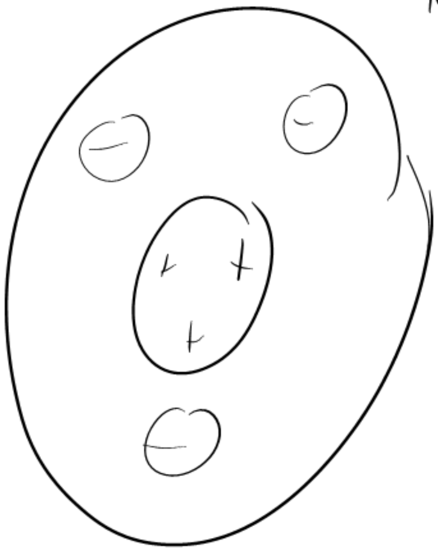
R_i, R_0



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

$$\xi = \frac{2}{r}\left[1 - k\tan\left(k\ln\frac{r}{R_m}\right)\right]$$

BC: $$1 = k\tan\left(k\ln\frac{R_0}{R_m}\right)$$

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

$$\ln\left(\frac{R_M}{R_i}\right) = \frac{1}{k}\tan^{-1}\left(\frac{\xi-1}{k}\right)$$

$$\ln\left(\frac{R_0}{R_M}\right) = \frac{1}{k}\tan^{-1}\left(\frac{1}{k}\right)$$

<u>Sum</u>: $\ln\left(\frac{R_0}{R_i}\right) = \frac{1}{k}\left\{\tan^{-1}\left(\frac{\xi-1}{k}\right) + \tan^{-1}\left(\frac{1}{k}\right)\right\}$

Consider $R_0 \longrightarrow \infty$ (large) $\Rightarrow k$ small

$\tan^{-1} \longrightarrow \pi/2 \Rightarrow \ln\frac{R_0}{R_i} \simeq \frac{1}{k}\pi$

$$\boxed{k = \frac{\pi}{\ln\left(\frac{R_o}{R_i}\right)}}$$

$$k \ln\left(\frac{R_m}{R_i}\right) = \tan^{-1} \frac{\xi - 1}{k} \Rightarrow \frac{\pi}{\ln\left(\frac{R_o}{R_i}\right)} \ln\left(\frac{R_m}{R_i}\right) = \frac{\pi}{2}$$

$$\ln \frac{R_m}{R_i} = \frac{1}{2} \ln\left(\frac{R_o}{R_i}\right) = \ln\left(\frac{R_o}{R_i}\right)^{1/2}$$

$$\frac{R_m}{R_i} \simeq \left(\frac{R_o}{R_i}\right)^{1/2} \qquad \boxed{R_m \equiv \sqrt{R_o R_i}}$$

$$\frac{R_m}{R_o} = \left(\frac{R_i}{R_o}\right)^{1/2}$$

concentration profile? PB theory:

$$-\vec{\nabla}^2 \psi = -4\pi l_B c \qquad \Rightarrow c = \frac{1}{4\pi l_B} \vec{\nabla}^2 \psi$$

we had: $\tilde{D}^2 \psi = \left[\rho'(r)\right]^2 \frac{\partial^2}{\partial \rho^2} \psi$

$\rho(r) = \ln r \Rightarrow (\rho'(r))^2 = \frac{1}{r^2}$

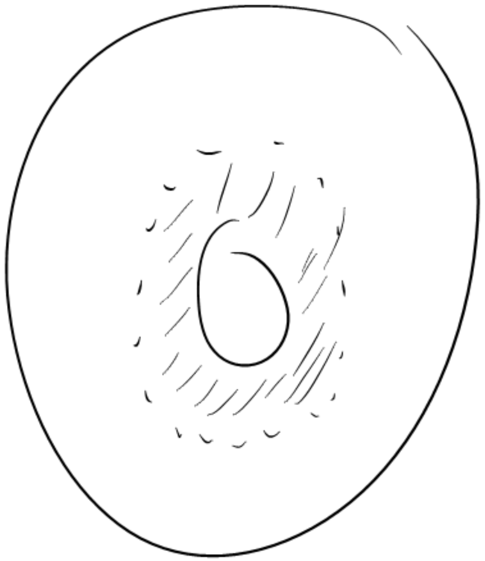
$\psi(\rho) = \psi_0 - 2\rho - 2\ln \cos[k(\rho+\delta)]$

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

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

$$\frac{\partial^2 \psi}{\partial \rho^2} = \frac{2k^2}{\cos^2[k(\rho+\delta)]} = \frac{2k^2}{\cos^2\left[k \ln \frac{r}{R_m}\right]}$$

$$\Rightarrow c(r) = \frac{1}{4\pi l_B r^2} \frac{2h^2}{\cos^2\left[h \ln \frac{r}{R_M}\right]}$$



rod: length L

charges on the rod: $\frac{\xi}{l_B} L$

counterions within the cylinder between R_i and R_M:

$$L \cdot \int_{R_i}^{R_M} dr \, 2\pi r \, c(r)$$

fraction of counterions in that cylinder

$$f = \frac{2\pi L \int_{R_i}^{R_M} dr\, r\, c(r)\, l_B}{\xi L} =$$

$$= \frac{1}{2\xi} \int_{R_i}^{R_M} dr\, 4\pi l_B\, c(r)\, r =$$

$$= \frac{1}{2\xi} \int_{R_i}^{R_M} dr\, \frac{2h^2}{r} \frac{1}{\cos^2\left[h \ln \frac{r}{R_M}\right]} =$$

$$= \frac{k^2}{\xi} \int_{R_i}^{R_m} \frac{dr}{r} \frac{1}{\cos^2\left[k \ln \frac{r}{R_m}\right]}$$

$$x := k \ln \frac{r}{R_m} \qquad dx = k \frac{dr}{r}$$

$$r = R_i \rightarrow x = k \ln \frac{R_i}{R_m} = -k \ln \frac{R_m}{R_i} = -\tan^{-1} \frac{\xi - 1}{k}$$

$$=: -x_0$$

$$r = R_m \rightarrow x = 0$$

$$f = \frac{k}{\xi} \int_{-x_0}^{0} dx \frac{1}{\cos^2 x} = \frac{k}{\xi} \tan x \Big|_{-x_0}^{0} = \frac{k}{\xi} \tan x_0$$

$$= \frac{k}{\xi} \frac{\xi - 1}{k} = \boxed{1 - \frac{1}{\xi} = f}$$

"Manning condensation": Phase transition at $\xi = 1$: A condensed phase occurs only for $\xi > 1$

Handwaving argument

$$F = E - TS = \text{Min.}$$

$$S \sim \ln V \sim \ln r$$

3d: $\phi \sim \frac{1}{r}$ $\rightsquigarrow$ S wins $\rightsquigarrow$ all ions evaporate

1d: $\phi \sim r$ $\rightsquigarrow$ E wins $\rightsquigarrow$ all ions adsorbed

2d: $\phi \sim \ln r$ $\rightsquigarrow$ delicate balance between energy & entropy $\longrightarrow$ phase transition "charge renormalization" "effective charge" $\rightarrow$

subtract the condensed ions to obtain an effective rod with smaller charge

bare charge: $\dfrac{\text{charge}}{\text{unit length}} = \dfrac{e\xi}{l_B}$

renormalized charge: $\dfrac{\text{effective charge}}{\text{unit length}} = \dfrac{e\xi}{l_B} - \dfrac{e\xi}{l_B} f$

$$= \frac{e\xi}{l_B}(1-f) = \frac{e\xi}{l_B}\frac{1}{\xi} = \frac{e}{l_B}$$

"You can never put more charges onto a rod than one per Bjerrum length"

When $R_0 \to \infty$

$$c(r) = \frac{1}{2\pi l_B r^2} \frac{1}{\left(\ln\frac{r}{R_i} + \frac{1}{\xi - 1}\right)^2}$$

$$\int_{R_i}^{\infty} dr\, 2\pi r\, c(r) = \frac{\xi}{l_B} \underbrace{\left(1 - \frac{1}{\xi}\right)}_{f}$$

8. Linearized Poisson-Boltzmann Theory [Debye-Hückel Theory]

Assume: External charges (or external fields) are weak $\Rightarrow$ Concentration profiles will be nearly homogeneous

Set $\bar{c}_a \equiv$ volume-averaged (constant) concentration

$$\bar{c}_a = \frac{N_a}{V} \Rightarrow c_a(\vec{r}) = \bar{c}_a + \delta c_a(\vec{r})$$

inhomogeneity

[NOT a statistical fluctuation!]

$$= \bar{c}_a \left[1 + \underbrace{\frac{\delta c_a(\vec{r})}{\bar{c}_a}}_{\ll 1} \right]$$

$$\ln c_a = \ln \bar{c}_a + \ln\left(1 + \frac{\delta c_a}{\bar{c}_a}\right) \simeq$$

$$\simeq \ln \bar{c}_a + \frac{\delta c_a}{\bar{c}_a}$$

$$\vec{\nabla} \ln c_a \simeq \frac{1}{\bar{c}_a} \vec{\nabla} \delta c_a = \frac{1}{\bar{c}_a} \vec{\nabla}\left(\bar{c}_a + \delta c_a\right)$$

$$= \frac{1}{\bar{c}_a} \vec{\nabla} c_a$$

Nonlinear PBE: $\vec{\nabla} \cdot \vec{\mathcal{E}} = 4\pi l_B \sum_a z_a c_a$

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

$\downarrow$

linearized PBE:

$$\boxed{\begin{aligned} \vec{\nabla} \cdot \vec{\mathcal{E}} &= 4\pi l_B \sum_a z_a c_a \\ \vec{\nabla} c_a &= z_a \bar{c}_a \vec{\mathcal{E}} \end{aligned}}$$

vector analysis

$$0 = \vec{\nabla} \times (\vec{\nabla} \times \vec{\mathcal{E}}) = \vec{\nabla}(\vec{\nabla} \cdot \vec{\mathcal{E}}) - \vec{\nabla}^2 \vec{\mathcal{E}}$$

$$\Rightarrow \quad \vec{\nabla}(\vec{\nabla} \cdot \vec{\mathcal{E}}) = \vec{\nabla}^2 \vec{\mathcal{E}}$$

$$\Rightarrow \vec{\nabla}^2 \vec{\mathcal{E}} = 4\pi l_B \sum_a z_a \tilde{\nabla} c_a = 4\pi l_B \sum_a z_a z_a \bar{c}_a \vec{\mathcal{E}}$$

<u>define</u>: Debye screening parameter

$$\boxed{\kappa^2 := 4\pi l_B \sum_a z_a^2 \bar{c}_a}$$

- unit: $\frac{1}{(\text{length})^2}$

- <u>all</u> ions contribute to κ^2
  - salt ions
  - counter ions

Debye screening length $\boxed{l_D = \frac{1}{\kappa}}$

$\rightsquigarrow \boxed{\vec{\nabla}^2 \tilde{\Sigma} = \kappa^2 \tilde{\Sigma}}$ Debye-Hückel equation for the field

$$\left(-\vec{\nabla}^2 + \kappa^2\right)\vec{E} = 0 \qquad \vec{E} = -\vec{\nabla}\varphi$$

$$\left(-\vec{\nabla}^2 + \kappa^2\right)\left(-\vec{\nabla}\varphi\right) = 0$$

$$\left(-\vec{\nabla}\right)\left(-\vec{\nabla}^2 + \kappa^2\right)\varphi = 0$$

$$\left(-\vec{\nabla}^2 + \kappa^2\right)\varphi = \text{const.} = A$$

Debye-Hückel eq. for the potential

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

$$\psi = \frac{1}{\kappa^2}\left[A - 4\pi l_B \sum_a z_a c_a\right] \quad \Big| \int d^3\vec{r}\,,\ \frac{1}{V}$$

choose normalization of ψ:

$$\int d^3\vec{r}\ \psi = 0$$

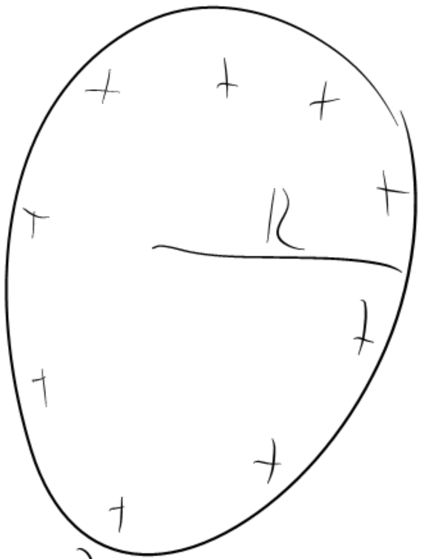
$$0 = \frac{1}{\kappa^2}\left[A - 4\pi l_B \sum_a z_a \bar{c}_a\right] \Rightarrow A = 4\pi l_B \sum_a z_a \bar{c}_a$$

$$\left(-\vec{\nabla}^2 + \kappa^2\right)\varphi = \underbrace{4\pi l_B \sum_a z_a \bar{c}_a}_{\substack{\text{volume-averaged ionic} \\ \text{charge density}}}$$

[is zero for infinite dilution

of the counterions}

field of a charged sphere



$\sigma = \frac{\text{charge}}{\text{area}}$

(salt ions)

$$(-\tilde{D}^2 + \kappa^2)\psi = 0$$

$$\psi(r \to \infty) = 0$$

$$(-\tilde{D}^2 + \kappa^2)\,\phi = 0, \quad \phi(r \to \infty) = 0$$

unscaled electrostatic potential

recall
$$\left(-\vec{\nabla}^2+\kappa^2\right)\underbrace{\frac{1}{4\pi r}e^{-\kappa r}}_{\text{Debye-Hückel (Yukawa) potential}}=\delta(\vec{r})$$

Ansatz

$$\phi(r)=A\,\frac{\exp(-\kappa r)}{4\pi r}$$

$$E=-\frac{\partial\phi}{\partial r}=-\frac{A}{4\pi}\left\{-\frac{1}{r^2}e^{-\kappa r}+\frac{1}{r}e^{-\kappa r}(-\kappa)\right\}=$$

$$= \frac{A}{4\pi r} e^{-\kappa r} \left(\kappa + \frac{1}{r}\right)$$

at $r = R$

$$E = \frac{\sigma}{\varepsilon}$$

$$\frac{\sigma}{\varepsilon} = \frac{A}{4\pi R} e^{-\kappa R} \left(\kappa + \frac{1}{R}\right)$$

$$A = \frac{\sigma}{\varepsilon} 4\pi R e^{+\kappa R} \frac{1}{\kappa + \frac{1}{R}}$$

$$= \frac{\sigma}{\varepsilon} 4\pi R^2 e^{\kappa R} \frac{1}{1 + \kappa R}$$

$\sigma \cdot 4\pi R^2 = Q$

total charge on the sphere

$$A = \frac{1}{\varepsilon} Q \frac{e^{\kappa R}}{1 + \kappa R}$$

$$\Phi(r) = \frac{Q}{4\pi \varepsilon r} \frac{\exp[-\kappa(r-R)]}{1 + \kappa R}$$

$r > R$

Green's fct. is $\frac{1}{4\pi \varepsilon r} e^{-\kappa r}$

effective point charge at the origin

$$Q_{eff} = Q \frac{e^{+\kappa R}}{1+\kappa R}$$

interaction between two such spheres

$r \gg R \rightsquigarrow$ point-particle approximation.

$$\boxed{U = \frac{Q^2}{4\pi\varepsilon r}\left(\frac{e^{\kappa R}}{1+\kappa R}\right)^2 e^{-\kappa r}}$$

add van der Waals interactions

→ DLVO model for charged colloids

↓

Derjaguin, Landau, Verwey, Overbeek