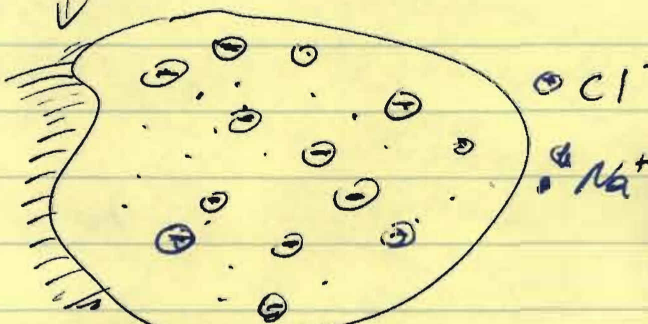
II The Poisson-Boltzmann Theory for Electrostatics

1. Some background. basics
2. Variational formulation. some new results
3. Application to solvation: dielectric boundary forces
4. Stat. mech foundation:
   from a lattice gas model
   to the mean-field model.
5. Remarks: size effect, numerics, etc.

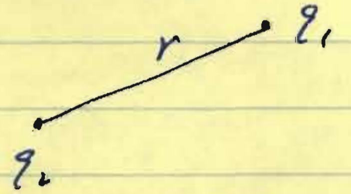
1. Some background, basics

charged surface

polarization



~~Coulomb~~
Coulomb's law



$$F = k_e \frac{q_1 q_2}{r^2}$$

$\cdot q_i$

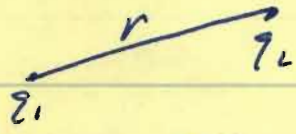
$\cdot q$ test charge

$$\vec{F}(\vec{r}) = \frac{q}{4\pi\varepsilon_0} \sum_{i=1}^{N} \frac{q_i\,(\vec{r}-\vec{r}_i)}{\cancel{k}\,|\vec{r}-\vec{r}_i|}$$

salted water
e.g. NaCl
Sodium Chloride
sodium ions Na^+
chloride ions Cl^-.

An ionic solution
an electrolyte.

charges from protein polarize the solvent.



force $F = \frac{q_1 q_2}{4\pi \varepsilon_0}$

potential energy (at q_1 by q_2)

$$E_{21} = \frac{1}{4\pi\varepsilon_0} \cdot \frac{q_1 q_2}{r}$$

potential (at q_1 by q_2

$$V_{21} = \frac{1}{4\pi\varepsilon_0}\frac{q_2}{r}. \qquad (E_{21} = q_1 V_{21})$$

Continuum. Poisson's equation

(A) $$\nabla \cdot \varepsilon \varepsilon_0 \nabla \psi = -\rho$$

ρ ← charge density

ε_0 ← vacuum permittivity

ε ← relative permittivity (dielectric coefficient)

or: $\nabla \cdot \varepsilon \nabla \psi = -4\pi\rho$

For an ionic solution

$$\rho = \rho_f + \rho_i$$

ρ_i ← induced charge density

ρ_f ← fixed charge density

(B) $$\rho_i(x) = \sum_{i=1}^{m} z_i e\, c_i(x)$$

z_i … valence of ith ionic species

e … elementary charge.

$c_i(x)$ … local concentration of ith ions.

(C) Boltzmann distributions for equilibrium ionic concentrations $c_1(x), \dots, c_m(x)$.

$$c_j(x) = c_j^{\infty} e^{-\beta z_j e \psi(x)}$$

$\psi(x)$ … electrostatic potential

$\beta = \frac{1}{k_B T}$.

k_B = the Boltzmann constant

T = temperature

c_j^∞ = bulk concentration of jth ions

(A)+(B)+(C): The Poisson-Boltzmann eq.

$$\boxed{\nabla\cdot\varepsilon\varepsilon_0\nabla\psi + \sum_{j=1}^{M} z_j e c_j^\infty e^{-\beta z_j e\psi(x)} = -\rho_f}$$

special cases.

(1) 1:1 salt. $z_1 = 1$. $z_2 = -1$. $c_1^\infty = c_2^\infty$

$$\sum_{j=1}^{M}(\cdots) = e c_1^\infty\left(e^{-\beta e\psi} - e^{\beta e\psi(x)}\right)$$

$$= 2ec_1^\infty \sinh\left(\cancel{e}^{-\beta e\psi}\right)$$

$$= -2ec_1^\infty \sinh(\beta e\psi)$$

$$\nabla\cdot\varepsilon\varepsilon_0\nabla\psi - 2ec_1^\infty\sinh(\beta e\psi) = -\rho_f$$

The ~~sh~~ sinh PB equation

(2) $$\sum_{j=1}^{M} z_j e c_j^\infty e^{-\beta z_j e\psi(x)}$$

$$= \sum_{j=1}^{M} z_j e c_j^\infty\left(1 - \beta z_j e\psi(x)\right) + \cdots$$

$$= \underbrace{\sum_{j=1}^{M} z_j e c_j^\infty}_{=0} - \beta\left[\sum_{j=1}^{M}(z_j e)^2 c_j^\infty\right]\psi + \cdots$$

charge neutrality!

$$\nabla\cdot\varepsilon\varepsilon_0\nabla\psi - \beta\left[\sum_{j=1}^{M}(z_j e)^2 c_j^\infty\right]\psi = -\rho_f$$

linearized PB eq!

$$\Delta\psi - \kappa^2\psi = -\tilde{\rho}_f$$

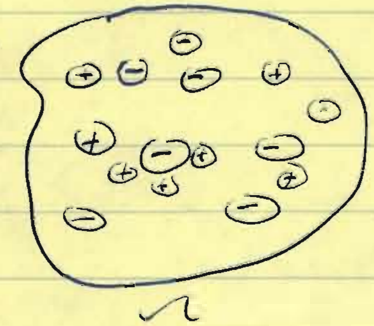
$$\kappa^2 = \frac{\beta\sum_{j=1}^{M}(z_j e)^2 c_j^\infty}{\varepsilon\varepsilon_0}$$

We are here at: *The Poisson-Boltzmann equation*

1. Background and the basics

$$\nabla\cdot\varepsilon\varepsilon_0\nabla\psi + \sum_{j=1}^{M} z_j e c_j^{\infty} e^{-\beta z_j e\psi} = -\rho_f \quad \text{in } \Omega$$

$c_j(x) = c_j^{\infty} e^{-\beta z_j e\psi(x)}$ ... concentrations of jth ions

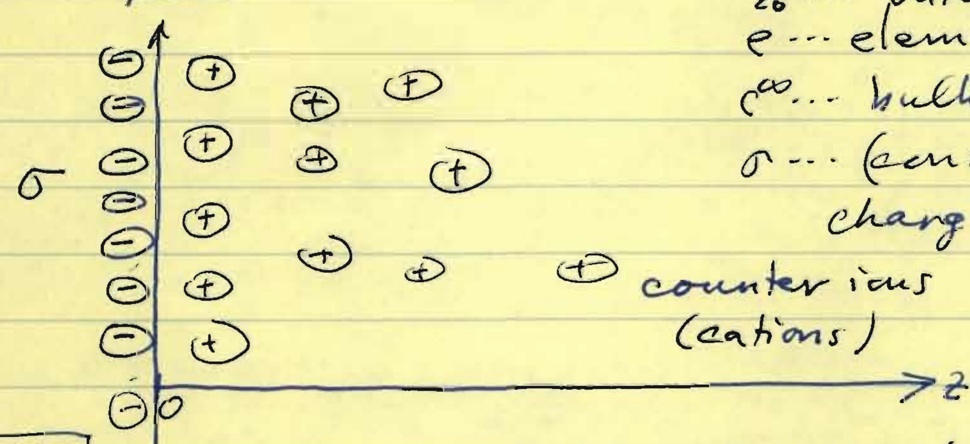


Special cases: see page $\boxed{22}$.

Some examples (w/ explicit analytical solutions)

Example 1

$c_0(z)$ ... counter ion concentration
z_0 ... valence $=1$
e ... elementary charge
c^{∞} ... bulk concentration
σ ... (constant) surface charge density



$$\boxed{c_0(z) = c_0^{\infty} e^{-e\psi/k_BT}}$$

$c_0(z)$ = concentration of counter ions
z_0 = valence $=1$ (assumption)

$$\begin{cases} \varepsilon\nabla^2\psi = -4\pi e c_0^{\infty} e^{-e\psi/k_BT} & (z>0) \\ \psi'(0) = -\dfrac{\sigma}{\varepsilon} & (\sigma<0) \\ \psi'(\infty) = 0 \end{cases}$$

After change of variables (still use ψ)

$$\begin{cases} 2\psi''(z) = -e^{-\psi} \\ \psi'(0) = 1 \\ \psi'(\infty) = 0 \end{cases}$$

$$2\psi'\psi'' = -e^{-\psi}\psi'$$

$$(\psi'^2)' = (e^{-\psi})'$$

$\psi'(1) = 1$: $\psi'^2 - 1 = e^{-\psi} - e^{-\psi_0}$

Let $u_0 = 1 - e^{-\psi_0}$.

$$\frac{dz}{d\psi} = \frac{1}{\sqrt{e^{-\psi} + u_0}}$$

Let $\eta = e^{-\psi}$ $\quad \frac{dz}{d\eta} = -\frac{1}{\eta\sqrt{\eta + u_0}}$.

Let $s^2 = \eta + u_0$ ...

Sol'n.

$$\begin{cases} \psi(z) = \frac{2k_B T}{e} \ln(z + b) + \psi_0 \\ c_0(z) = \frac{1}{2\pi l} \cdot \frac{1}{(z+b)^2} \end{cases}$$

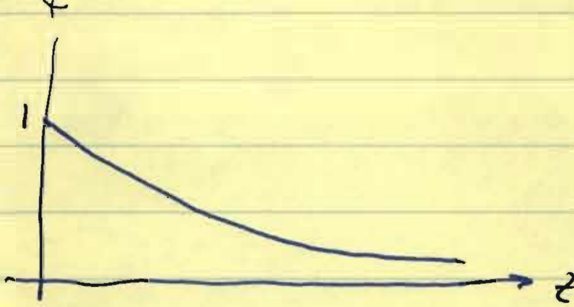
$b = \frac{e}{2\pi|\sigma| l}$.

— Gouy-Chapman length

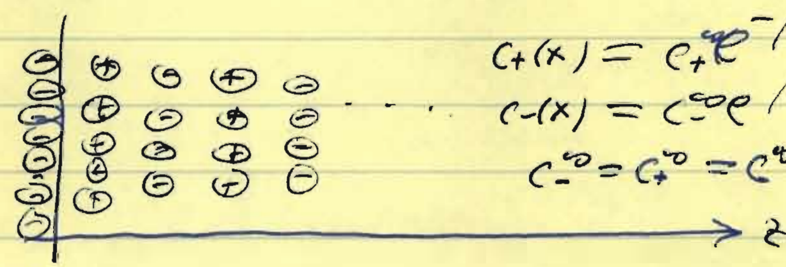
$l = \frac{e^2}{\varepsilon k_B T} \sim 7\text{Å}$

Bjerrum length

Example



Example 2



$$c_+(x) = c_+^{\infty} e^{-\beta e\psi}$$
$$c_-(x) = c_-^{\infty} e^{\beta e\psi}$$
$$c_-^{\infty} = c_+^{\infty} = c^{\infty}$$

$z_+ = 1$, $z_- = -1$.

$$\begin{cases} \psi''(z) = \frac{8\pi e c^{\infty}}{\varepsilon} \sinh\left(\frac{e\psi}{k_B T}\right) \\ \psi'(0) = -\frac{\sigma}{\varepsilon} > 0 \end{cases}$$

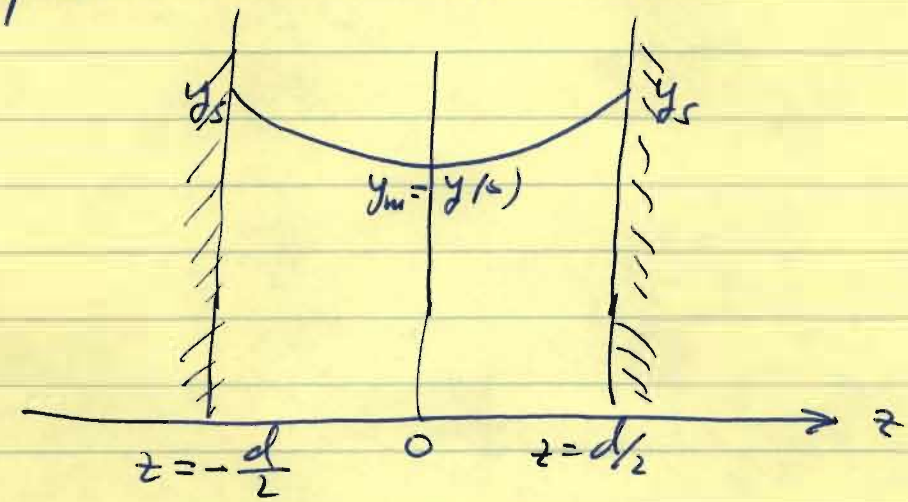
$$\psi(z) = -\frac{2k_BT}{e} \ln \frac{1+\gamma e^{-z/\lambda_D}}{1-\gamma e^{-z/\lambda_D}}$$

$$\gamma^2 + \frac{2b}{\lambda_D}\gamma - 1 = 0 \qquad \gamma > 0.$$

$$\lambda_D = \kappa^{-1} = \left(\frac{8\pi c^\infty e^2}{\varepsilon k_B T}\right)^{-\frac{1}{2}} \sim (c^\infty)^{-\frac{1}{2}}.$$

Debye-Hückel screen length.

<u>Example 3</u> Two flat, charged memberanes

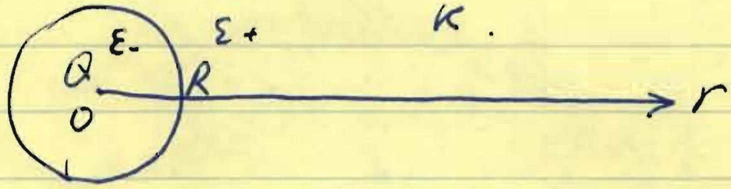


BC: $\psi(\pm \frac{d}{2}) = \psi_s$

$$\begin{cases} y''(z) = \lambda_D^{-2} \sinh y \\ \left.\frac{\partial y}{\partial z}\right|_{z=\frac{d}{2}} = \frac{2}{b} \quad \left.\frac{\partial y}{\partial z}\right|_{z=0} = 0 \end{cases} \Rightarrow \frac{2}{b^2}\lambda_D^2 = \cosh y_s - \cosh y_m.$$

$$\Rightarrow z = \lambda_D \int_{y_m}^{y} \frac{dy'}{\sqrt{2\cosh y' - 2\cosh y_m}}$$

Example 4



$\chi_+ = \chi_{\{r>R\}}$

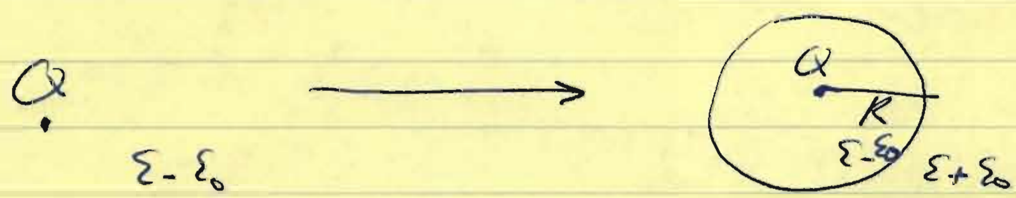
$$\begin{cases} \nabla\cdot\varepsilon\varepsilon_0\nabla\psi - \chi_+\varepsilon_+\varepsilon_0\kappa^2\psi_2 = -Q\delta & \mathbb{R}^3 \\ \psi(\infty)=0 \end{cases}$$

$$\begin{cases} \varepsilon_-\varepsilon_0\Delta\psi = -Q\delta & r<R \\ \Delta\psi - \kappa^2\psi = 0 & r>R \\ [\![\psi]\!]_R = 0 \\ [\![\varepsilon\psi']\!]_R = 0 \\ \psi(\infty)=0 \end{cases}$$

$$\psi(r) = \begin{cases} \dfrac{Q}{4\pi\varepsilon_+\varepsilon_0 R(1+\kappa R)} + \dfrac{Q}{4\pi\varepsilon_-\varepsilon_0}\left(\dfrac{1}{r}-\dfrac{1}{R}\right) & (r\le R) \\[2ex] \dfrac{Q}{4\pi\varepsilon_+\varepsilon_0(1+\kappa R)}\,\dfrac{1}{r}e^{-\kappa(r-R)} & (r>R) \end{cases}$$

The Coulomb ~~field~~ (potential):

$$\psi_c(r) = \frac{Q}{4\pi\varepsilon_-\varepsilon_0 r}$$



Born's cycle

Define the reaction field

$$\phi_r(r) = \phi(r) - \phi_c(r)$$

$$= \begin{cases} \dfrac{Q}{4\pi\varepsilon_+\varepsilon_0 R(1+\kappa R)} - \dfrac{Q}{4\pi\varepsilon_-\varepsilon_0 R} & (r<R) \\ \dfrac{Q}{4\pi\varepsilon_+\varepsilon_0(1+\kappa R)r}e^{-\kappa(r-R)} & (r>R) \end{cases}$$

$$= \begin{cases} \dfrac{Q}{4\pi\varepsilon_0 R}\left[\dfrac{1}{\varepsilon_+(1+\kappa R)} - \dfrac{1}{\varepsilon_-}\right] & (r<R) \\ \dfrac{Q}{4\pi\varepsilon_+\varepsilon_0(1+\kappa R)r}e^{-\kappa(r-R)} & (r>R) \end{cases}$$

Solvation energy of an ion:

$$E = \frac{1}{2}Q\phi_r(0) = \frac{Q^2}{8\pi\varepsilon_0 R}\left[\frac{1}{\varepsilon_+(1+\kappa R)} - \frac{1}{\varepsilon_-}\right].$$

If $\kappa = 0$ (no salt) Then

$$E = \frac{Q^2}{8\pi\varepsilon_0 R}\left(\frac{1}{\varepsilon_+} - \frac{1}{\varepsilon_-}\right)$$ — Born's formula (1920).