Poisson-Boltzmann theory

$\rho(\vec{r})\,,\quad \vec{E}(\vec{r})\,,\quad \phi(\vec{r})$

$$\Big\downarrow \; \langle \ldots \rangle \quad \text{thermal average}$$

$\langle \rho(\vec{r}) \rangle\,,\quad \langle \vec{E}(\vec{r}) \rangle\,,\quad \langle \phi(\vec{r}) \rangle$

$$\rho(\vec{r}) = \langle \rho(\vec{r}) \rangle + \delta\rho(\vec{r}) \qquad \phi(\vec{r}) = \langle \phi(\vec{r}) \rangle + \delta\phi(\vec{r})$$

$$\vec{E}(\vec{r}) = \langle \vec{E}(\vec{r}) \rangle + \delta\vec{E}(\vec{r})$$

$$\mathcal{H} = \frac{\varepsilon}{2} \int d^3\vec{r}\ \vec{E}^2(\vec{r})$$

$$\vec{E}^2 = \left(\langle \vec{E} \rangle + \delta \vec{E} \right)^2 = \underbrace{\langle \vec{E} \rangle^2}_{\substack{\text{discard} \\ \text{constant} \\ \text{offset}}} + \underbrace{\delta \vec{E}^2}_{\substack{\text{neglect} \\ \text{(MEAN FIELD} \\ \text{APPROXIMATION)}}} + 2 \langle \vec{E} \rangle \delta \vec{E}$$

$$\mathcal{H} \to \frac{\varepsilon}{2} \int d^3\vec{r}\ 2 \langle \vec{E} \rangle \delta \vec{E} = \varepsilon \int d^3\vec{r} \langle \vec{E} \rangle \left[\vec{E} - \underbrace{\langle \vec{E} \rangle}_{\substack{\text{discard} \\ \text{const. offset}}} \right]$$

$$\to \varepsilon \int d^3\vec{r} \langle \vec{E} \rangle \cdot \vec{E} = \mathcal{H}_{MF}$$

$$\mathcal{H}_{MF} = \varepsilon \int d^3\vec{r}\, \underbrace{\langle \vec{E} \rangle}_{-\vec{\nabla}\langle \phi \rangle} \cdot \vec{E} = \varepsilon \int d^3\vec{r}\, \langle \phi \rangle \underbrace{\vec{\nabla} \cdot \vec{E}}_{\frac{1}{\varepsilon}\rho}$$

part. Int.

$$\boxed{\mathcal{H}_{MF} = \int d^3\vec{r}\, \langle \phi(\vec{r}) \rangle\, \rho(\vec{r})}$$

$$\rho(\vec{r}) = \sum_i z_i e\, \delta(\vec{r} - \vec{r}_i)$$

$$\mathcal{H}_{MF} = \sum_i z_i e \langle \phi(\vec{r}_i) \rangle$$

$\langle \phi(\vec{r}) \rangle$ should be viewed as an EXTERNAL potential! StatMech of such a system is MUCH EASIER!

<u>Abbr.:</u> $c_k(\vec{r}) = \langle \delta(\vec{r} - \vec{r}_k) \rangle$

"average concentration of particle k"

$$c_k(\vec{r}) = \frac{\int d^3\vec{r}_1 \int d^3\vec{r}_2 \ldots \int d^3\vec{r}_N \; \delta(\vec{r}-\vec{r}_k) \; \exp(-\beta \mathcal{H}_{MF})}{\int d^3\vec{r}_1 \ldots \int d^3\vec{r}_N \; \exp(-\beta \mathcal{H}_{MF})}$$

within Mean Field

$$\exp(-\beta \mathcal{H}_{MF}) = e^{-\beta z_1 e \langle \phi(\vec{r}_1) \rangle} \ldots e^{-\beta z_N e \langle \phi(\vec{r}_N) \rangle}$$

factorizes!

$$c_k(\vec{r}) = \frac{\int d^3\vec{r}_k \; \delta(\vec{r}-\vec{r}_k) \; \exp[-\beta z_k e \langle \phi(\vec{r}_k) \rangle]}{\int d^3\vec{r}_k \; \exp[-\beta z_k e \langle \phi(\vec{r}_k) \rangle]}$$

$$c_k(\vec{r}) = \frac{\exp[-\beta z_k e \langle \phi(\vec{r}) \rangle]}{\int d^3\vec{r}\, \exp[-\beta z_k e \langle \phi(\vec{r}) \rangle]}$$

Self-consistency equation $\equiv$ Poisson-Boltzmann equation

$$\Rightarrow \langle \rho(\vec{r}) \rangle = \sum_k z_k e\, c_k(\vec{r}) =$$

$$\boxed{\sum_k z_k e \frac{\exp(-\beta z_k e \langle \phi(\vec{r}) \rangle)}{\int d^3\vec{r}\, \exp(-\beta z_k e \langle \phi(\vec{r}) \rangle)} = -\varepsilon \vec{\nabla}^2 \langle \phi(\vec{r}) \rangle}$$

introduce: reduced potential $\Psi(\vec{r}) = \beta e\, \phi(\vec{r})$

dimensionless

discard $\langle \ldots \rangle$

PBE:

$$-\varepsilon \vec{\nabla}^2 \Psi(\vec{r}) = \sum_i \frac{z_i \beta e^2 \exp(-z_i \Psi)}{\int d^3 r \, \exp(-z_i \Psi)}$$

$$\frac{\beta e^2}{\varepsilon} = 4\pi \frac{e^2}{4\pi \varepsilon k_B T} = 4\pi l_B$$

$$-\vec{\nabla}^2 \Psi = 4\pi l_B \sum_i \frac{z_i \exp(-z_i \Psi)}{\int d^3 r \, \exp(-z_i \Psi)}$$

ionic species a : $\sum_i = \sum_a \sum_{i \in a}$

$\sum_{i \in a} 1 = N_a$ # of ions in species a

$$\boxed{-\vec{\nabla}^2 \psi = 4\pi l_B \sum_a \frac{N_a z_a \exp(-z_a \psi)}{\int d^3\vec{r} \exp(-z_a \psi)}}$$

define $c_a(\vec{r}) = \sum_{k \in a} c_k(\vec{r}) = \dfrac{N_a \exp(-z_a \psi)}{\int d^3\vec{r} \exp(-z_a \psi)}$

$$-\vec{\nabla}^2 \psi = 4\pi l_B \sum_a z_a c_a$$

$$\ln c_a = \ln N_a - z_a \psi - \ln \int d^3\vec{r}\, \exp(-z_a \psi) \quad | \vec{\nabla}$$

$$\vec{\nabla} \ln c_a = -z_a \vec{\nabla} \psi$$

reduced field $\vec{\mathcal{E}} := \beta e \vec{E} = -\vec{\nabla}\psi$

$$\boxed{\begin{aligned} &\vec{\nabla}\cdot\vec{\mathcal{E}} = 4\pi l_B \sum_a z_a c_a \\ &(\vec{\nabla}\times\vec{\mathcal{E}} = 0) \\ &\vec{\nabla}\ln c_a = z_a \vec{\mathcal{E}} \end{aligned}}$$

PBE in terms of fields

Maggs-style variational formulation

finite volume V $\qquad \int d^3\vec{r}\, 1 = V$

Constraints:

(i) particle numbers: $\int d^3\vec{r}\, c_a(\vec{r}) = N_a$

$$\int d^3\vec{r} \left[c_a - \frac{N_a}{V} \right] = 0$$

↳ Lagrange multiplier μ_a (number)

(ii) Gauss' law: $\vec{\nabla} \cdot \vec{\mathcal{E}} - 4\pi l_B \sum_a z_a c_a = 0$

↳ Lagrange multiplier ψ (field)

Λ^3: normalization volume to define entropy

$$F = \int d^3\vec{r} \left\{ \underbrace{\frac{1}{2} \vec{\mathcal{E}}^2}_{\text{energy}} + \underbrace{4\pi l_B \sum_a c_a \ln(\Lambda^3 c_a)}_{\text{entropy}} \right.$$

$$\left. - \underbrace{\psi \left[\vec{\nabla} \cdot \vec{\mathcal{E}} - 4\pi l_B \sum_a z_a c_a \right]}_{\text{constraint (ii)}} - \underbrace{\sum_a \mu_a \left[c_a - \frac{N_a}{V} \right]}_{\text{constraint (i)}} \right\}$$

$\vec{\mathcal{E}}$ and c_a : independent degrees of freedom

$$\frac{\delta F}{\delta \Psi} = 0 \Rightarrow \boxed{\vec{\nabla} \cdot \vec{\mathcal{E}} = 4\pi l_B \sum_a z_a c_a}$$

$$\frac{\partial F}{\partial \mu_a} = 0 \Rightarrow \boxed{\int d^3\vec{r}\, c_a = N_a}$$

$$\frac{\delta F}{\delta \mathcal{E}_\alpha} = 0 \Rightarrow 0 = \mathcal{E}_\alpha + \partial_\beta \left(\Psi\, \delta_{\alpha\beta} \right) \Rightarrow \boxed{\vec{\mathcal{E}} = -\vec{\nabla}\Psi}$$

$$\vec{\nabla} \cdot \vec{\mathcal{E}} = \partial_\beta \mathcal{E}_\alpha \delta_{\alpha\beta} \qquad \Rightarrow \boxed{\vec{\nabla} \times \vec{\mathcal{E}} = 0}$$

$$\frac{\delta F}{\delta c_a} = 0 \Rightarrow 0 = 4\pi l_B \left\{ \ln\left(\Lambda^3 c_a\right) + c_a \frac{1}{\Lambda^3 c_a} \Lambda^3 \right\} + 4\pi l_B \Psi z_a - \mu_a$$

$$\frac{\mu_a}{4\pi l_B} = \ln\left(\Lambda^3 c_a\right) + 1 + z_a \Psi \qquad \Big| \ \vec{\nabla}$$

$$0 = \vec{\nabla} \ln c_a + z_a \vec{\nabla} \Psi = \vec{\nabla} \ln c_a - z_a \vec{E}$$

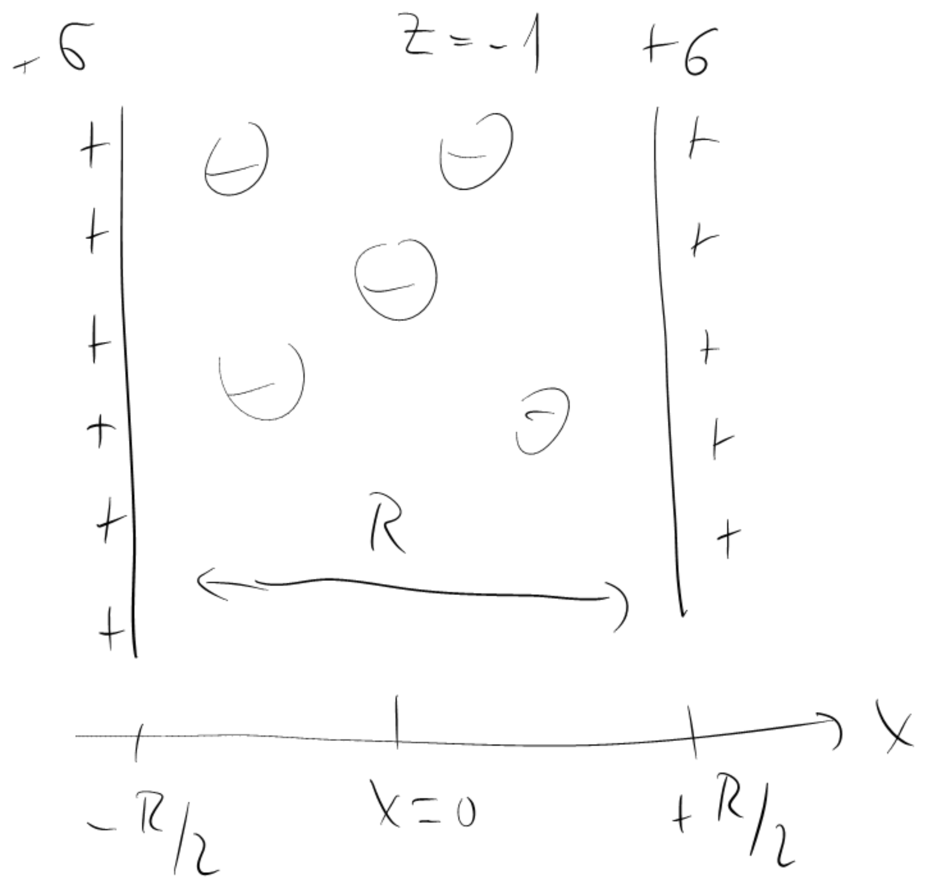
$$\boxed{\vec{\nabla} \ln c_a = z_a \vec{E}}$$

$\uparrow$ PBE recovered

It can be shown: This is a minimum

M. Baptista et al. PRE 2009

6. Counterions in a 1d capacitor



at $x = -\frac{R}{2}$:

$$\vec{E} = E\hat{e}_x = \frac{\sigma}{\varepsilon}$$

$$\mathcal{E} = \frac{\beta e \sigma}{\varepsilon}$$

N: # of counterions

system as a whole is charge neutral !

PBE: $$-\vec{\nabla}^2 \psi = 4\pi l_B \frac{-N \exp(+\psi)}{\int d^3\vec{r} \exp(+\psi)}$$

$$\frac{d^2}{dx^2}\psi = A \exp(+\psi) = -\frac{d}{d\psi}\left[-A \exp(+\psi)\right]$$

$$A = \frac{N 4\pi l_B}{\int d^3\vec{r}\, e^{+\psi}}$$ some normalization constant (taken care of later)

cf. $m\frac{d^2}{dt^2}x = -\frac{d}{dx}U$ Newton!

"energy conservation"

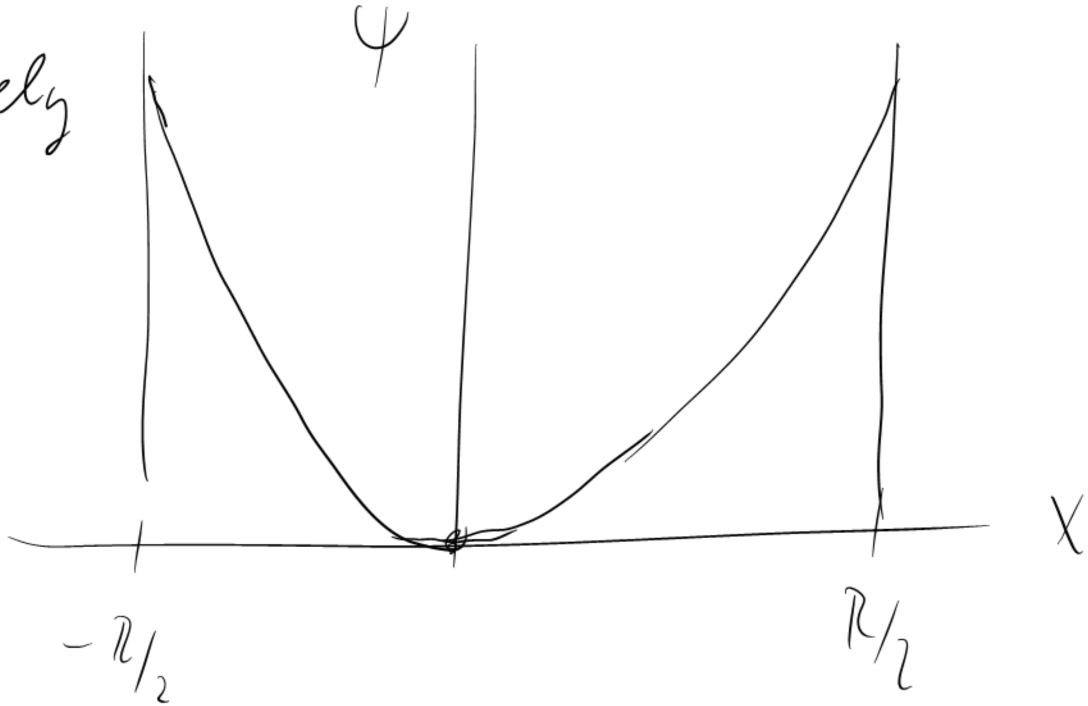
$$\underbrace{\frac{1}{2}\left(\frac{d\psi}{dx}\right)^2}_{\text{"kinetic energy"}} + \left[-A\exp(+\psi)\right] = \text{const.} = -A$$

normalize potential : $\psi(0) = 0$

symmetry: $\left.\frac{d\psi}{dx}\right|_{x=0} = 0$

$$\left(\frac{d\psi}{dx}\right)^2 = 2A\left[\exp(\psi) - 1\right]$$

qualitatively



$$\underline{\underline{x > 0}} \Rightarrow \frac{d\psi}{dx} > 0 \Rightarrow \frac{d\psi}{dx} = \sqrt{2A}\sqrt{e^{\psi} - 1}$$

$$dx = \frac{d\psi}{\sqrt{2A}\sqrt{\exp(\psi)-1}} \qquad \Big| \int$$

Wolfram Alpha

$$x = \int_0^{\psi} \frac{d\varphi}{\sqrt{2A}\sqrt{\exp(\varphi)-1}} =$$

$$= \frac{1}{\sqrt{2A}} \cdot 2 \underbrace{\tan^{-1}}_{\text{inverse fct. of tan}} \sqrt{e^{\varphi}-1} \, \Bigg|_{\varphi=0}^{\varphi=\psi}$$

no contrib

$$\boxed{x = \sqrt{\frac{2}{A}}\, \tan^{-1} \sqrt{e^{\psi} - 1}}$$

$$\sqrt{e^{\psi} - 1} = \tan\left(\sqrt{\frac{A}{2}}\, x\right)$$

$$e^{\psi} = 1 + \tan^2\left(\sqrt{\frac{A}{2}}\, x\right) = \frac{1}{\cos^2\left(\sqrt{\frac{A}{2}}\, x\right)}$$

$$\boxed{\psi = -2 \ln \cos\left(\sqrt{\frac{A}{2}}\, x\right)}$$

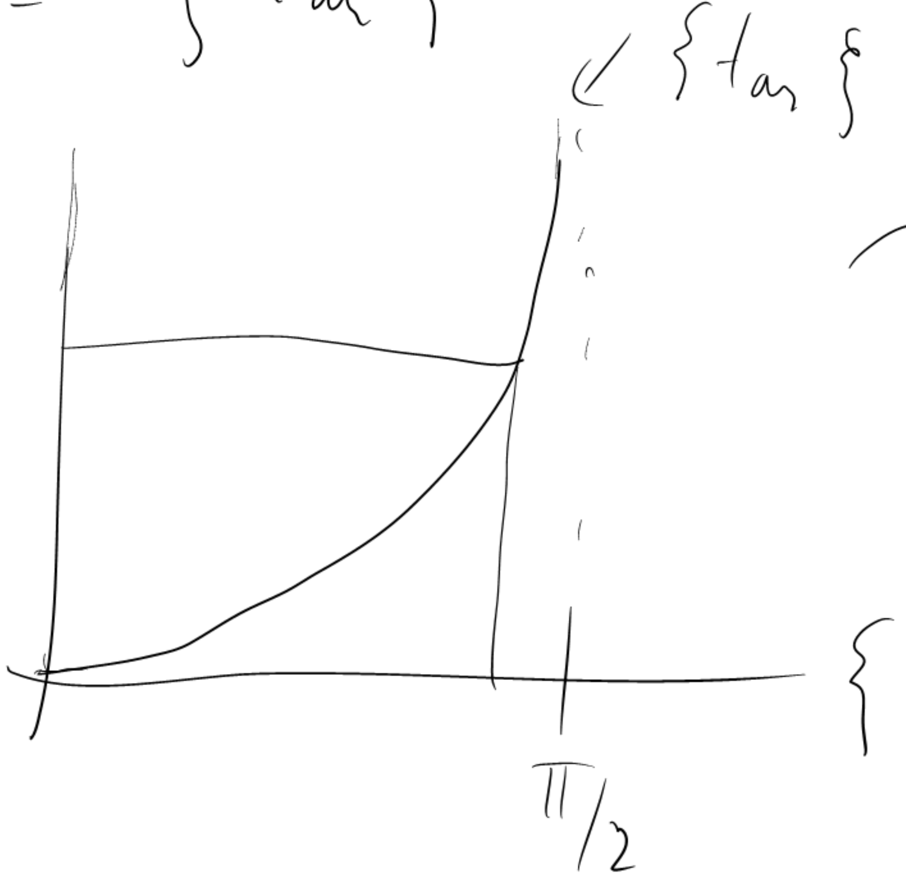
$$\varepsilon = -\frac{d\psi}{dx} = -2\,\frac{1}{\cos\left(\sqrt{\frac{A}{2}}\,x\right)}\,\sin\left(\sqrt{\frac{A}{2}}\,x\right)\sqrt{\frac{A}{2}}$$

$$= -\sqrt{2A}\,\tan\left(\sqrt{\frac{A}{2}}\,x\right)$$

$$x = -\frac{R}{2} \Rightarrow \varepsilon = \frac{\beta e \sigma}{\varepsilon} = \sqrt{2A}\,\tan\left(\sqrt{\frac{A}{2}}\,\frac{R}{2}\right)$$

$$= \frac{4}{R}\underbrace{\sqrt{\frac{A}{2}}\,\frac{R}{2}}_{\xi}\,\tan\left(\underbrace{\sqrt{\frac{A}{2}}\,\frac{R}{2}}_{\xi}\right)$$

$$\frac{\beta e G R}{4\varepsilon} = \xi \tan \xi$$



$$\rightsquigarrow \xi = \sqrt{\frac{A}{2}}\,\frac{R}{2}$$

$$\rightsquigarrow \underline{\underline{A}}$$