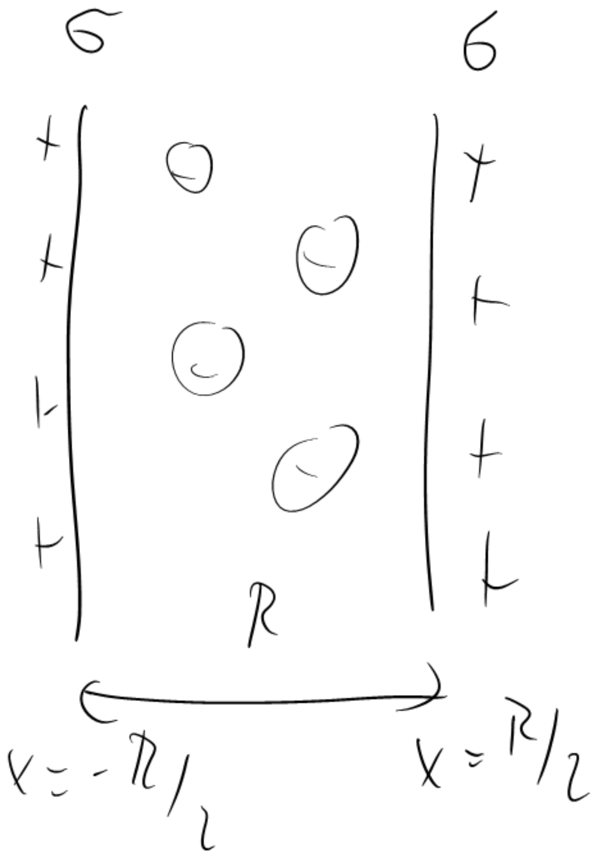
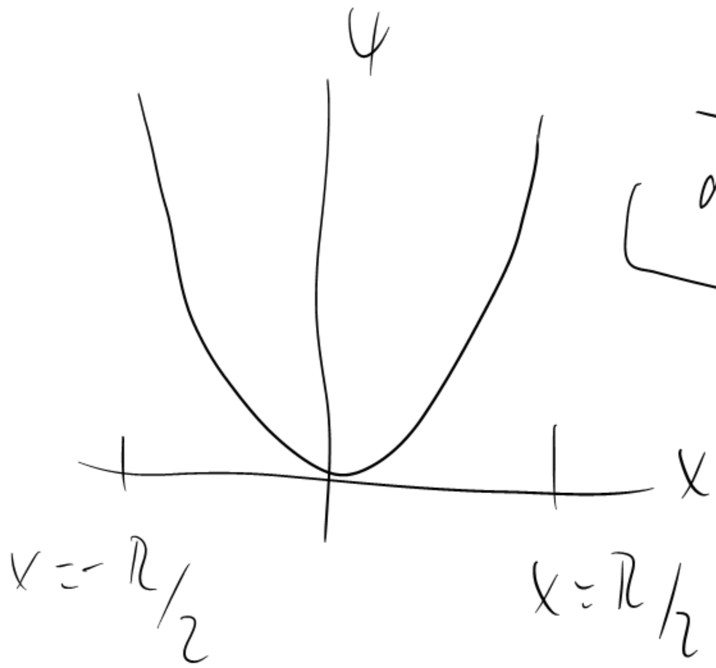


charge neutral



$$\frac{d^2}{dx^2}\psi = A\exp(+\psi)$$

solve $$\frac{\beta e \sigma R}{4\varepsilon} = \left(\sqrt{\frac{A}{2}}\,\frac{R}{2}\right)\tan\left(\sqrt{\frac{A}{2}}\,\frac{R}{2}\right)$$

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

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

$$\frac{d}{dx}\mathcal{E} = -\sqrt{2A}\,\frac{1}{\cos^2\left(\sqrt{\frac{A}{2}}\,x\right)}\sqrt{\frac{A}{2}} = -\frac{A}{\cos^2\left(\sqrt{\frac{A}{2}}\,x\right)}$$

$$\overset{!}{=} 4\pi l_B\left(-c\right) \Rightarrow \boxed{c(x) = \frac{A}{4\pi l_B \cos^2\left(\sqrt{\frac{A}{2}}\,x\right)}}$$

Is the system charge-neutral? If yes, then

$$2\sigma\, d(\text{area}) = \text{charge} = d(\text{area}) \int_{-R/2}^{+R/2} dx\, c(x)\cdot e$$

or $\quad \frac{\sigma}{e} = \int_0^{R/2} dx\, c(x)$ Does this hold?

r.h.s. $\int_0^{R/2} dx\, c(x) = \frac{A}{4\pi l_B} \int_0^{R/2} \frac{dx}{\cos^2\left(\sqrt{\frac{A}{2}}\, x\right)} \overset{\xi=\sqrt{\frac{A}{2}}x}{=}$

$$= \frac{A}{4\pi l_B} \sqrt{\frac{2}{A}} \int_0^{\sqrt{\frac{A}{2}}\frac{R}{2}} \frac{d\xi}{\cos^2 \xi} =$$

$$= \frac{A}{4\pi l_B} \sqrt{\frac{2}{A}} \tan\left(\frac{\sqrt{A}}{2} \frac{R}{2}\right) =$$

$$= \frac{1}{4\pi l_B} \frac{4}{R} \underbrace{\left(\sqrt{\frac{A}{2}\frac{R}{2}}\right) \tan\left(\sqrt{\frac{A}{2}\frac{R}{2}}\right)}_{= \frac{\beta e \sigma R}{4\varepsilon}} =$$

$$= \frac{1}{4\pi l_B} \frac{\beta e \sigma}{\varepsilon} =$$

$$= \frac{\beta e \sigma}{\varepsilon} \frac{1}{4\pi} \left(\frac{e^2}{4\pi\varepsilon k_B T}\right)^{-1} = \frac{\sigma}{e} \quad \checkmark$$

OK!

$$\frac{\beta e \sigma R}{4\varepsilon} = \left(\sqrt{\frac{A}{2}}\,\frac{R}{2}\right) \tan\left(\sqrt{\frac{A}{2}}\,\frac{R}{2}\right)$$

re-parametrization $A \to \xi = \sqrt{\frac{A}{2}}\,\frac{R}{2}$

$$\frac{\beta e \sigma R}{4\varepsilon} = \pi \underbrace{\frac{e^2}{4\pi\varepsilon k_B T}}_{\ell_B} \frac{1}{e}\,\sigma R = \frac{1}{2} \underbrace{\frac{2\pi \ell_B \sigma}{e}}_{1/\lambda} R$$

introduce so-called Gouy-Chapman length

$$\boxed{\lambda = \frac{e}{2\pi l_B \sigma}}$$

as a measure for the surface charge

$$\frac{\beta e \sigma R}{4\varepsilon} = \frac{R}{2\lambda} \Rightarrow \boxed{\frac{R}{2\lambda} = \xi \tan \xi}$$

$R \to \infty \Rightarrow \xi \to \frac{\pi}{2} \Rightarrow$ write $\xi = \frac{\pi}{2} - \eta$

small

$$\tan \xi = \tan\left(\frac{\pi}{2} - \eta\right) = \cot \eta$$

$$\frac{R}{2\lambda} = \left(\frac{\pi}{2} - \eta\right) \cot \eta \qquad \Big| \cdot \tan \eta \cdot \frac{2\lambda}{R}$$

$$\tan \eta = \left(\frac{\pi}{2} - \eta\right) \frac{2\lambda}{R}$$

leading order : $\eta = \frac{\pi}{2} \frac{2\lambda}{R}$ (neglect terms of order $\frac{1}{R^2}$)

$$= \frac{\pi \lambda}{R}$$

$$\xi = \frac{\pi}{2} - \frac{\pi\lambda}{R} \qquad \sqrt{\frac{A}{2}} = \frac{2}{R}\xi = \frac{\pi}{R}$$

again, neglect terms $O\left(\frac{1}{R^2}\right)$

$$\boxed{A = 2\frac{\pi^2}{R^2}}$$

near the right plane $\quad x = \frac{R}{2} - y \qquad y > 0$, y small

$$\sqrt{\frac{A}{2}}\,x = \sqrt{\frac{A}{2}}\,\frac{R}{2} - \sqrt{\frac{A}{2}}\,y \simeq \xi - \frac{\pi}{R}y \simeq \frac{\pi}{2} - \frac{\pi\lambda}{R} - \frac{\pi y}{R} =$$

$$= \frac{\pi}{2} - \frac{\pi}{R}\left(y+\lambda\right)$$

$$\cos\left(\sqrt{\frac{A}{2}}\,x\right) \simeq \cos\left(\frac{\pi}{2} - \frac{\pi}{R}\left(y+\lambda\right)\right) = \sin\left[\frac{\pi}{R}\left(y+\lambda\right)\right]$$

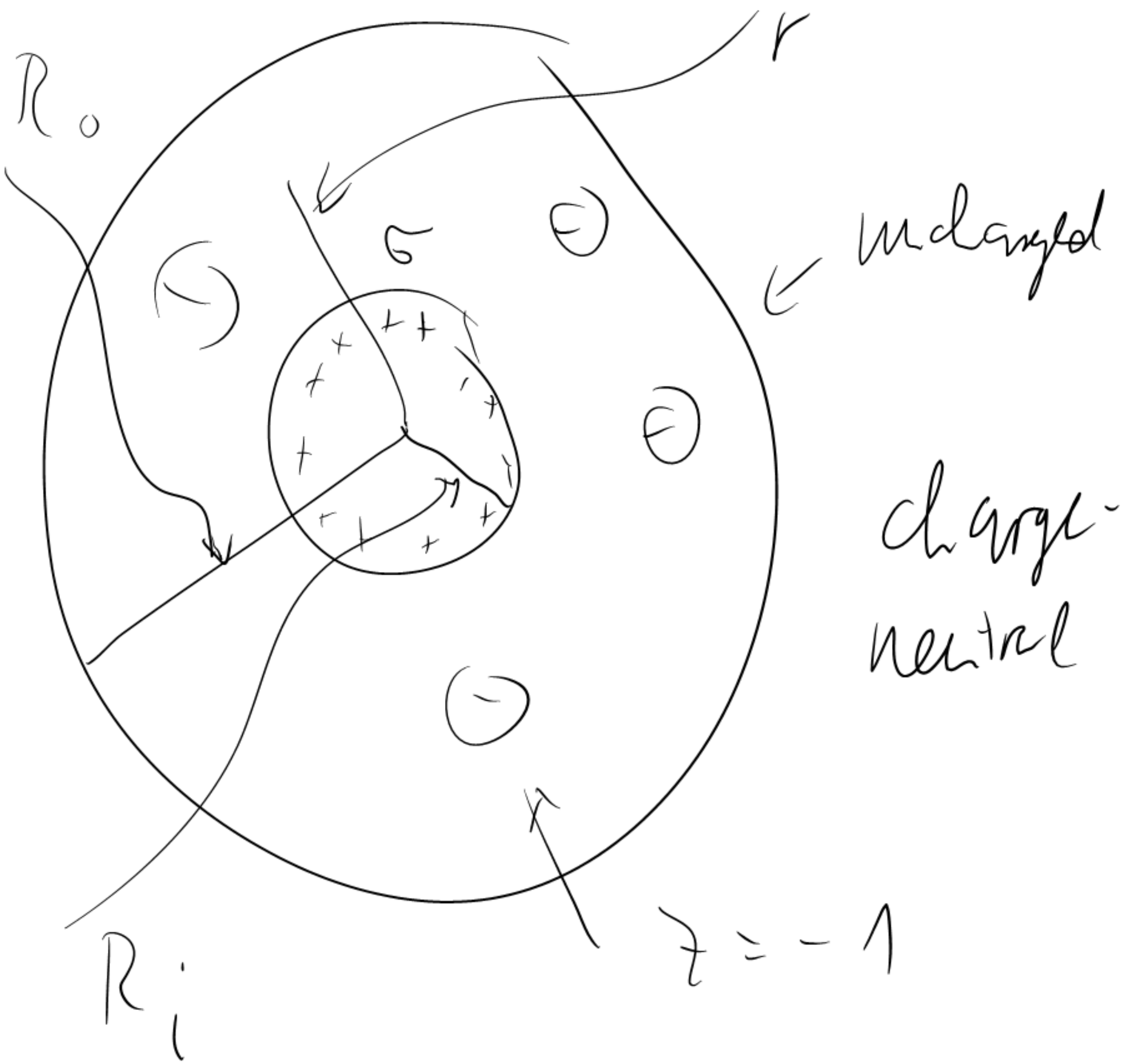
$$\simeq \frac{\pi}{R}\left(y+\lambda\right) \Rightarrow \text{conc. profile:}$$

$$c(x) = \frac{1}{4\pi \ell_B} A \frac{1}{\cos^2\left(\sqrt{\frac{A}{2}}\,x\right)} \simeq \frac{1}{4\pi \ell_B} 2\frac{\pi^2}{R^2} \frac{1}{\frac{\pi^2}{R^2}\left(y+\lambda\right)^2}$$

c)

$$\boxed{c(y) = \frac{1}{2\pi l_B (y+\lambda)^2}}$$

7. Counterions in 2d, 3d spherical capacitors



$$-\vec{\nabla}^2 \psi = A \exp(\psi)$$

We know solutions of

$$\vec{\nabla}^2 \psi = 0$$

$\psi(r)$

$d = 2, 3$ spatial dimension

α: Cartesian index, Einstein Σ conv.

$$r^2 = x_\alpha x_\alpha \qquad 2r\,dr = 2x_\alpha\,dx_\alpha \qquad \underbrace{dr = \frac{x_\alpha}{r}\,dx_\alpha}$$

$\psi = \psi(r)$

$$\partial_\alpha \psi = \frac{\partial}{\partial x_\alpha}\psi = \frac{\partial \psi}{\partial r}\frac{\partial r}{\partial x_\alpha} = \frac{x_\alpha}{r}\frac{\partial \psi}{\partial r}$$

$$\partial_\alpha = \frac{x_\alpha}{r}\frac{\partial}{\partial r} \Rightarrow \vec{\nabla}^2 \psi = \frac{x_\alpha}{r}\frac{\partial}{\partial r}\frac{x_\alpha}{r}\frac{\partial}{\partial r}\psi =$$

$$= \frac{x_\alpha}{r}\left[\frac{1}{r}\frac{\partial x_\alpha}{\partial r} + x_\alpha\frac{\partial}{\partial r}r^{-1} + \frac{x_\alpha}{r}\frac{\partial}{\partial r}\right]\frac{\partial}{\partial r}\psi =$$

$$= \left(\frac{x_\alpha}{r^2} \frac{r}{x_\alpha} + r(-1)\frac{1}{r^2} + \frac{r^2}{r^2} \frac{\partial}{\partial r} \right) \frac{\partial}{\partial r} \psi =$$

$$= \left(\frac{1}{r} d - \frac{1}{r} + \frac{\partial}{\partial r} \right) \frac{\partial}{\partial r} \psi = \left(\frac{d-1}{r} + \frac{\partial}{\partial r} \right) \frac{\partial}{\partial r} \psi$$

nonlinear transformation

$r \longrightarrow \rho(r)$ (some invertible fct. of r)

$$\frac{d\rho}{dr} = \rho'(r)$$

$$\frac{\partial \psi}{\partial r} = \frac{\partial \psi}{\partial \rho} \rho'(r) \qquad \frac{\partial}{\partial r} = \rho'(r) \frac{\partial}{\partial \rho}$$

$$\frac{\partial^2 \psi}{\partial r^2} = \rho''(r) \frac{\partial \psi}{\partial \rho} + \rho'(r) \frac{\partial}{\partial r}\left(\frac{\partial \psi}{\partial \rho}\right) =$$

$$= \rho''(r) \frac{\partial \psi}{\partial \rho} + \left[\rho'(r)\right]^2 \frac{\partial^2 \psi}{\partial \rho^2}$$

$$\vec{\nabla}^2 \psi = \frac{d-1}{r} \rho'(r) \frac{\partial \psi}{\partial \rho} + \rho''(r) \frac{\partial \psi}{\partial \rho} + \left[\rho'(r)\right]^2 \frac{\partial^2}{\partial \rho^2} \psi =$$

$$= \left[\vec{\nabla}^2 \rho\right] \frac{\partial \psi}{\partial \rho} + \left[\rho'(r)\right]^2 \frac{\partial^2}{\partial \rho^2} \psi$$

1) choose ρ such that $\tilde{\nabla}^2 \rho = 0$

$$\Rightarrow \quad \rho(r) = \begin{cases} \ln r & d=2 \\ -1/r & d=3 \end{cases}$$

$$\Rightarrow \text{PBE}: \quad \left(\rho'(r)\right)^2 \frac{\partial^2 \psi}{\partial \rho^2} = A \exp(\psi)$$

$$\psi = \psi_1 + \psi_2$$

$$\rho'^2 \frac{\partial^2}{\partial \rho^2} \psi = A e^{\psi_1} e^{\psi_2}$$

$\Rightarrow$ choose ψ_1 such that $e^{\psi_1} = \rho'^2$

i.e. $\psi_1 = \ln(\rho'^2) = 2 \ln \rho'$

$$\frac{\partial^2}{\partial \rho^2} \left[2 \ln \rho' + \psi_2 \right] = A e^{\psi_2}$$

$$\frac{\partial^2}{\partial \rho^2}\psi_2 = A\exp(\psi_2) - 2\frac{\partial^2}{\partial \rho^2}\ln \rho'$$

inertia

force from an external potential

force with an explicit time dependence

<u>check:</u> 3d: $\rho = -\frac{1}{r}$, $\rho' = +\frac{1}{r^2} = \rho^2$

$$\ln \rho' = \ln \rho^2 = 2 \ln \rho$$

$$\frac{\partial}{\partial \rho} \ln \rho' = \frac{2}{\rho}$$

$$\frac{\partial^2}{\partial \rho^2} \ln \rho' = -\frac{2}{\rho^2} \qquad -2 \frac{\partial^2}{\partial \rho^2} \ln \rho' = +\frac{4}{\rho^2}$$

time-dependent force $\rightarrow$ no closed analytic solution is known.

Approximate solution

Lee White, 1977

apart from that: numerics

2d: $\rho = \ln r \quad \rho' = \frac{1}{r} \quad \ln \rho' = -\ln r = -\rho$

$\frac{\partial}{\partial \rho} \ln \rho' = -1 \quad \frac{\partial^2}{\partial \rho^2} \ln \rho' = 0$

$\rightsquigarrow$ lucky: time-dependent force is ZERO B_0

PBE: $\boxed{\frac{\partial^2}{\partial \rho^2} \psi_2 = A \exp(\psi_2)}$ as in 1d B_0

Ansatz:

$$\Psi_2(\rho) = \Psi_0 - 2 \ln \cos\left[k(\rho+\delta)\right]$$

Ψ_0, k, δ : constants

$$\frac{\partial \Psi_2}{\partial \rho} = -2 \frac{1}{\cos\left[k(\rho+\delta)\right]} \left\{ -\sin\left[k(\rho+\delta)\right] \right\} k =$$

$$= 2k \tan\left[k(\rho+\delta)\right]$$

$$\frac{\partial^2 \psi_2}{\partial p^2} = 2k \frac{1}{\cos^2\left[k(p+\delta)\right]} k = \frac{2k^2}{\cos^2\left[k(p+\delta)\right]}$$

$$A \exp(\psi_2) = A \exp(\psi_0) \frac{1}{\cos^2\left[k(p+\delta)\right]}$$

$$\boxed{A \exp(\psi_0) = 2k^2}$$

$$\psi_1 = 2 \ln p' = -2p$$

$$\psi = \psi_0 - 2p - 2 \ln \cos\left[k(p+\delta)\right]$$

$$\boxed{\psi = \psi_0 - 2\ln r - 2\ln \cos\left[k(\ln r + \delta)\right]}$$

with $\boxed{k^2 = \frac{\Delta}{2} \exp(\psi_0)}$

re-parametrization $\quad \delta =! -\ln R_M$

R_M: "Manning radius"

$$\ln r + \delta = \ln r - \ln R_M = \ln \frac{r}{R_M}$$

$$k^2 = \frac{A}{2} \exp(\psi_0) \qquad \exp(\psi_0) = \frac{2}{A} k^2 = \left(\sqrt{\frac{2}{A}}\, k\right)^2$$

$$\psi_0 = -2 \ln\left(\sqrt{\frac{A}{2}} \frac{1}{k}\right)$$

$$\psi = -2\ln\left[\sqrt{\frac{A}{2}}\,\frac{1}{k}\right] - 2\ln r - 2\ln\cos\left[k\ln\frac{r}{R_M}\right]$$

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

$$\mathcal{E} = -\frac{\partial\psi}{\partial r} = \frac{2}{r} + \frac{2}{\cos\left[k\ln\frac{r}{R_M}\right]}\left\{-\sin\left[k\ln\frac{r}{R_M}\right]\right\}k\,\frac{1}{r}$$

$$\mathcal{E} = \frac{2}{r}\left\{ 1 - k \tan\left[k \ln \frac{r}{R_m} \right] \right\}$$

$$r = R_0 \Rightarrow \mathcal{E} = 0 \Rightarrow \boxed{k \tan\left[k \ln \frac{R_0}{R_m} \right] = 1}$$

$$r = R_i \Rightarrow E = \frac{\sigma}{\varepsilon} \Rightarrow \underline{\underline{\mathcal{E}}} = \frac{\beta e \sigma}{\varepsilon} =$$

$$= \frac{1}{e} \sigma \frac{e^2}{\varepsilon k_B T} = \frac{1}{e} \sigma 4 \pi l_B = 2 \frac{2 \pi l_B \sigma}{e} = \underline{\underline{\frac{2}{\lambda}}}$$

Gouy-Chapman

$$\Rightarrow \frac{2}{\lambda} = \frac{2}{R_i} \left\{ 1 - \tan\left(k \ln \frac{R_i}{R_m} \right) \right\}$$

define Manning parameter $\xi \equiv$

\# of elementary charges on the rod per Bjerrum length

$$2\pi R_i l_B \sigma = e \xi \Rightarrow \boxed{\xi = \frac{R_i}{\lambda}}$$

$$\xi = 1 - h \tan\left[k \ln \frac{R_i}{R_M}\right]$$

$$\xi - 1 = h \tan\left[h \ln \frac{R_M}{R_i}\right]$$ BC interior

$$1 = h \tan\left[h \ln \frac{R_o}{R_M}\right]$$ BC exterior

consider $\xi > 1$ strongly charged case