One Hundred Years of Electrified Interfaces:

What's new with the theories of Debye & Onsager?

David Andelman

October 30, 2022

TEL AVIV UNIVERSITY

Let’s start with a short story

of 100 years ago…

One day in 1925, Peter Debye was sitting in his office …

Let’s start with a short story

of 100 years ago…

“Professor Debye, your theory on electrolytes is incorrect” …

Let’s start with a short story

of 100 years ago…

Whereupon Professor Debye, after begging the stranger to sit down and inviting him to discuss his objections, offered him an assistantship for the following year…

~1920

Lars Onsager

1903-1976

~1968

The young man's name was **Lars Onsager**…

43 years later (1968), Onsager was awarded the Nobel Prize for the "***discovery of the (Onsager) reciprocal relations, which are fundamental for the thermodynamics of irreversible processes***".

J.C. Longuet-Higgins & M.E. Fisher, J. Stat. Phys. (1995)

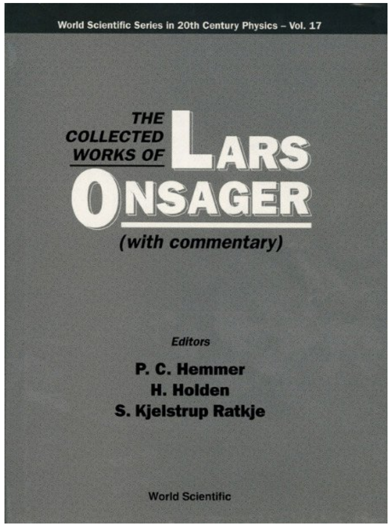
Lars Onsager

Probably the greatest statistical physicist of the 20th century

- Onsager's reciprocal relations - Nobel Prize
- Exact solution of the 2d Ising model
- The isotropic-to-nematic transition - Liquid Crystals
- Many works on *ions in solutions* (electrolytes)

95 publications including:

ice and water, dielectrics, turbulence, He II,
de Haas - van Alphen effect in metals, …



World Scientific Series in 20th Century Physics – Vol. 17

THE COLLECTED WORKS OF LARS ONSAGER

(with commentary)

Editors

P. C. Hemmer
H. Holden
S. Kjelstrup Ratkje

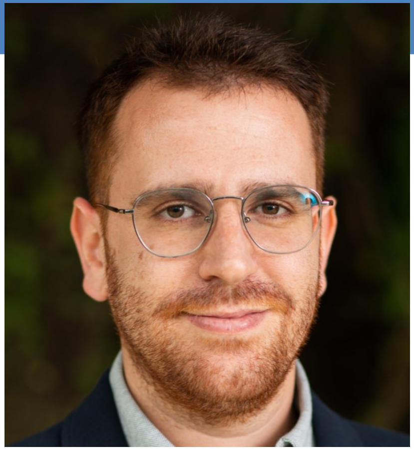
World Scientific

100 years of Electrified Interfaces:

What's new with the theories of Debye & Onsager?

- Introduction: the 100-year old Poisson-Boltzmann Theory
- Dielectric properties of electrolytes (Debye, *Onsager*, Kirkwood)
- Surface tension of electrolytes (*Onsager*-Samaras)
- Conductivity of Electrolytes (Debye & Hückel, *Onsager*)

Thanks



R. Adar

College de France

Y. Avni

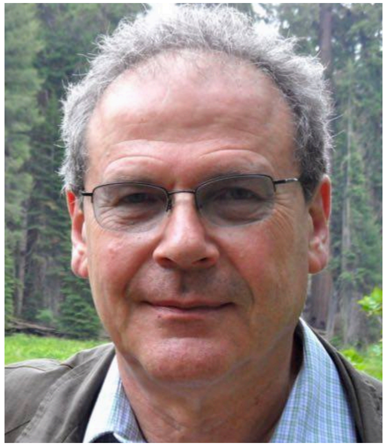
TAU & Chicago U

T. Markovich

TAU, Eng.

H. Orland

Saclay



R. Podgornik

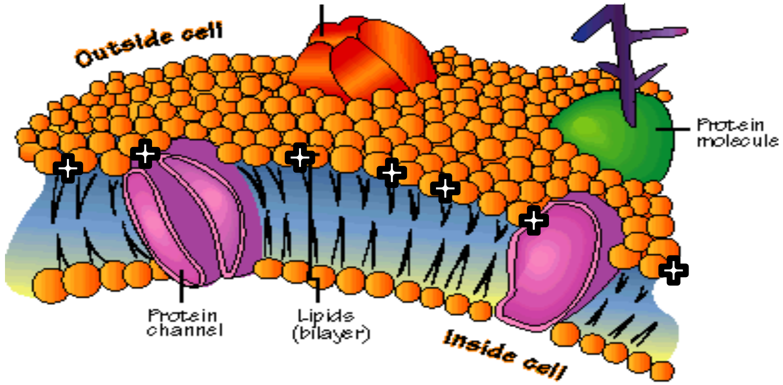
Beijing

Why electrostatics?

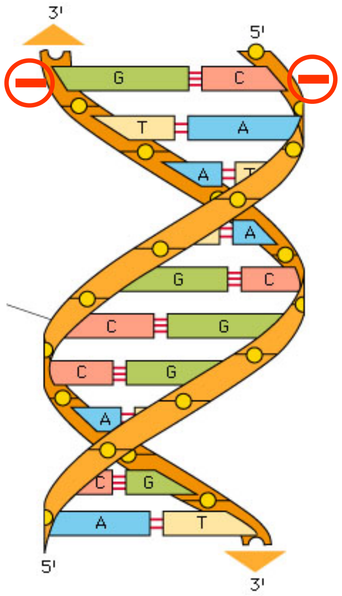
Biology: *water is the universal solvent*

- Ions in the cell/blood: $\mathrm{Na}^+, \mathrm{Cl}^-, \ldots$
- Cell membrane: charged lipids
- DNA, RNA, charged polymers, proteins

Cell membrane



DNA



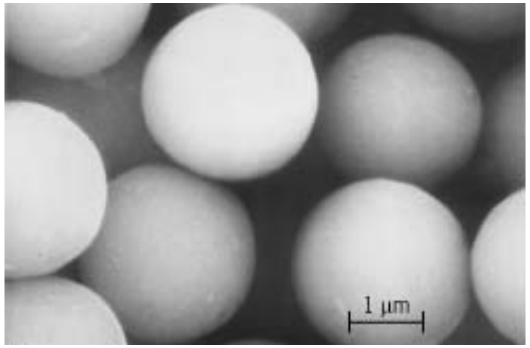
Why electrostatics?

Industry/chemistry

- Stabilization of colloids, paints, aerosols, emulsions
- Anionic/cationic detergents & soaps

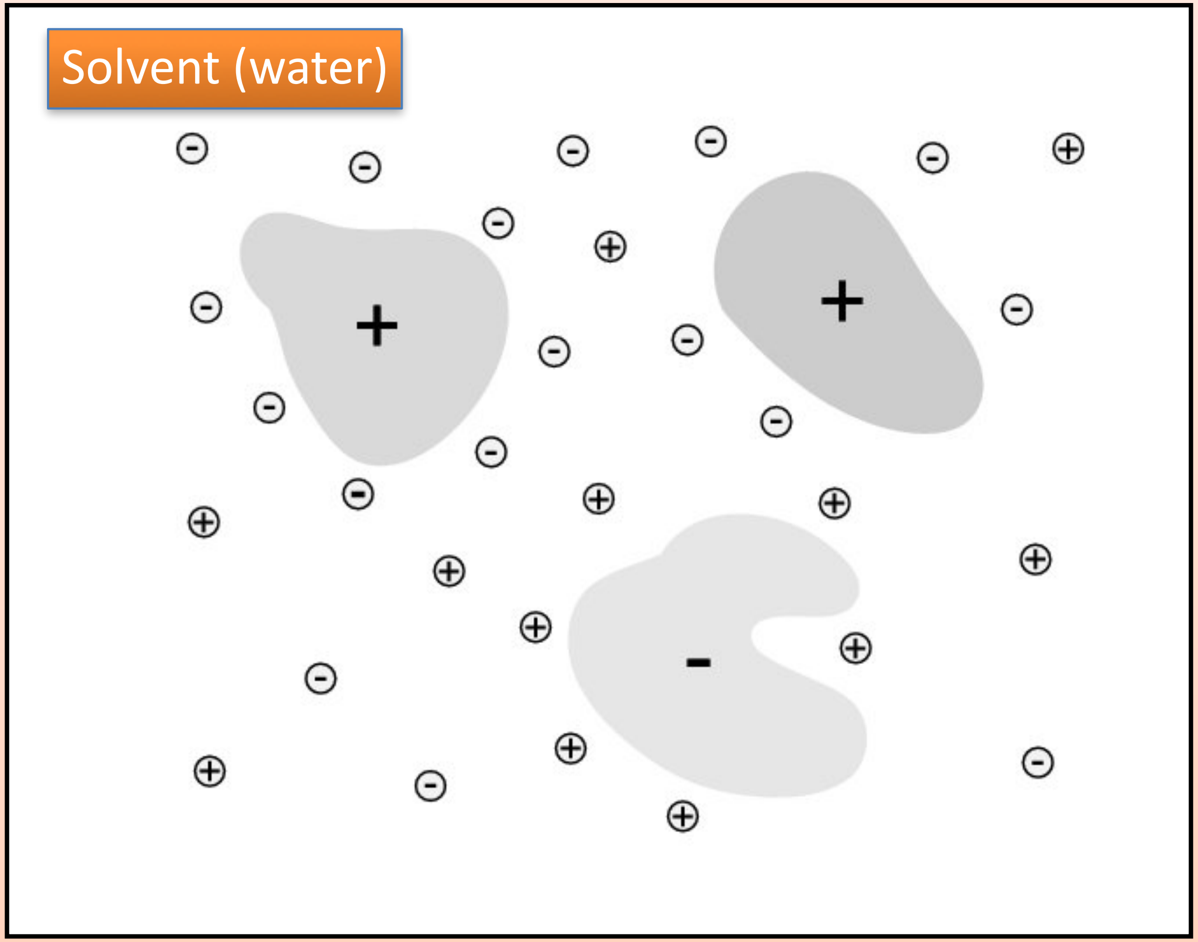
soap

Colloids

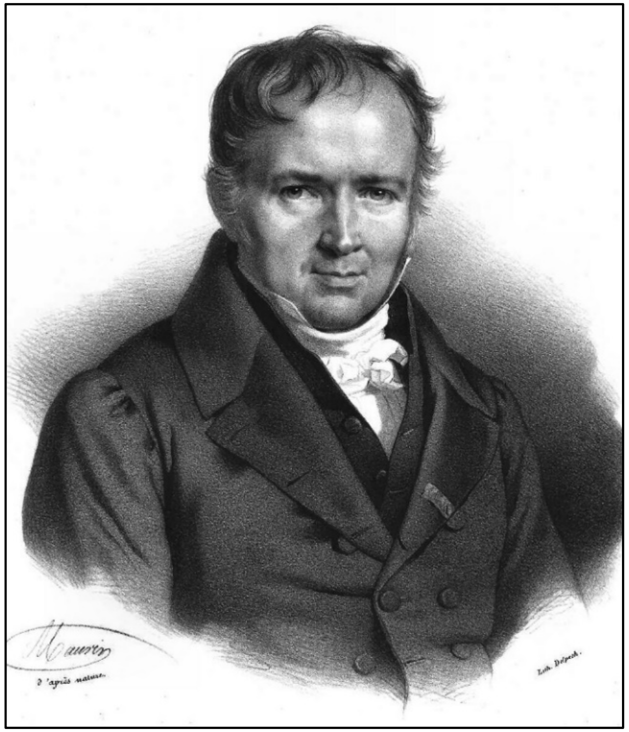


paint

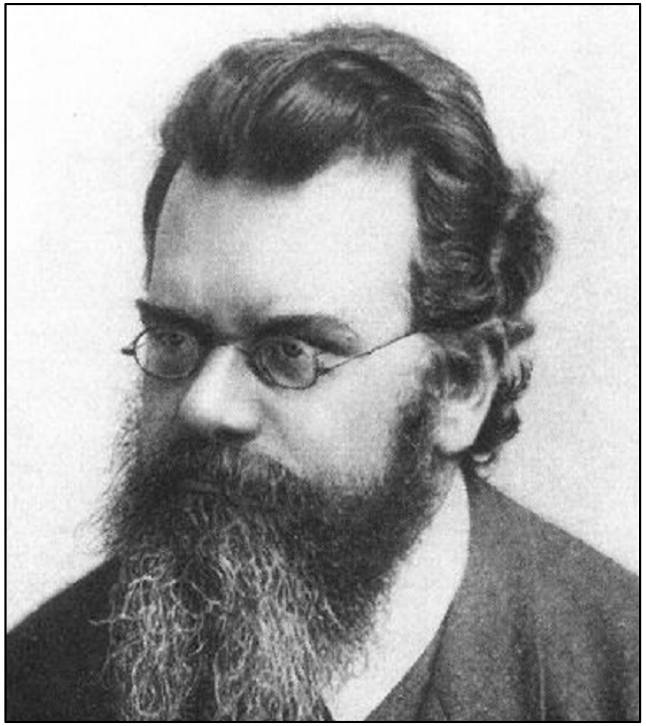
The “Grand” Problem
Statistical Mechanics of Coulombic Systems



- Entropy of ions ~ *kT*
- Dielectric solvent (water molecules)
- Mobile ions around macro & charged objects
- Screening of Elec. Int.
- Coupling between conformation & ionic degrees of freedom



Simeon Denis Poisson
1781-1840



Ludwig Boltzmann
1844-1906

The Poisson-Boltzmann Theory

Poisson-Boltzmann Equation

- Boltzmann distribution for mobile ion densities: (1:1 salt)

$$n_{\pm}(r) = n_{\mathrm{bulk}} \mathrm{e}^{\mp e\psi(r)/kT}$$

- Poisson equation for the potential ψ :

$$\nabla^2 \psi = -\frac{e}{\varepsilon_w}\left(n_+ - n_-\right)$$

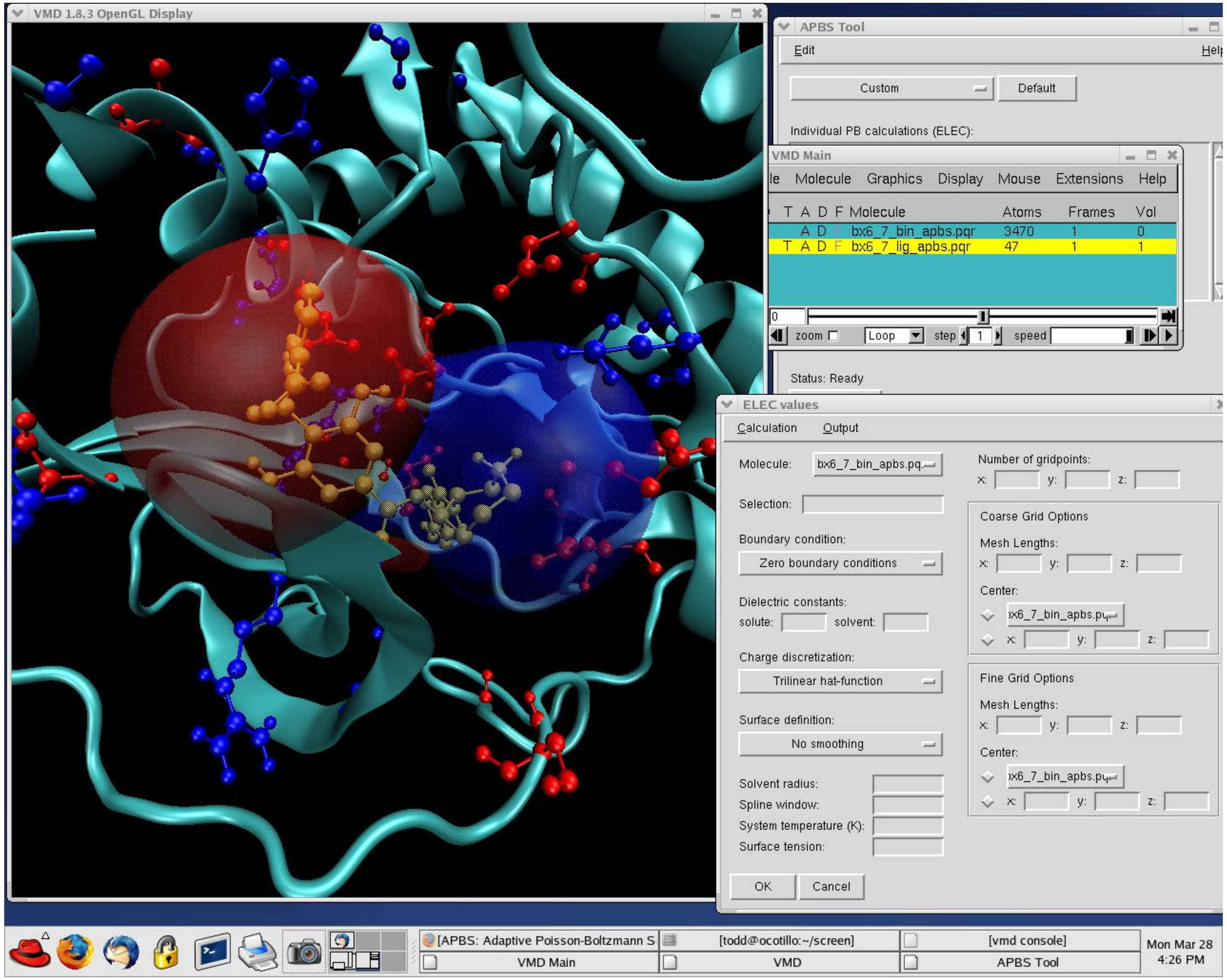
- Poisson-Boltzmann equation (non-linear):

$$\boxed{\nabla^2 \psi = \frac{2n}{\varepsilon_w} \sinh(e\psi/kT)}$$

- Mean-field densities of ions & electric potentials
- Boundary conditions: Dirichlet (CP), Neumann (CC),
  Charge regulation (CR), …

Adaptive Poisson-Boltzmann Solver (APBS)

Software for evaluating the electrostatic properties of nanoscale biomolecular systems



T	A	D	F	Molecule	Atoms	Frames	Vol
	A	D	F	bx6_7_bin_apbs.pqr	3470	1	0
T	A	D	F	bx6_7_lig_apbs.pqr	47	1	1

Status: Ready

Molecule: bx6_7_bin_apbs.pq

Selection:

Boundary condition: Zero boundary conditions

Dielectric constants: solute: solvent:

Charge discretization: Trilinear hat-function

Surface definition: No smoothing

Solvent radius:

Spline window:

System temperature (K):

Surface tension:

Number of gridpoints: x: y: z:

Coarse Grid Options
Mesh Lengths: x: y: z:
Center:
◇ x6_7_bin_apbs.pq
◇ x: y: z:

Fine Grid Options
Mesh Lengths: x: y: z:
Center:
◇ x6_7_bin_apbs.pq
◇ x: y: z:

[APBS: Adaptive Poisson-Boltzmann S

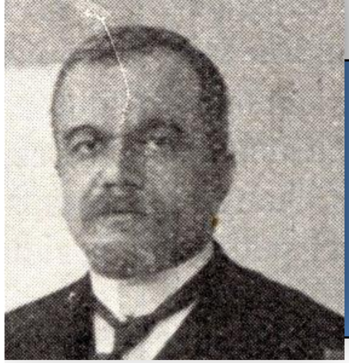
[todd@ocotillo:~/screen]

https://www.poissonboltzmann.org (NIH)

Also:

Delarue, Koehl, Orland

AQUASOL (Inst. Pasteur)



One surface & counter-ions

Gouy 1910; Chapman 1913

$$\Psi = 2\ln(1 + z/l^*)$$

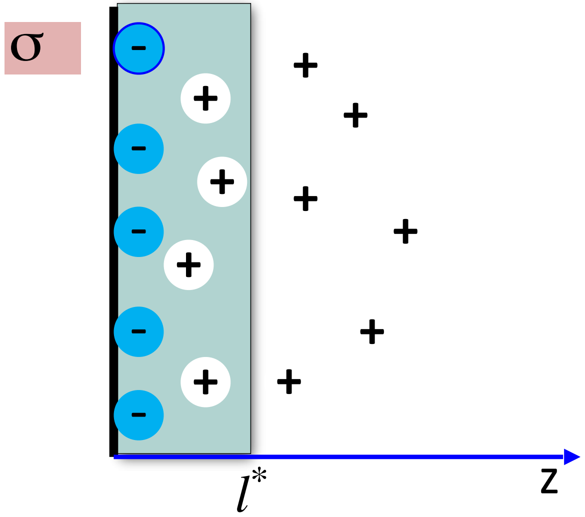
Electrostatic potential

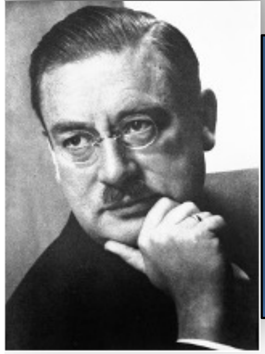
$$l^* = \frac{2\varepsilon_w kT}{e\sigma} \sim \sigma^{-1}$$

Gouy-Chapman Length

$$n(z) \sim \frac{1}{(z + l^*)^2} \sim 1/z^2$$

Ion profile





Debye-Hückel

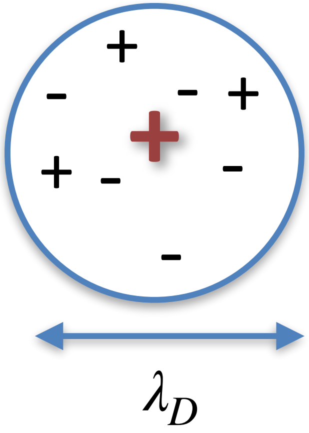
screening - 1923

The Debye screening length

$$\lambda_D = 1/\sqrt{\frac{2e^2 n}{\varepsilon_w kT}} = 3\text{Å}/\sqrt{n[\text{molar}]}$$

$$\lambda_D = 3\text{Å} \ \text{for} \ 1\text{M} \ \rightarrow \ 1\mu m \ \text{for} \ 10^{-7}\text{M}$$

ionic cloud



Electrostatic potential

$$\nabla^2 \psi = \lambda_D^{-2} \psi$$

linear; small ψ

$$\psi(z) \sim \exp(-z/\lambda_D)$$

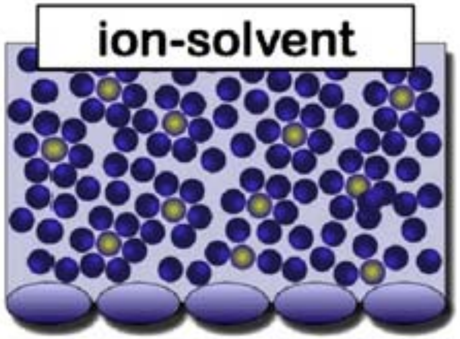
The Bjerrum Length

$$l_B = e^2/(4\pi\varepsilon_w kT) \approx 7\text{Å}$$

$$\lambda_D = 1/\sqrt{8\pi l_B n}$$

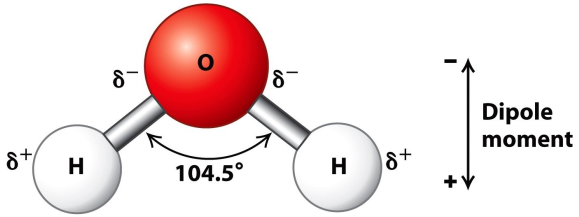
Ion hydration shell

Dielectric decrement

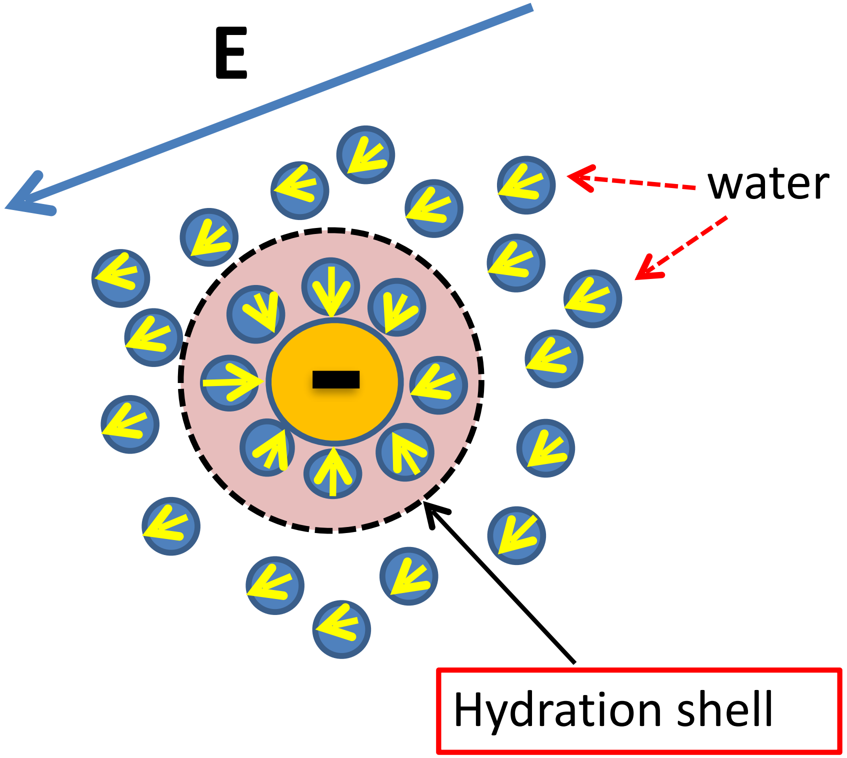


Hydration shell around ions

- Ion surrounded by dipolar water molecules



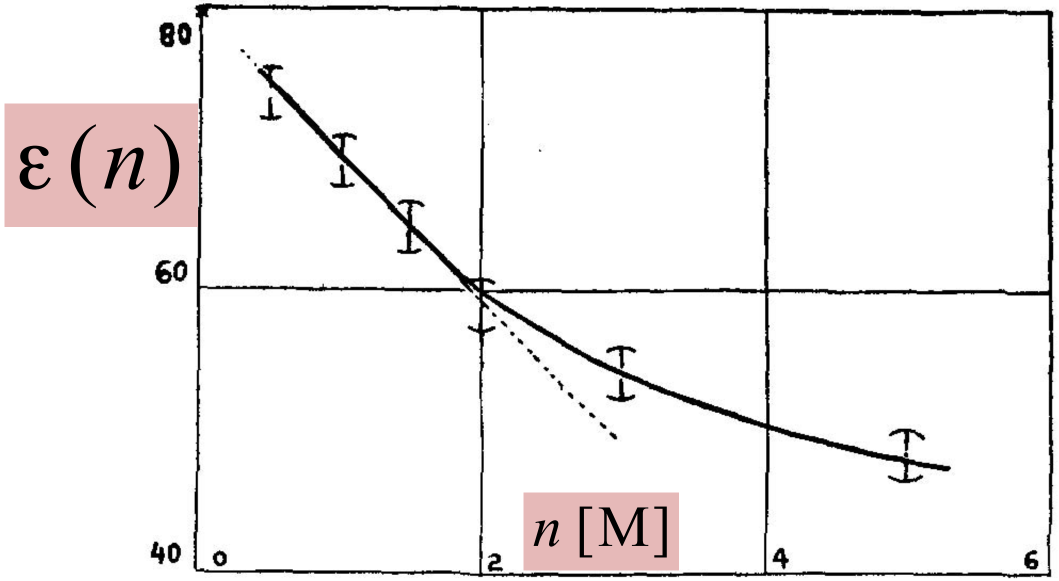
- Response to the E field is reduced: dielectric decrement



$$\boxed{\varepsilon(n) < \varepsilon_w}$$

Dielectric decrement

Salt conc.



Hasted, Ritson and Collie, 1948

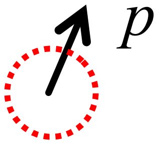
$$\varepsilon(n) \simeq \varepsilon_w - \gamma n$$

Salt	$\gamma\ [\mathrm{M}^{-1}]$
HCl	10
LiCl	7
NaCl	5.5
KCl	5
RbCl	5
KF	6.5
NaI	8

The Dipolar Poisson-Boltzmann

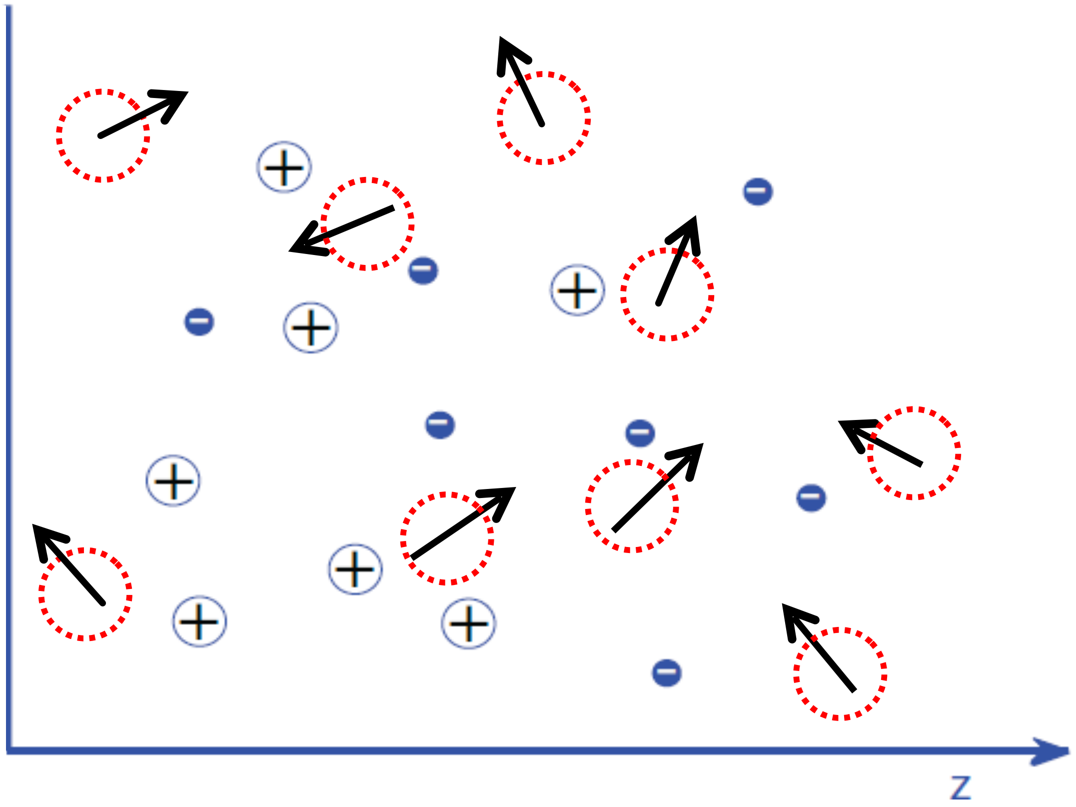
A mixture of:

permanent dipoles (water)



bulk concentration n_d

Ions +, - bulk concentration n_0



Abrashkin, Orland, Andelman, PRL ’07
Levy, Orland, Andelman, PRL ’12

The Dipolar PB

The free energy of point-like ions and dipoles

$$F = \int \mathrm{d}^3 \mathrm{r} \left\{ \frac{\varepsilon}{8\pi kT} [E(\mathbf{r})]^2 + 2n_0 \cosh[\beta e\psi(\mathbf{r})] + \right.$$

$$E = -|\nabla\psi(\mathbf{r})| \quad \text{Elec. field}$$

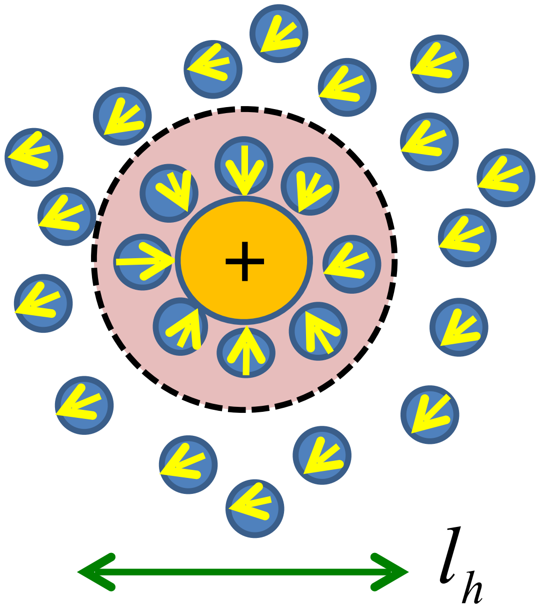
Φ

Mean-Field: the ***Dipolar PB*** equation

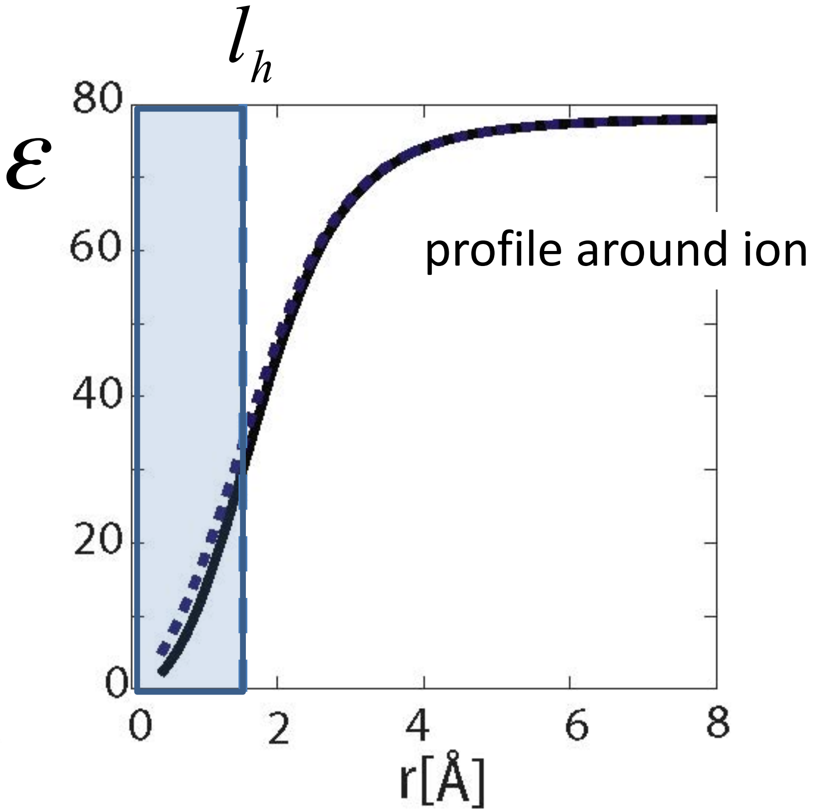
$$-\frac{\varepsilon}{4\pi}\nabla^2\psi = \underbrace{-2n_0 e \sinh\left[\beta e\psi\right]}_{\text{ions}} +$$

Hydration layer

Solve the Dipolar PB around a point ion



hydration layer thickness



$$\boxed{l_h \sim \sqrt{\frac{p}{e} l_B} \approx [1-2]\text{Å}}$$

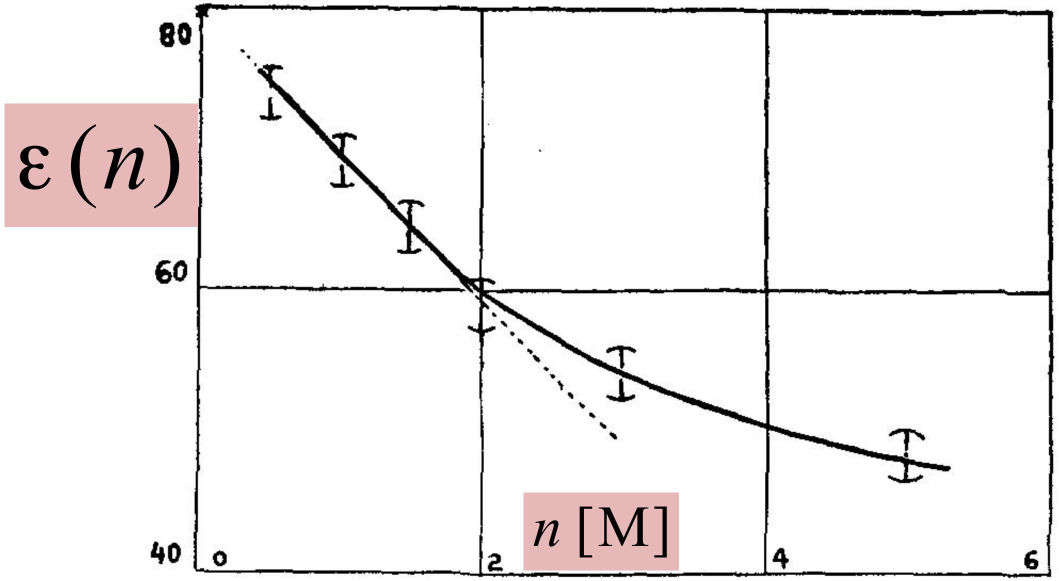
$l_B = e^2/\varepsilon_w kT \simeq 7\text{Å}$ Bjerrum

Levy, Orland, Andelman, PRL '12; JCP '13

Back to dielectric decrement

$$\varepsilon(n) = \varepsilon_0 - \gamma n$$

Salt conc.



Hasted, Ritson, Collie, 1948

Salt	$\gamma\ [\mathrm{M}^{-1}]$
HCl	10
LiCl	7
NaCl	5.5
KCl	5
RbCl	5
KF	6.5
NaI	8

Dipolar PB:
one-loop expansion

- Field-theory expansion of the free energy
- Fluctuations in dipole and ion densities; finite ion size a
- One loop produces a closed analytical formula

complex expression - not shown

Simple expression for low salt concentration n

$$\boxed{\varepsilon(n) \approx \varepsilon_w - \gamma n + \zeta n^{3/2} + \ldots}$$

Dielectric decrement

γ and ζ are functions of : l_B, ε_w, and a

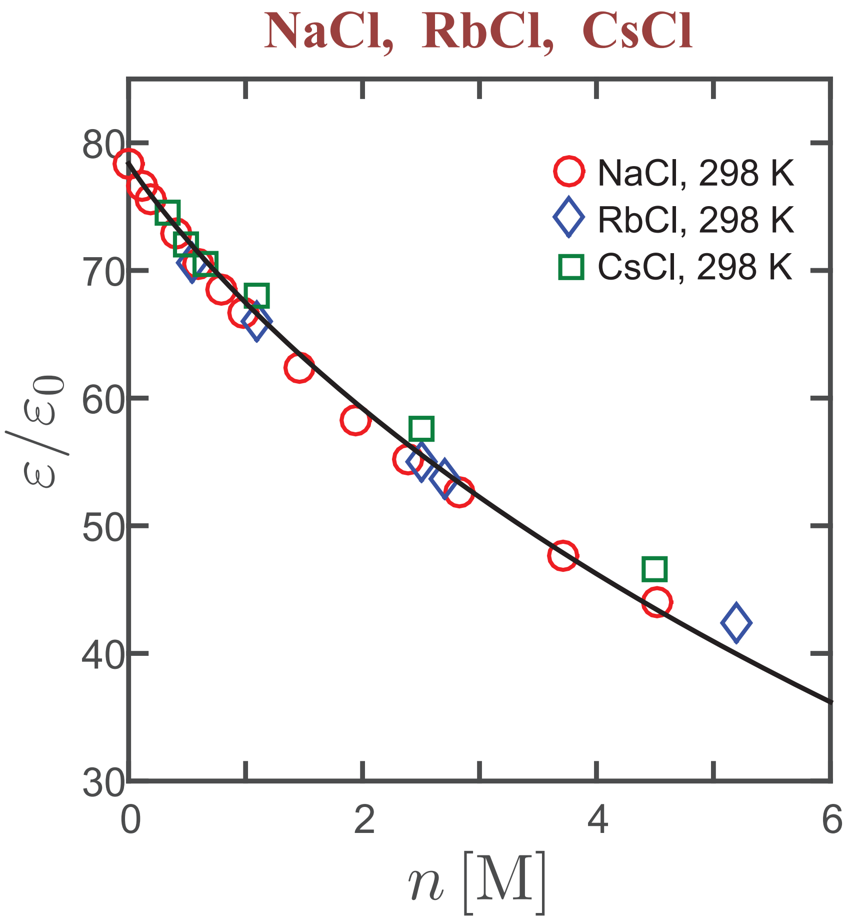
$$\gamma = 2a^3\varepsilon_w\left(1 + \frac{4l_B}{3a}\right) \quad ; \quad \zeta \simeq 5.2\varepsilon_w l_B^{3/2} a^3$$

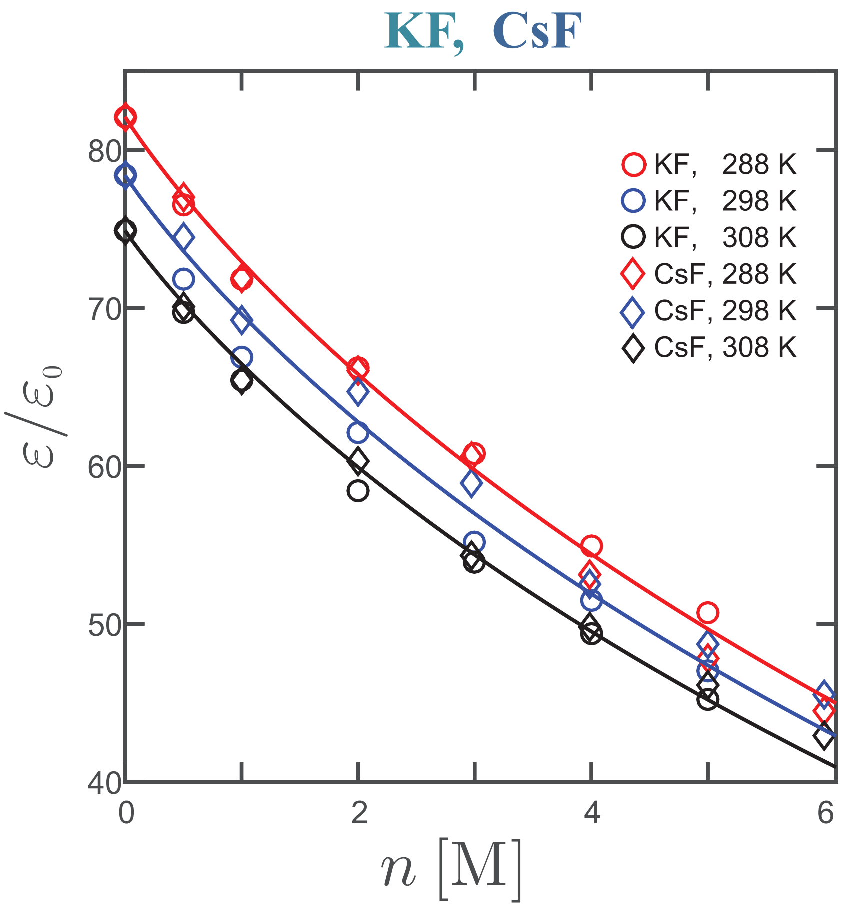
Adar, Markovich, Orland, Andelman, JCP ’18
Levy, Orland, Andelman, PRL ‘12

Comparison with Experiments

Dielectric constant of simple salts:

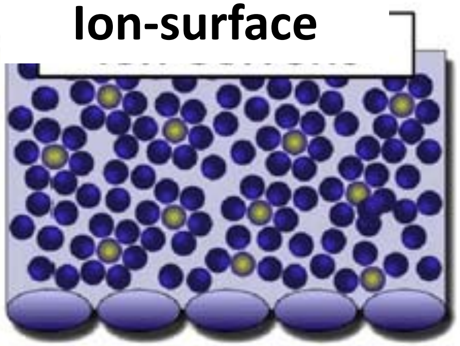
extrapolating to static behavior from high frequencies





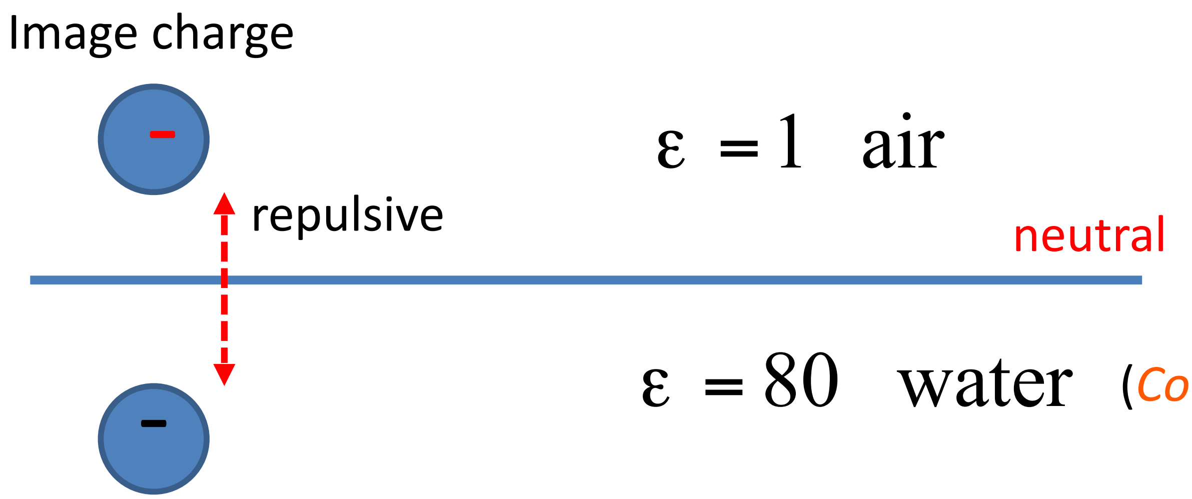
Surface Tension of ionic Solutions:

Beyond Onsager-Samaras



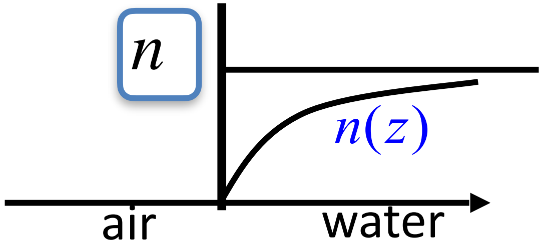
Surface Tension of electrolytes:

Onsager-Samaras (1934)



$\varepsilon = 1$ air

$\varepsilon = 80$ water (*Continuum*)



- Ion depletion from neutral interface $\varepsilon_{\text{water}} > \varepsilon_{\text{air}}$

- Onsager-Samaras

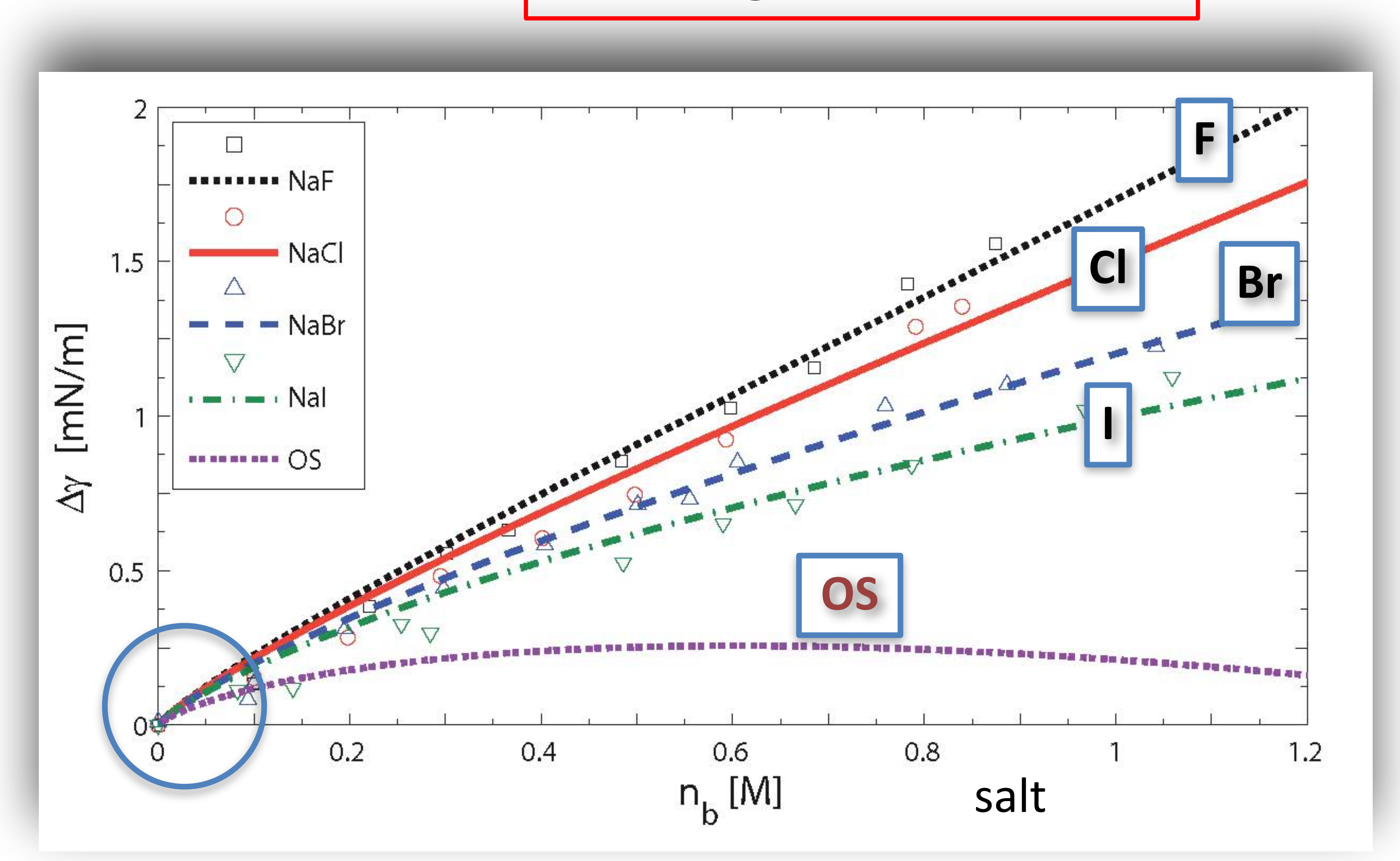
  Dielectric discontinuity & Debye-Hückel theory $n \sim \lambda_D^{-2}$

$\gamma \approx kTn \ln n$ $\boxed{\text{increase tension with salt conc.}}$ ***Non-specific***

Water/Air Surface Tension:
Ion Specificity

Hofmeister series

$$F^- > Cl^- > Br^- > I^-$$



Onsager-Samaras works only at very low salinity

$$\leq 10\text{mM}$$

Exp: Matubayasi et al (2001)

Hofmeister Series:

Ionic specific effects (1888)

- Experiments on protein precipitation
- Many chemical and biological systems
- Ionic specific (not only the charge)

most stabilizing

strongly hydrated anions

most destabilizing

weakly hydrated anions

$$\text{citrate}^{3-} > \text{sulfate}^{2-} > \text{phosphate}^{2-} > F^- > Cl^- > Br^- > I^- > NO_3^- > ClO_4^-$$

$$N(CH_3)_4^+ > NH_4^+ > Cs^+ > Rb^+ > K^+ > Na^+ > H^+ > Ca^{2+} > Mg^{2+} > Al^{3+}$$

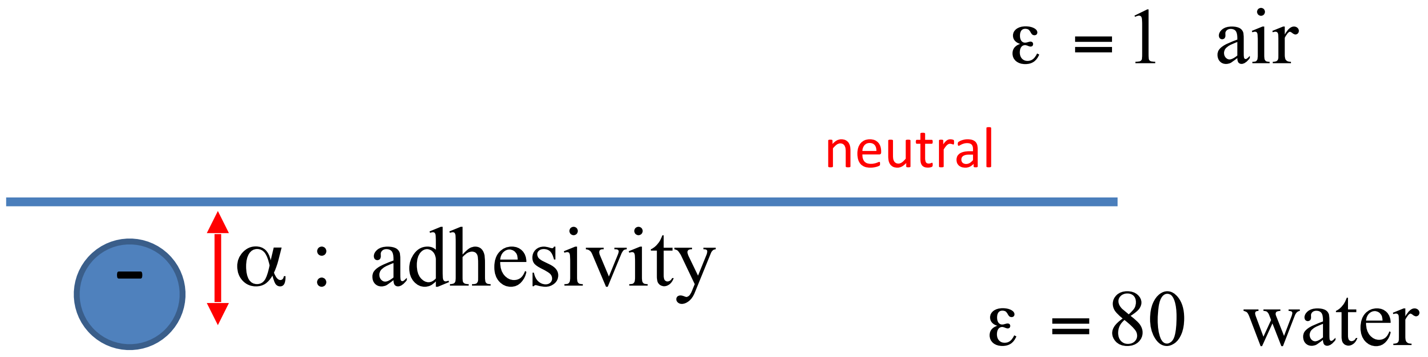
weakly hydrated cations

strongly hydrated cations

F. Hofmeister, Arch. Exp. Pathol. Pharmakol. (1888)

Self-Consistent Field Theory:

Surface-ion interaction



$$\gamma = \gamma_{\mathrm{os}} + \gamma_{\mathrm{ion\ spec.}}$$

analytical

- One-loop expansion:

  OS and ion specific effects

Markovich, Andelman, Podgornik (JCP ’15)

Surface Tension of Electrolytes:

analytical results

- a: distance of closest approach (ion “size”)

  Analytical results for small a

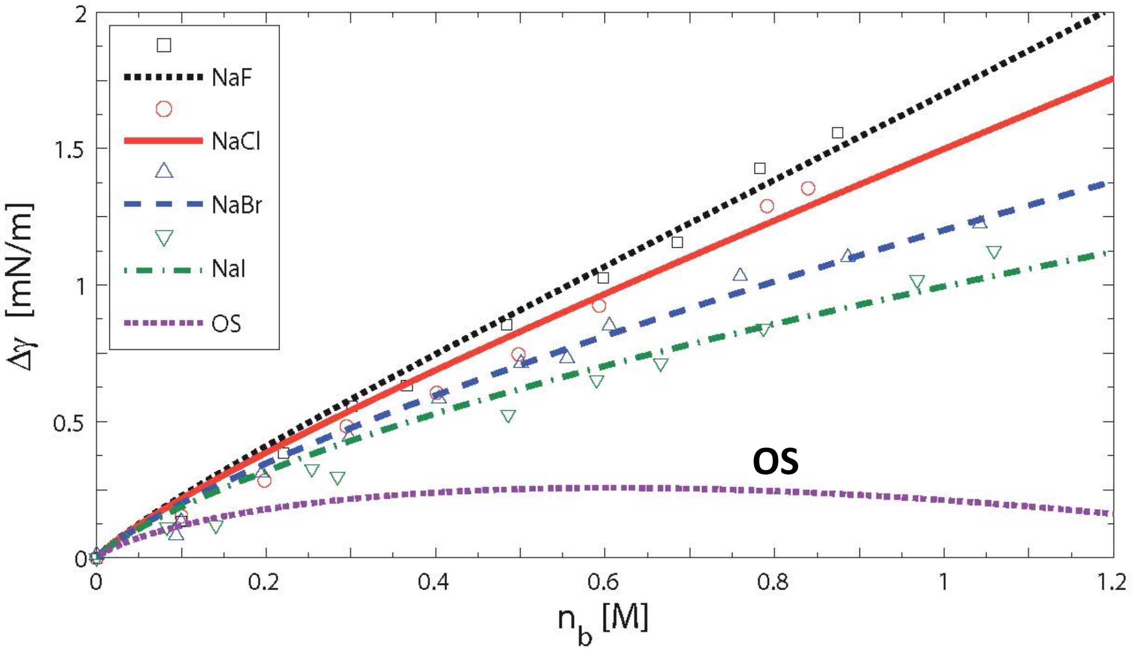
$$\frac{\gamma}{kT} = \underbrace{-\frac{\lambda_D^{-2}}{16\pi}\frac{1-\varepsilon}{1+\varepsilon}\ln(a/\lambda_D)}_{\text{Onsager-Samaras}} + \underbrace{const \times \frac{\sigma_e^2(\alpha)}{(\varepsilon+1)^2}\ln(a/\lambda_D)}_{\text{Ion-specific}}$$

- Effective surface charge $\sigma_e \sim n_0(\alpha / kT)$ small

Markovich, Andelman, Podgornik (JCP ’15)

Self-Consistent Theory:
Fit with experiments

air-water interface



Hofmeister Series α

$$\boxed{F^- > Cl^- > Br^- > I^-}$$

Strong fluctuation effect

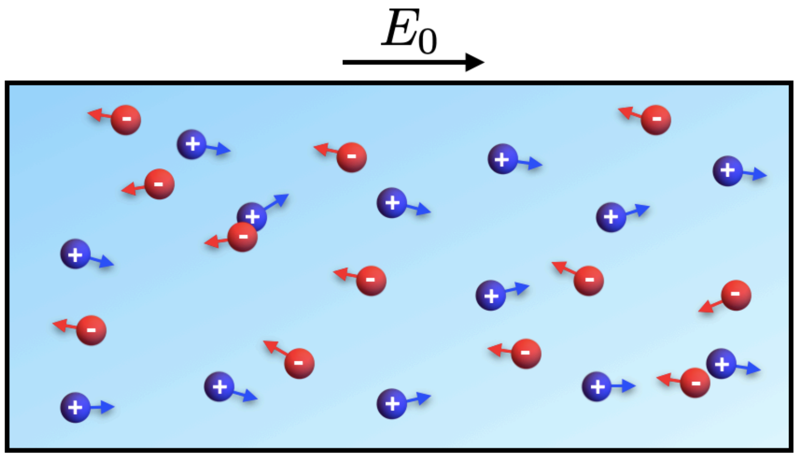
$\alpha / kT \approx 0.18$ (NaF) → 0.02 (NaI)   ions at air/water

ionic size = $r_+ + r_- \approx 6.9 - 7.1$Å

Markovich, Andelman, Podgornik (JCP ’15)

Conductivity of Concentrated Ionic Solutions

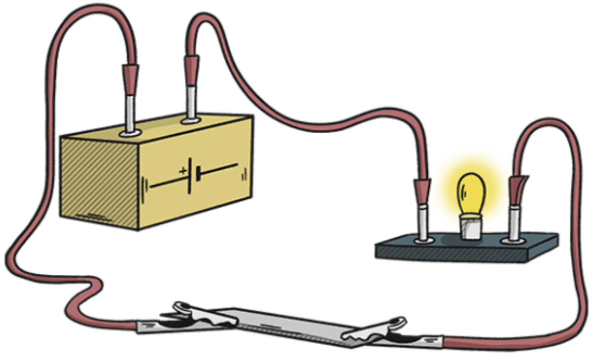
Conductivity of Ionic Solutions



Monovalent ions: $\pm e$

$$\langle n_+ \rangle = \langle n_- \rangle = n$$

Conductivity $\kappa = \dfrac{\langle J \rangle}{E_0}$

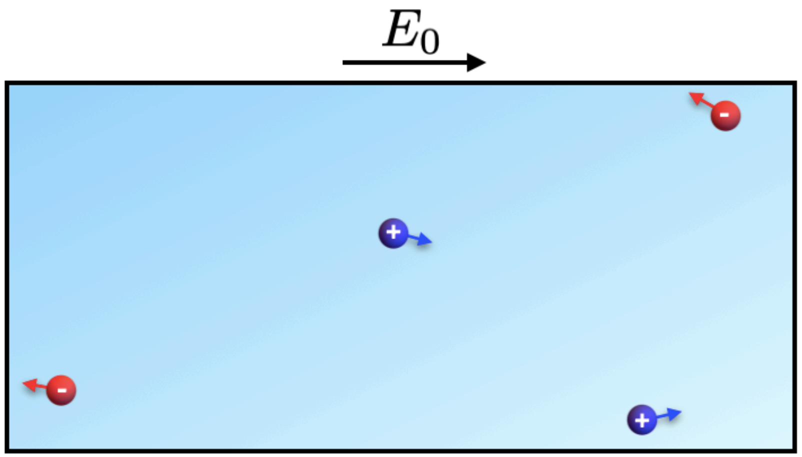


Linear response $\langle J \rangle \propto E_0$

$$E_0 \to 0$$

Dilute Limit

No interactions: $n \to 0$



$$\kappa = \frac{\langle J \rangle}{E_0}$$

Conductivity

$$\boxed{\kappa_0 = 2e^2 \mu_{\mathrm{av}} n}$$

The conductivity is linear in the concentration

$$\mu_{\mathrm{av}} = \frac{\mu_+ + \mu_-}{2}$$

Mobility

Beyond the Dilute Limit:

Hydrodynamics & Correlations

P. Debye *E. Hückel* *L. Onsager*

DHO Theory

$$\kappa\left(\lambda_D\right) = \kappa_0\left(1 - \underbrace{\frac{r_s}{\lambda_D}}_{\text{Hydrodynamically mediated electrostatic interactions}} - \underbrace{\frac{1}{3}\left(1 - \frac{1}{\sqrt{2}}\right)\frac{l_B}{\lambda_D}}_{\text{Direct electrostatic interactions}}\right)$$

Reduced Stokes

$$r_s = \frac{1}{6\pi\eta\mu_{\text{av}}}$$

η = viscosity

λ_D = **Debye Screening length**

l_B = **Bjerrum length**

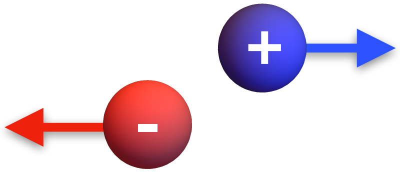
Beyond the Dilute Limit:

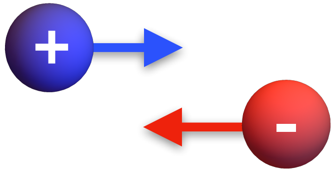
Hydrodynamics & Correlations

P. Debye E. Hückel L. Onsager

DHO Theory

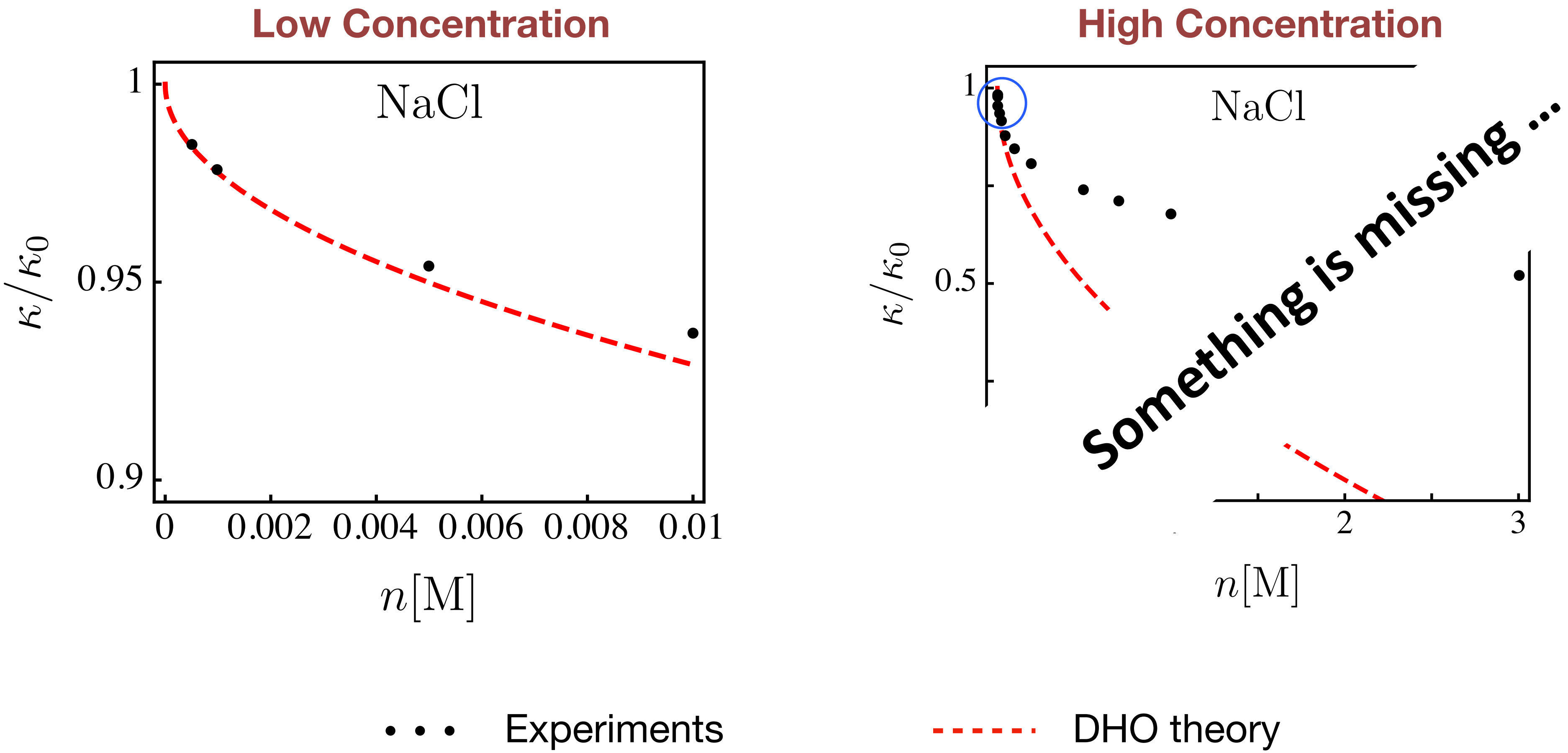
$$\boxed{\kappa\left(\lambda_D\right) = \kappa_0 \left(1 - \underbrace{\frac{r_s}{\lambda_D}}_{\text{Hydrodynamically mediated electrostatic interactions}} - \frac{1}{3}\underbrace{\left(1 - \frac{1}{\sqrt{2}}\right)\frac{l_B}{\lambda_D}}_{\text{Direct electrostatic interactions}}\right)}$$





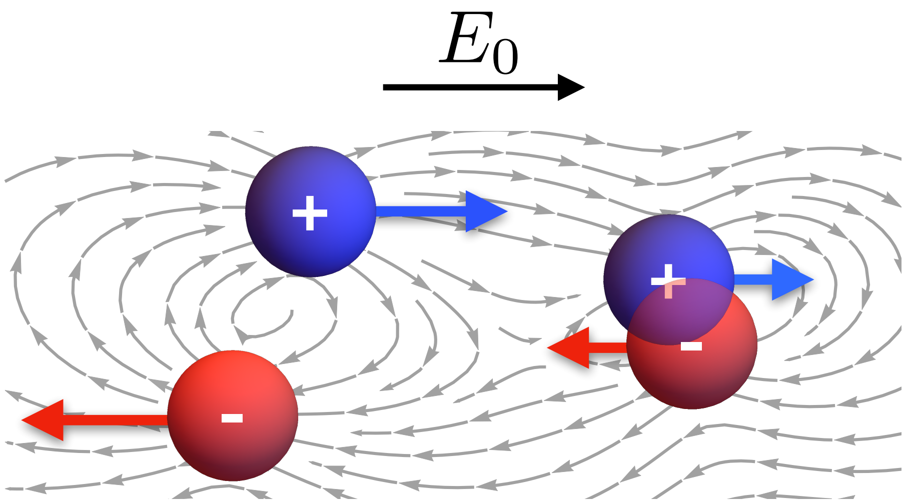
$$\boxed{\frac{\kappa(n)}{\kappa_0} < 1}$$

DHO equation works only for very dilute solutions



Something is missing ...

Finite ion size: beyond DHO



concentrated solutions

$$\mathbf{j}_\pm = \underbrace{\mathbf{u}n_\pm}_{\text{advection}} - \underbrace{D_\pm \nabla n_\pm}_{\text{diffusion}} + \underbrace{\mu_\pm \mathbf{f}_\pm}_{\text{electrostatic}} - \underbrace{\sqrt{2D_\alpha n_\pm}\,\zeta_\pm}_{\text{stochastic current}}$$

- Stochastic density functional theory

  Dean ’96; Dèmery & Dean ’16; Pèraud et al. ’17

- Accounting for ion size through a modified ion-ion potential

Avni, Adar, Orland & Andelman, PRL ‘22

The Conductivity:
Simple correction to DHO

In the limit of $a/\lambda_D \ll 1$

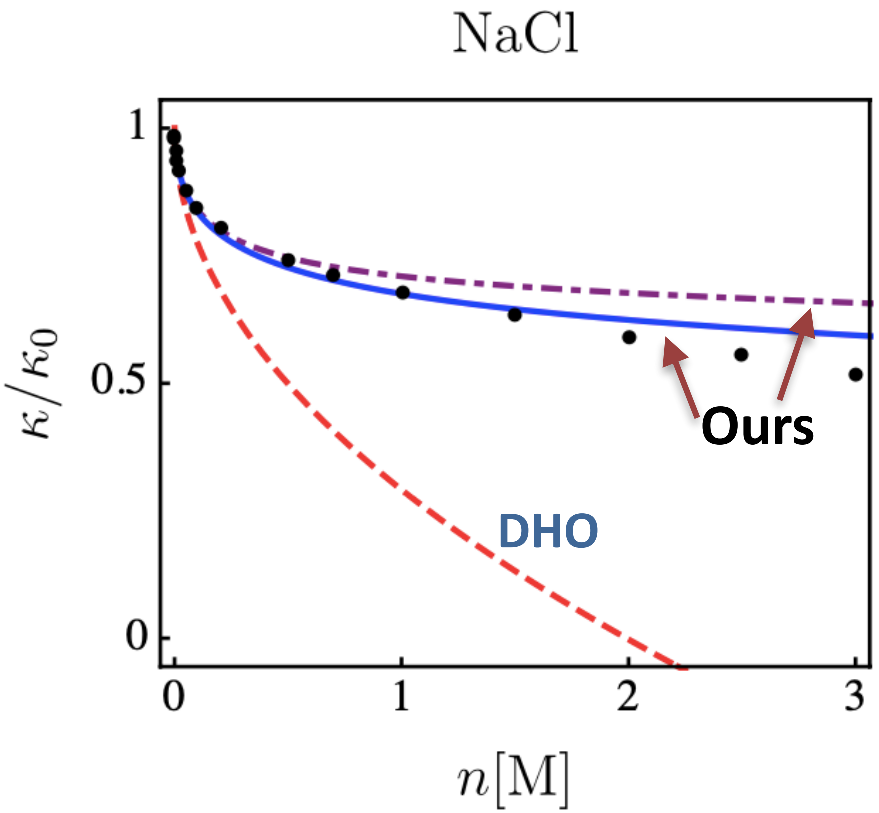
$$\kappa\left(\lambda_{\mathrm{D}}\right) \approx \kappa_0\left(1-\underline{\frac{r_{\mathrm{s}}}{\lambda_{\mathrm{D}}}\mathrm{e}^{-a/\lambda_{\mathrm{D}}}}-\frac{1}{6}\left(\underline{1-\frac{1}{\sqrt{2}}+\mathrm{e}^{-2a/\lambda_{\mathrm{D}}}-\frac{1}{\sqrt{2}}\mathrm{e}^{-\sqrt{2}a/\lambda_{\mathrm{D}}}}\right)\frac{l_{\mathrm{B}}}{\lambda_{\mathrm{D}}}\right)$$

DHO equation:

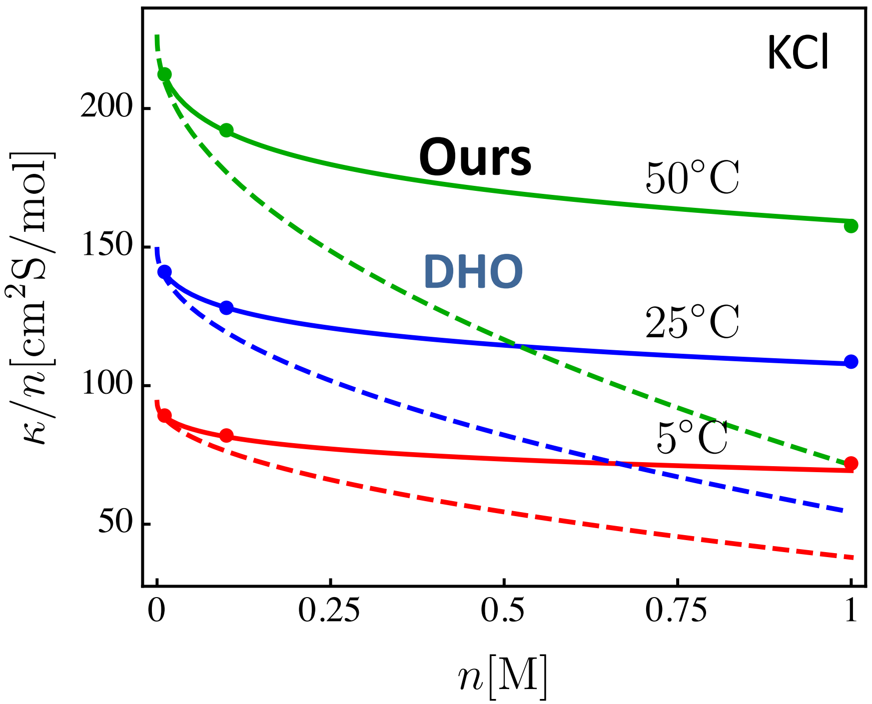
$$\kappa\left(\lambda_D\right)=\kappa_0\left(1-\underline{\frac{r_s}{\lambda_D}}-\underline{\frac{1}{3}\left(1-\frac{1}{\sqrt{2}}\right)}\frac{l_B}{\lambda_D}\right)$$

Avni, Adar, Orland & Andelman, PRL '22

Comparison with experiments



Temperature dependence

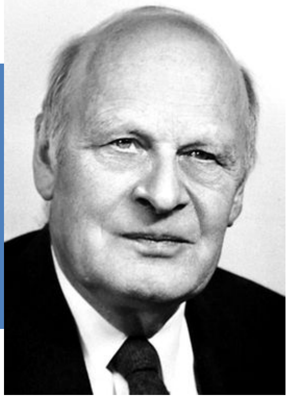


No fit parameters!

Avni, Adar, Orland & Andelman, PRL ’22
Avni, Orland, Andelman, JCP ‘22

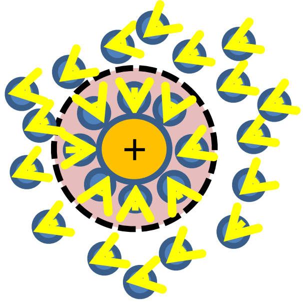
Conclusions

Going beyond Onsager's theories



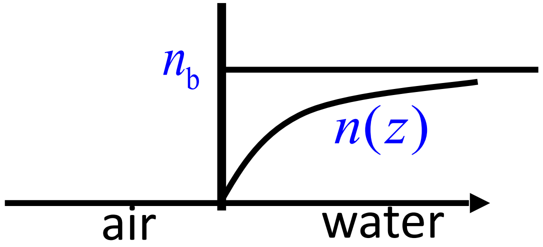
- Interaction of ions and dipoles

  Hydration shells & dielectric decrement



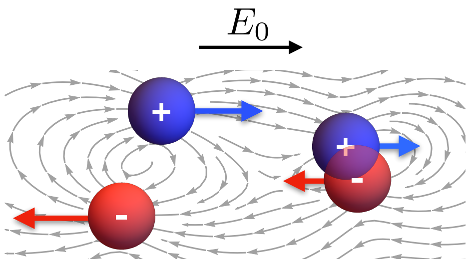
- Ion specific effects at interfaces

  Surface tension of electrolytes

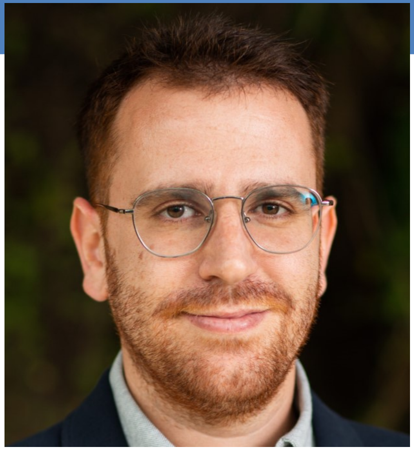


- Conductivity of concentrated solutions

  Finite size of ions



Thanks



R. Adar

College de France

Y. Avni

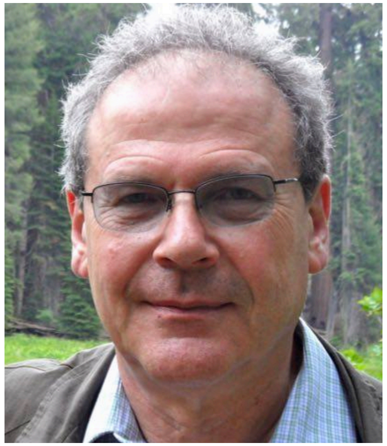
TAU & Chicago U

T. Markovich

TAU, Eng.

H. Orland

Saclay



R. Podgornik

Beijing