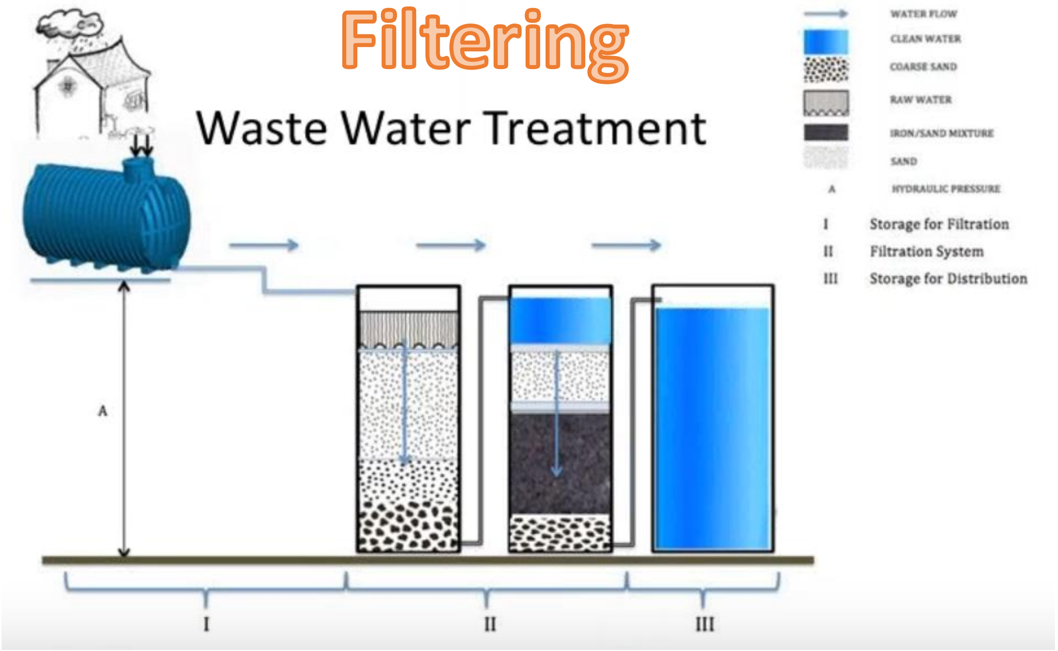
Industrial relevance

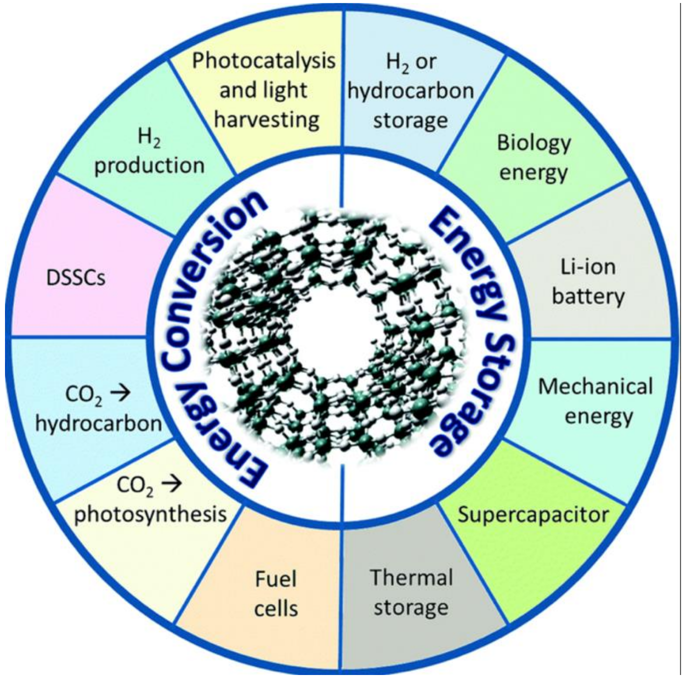
methane and hydrogen storage, air purification, decaffeination, gold purification, metal extraction, water purification, air filters, ...

Production & Storage

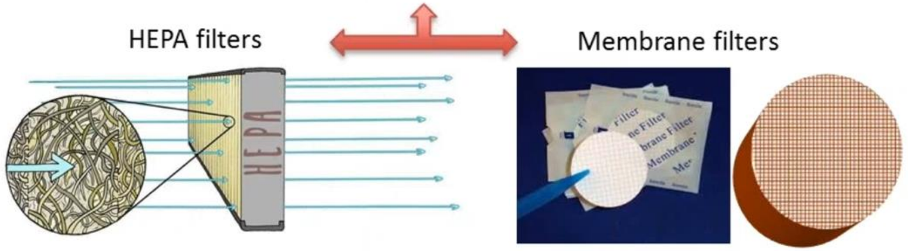


Filtering



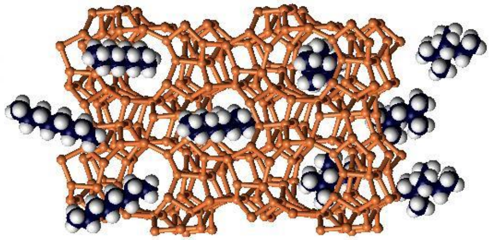


Sterile Products

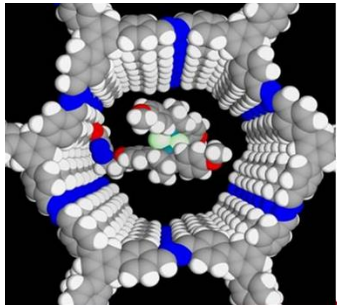


Catalysis

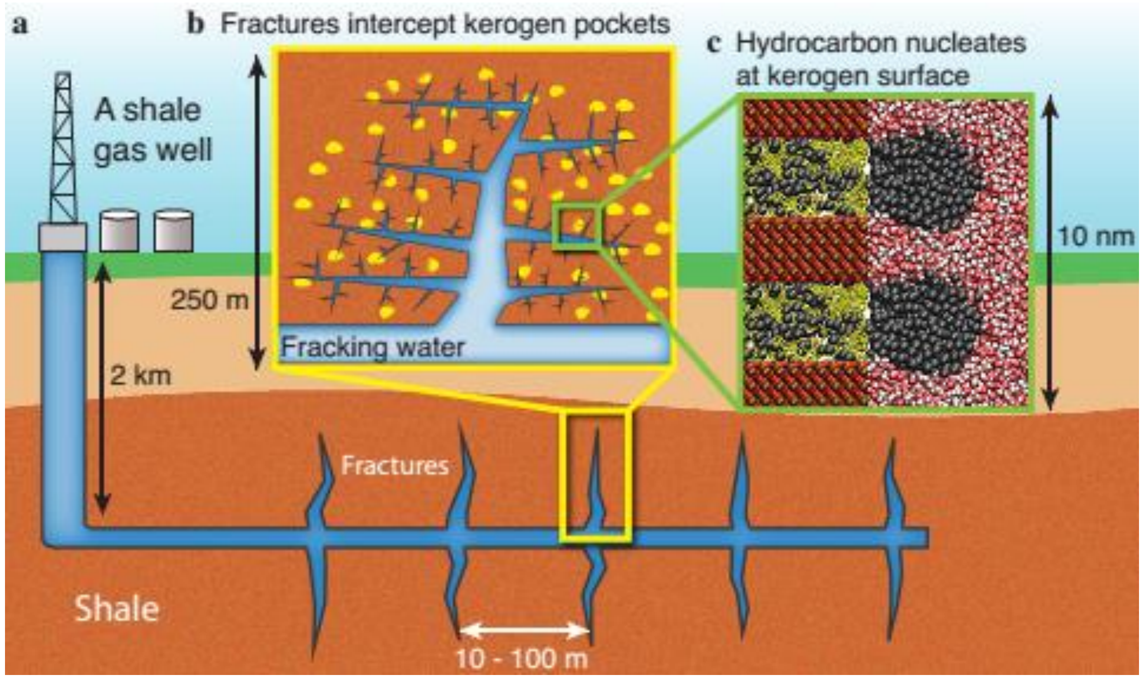
Catalytic Convertors



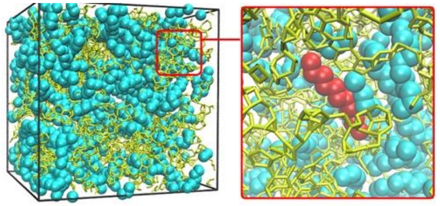
Cracking, isomerisation and hydrocarbon synthesis for oil industry, electrocatalysis, biomolecular rections



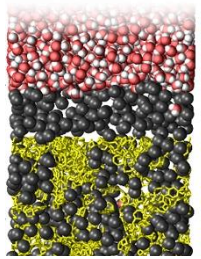
Multiscale physics: e.g. fracking



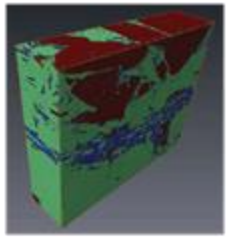
- Nanoporosity (nm):
  Kerogen is a nanoporous organic material filled with hydrocarbon
- Interfacial transport (10 nm)
  Hydrocarbon migrates from the intrinsic porosity of kerogen to the fracture network
- (> 100 nm) Transport in the fracture network to the surface of the well



~ nm



~ 10 nm



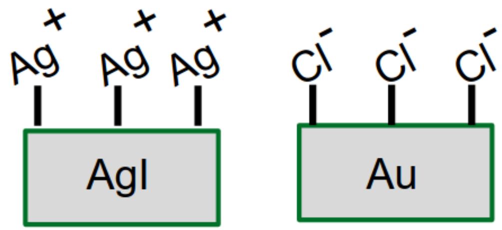
> 100 nm

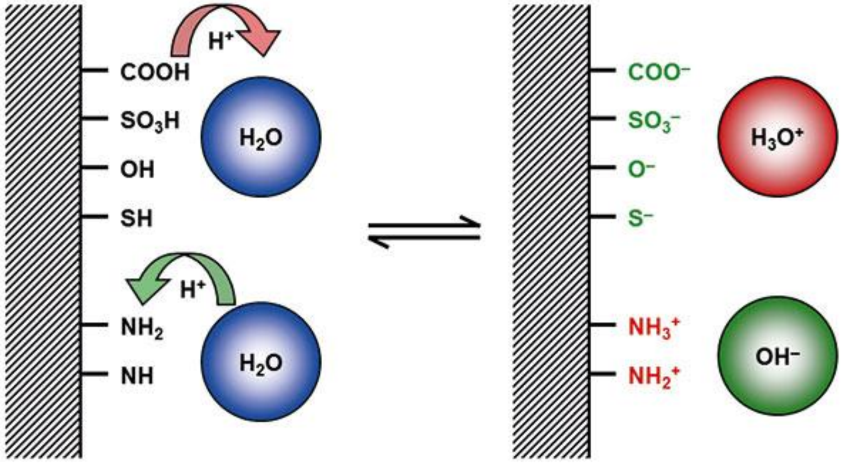
Length scales

Surface charges: interfaces

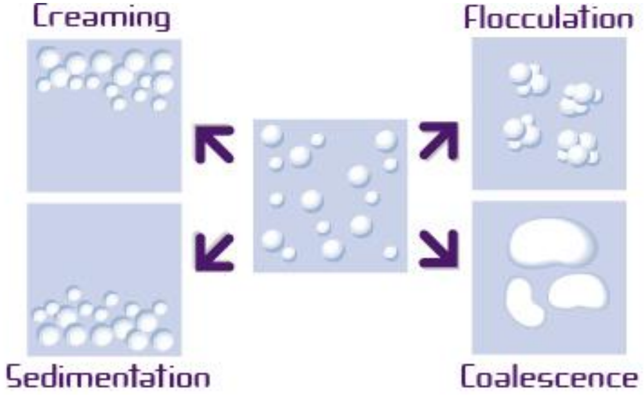
What is the origin of surface charges?

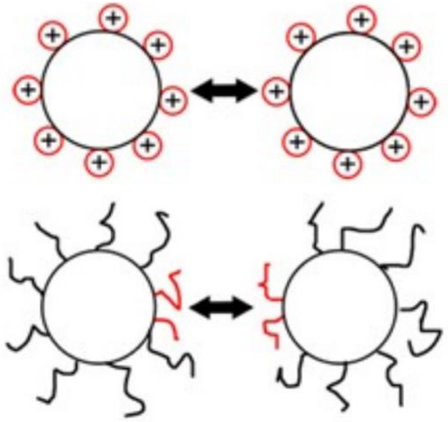
- Preferential adsorption of charges species
- Dissociation or ionization of surface groups





Driving force of colloidal stability and self-organization

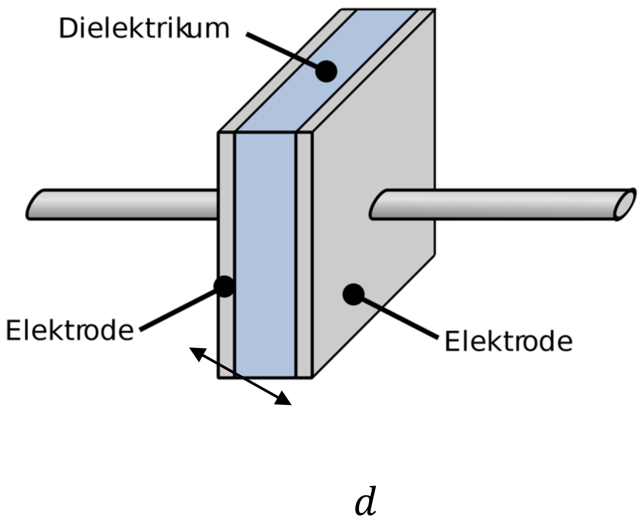




Electrostatic stabilization

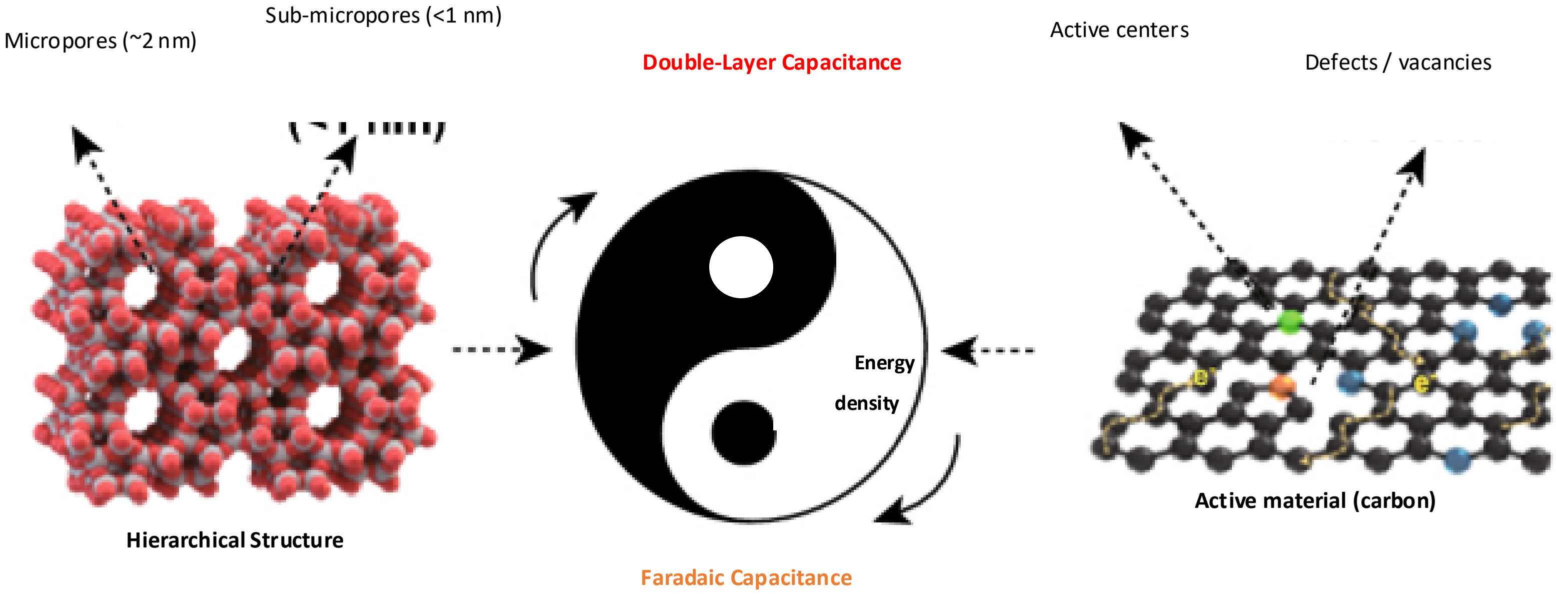
Steric stabilization

Electrodes



- Energy $W = \frac{1}{2} C U^2$
- Capacitance $C = \frac{\varepsilon_0 \varepsilon_r A}{d} = \frac{Q}{U}$
- Energy density $\frac{W}{V} = \frac{\frac{1}{2}\varepsilon_0 \varepsilon_r U^2}{d^2}$

[https://de.wiktionary.org/wiki/Plattenkondensator#/media/Datei:Plate_Capacitor_DE.svg]



- **Good** ionic transport
- **Efficient** pore structure

- **Good** electron transport
- **Reversible** redox reactions

Optimal energy density

Electrostatics in polarizable media: Maxwell equations

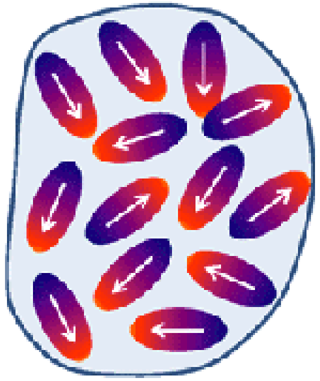
1st Maxwell equation in vacuum

$$\nabla \cdot \mathbf{E} = \frac{1}{\epsilon_o}\rho$$

$$\rho = \rho_f + \rho_b = \rho_f - \nabla \cdot \mathbf{P}$$

1st Maxwell equation in media:

$$\epsilon_o \nabla \cdot \mathbf{E} = \rho_f - \nabla \cdot \mathbf{P}$$



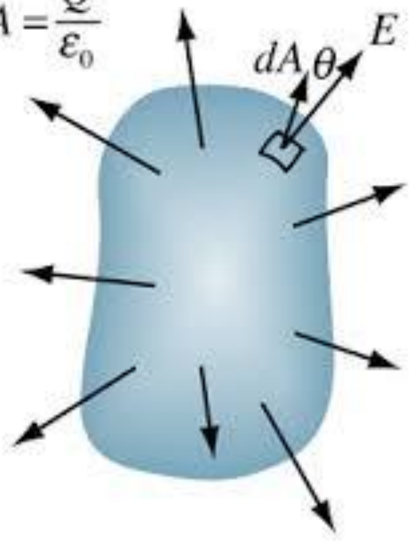
Polarizable medium:
Bound charge density

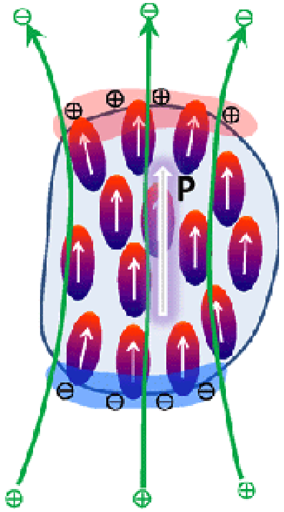
$$\rho_b = -\nabla \cdot \mathbf{P}$$

$\boldsymbol{P}$: polarization

Gauss' law

$$\oint \vec{E} \cdot \vec{dA} = \frac{Q}{\varepsilon_0}$$





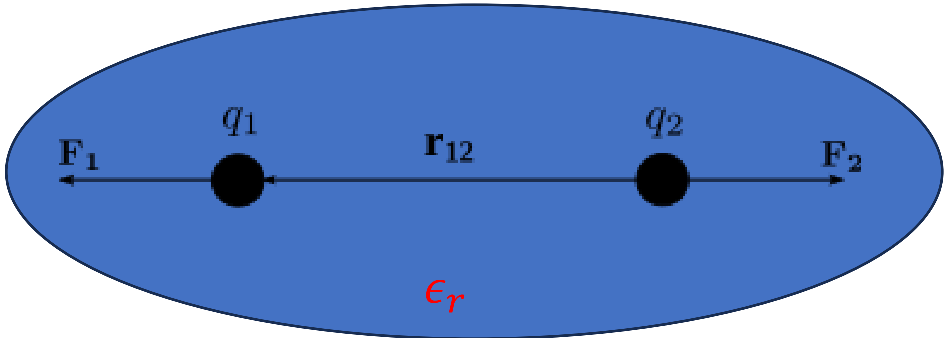
Define dielectric displacement field $\mathbf{D} = \epsilon_o \mathbf{E} + \mathbf{P}$: $\nabla \cdot \mathbf{D} = \rho_f$

How large is the polarization?
Linear relation in isotropic medium: $\boldsymbol{P} = \chi \epsilon_0 \boldsymbol{E}$

$\rightarrow \boldsymbol{D} = (1 + \chi)\epsilon_0 \boldsymbol{E} = \epsilon_r \epsilon_0 \boldsymbol{E}$

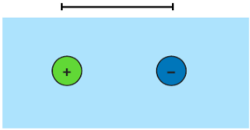
Electrostatic interactions are screened in polarizable media:

$$\boldsymbol{F}_1 = \frac{q_1 q_2}{4\pi \epsilon_r \epsilon_0} \frac{\hat{\boldsymbol{r}}_{12}}{|\boldsymbol{r}_{12}|^2}$$



CAVE: continuum picture!

Plate capacitor revisited…



Electrostatic Hamiltonian $$H_{\mathrm{el}} = \frac{1}{4\pi\varepsilon\varepsilon_0} \sum_{j=1}^{N} \sum_{i>j}^{N} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}$$

At interfaces dielectric constant is tensorial!

$$\varepsilon \rightarrow \hat{\boldsymbol{\varepsilon}} = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{xy} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{pmatrix}$$

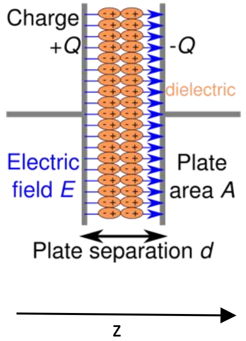
→ symmetry:

Local dielectric permittivity tensor $\varepsilon_{\|}, \varepsilon_{\perp}$

Maxwell equations:

$$\boxed{\begin{aligned} \nabla \cdot \mathbf{D}(z) &= \rho_f \\ \nabla \times \mathbf{E}(z) &= 0 \end{aligned}}$$

Parallel E-field is const.



Linear response:

$$\Delta D_{\|}(z) = \varepsilon_0 \varepsilon_{\|}(z) \Delta E_{\perp}$$

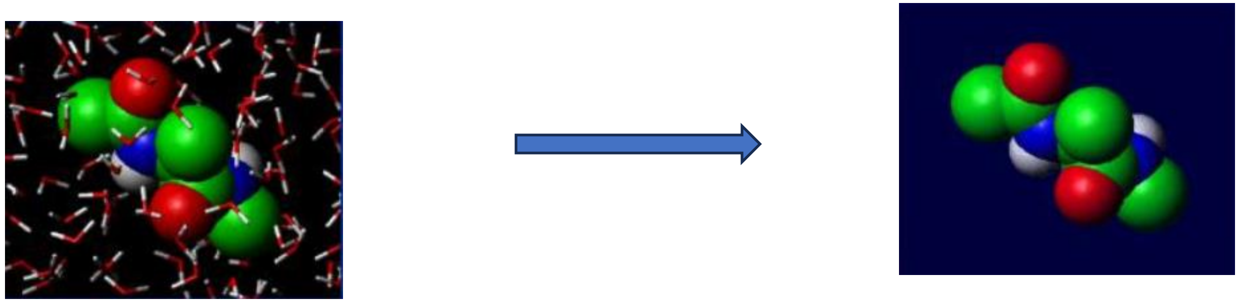
$$\Delta E_{\perp}(z) = \varepsilon_0^{-1} \varepsilon_{\perp}^{-1}(z) \Delta D_{\perp}$$

Perpendicular D-field is const. in absence of free charges

Fully consistent with non-local electrostatics!

Coarse-graining to the meso-scale: Implicit solvent

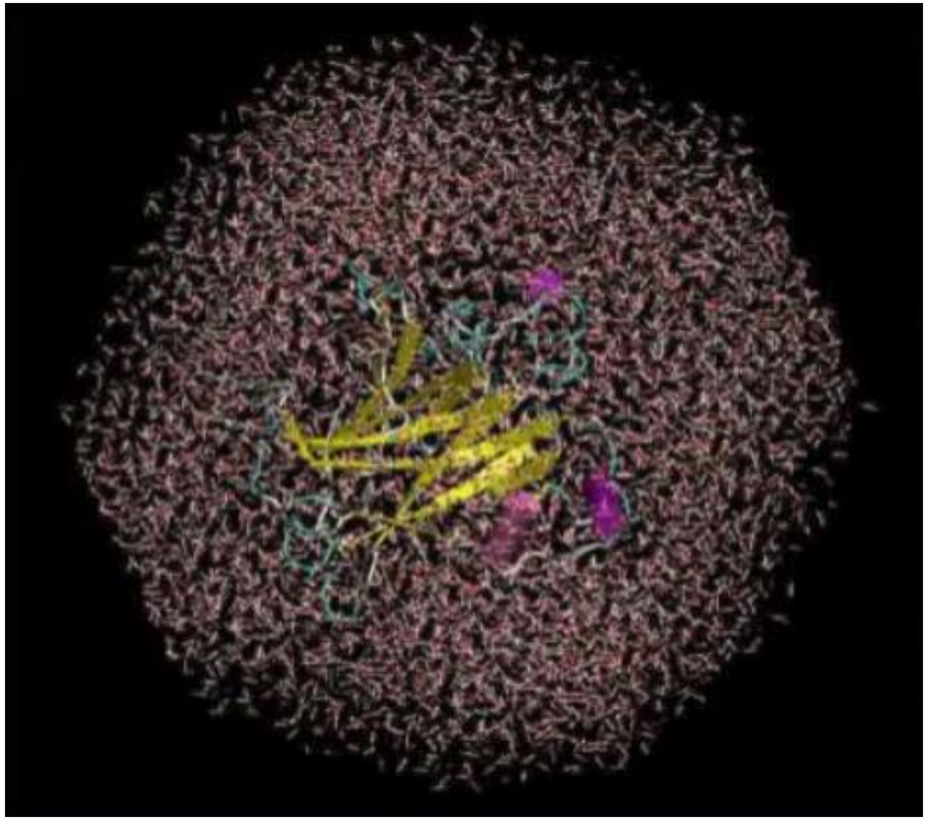
- Typical soft matter system: $> 10^6$ solvent molecules (water)
- Implicit solvent: Reduce phase space!



$$P(\mathbf{r}_u,\mathbf{r}_v)=\frac{\exp[-\beta U(\mathbf{r}_u,\mathbf{r}_v)]}{\int d\mathbf{r}_u d\mathbf{r}_v \exp[-\beta U(\mathbf{r}_u,\mathbf{r}_v)]}$$

$$\exp[-\beta W(\mathbf{r}_u)]=\int d\mathbf{r}_v \exp[-\beta U(\mathbf{r}_u,\mathbf{r}_v)]$$

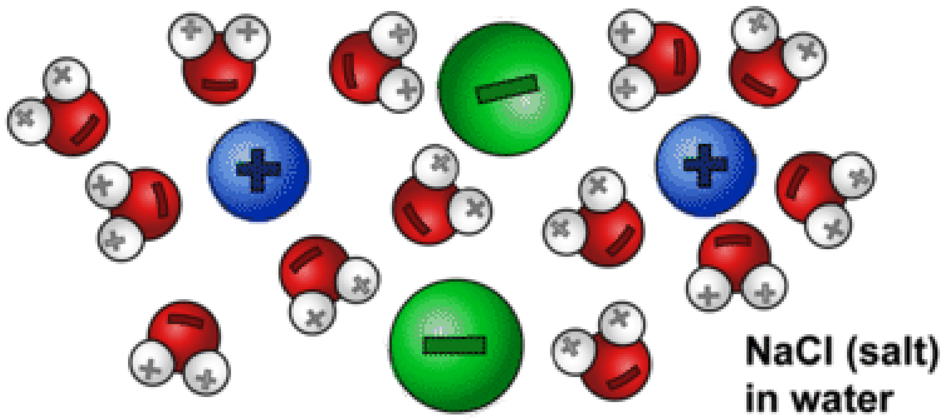
$$P(\mathbf{r}_u)=\frac{\exp[-\beta W(\mathbf{r}_u)]}{\int d\mathbf{r}_u \exp[-\beta W(\mathbf{r}_u)]}$$



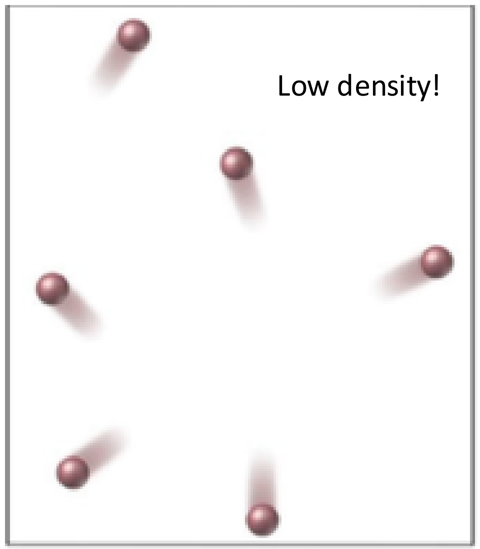
- Homogeneous, isotropic and structureless solvent

<u>Meso-scale</u>: A length- or time-scale for which all degrees of freedom on smaller scales can be considered to be in equilibrium (no relevant processes on smaller scales for the evolution on the meso-scale).

Statistical Mechanics



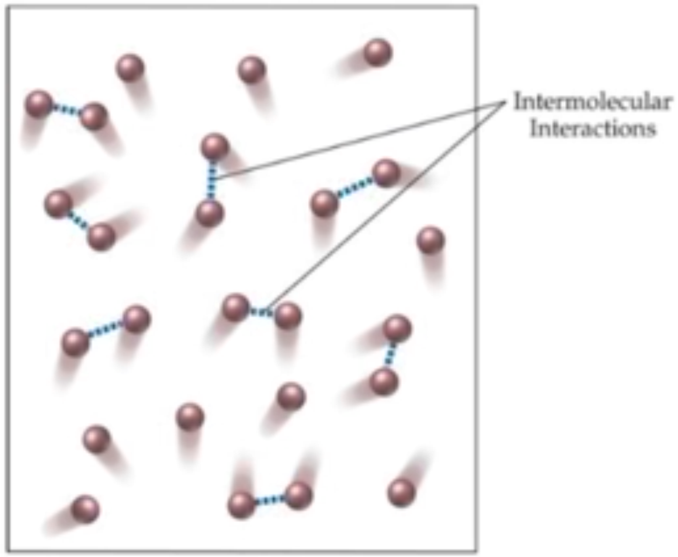
Ideal gas: non-interacting particles



Implicit solvent ✅
But how about the salt?

Poor physicists approach: Ideal gas

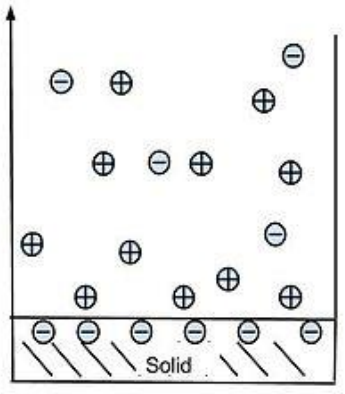
Real gas



Mean-field approach

Effective interaction such that the potential of mean-force is reproduced:

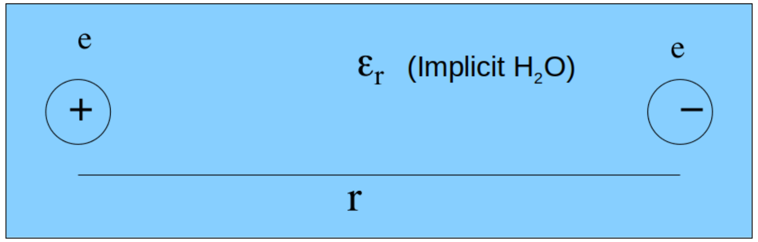
$$c_i = c_i^0 \cdot e^{\frac{-W_i}{k_B T}}$$



c_i: ion concentration in the bulk
W_i: work required to move an ion closer to the surface from an infinitely far distance

Coarse-graining electrostatic interactions

- Treat the solvent (water) implicitly via dielectric background (ϵ_r)
- Assume point-charges (valency *z*) with no other interactions than the electrostatic ones
- In general: Minimize the Gibbs free energy (**challenging!**)



Coulomb energy

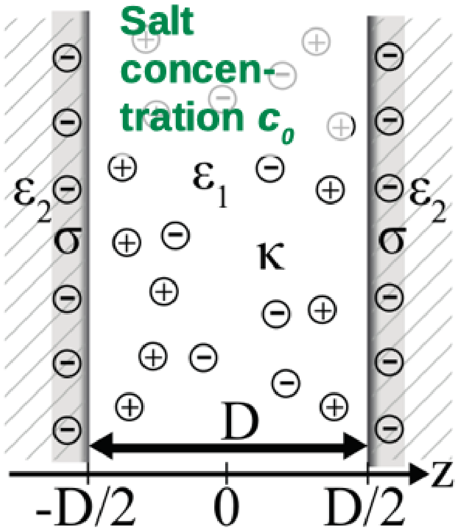
$$\frac{1}{4\pi\epsilon_0\epsilon_r}\frac{q_1 q_2}{|r_1 - r_2|} = k_B T\, \ell_B \frac{1}{|r_1 - r_2|}$$

- Bjerrum length $\ell_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}$: electrostatic prefactor
- Thermal energy $k_B T$: energy scale
- Often: $\epsilon = \epsilon_0\epsilon_r$

$$\mathcal{F} = \frac{1}{2}\iint \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \frac{1}{4\pi\varepsilon}\frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + k_B T \int \mathrm{d}\boldsymbol{r} \left[c_+(\boldsymbol{r})\left(\ln\frac{c_+(\boldsymbol{r})}{c_0} - 1\right) + c_-(\boldsymbol{r})\left(\ln\frac{c_-(\boldsymbol{r})}{c_0} - 1\right) + 2c_0 \right]$$

Electrostatic interactions

Ideal gas free energy



- Mean-field approach: Each charge only feels the mean potential

$$\phi(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}' \frac{1}{4\pi\varepsilon}\frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

- Minimize free energy → Boltzmann distribution $c_\pm(\mathbf{r}) = c_0 \mathrm{e}^{\mp\frac{e v_\pm \phi(\mathbf{r})}{k_B T}}$

Poisson-Boltzmann theory

Mean potential $\phi(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}' \, \frac{1}{4\pi\varepsilon} \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$, insert to Bolltzmann distribution $c_\pm(\mathbf{r}) = c_0 \mathrm{e}^{\mp \frac{e v_\pm \phi(\mathbf{r})}{k_\mathrm{B}T}}$

→ Insert to Poisson’s equation: $\nabla^2\phi = -\rho/\varepsilon$

$$\boxed{\varepsilon\nabla^2\phi = -\rho(\mathbf{r}) = -ec_0\left(\mathrm{e}^{-\frac{v_- e\phi(\mathbf{r})}{k_\mathrm{B}T}} - \mathrm{e}^{+\frac{v_+ e\phi(\mathbf{r})}{k_\mathrm{B}T}}\right) - \rho_\mathrm{f}(\mathbf{r})}$$

Fixed charge distribution
(~ surface charge)

Poisson Boltzmann equation
(for species of valency $\nu_\pm$)

- Point-like ions: No excluded volume
- Mean-field: no correlations between charges (fails typically for valency *v*>1)
- 2nd order partial differential equation: closed solution only for few simple geometries (planar walls, cylinders, …)
- Many extensions: Finite-sized ions, dielectric effects, correlations, ...

1:1 electrolyte: $v_- = v_+ = v = 1$ reduced potential: $\varphi(\mathbf{r}) = \frac{e\phi}{k_\mathrm{B}T}$

$$\boxed{\nabla^2\varphi(\mathbf{r}) = \kappa^2 \sinh\varphi(\mathbf{r}) - \frac{e\rho_\mathrm{f}(\mathbf{r})}{\varepsilon k_\mathrm{B}T}}$$

with $\kappa^2 = 2e^2c_0/\varepsilon k_\mathrm{B}T$

Semi-infinite charged plate: Gouy-Chapman theory

Consider semi-infinite plane with surface charge density $\sigma > 0$ and neutralizing counterions of valence v ("salt-free") in half-space $x > 0$ (Gouy [1910] and Chapman [1913]).

1d PB equation: $\psi''(x) = \frac{ve_0}{\epsilon} n(0)\, \mathrm{e}^{\beta e_0 v \psi(x)}$

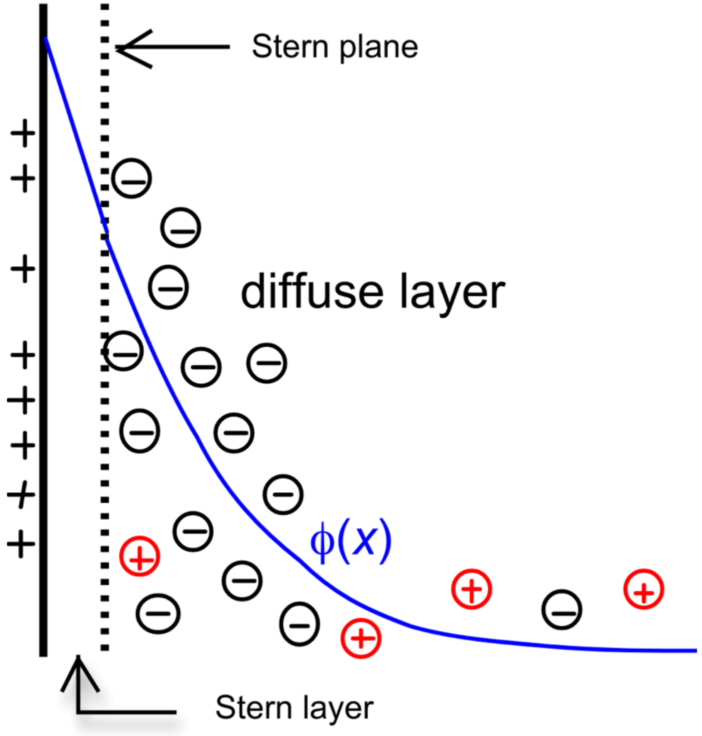
Boundary conditions: $\psi'(0) = -\frac{\sigma}{\epsilon} \qquad \lim_{x\to\infty} \psi'(x) = 0$

Is solved by: $y(x) = \beta e_0 v \psi(x) = -2 \ln\left(1 + \frac{x}{\lambda_{GC}}\right)$

With the Gouy-Chapman length $\lambda_{GC} := \frac{e_0}{2\pi \ell_\mathrm{B} v \sigma}$

Ion density *n*(*x*) and the integrated ion distribution *P*(*x*) then directly follow as

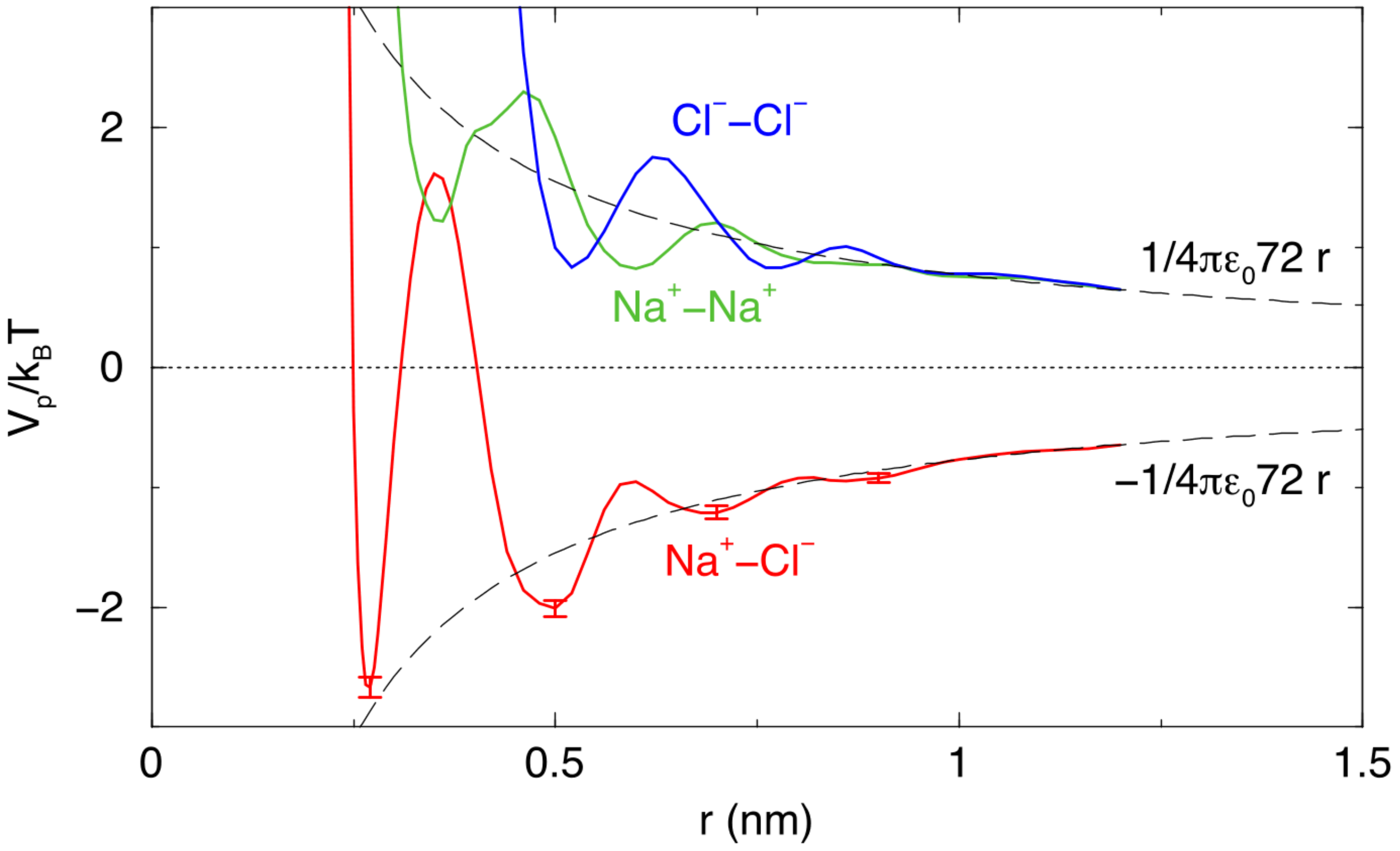
$n(x) = \frac{(2\pi\ell_\mathrm{B} v^2)^{-1}}{(x+\lambda_{GC})^2}$ and $P(x) = \frac{ve_0}{\sigma}\int_0^x \mathrm{d}\bar{x}\; n(\bar{x}) = 1 - \left(1 + \frac{x}{\lambda_{GC}}\right)^{-1}$



Note that $P(\lambda_\mathrm{GC})$=1/2: strong ion localization!
Motivation for Stern layer to describe surface capacitance (later refined by Grahame and many others).

How good is the implicit solvent approximation?

- Na-Cl ion pair in water
- 1000 explicit SPC water molecules



Linearization: Debye-Hückel

$$\nabla^2\varphi(\mathbf{r}) = \kappa^2 \sinh\varphi(\mathbf{r}) - \frac{e\rho_\mathrm{f}(\mathbf{r})}{\varepsilon k_\mathrm{B}T} \approx \kappa^2\varphi(\mathbf{r}) - \frac{e\rho_\mathrm{f}(\mathbf{r})}{\varepsilon k_\mathrm{B}T}$$

- Valid for $\varphi < 1$: $e\phi < k_\mathrm{B}T$
- Exponentially screened solution: $\varphi(r) = A\mathrm{e}^{-\kappa r}$

where $\boxed{\kappa^{-1} = \lambda_\mathrm{D} = \sqrt{\frac{\varepsilon k_\mathrm{B}T}{2e^2c_0}}}$ **Debye screening length**

(~range of electrostatic interactions in the salt)

- Dependence on salt concentration: $\sim \frac{1}{\sqrt{c_0}}$
- 3 Å for 1 Mol NaCl in water
- 10 Å for 100 mMol (1:1) salt → physiological conditions
- 1 µm for pure water ($c_0 \approx 10^{-7}$Mol due to auto-ionization of water 2 H2O → OH- + H3O+)

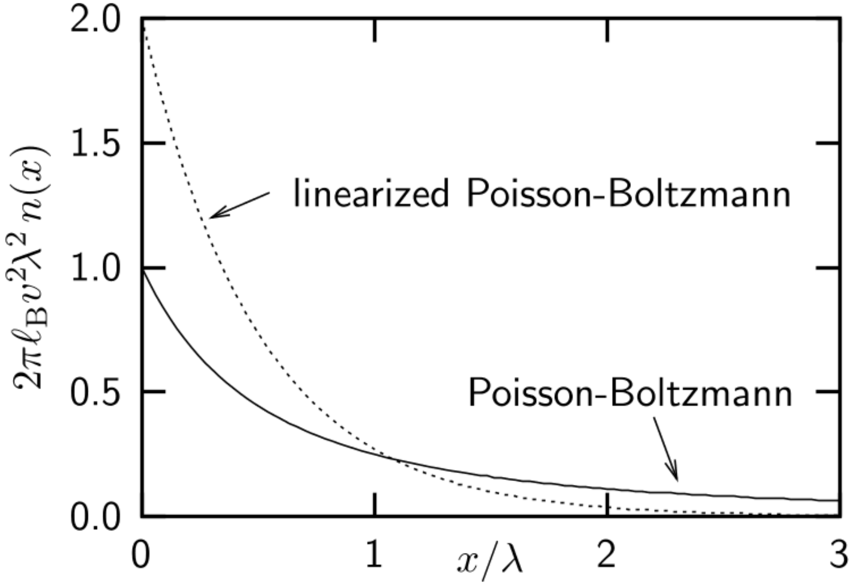
Linearized Gouy—Chapman theory

Within the linearized Poisson-Boltzmann equation the solution for the semi-infinite plane reads

$$y(x) = \mathrm{e}^{-2x/\lambda_{GC}} - 1$$

and the ion distribution

$$n(x) = \frac{1}{\pi \ell_{\mathrm{B}} v^2 \lambda_{GC}^2}\,\mathrm{e}^{-2x/\lambda_{GC}}.$$



→ Exponential rather than algebraic decay!

Overestimates contact density n(0) by a factor two independent of the surface charge density *σ*.

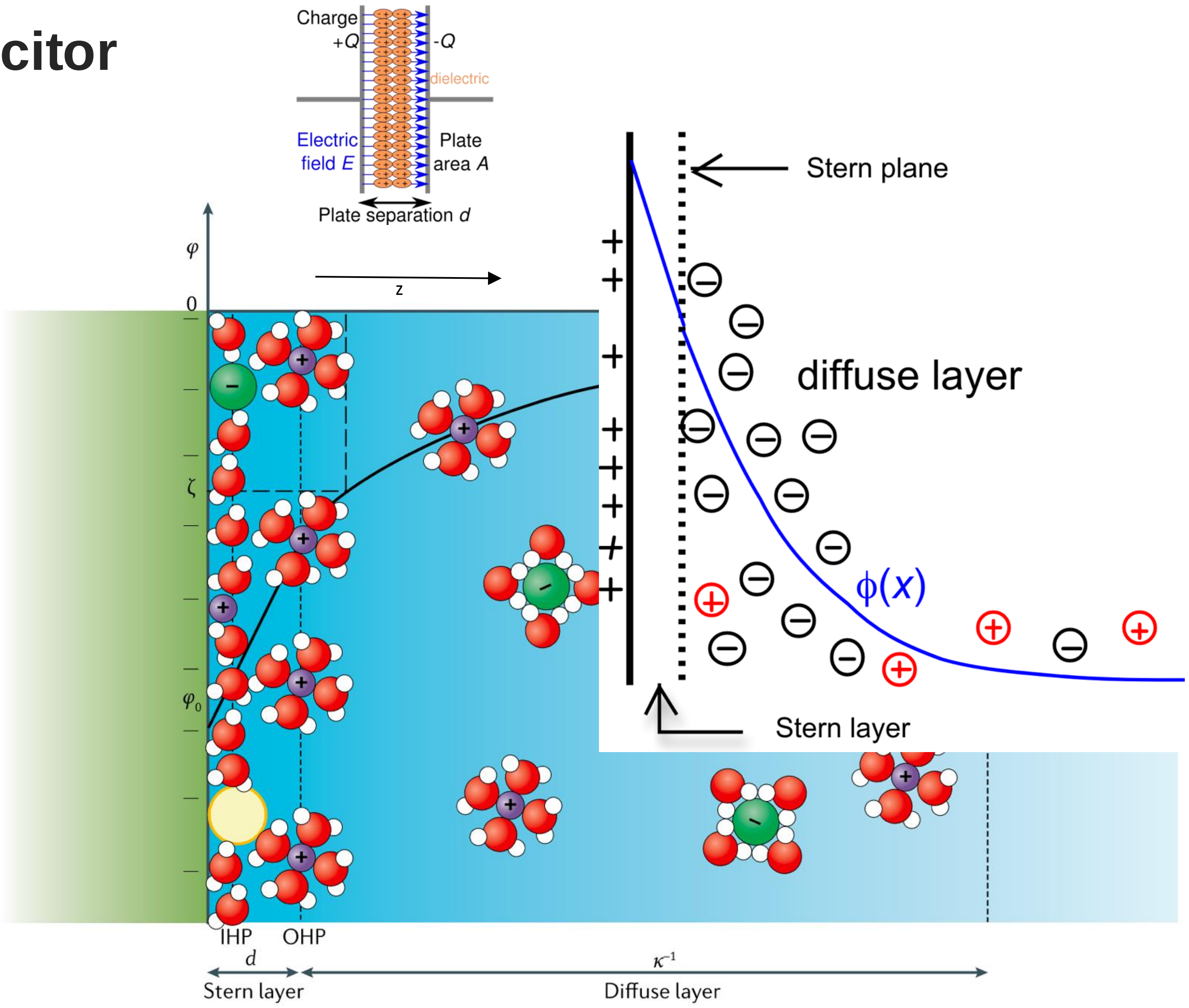
Thus, the linearized PB theory in the salt-free case fails already atarbitrarily small *σ*.

The electric double layer capacitor

Gouy–Chapman–Stern model:

- monolayer of solvent molecules forms the inner Helmholtz plate (IHP)
- Counter-charge is strongly localized within the outer Helmholtz plate (OHP): Stern layer

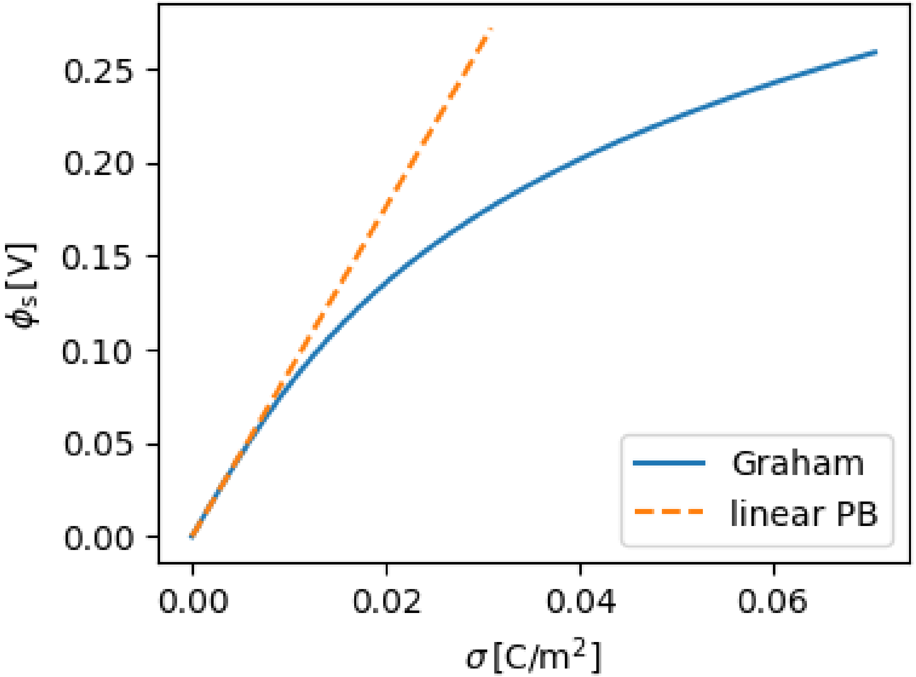
- In general no closed solution, interfacial details
  <u>but</u> within Gouy-Chapman (Counter-ions only, i.e. no added salt):
  - ➢ At large distances from the interface the electric field vanishes
  - ➢ Use additivity of electrostatic potentials, seperation D between plates:
    $\phi(z) = \phi_1(z) + \phi_2(D - z)$

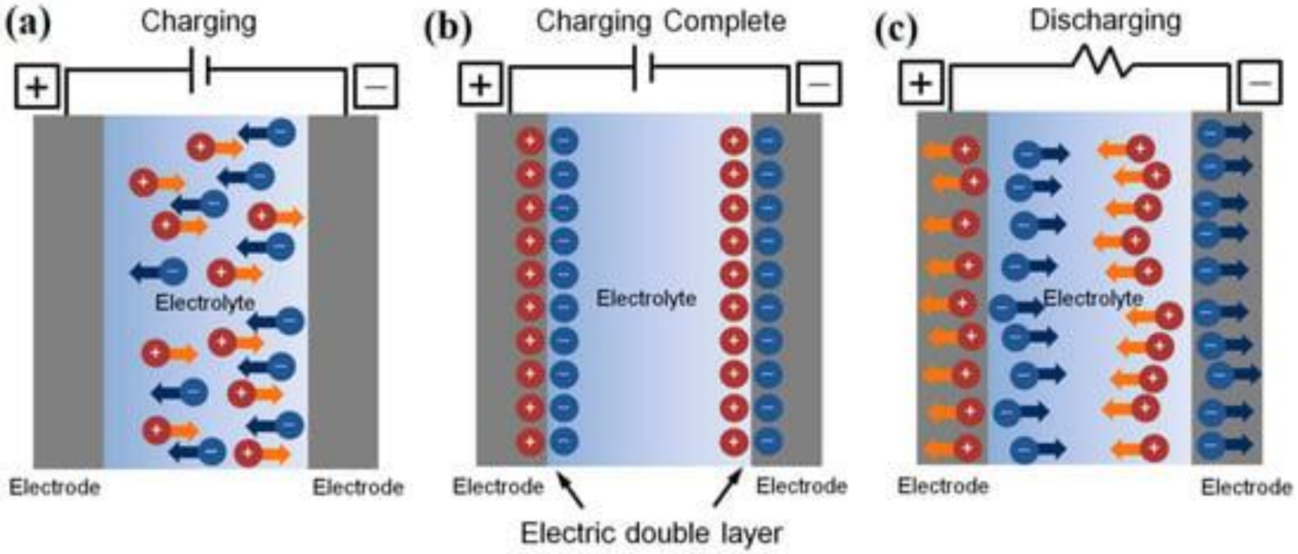


Differential capacitance

Characteristic parameter for efficiency of energy storage:

$$C_{\mathrm{diff}} = \frac{\mathrm{d}\sigma}{d\phi}$$





Liu, Chen, Wan, *Sensors* **2019**, *19* (15), 3425.

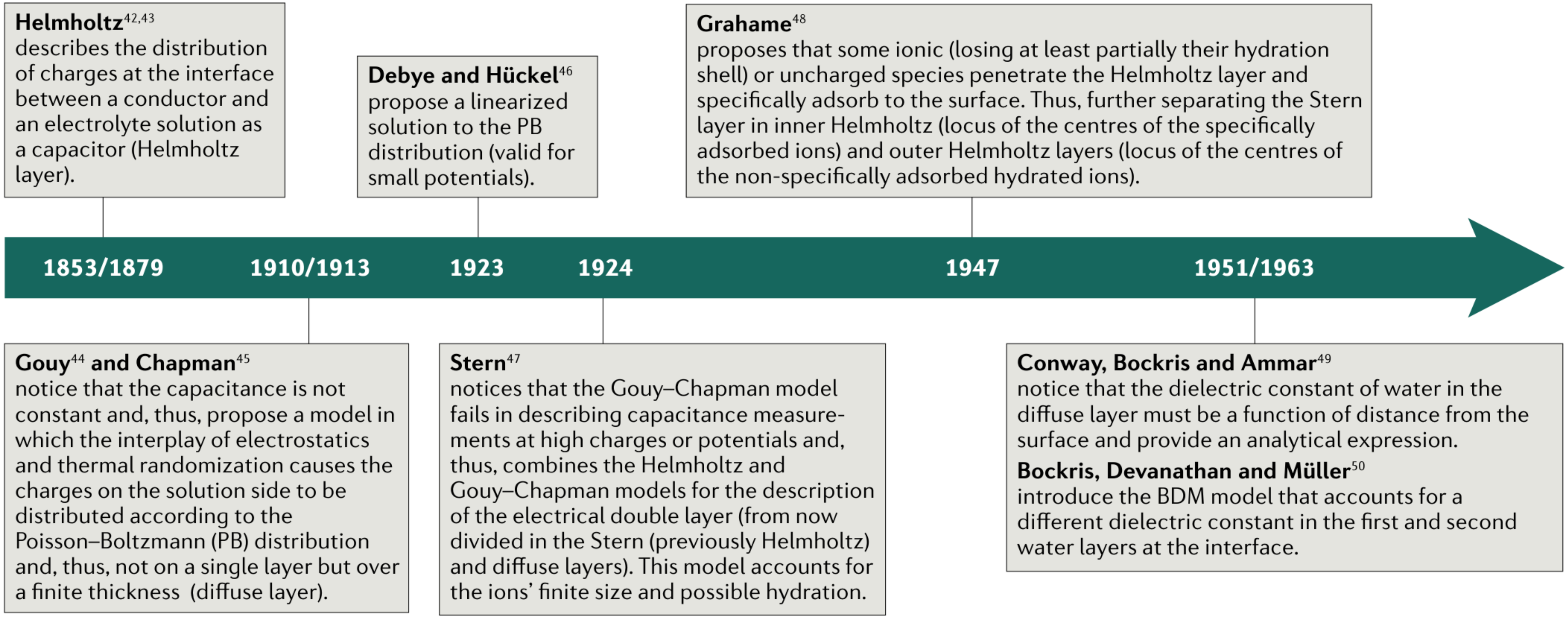
Within Gouy-Chapman theory (Graham equation):

$$\sigma = \sqrt{8c_0\epsilon_0\epsilon_r k_{\mathrm{B}}T}\,\sinh\left(\frac{ze\phi_{\mathrm{s}}}{2k_{\mathrm{B}}T}\right)$$

Linearization:

$$\sigma = \frac{\epsilon_0\epsilon_r\phi_{\mathrm{s}}}{\lambda_{\mathrm{D}}}$$

The electric double layer capacitor: History



1853/1879

Helmholtz[42,43]
describes the distribution of charges at the interface between a conductor and an electrolyte solution as a capacitor (Helmholtz layer).

1910/1913

Gouy[44] **and Chapman**[45]
notice that the capacitance is not constant and, thus, propose a model in which the interplay of electrostatics and thermal randomization causes the charges on the solution side to be distributed according to the Poisson–Boltzmann (PB) distribution and, thus, not on a single layer but over a finite thickness (diffuse layer).

1923

Debye and Hückel[46]
propose a linearized solution to the PB distribution (valid for small potentials).

1924

Stern[47]
notices that the Gouy–Chapman model fails in describing capacitance measurements at high charges or potentials and, thus, combines the Helmholtz and Gouy–Chapman models for the description of the electrical double layer (from now divided in the Stern (previously Helmholtz) and diffuse layers). This model accounts for the ions' finite size and possible hydration.

1947

Grahame[48]
proposes that some ionic (losing at least partially their hydration shell) or uncharged species penetrate the Helmholtz layer and specifically adsorb to the surface. Thus, further separating the Stern layer in inner Helmholtz (locus of the centres of the specifically adsorbed ions) and outer Helmholtz layers (locus of the centres of the non-specifically adsorbed hydrated ions).

1951/1963

Conway, Bockris and Ammar[49]
notice that the dielectric constant of water in the diffuse layer must be a function of distance from the surface and provide an analytical expression.

Bockris, Devanathan and Müller[50]
introduce the BDM model that accounts for a different dielectric constant in the first and second water layers at the interface.

Gonella, Backus, Nagata, Bonthuis, Loche, Schlaich, Netz, Kühnle, McCrum, Koper, Wolf, Winter, Meijer, Campen, Bonn, *Nat Rev Chem* **2021**, 1–20

DLVO theory

Attractive/repulsive force balance explains colloidal stability

- Screened electrostatic repulsion / double layer forces (Yukawa potential)

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

Derjaugin approximation: $a \to \infty$

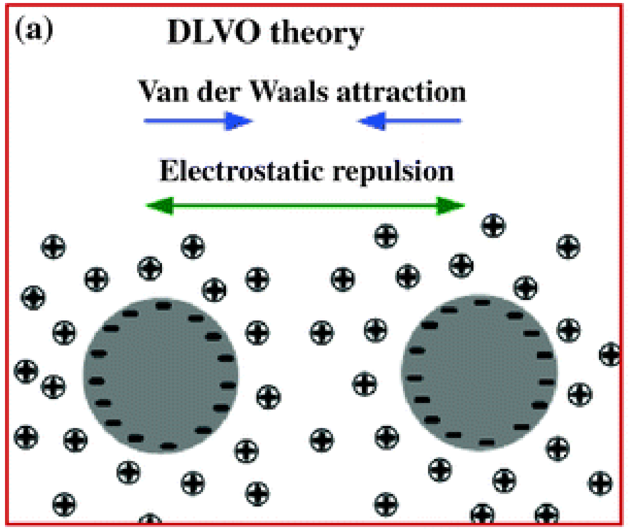
- Van der Waals (vdW) forces due to induced dipole interactions

$$U(r; R_1, R_2) = -\frac{A R_1 R_2}{(R_1 + R_2) 6r}$$

(R_1, R_2): radii of colloids, A: Hamaker constant)

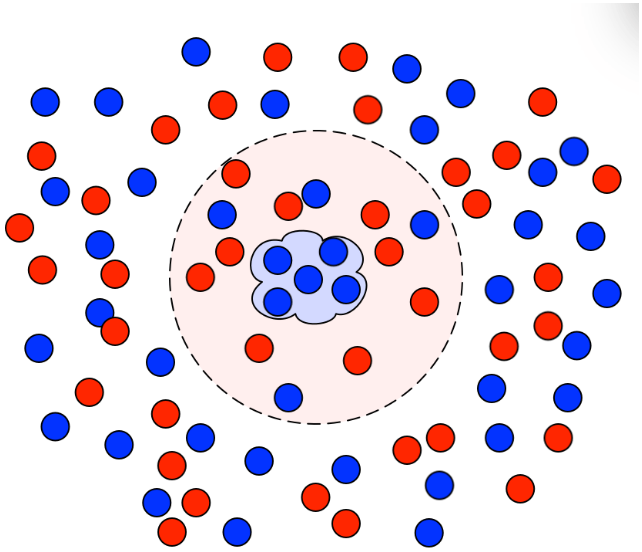
- In simulations typically a short-range repulsion is included (Pauli exclusion):

  Lennard-Jones or Buckingham potentials



Complex systems: The cell model

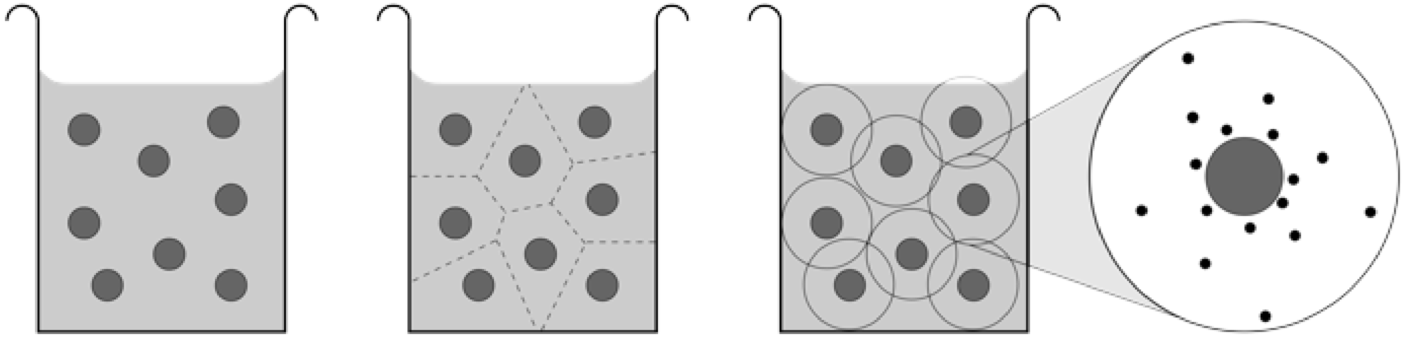
- Consider colloidal-like problem: sphere of radius a and effective charge Z_{eff}

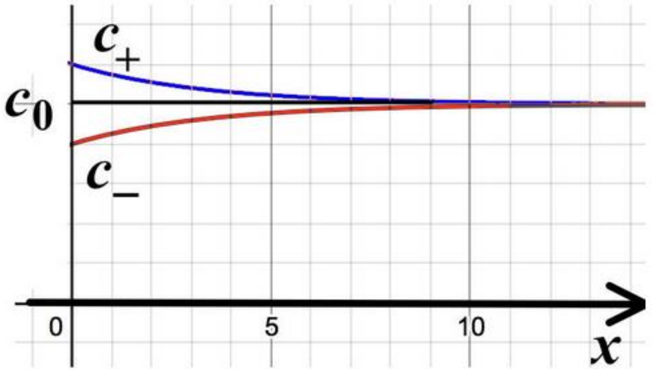


$$V_{\mathrm{DLVO}}(x) = Z_{\mathrm{eff}}^2 \ell_B \left(\frac{e^{\kappa_{\mathrm{eff}} a}}{1 + \kappa_{\mathrm{eff}} a} \right)^2 \frac{e^{\kappa_{\mathrm{eff}} x}}{x}$$

- **DLVO (Derjaugin, Landau, Verwey, Overbeek) theory:** Heart of colloidal stability!
- Exact within the limits of linearized PB theory!

Debye screening length $\lambda_{\mathrm{D}} = \kappa^{-1} = \left(4\pi\, \ell_{\mathrm{B}} \sum_{j=1}^{N} c_j^0\right)^{-\frac{1}{2}}$

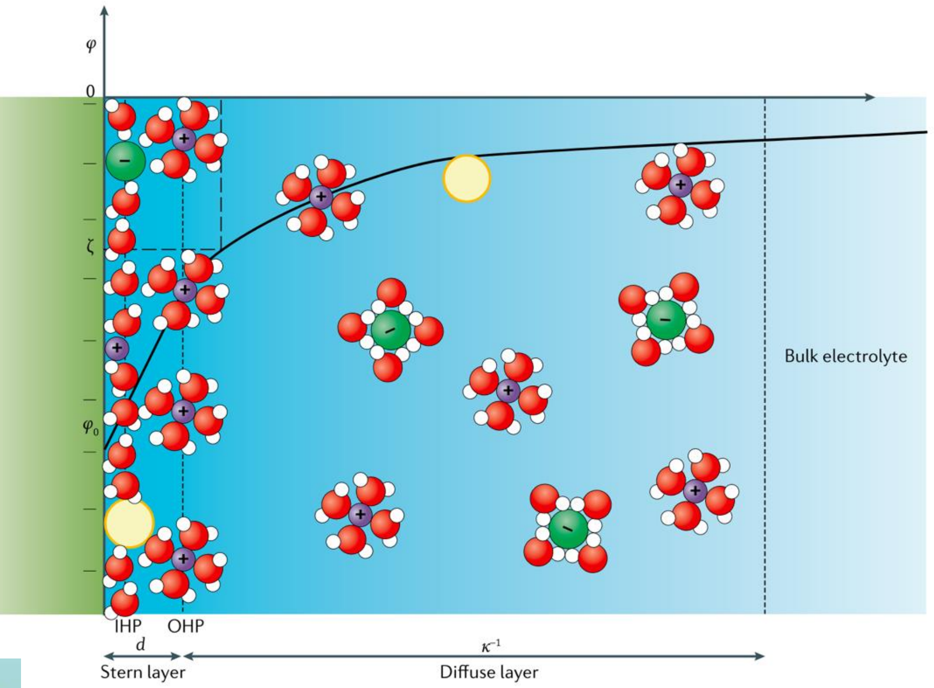


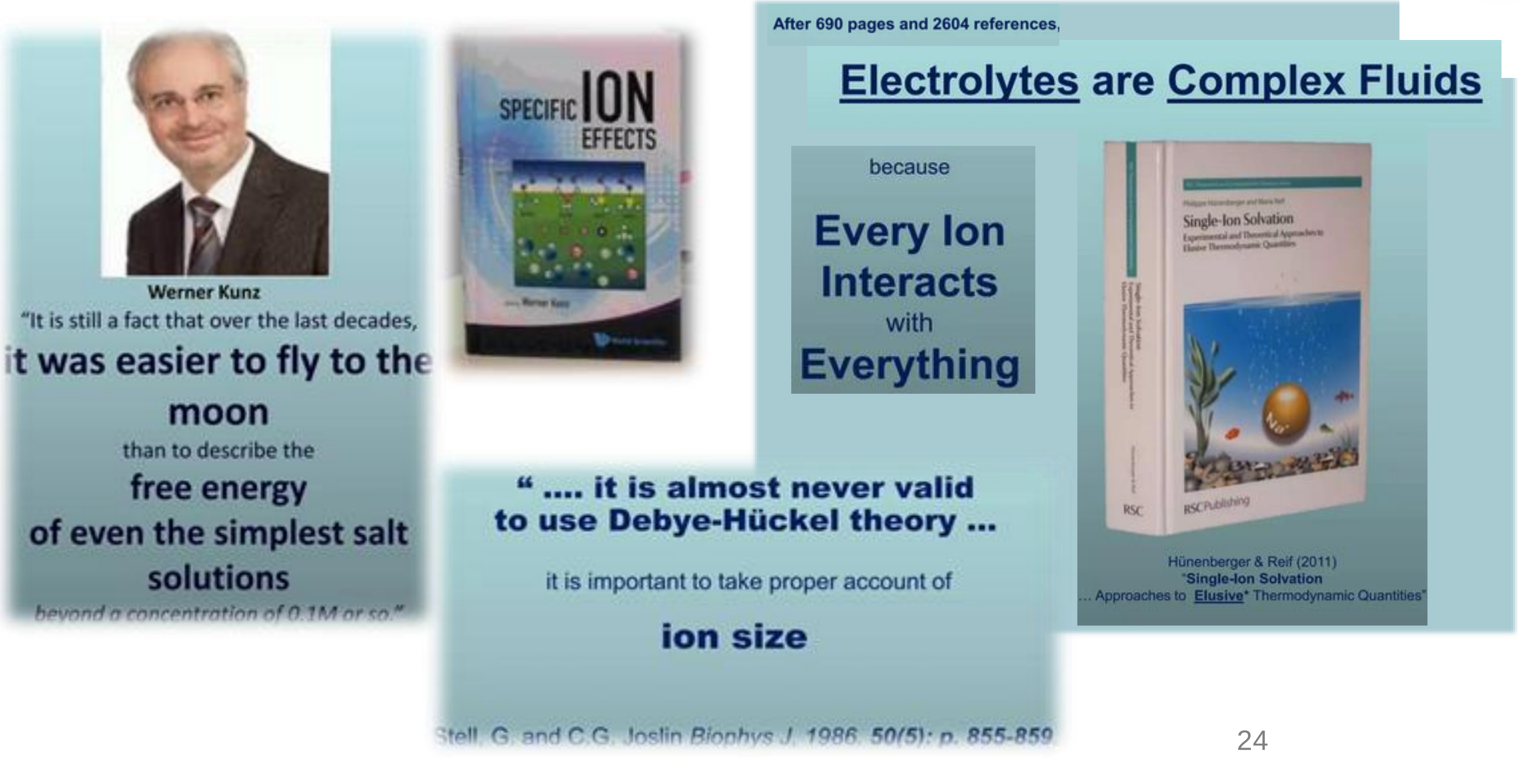


Systematic shortcomings of PB theory

- Ions are treated as point charges
- Homogeneous, isotropic dielectric background
- No solvent polarization, layering

- Many, many, many (!) extensions/corrections
- Still active research
- But need to connect to molecular details!





Werner Kunz

"It is still a fact that over the last decades,

it was easier to fly to the moon

than to describe the

free energy

of even the simplest salt solutions

beyond a concentration of 0.1M or so."

After 690 pages and 2604 references,

Electrolytes are Complex Fluids

because

Every Ion Interacts with Everything

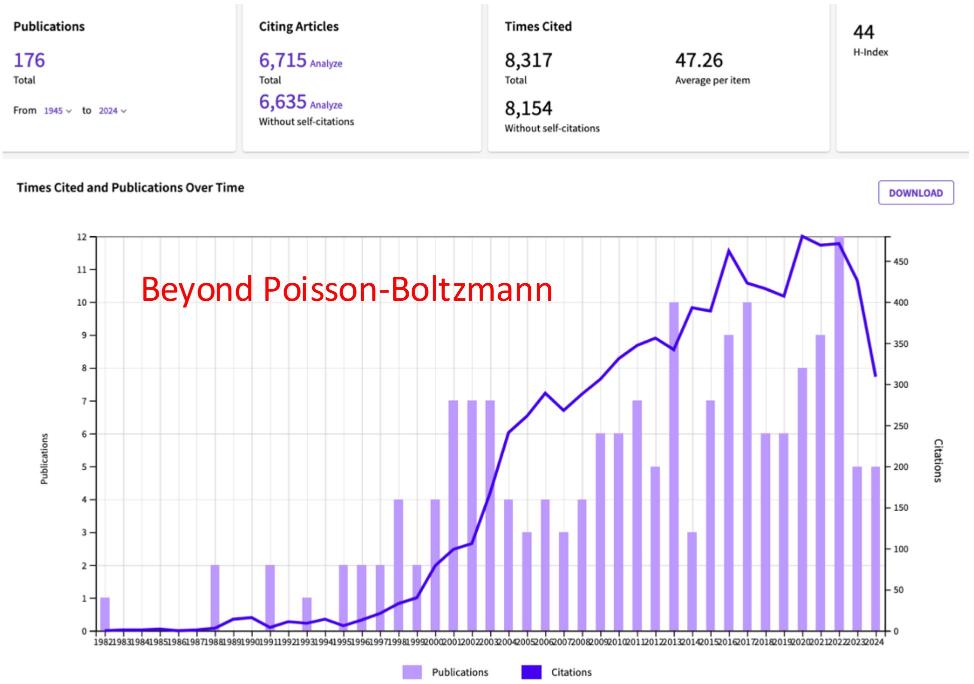
Hünenberger & Reif (2011)
"Single-Ion Solvation
... Approaches to Elusive" Thermodynamic Quantities"

" .... it is almost never valid to use Debye-Hückel theory ...

it is important to take proper account of

ion size

Stell, G. and C.G. Joslin Biophys J, 1986, 50(5): p. 855-859



Publications
176
Total
From 1945 to 2024

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Total
6,635 Analyze
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Total
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44
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Times Cited and Publications Over Time

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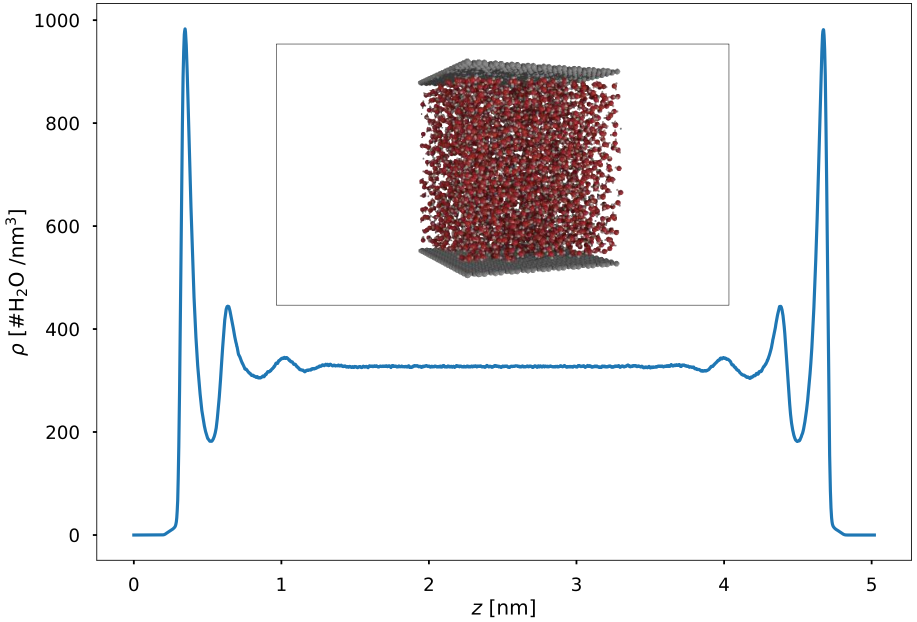
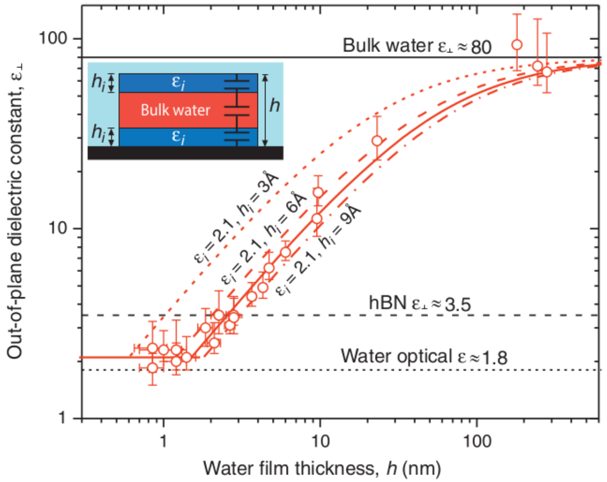
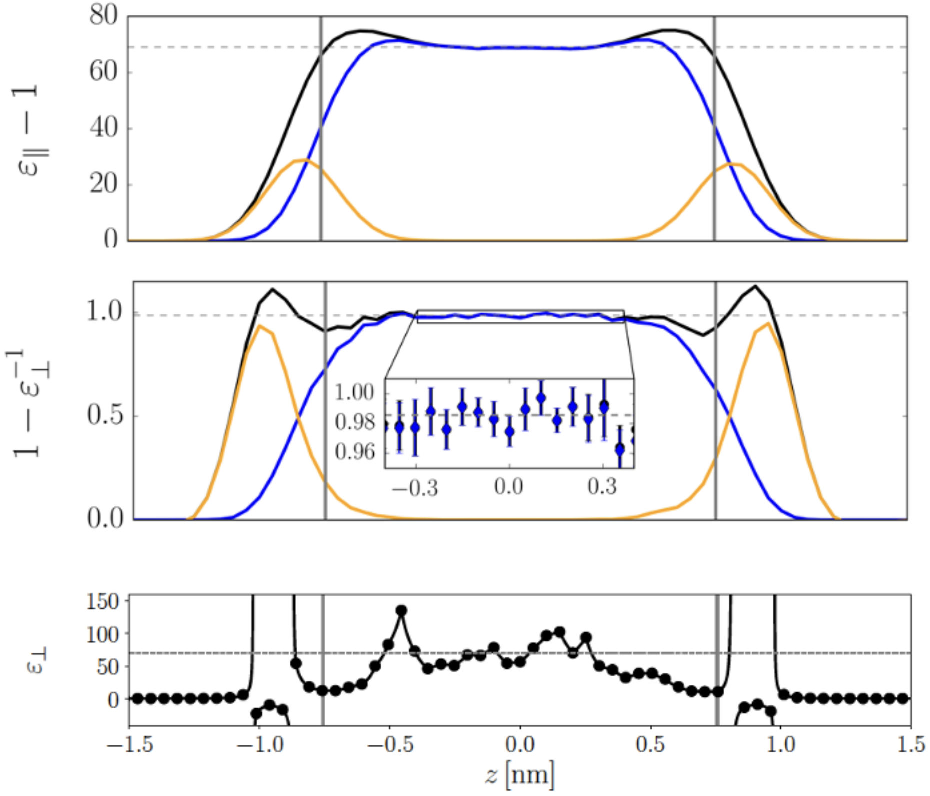
Beyond Poisson-Boltzmann

Insights from simulations







Schlaich, Knapp, and Netz, *Phys. Rev. Lett.* **117**, 48001 (2016).
P. Loche, C. Ayaz, A. Wolde-Kidan, A. Schlaich & R.R. Netz, *J. Phys. Chem B* (2020)
Fumagalli, Esfandiar, Fabregas, Hu, Ares, Janardanan, Yang, Radha, Taniguchi, Watanabe, Gomila, Novoselov, Geim, *Science* **2018**, *360* (6395), 1339–1342.

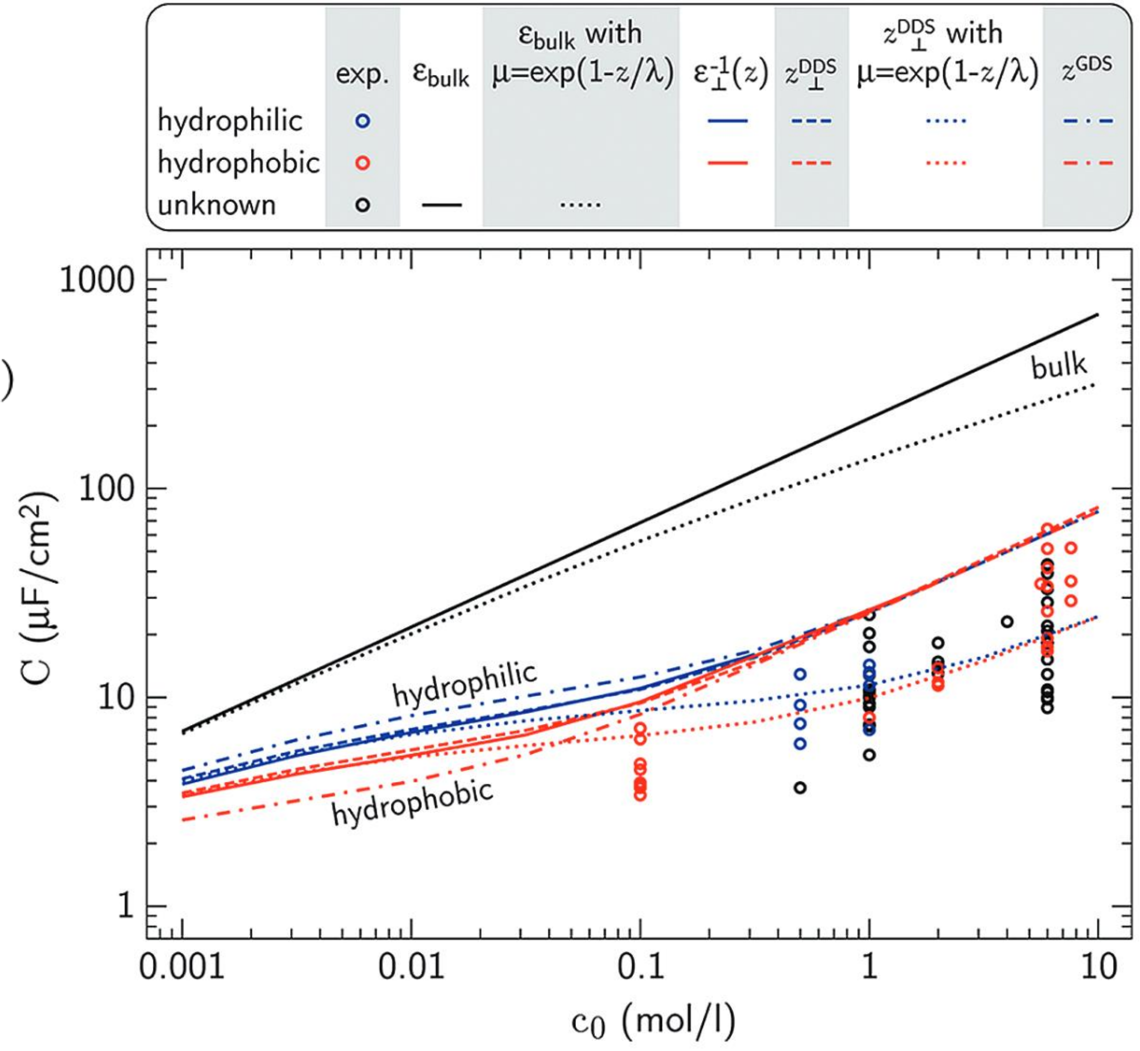
Double layer capacitance: influence of dielectric profile

Microscopic insight from simulations reveals macroscopic effects on the double layer capacitance!

Modified Poisson-Boltzmann approach

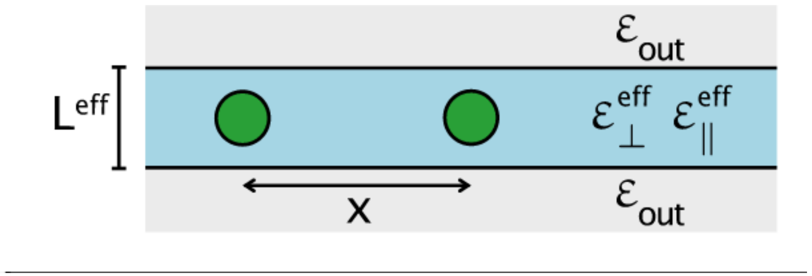
$$\varepsilon_0 \frac{d^2\psi}{dz^2} = -D_\perp(z)\frac{d\varepsilon_\perp^{-1}}{dz} - 2ec_0\beta e\psi(z)\exp[-\mu(z)]\varepsilon_\perp^{-1}(z)$$

- Dielectric profile
- External/surface potential to incorporate ion-specific effects



Bonthuis, Gekle, Netz, *Phys. Rev. Lett.* **2011**, *107* (16), 166102.
Schlaich, dos Santos, Netz, *Langmuir* **2019**, *35* (2), 551–560.

Anisotropic Green’s function



Solve Poisson equation via Green‘s formalism

$$\nabla \cdot \hat{\boldsymbol{\varepsilon}} \nabla \mathcal{G}(\boldsymbol{r}) = -\frac{\varrho(\boldsymbol{r})}{\varepsilon_0}$$

With dielectric tensor $\hat{\boldsymbol{\varepsilon}} = \mathrm{diag}(\varepsilon_{\parallel}, \varepsilon_{\parallel}, \varepsilon_{\perp})$

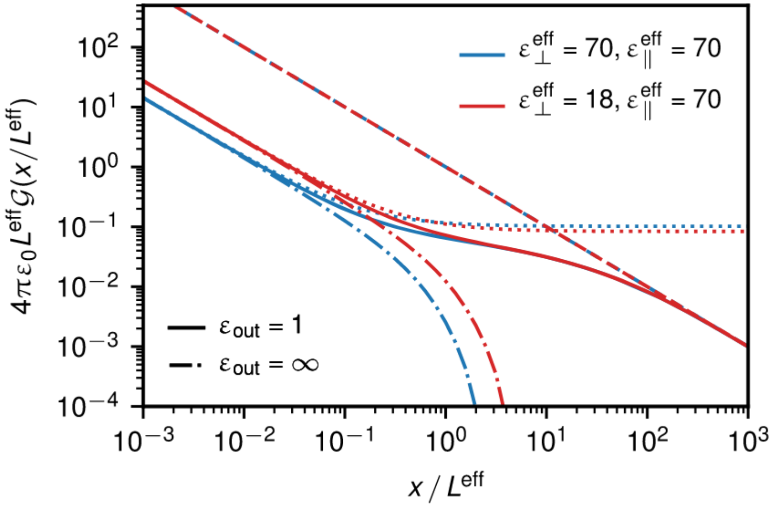
yields $$4\pi\varepsilon_0\varepsilon_{\parallel}^{(2)} L^{\text{eff}}\, \mathcal{G}(\tilde{x},0,0) = \frac{1}{|\tilde{x}|} + \frac{\Delta_{21}}{\sqrt{\tilde{x}^2+1}} + \Delta_{23} \sum^{\infty} \sum^{2} \binom{2}{k} \frac{\Delta_{23}^{n}\Delta_{21}^{n+k}}{\sqrt{\tilde{x}^2+(2n+k+1)^2}},$$

with $$\tilde{x} = \frac{x}{\gamma_2 L^{\text{eff}}} \qquad \gamma_2 = \sqrt{\frac{\varepsilon_{\parallel}^{(2)}}{\varepsilon_{\perp}^{(2)}}} \qquad \Delta_{ij} = \frac{\sqrt{\varepsilon_{\parallel}^{(i)}\varepsilon_{\perp}^{(i)}} - \sqrt{\varepsilon_{\parallel}^{(j)}\varepsilon_{\perp}^{(j)}}}{\sqrt{\varepsilon_{\parallel}^{(i)}\varepsilon_{\perp}^{(i)}} + \sqrt{\varepsilon_{\parallel}^{(j)}\varepsilon_{\perp}^{(j)}}} < 1$$

In the metallic limit $\Delta_{ij} = -1$ and thus $$4\pi\varepsilon_0\varepsilon_{\parallel}^{(2)} L^{\text{eff}}\, \mathcal{G}(\tilde{x}) = \sum_{n=-\infty} \frac{(-1)^n}{\sqrt{\tilde{x}^2+n^2}}$$

For small separations $\bar{x} \to 0$: $$\lim_{\tilde{x}\to 0} 4\pi\varepsilon_0\varepsilon_{\parallel}^{(2)} L^{\text{eff}}\, \mathcal{G}(\tilde{x}) = \frac{1}{|\tilde{x}|}$$

For large separations $\bar{x} \to \infty$: $$\boxed{\lim_{\tilde{x}\to\infty} 4\pi\varepsilon_0\varepsilon_{\parallel}^{(2)} L^{\text{eff}}\, \mathcal{G}(\tilde{x}) = \sqrt{\frac{8}{\tilde{x}}}\, e^{-\pi\tilde{x}}}$$

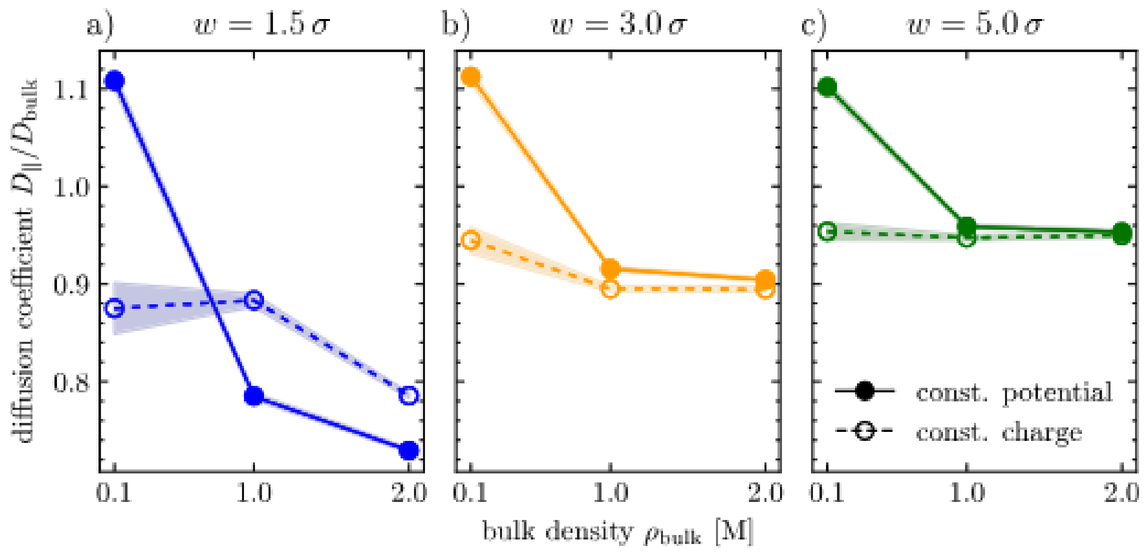


Loche, Ayaz, Schlaich, Bonthuis.; Netz, *J. Phys. Chem. Lett*. **2018**, *9* (22), 6463–6468
Loche, Ayaz, Wolde-Kidan, Schlaich, Netz, *J. Phys. Chem. B* **2020**, *124* (21), 4365–4371.

Exponential decay!

Electrode models

Do we really need ICC or other methods?



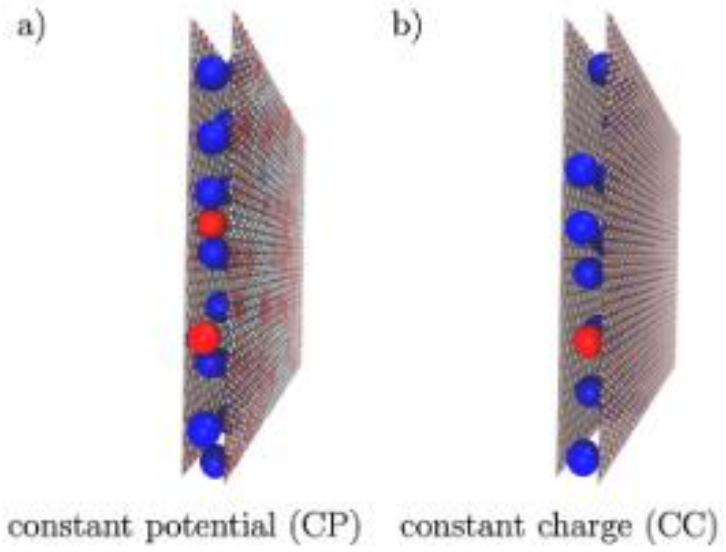
For small pores and low densities drastic effects on structure and dynamics!

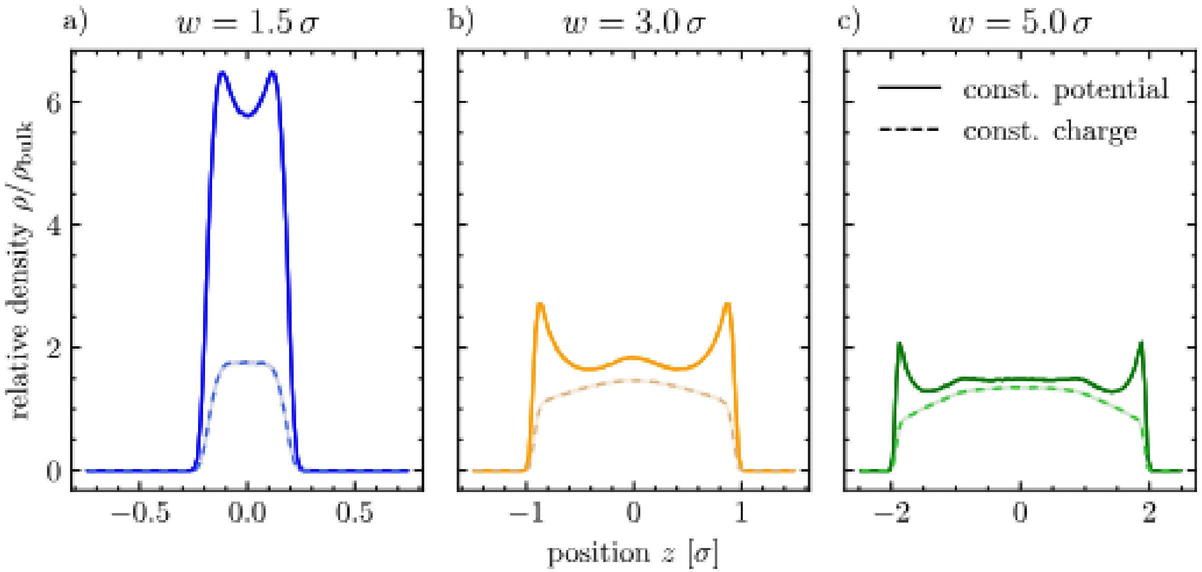
Constant potential methods: Image charge attraction vs. dielectric exclusion (CC methods)

Important quantity: pore size w/σ!

Locally induced charges!

Homogeneous charge density!





Conclusions

- Confinement: Host/guess ratio
- Continuum electrostatics: Maxwell
- Poisson-Boltzmann & Gouy-Chapman theory
- Graham equation for differential capacitance
- Tensorial, anisotropic electrostatics
- Limitations of constant-charge, constant-potential, … approaches
- Recent developments towards modeling electrochemical interfaces