Khokhlov / Khatchaturian 1982

Gaussian chain + Yukawa charges

large l_D: blob pole $R_E \sim N b (f^2 u)^{1/3}$

until $l_D \sim N^{1/2} b$

from then on: semiflexible chain

$$R_E \sim N^{1/2} l_D (f^2 u)^{1/3} \qquad l_p \sim \frac{l_D^2}{\xi_{el}}$$

excluded volume between "rods": $l_p^2 \, l_D$

# of rods $\sim \dfrac{R_E \text{ (blob pole)}}{l_p} \sim \dfrac{N b^2}{l_D^2}$

total excluded volume: # rods × excluded volume of rod

$$\frac{N b^2}{l_D^2} l_p^2 l_D \sim \frac{N b^2}{l_D} \frac{l_D^4}{\xi_{el}^2} \sim N l_D^3 \frac{b^2}{b^2 (f^2 u)^{-2/3}} \sim$$

$N l_D^3 (f^2 u)^{2/3}$; total volume of chain:

$$R_E^3 \sim N^{3/2} l_D^3 (f^2 u)$$

fraction of excluded volume: $\equiv$ probability for contact

$$\frac{N\,(f^2 u)^{2/3}\, l_D^3}{N^{3/2}\,(f^2 u)\, l_D^3} \sim N^{-1/2}\,(f^2 u)^{-1/3}$$

rod-rod contacts: probability $\times$ # of rods

$$\sim N^{-1/2}\,(f^2 u)^{-1/3}\,\frac{N b^2}{l_D^2} \sim N^{1/2}\,\frac{b^2}{l_D^2}\,(f^2 u)^{-1/3}$$

excluded volume becomes important when this is of order one:

$$N^{1/2} \frac{b^2}{l_D^2} \left(f^2 u\right)^{-1/3} \overset{!}{\sim} 1$$

$$\boxed{l_D \sim N^{1/4}\, b \left(f^2 u\right)^{-1/6}}$$

for l_D smaller than this, one has SAW behavior, $R_E = ?$

$$R_E \sim A\, N^{\nu} \quad \nu = 0.588$$

matching: $A N^{\nu} \stackrel{!}{=} N^{1/2} l_D (f^2 n)^{1/3}$

for $l_D = b N^{1/4} (f^2 n)^{-1/6}$ or

$$N = \left(\frac{l_D}{b}\right)^4 (f^2 n)^{+2/3}$$

$$A \left\{ \left(\frac{l_D}{b}\right)^4 (f^2 n)^{2/3} \right\}^{\nu} = \left(\frac{l_D}{b}\right)^2 (f^2 n)^{1/3} l_D (f^2 n)^{1/3}$$

$$A = l_D \left(\frac{l_D}{b}\right)^{2-4\nu} (f^2 n)^{(2-2\nu)/3}$$

$$\boxed{R_E \sim l_D \left(\frac{b}{l_D}\right)^{4\nu-2} (f^2 n)^{(2-2\nu)/3} N^{\nu}}$$

decrease l_D further $\Rightarrow$ finally, l_p is of order

ξ_{el} $\rightsquigarrow$ no notion of stiffness left!

$\rightsquigarrow$ "conventional" excluded volume from

electrostatic repulsion between the blobs

$$l_p \overset{!}{\sim} \xi_{el} \Rightarrow \frac{l_D^2}{\xi_{el}} \sim \xi_{el} \Rightarrow \underline{\underline{l_D \sim \xi_{el}}}$$

$$l_D \sim b\left(f^2 u\right)^{-1/3}$$

$\Rightarrow$ look at 2nd virial coefficient v (dim.: volume)

$$v = 2\pi \int_0^\infty dr\, r^2 \left\{ 1 - \exp\left(- \frac{U(r)}{k_B T} \right) \right\}$$

in our case: U is weak $U/k_BT \ll 1$

$$v \simeq 2\pi \int_0^\infty dr\, r^2 \frac{U(r)}{k_B T} = 2\pi \int_0^\infty dr\, r^2 \frac{l_B f^2}{r} e^{-\kappa r} =$$

$$= 2\pi f^2 l_B \int_0^\infty dr\, r\, e^{-\kappa r} = \quad \angle x > \kappa r$$

$$= 2\pi f^2 l_B l_D^2 \int_0^\infty dx\, x\, e^{-x}$$

$$\boxed{v \sim l_D^2 b f^2 u}$$

"competition" between b and $v^{1/3}$

Flory theory

$$\frac{F}{k_B T} \simeq \underbrace{\frac{R_E^2}{N b^2}}_{\text{entropic elasticity}} + v \underbrace{\left(\frac{N}{R_E^3}\right)}_{\hookrightarrow \text{ concentration}}^2 R_E^3 = \frac{R_E^2}{N b^2} + v \frac{N^2}{R_E^3}$$

$$R_E \sim N^{1/2} b \, \alpha$$

swelling factor

$$\Downarrow \quad \alpha^2 + v N^{1/2} \frac{1}{b^3 \alpha^3} \stackrel{!}{=} \text{Min. wrt } \alpha$$

$$z := \frac{v}{b^3} N^{1/2} \quad \text{solvent strength}$$

$$\boxed{\alpha^2 + \frac{z}{\alpha^3} \stackrel{!}{=} \text{Min.}}$$

$$2\alpha - 3 z \alpha^{-4} = 0$$

$$\boxed{\alpha \sim z^{1/5}}$$

$$R_E \sim b N^{1/2} z^{1/5}$$

$$\sim b N^{1/2} \left(\frac{v}{b^3} N^{1/2} \right)^{1/5}$$

Correct exponent of z is $2\nu - 1$

$$R_E \sim b\, N^{1/2}\, z^{2\nu - 1}$$

in our case $z \sim N^{1/2} \frac{1}{b^3} \ell_D^2\, b \left(f^2 u\right)$

$$\sim N^{1/2} \left(\frac{\ell_D}{b}\right)^2 \left(f^2 u\right)$$

$$\boxed{R_E \sim b\, N^{\nu} \left\{ \left(\frac{\ell_D}{b}\right)^2 \left(f^2 u\right) \right\}^{2\nu - 1}}$$

$l_D \downarrow$: finally, interaction becomes so weak

that it does not even swell the chain,

This happens at $z \sim 1$ or

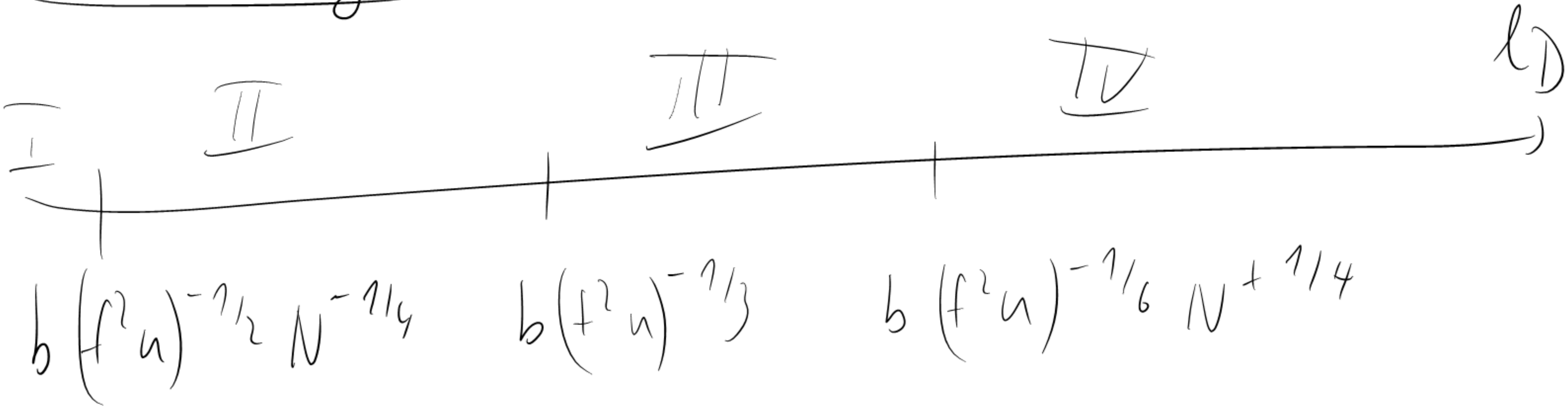
$$N^{1/2} \left(\frac{l_D}{b}\right)^2 (f^2 n) \sim 1 \quad \text{or}$$

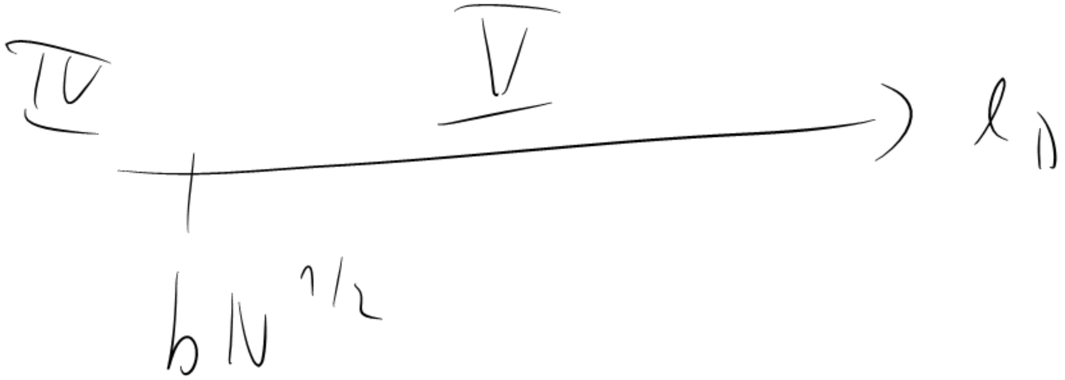
$$\boxed{l_D \sim b\,(f^2 n)^{-1/2} N^{-1/4}}$$

if l_D is smaller than that $\rightarrow$ unperturbed RW

$R_E \sim b N^{1/2}$

Summary





I. unperturbed RW $\quad R_E \sim b N^{1/2}$

II. electrostatic swelling

$$R_E \sim b N^{\nu} \left[(f^2 u) \left(\frac{l_D}{b} \right)^2 \right]^{2\nu - 1}$$

III. electrostatic swelling + el.st. stiffening

$$R_E \sim l_D N^{\nu} \left[(f^2 u)^{2/3} \right]^{1-\nu} \left(\frac{b}{l_D} \right)^{4\nu - 2}$$

IV. semiflexible chain

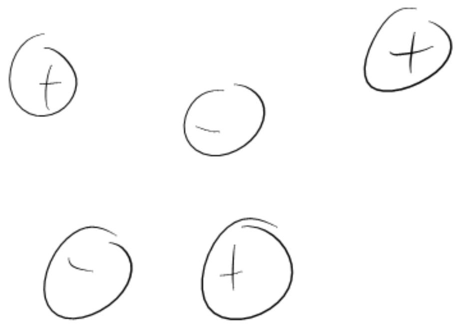
$$R_E \sim l_D N^{1/2} (f^2 u)^{1/3}$$

V. blob pole

$$R_E \sim b N (f^2 u)^{1/3}$$

14. Electrokinetics

fluid



various ionic species floating around

thermal energy k_BT

solvent dielectric constant ε

" viscosity η

ionic species a

concentrations c_a

ionic diffusion constant D_a

" mobility $\mu_a = D_a/(k_BT)$

Einstein

valency z_a

Poisson equation for electrostatic potential ϕ

$$-\vec{\nabla}^2 \phi = \frac{1}{\varepsilon} \sum_a z_a e c_a \qquad (EK1)$$

$\vec{v}$: velocity flow field of the fluid

current density of species a: $\vec{j}_a$

$$\vec{j}_a = -D_a \vec{\nabla} c_a - \frac{D_a}{k_B T} z_a e c_a \vec{\nabla} \phi + c_a \vec{v}$$

diffusive current

drift velocity due to electric force

convective current from the flow field

$$\frac{\partial}{\partial t} c_a + \vec{\nabla} \cdot \vec{j}_a = 0$$

$$\underbrace{\frac{\partial}{\partial t} c_a + \vec{\nabla} \cdot (c_a \vec{v}) = D_a \vec{\nabla} \cdot \left\{ \vec{\nabla} c_a + \frac{z_a e}{k_B T} c_a \vec{\nabla} \phi \right\}}_{\text{convection-diffusion eq. / Nernst-Planck eq.}} \quad \text{(EK2)}$$

fluid flow is incompressible: $\boxed{\vec{\nabla} \cdot \vec{v} = 0}$ (Ek 3)

dynamics of fluid: Navier-Stokes

$$\frac{\partial}{\partial t}(\rho \vec{v}) + \vec{\nabla}\underbrace{(\rho \vec{v} \otimes \vec{v})}_{\text{convective stress}} = -\vec{\nabla} p + \eta \vec{\nabla}^2 \vec{v} - e \vec{\nabla} \phi \sum_a z_a c_a \quad \text{(Ek 4)}$$

ρ: mass density

$-\vec{\nabla} p$: pressure

$\eta \vec{\nabla}^2 \vec{v}$: viscous dissipation

$- e \vec{\nabla} \phi \sum_a z_a c_a$: electric force

(Ek1) – (Ek4) : "electrokinetic equations"

equilibrium : $\frac{\partial}{\partial t}(\dots) = 0 \quad \vec{v} = 0$

Navier-Stokes : just an equation for the pressure p

"hydrostatics" $\rightarrow$ uninteresting

Poisson + Nernst-Planck :

$$\boxed{-\vec{\nabla}^2 \phi = (1/\varepsilon) \sum_a z_a e c_a} \qquad \vec{E} = -\vec{\nabla}\phi$$

Current is zero

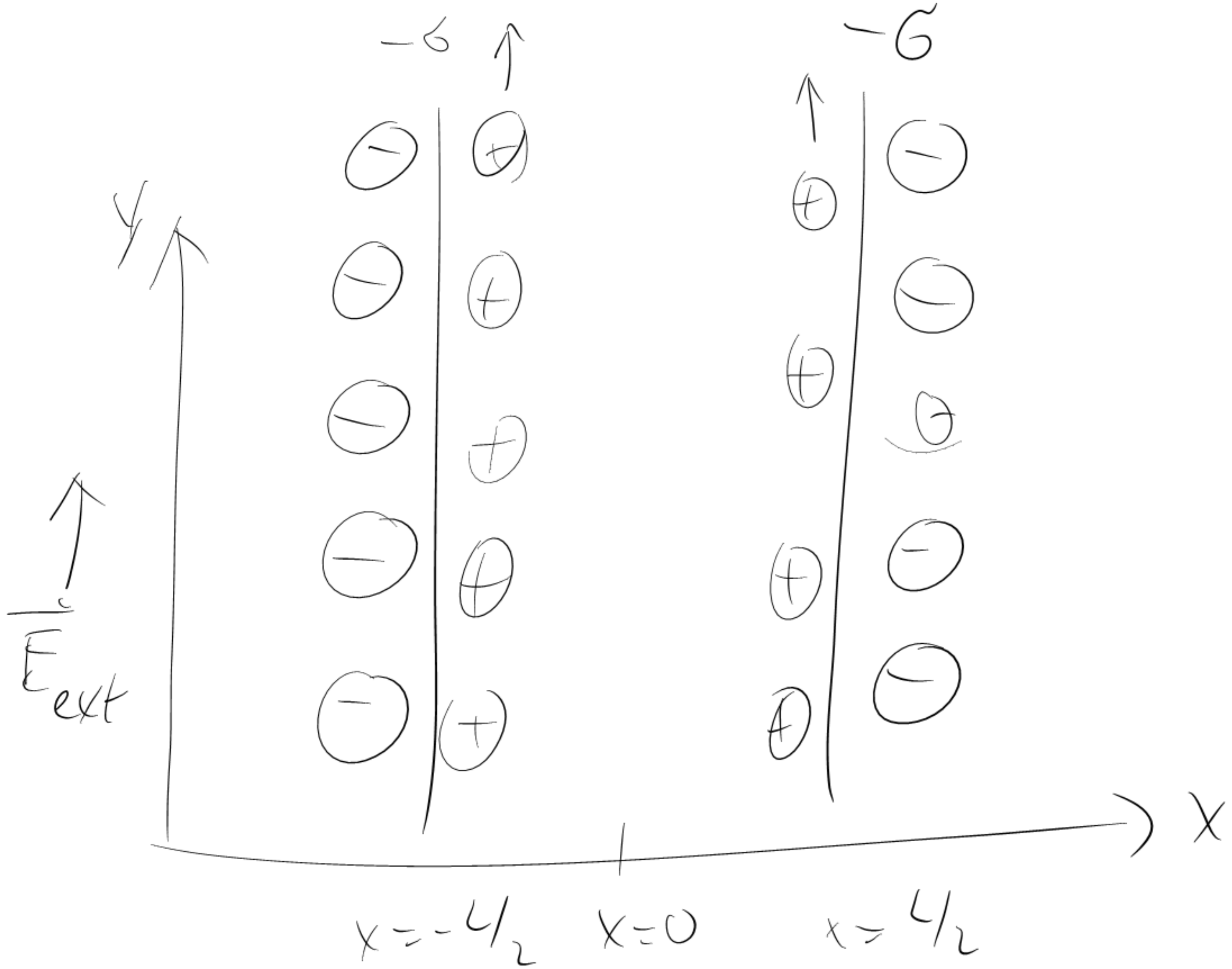
$$\vec{\nabla} c_a + \frac{z_a e}{k_B T} c_a \vec{\nabla} \phi = 0 \qquad | : c_a$$

$$\boxed{\vec{\nabla} \ln c_a = \frac{z_a e}{k_B T} \vec{E}}$$

$\wedge$ this is the (nonlinear) Poisson-Boltzmann eq. !, $\leadsto$ (EK1) - (EK4) is dynamic generalization of Poisson-Boltzmann theory !

electro-osmotic flow

σ: charge density



$$\vec{E} = \vec{E}_{int} + \vec{E}_{ext}$$

$$\vec{\nabla} \cdot \vec{E}_{ext} = 0 \qquad \vec{\nabla} \times \vec{E}_{ext} = 0$$

$$\vec{v} = v(x)\, \hat{e}_y \quad \Rightarrow \quad \vec{\nabla} \cdot \vec{v} = 0$$

$$\vec{\nabla} c_a \propto \hat{e}_x$$

$$\vec{\nabla} \cdot (c_a \vec{v}) = \underbrace{\vec{v} \cdot \vec{\nabla} c_a}_{0} + c_a \underbrace{\vec{\nabla} \cdot \vec{v}}_{=0} = 0$$

$$(\partial/\partial t)\, c_a = 0$$

Poisson: $\vec{\nabla} \cdot \vec{E}_{int} = \left(1/\varepsilon\right) \sum_a z_a e c_a$

Nernst-Planck:

$$0 = \vec{\nabla} \cdot \left\{ \vec{\nabla} c_a - \frac{z_a e}{k_B T} c_a \left(\vec{E}_{int} + \vec{E}_{ext} \right) \right\}$$

$\vec{\nabla} \cdot \left(c_a \vec{E}_{ext} \right) = 0$ (analogous to $\vec{\nabla} \cdot (c_a \vec{v})$)

$\rightsquigarrow$ Poisson + Nernst-Planck identical to equilibrium

→ first, solve PBE ⟶ $\vec{E}_{int}$, c_a

suppose this is done → into NS

$$\frac{\partial}{\partial t}(\rho \vec{v}) = 0, \quad \underbrace{\vec{\nabla}}_{\hat{e}_x} \cdot (\rho \vec{v} \otimes \vec{v}) = 0$$

$\vec{v} \parallel \hat{e}_y$

$$\vec{\nabla} p = \vec{\nabla} p_{int} + \underbrace{\vec{\nabla} p_{ext}}_{=0}$$

$p_{int}(x)$

no external pressure applied

$$0 = \underbrace{-\vec{\nabla} p_{int}}_{\parallel \hat{e}_x} \underbrace{-\vec{\nabla} p_{ext}}_{0} + \underbrace{\eta \vec{\nabla}^2 \vec{v}}_{\parallel \hat{e}_y} + \Big(\underbrace{\vec{E}_{int}}_{\parallel \hat{e}_x} + \underbrace{\vec{E}_{ext}}_{\parallel \hat{e}_y}\Big) \sum_a e z_a c_a$$

$\vec{E}_{int} \longleftrightarrow \vec{\nabla} p_{int}$ uninteresting hydrostatics

$$0 = \eta \vec{\nabla}^2 \vec{v} + \vec{E}_{ext} \sum_a e z_a c_a$$

$$\boxed{-\frac{d^2}{dx^2} v = \frac{E_{ext}}{\eta} \sum_a e z_a c_a}$$

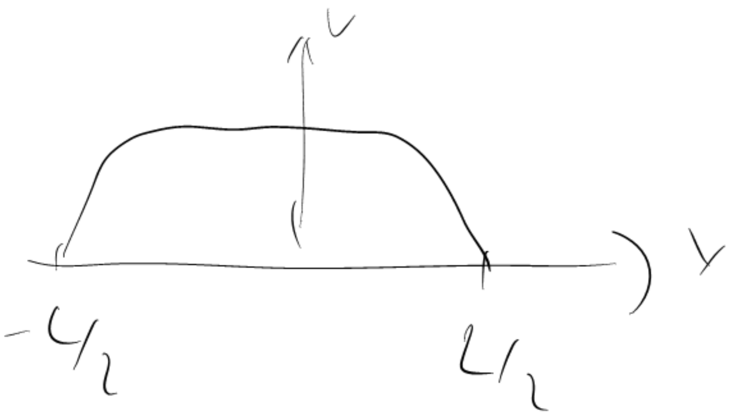
cf. with Poisson:

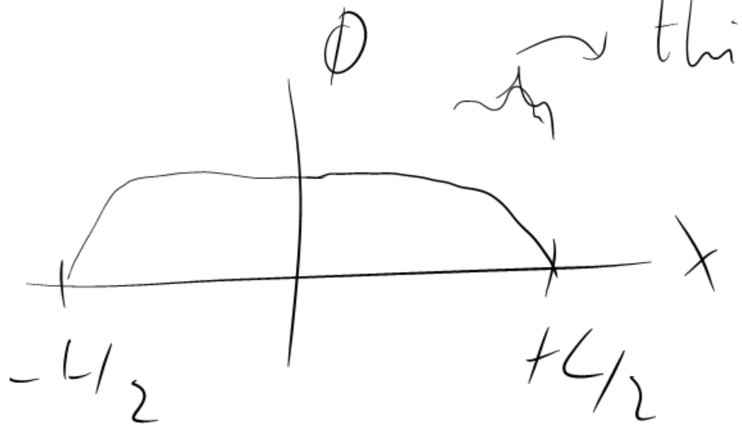
$$-\frac{d^2}{dx^2}\phi = \frac{1}{\varepsilon}\sum_a e z_a c_a$$

Same eq. → same solution

Stick boundary cond. $v(\text{boundary}) = 0$

normalize ϕ $\qquad \phi(\text{boundary}) = 0$





thickness of Debye layer

$$\boxed{v = \frac{E_{ext}\,\varepsilon}{\eta}\,\phi}$$

ϕ is just the PBE solution

strong screening $l_D \ll L$

$\rightsquigarrow$ profile in the center is flat

Introduce <u>Zeta Potential</u>

$$\zeta \equiv \phi(\text{center}) - \phi(\text{boundary})$$

$$\boxed{v(\text{center}) = \frac{E_{ext}\,\varepsilon\,\zeta}{\eta}}$$

electro-osmotic mobility

$$\mu = \frac{v(\text{center})}{e\,E_{ext}} = \frac{\varepsilon\,\zeta}{e\,\eta}$$