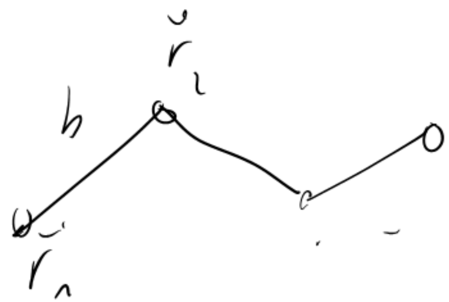
12. Polyelectrolyte Conformations IV: Electrostatic Persistence Length of a Freely Jointed Chain with Yukawa Interactions

$$\mathcal{H} = \frac{f^2 e^2}{4\pi\varepsilon} \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} \exp\left[-\kappa |\vec{r}_i - \vec{r}_j|\right]$$

$$|\vec{r}_{i+1} - \vec{r}_i| = b$$



$$\beta \mathcal{H} = f^2 \ell_B \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} \exp\left[-\kappa |\vec{r}_i - \vec{r}_j|\right]$$

$$= f^2 u \sum_{i<j} \frac{b}{|\vec{r}_i - \vec{r}_j|} \exp\left[-\kappa |\vec{r}_i - \vec{r}_j|\right]$$

$$\vec{r}_i = b \, \vec{x}_i \qquad |\vec{x}_{i+1} - \vec{x}_i| = 1$$

$$\kappa b =: \mu$$

$$\frac{\beta \mathcal{H}}{f^2 n} = \sum_{i<j} \frac{1}{|\vec{x}_i - \vec{x}_j|} \exp\left[-\kappa |\vec{x}_i - \vec{x}_j|\right]$$

assume: Debye length >> bond length

$$\kappa^{-1} \gg b$$

$$1 \gg \kappa b$$

$$\boxed{u \ll 1}$$

ground state: chain is stretched

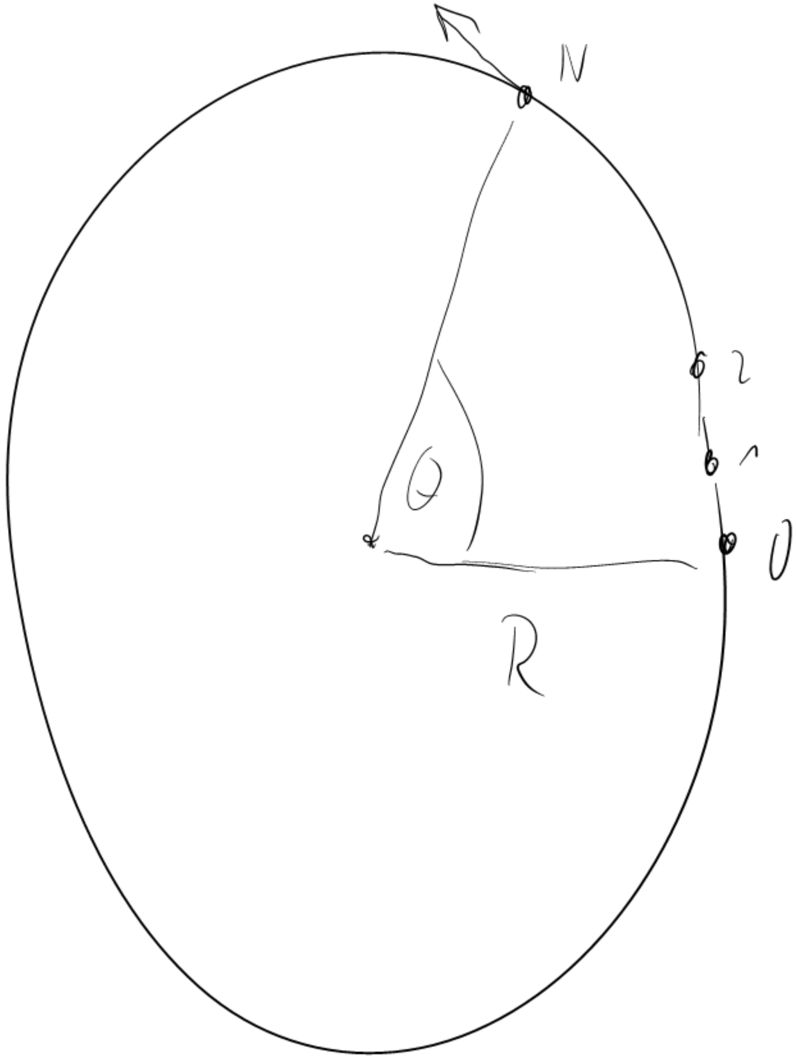
$\vec{x}_i = i\,\hat{n}$ ← unit vector

$i = 0, \ldots, N$ → N bonds

→ $N+1$ monomers

Energy cost of bending? Assume bending

on an ARC



θ is ∢ between 1st and last tangent vector

$$\bar{x}_n = R \begin{pmatrix} \cos\left(\frac{\theta n}{N}\right) \\ \sin\left(\frac{\theta n}{N}\right) \\ 0 \end{pmatrix}$$

$$|\bar{x}_n - \bar{x}_m| = ?$$

complex calculus: $z_n = \exp\left(i \frac{\theta n}{N}\right)$

$$z_n - z_m = \exp\left(i\frac{\theta n}{N}\right) - \exp\left(i\frac{\theta m}{N}\right) =$$

$$= \exp\left[i\frac{\theta m}{N}\right]\left\{\exp\left(i\frac{\theta}{N}(n-m)\right) - 1\right\} =$$

$$= \exp\left[i\frac{\theta m}{N}\right]\exp\left(i\frac{\theta}{2N}(n-m)\right)\left\{\exp\left(i\frac{\theta}{2N}(n-m)\right) - \exp\left[-i\frac{\theta}{2N}(n-m)\right]\right\}$$

$$= \exp\left(i\frac{\theta m}{N}\right)\exp\left(i\frac{\theta}{2N}(n-m)\right) 2i\sin\left[\frac{\theta}{2N}(n-m)\right]$$

$$|z_n - z_m| = 2\sin\left(\frac{\theta}{2N}(n-m)\right)$$ assume $n > m$

$$= |\breve{x}_n - \breve{x}_m| \frac{1}{R}$$

$$|\breve{x}_n - \breve{x}_m| = 2R\sin\left(\frac{\theta}{2N}(n-m)\right)$$

$n - m = 1$

$\Rightarrow |\breve{x}_n - \breve{x}_m| = 1$

$$1 = 2R\sin\left(\frac{\theta}{2N}\right)$$

$$|\breve{x}_n - \breve{x}_m| = \frac{\sin\left(\frac{\theta}{2N}(n-m)\right)}{\sin\left(\frac{\theta}{2N}\right)}$$

now $\theta \ll 1$, $N \gg 1$

set $\alpha := \frac{\theta}{2N}$ $\Rightarrow$ $|\bar{x}_n - \bar{x}_m| = \frac{\sin(\alpha\,|n-m|)}{\sin\alpha}$

$\alpha \ll 1$

small deformations $\Rightarrow$ harmonic expansion wrt α

$$\frac{\beta \mathcal{H}}{f^2 n} = \sum_{m<n} \frac{\sin\alpha}{\sin(\alpha\,|n-m|)} \exp\left[-\mu \frac{\sin(\alpha\,|n-m|)}{\sin\alpha}\right] =$$

MAXIMA

$$= \sum_{m<n} \left\{ \underbrace{\frac{e^{-\mu k}}{k}}_{\text{ground state contribution}} + \frac{\alpha^2}{6} \frac{e^{-\mu k}}{k} \left[\mu (k^3 - k) + k^2 - 1 \right] \right\} + O(\alpha^4)$$

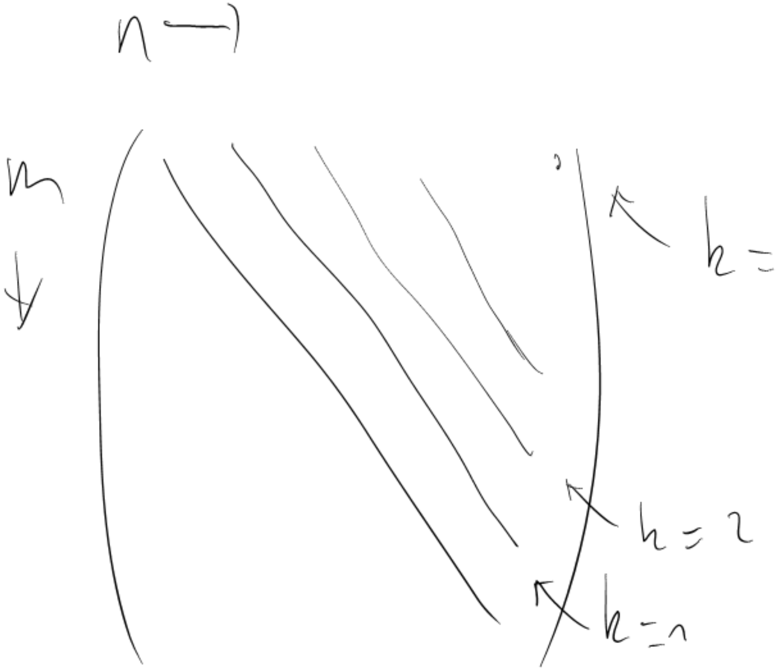
$k = n - m$

in harmonic approx :

$$\frac{\beta \Delta \mathcal{H}}{f^2 u} = \frac{\alpha^2}{6} \sum_{m<n} \frac{e^{-\mu k}}{k} \left[\mu (k^3 - k) + k^2 - 1 \right]$$

assume : Debye length << stretched chain length

$\kappa^{-1} << Nb \qquad \kappa b N >> 1 \qquad \mu N >> 1$



$e^{-\mu N} \ll 1$ negligible

# of elements $O(N)$

$$\rightsquigarrow \frac{\beta \Delta \mathcal{H}}{f^2 n} = \frac{\alpha^2 N}{6} \sum_{k=1}^{\infty} \frac{e^{-\mu k}}{k} \left[\underbrace{\mu (k^3 - k) + k^2}_{\text{"nice" part}} - 1 \right]$$

"nasty" part

"nasty" part:

$$\sum_{k=1}^{\infty} \frac{e^{-\mu k}}{k} \simeq \int_{0.5}^{\infty} dx\, \frac{e^{-\mu x}}{x} = \int_{0.5\mu}^{\infty} dy\, \frac{e^{-y}}{y} =$$

$y = \mu x$

$$= \underbrace{\int_{0.5\mu}^{1} dy\, \frac{1}{y}}_{-\ln(0.5\mu)} + \underbrace{\int_{0.5\mu}^{1} dy\, \frac{e^{-y}-1}{y}}_{} + \underbrace{\int_{1}^{\infty} dy\, \frac{e^{-y}}{y}}_{-Ei(-1)}$$

$$\simeq \int_0^1 \frac{dy}{y}\left(e^{-y}-1\right) = Ei(-1) - \gamma$$

Euler-Mascheroni

exponential integral

$$\sum_{k=1}^{\infty} \frac{e^{-\mu k}}{k} \simeq \ln\frac{2}{\mu} - \gamma$$

"nice" part:

$$y = \mu x$$

$$\sum_{k=1}^{\infty} e^{-\mu k}\left[\mu(k^2-1)+k\right] \simeq \int_{0.5}^{\infty} dx\, e^{-\mu x}\left[\mu(x^2-1)+x\right] =$$

$$= \frac{1}{\mu}\int_{0.5\mu}^{\infty} dy\, e^{-y}\left[\mu\left(\frac{y^2}{\mu^2}-1\right)+\frac{y}{\mu}\right]$$

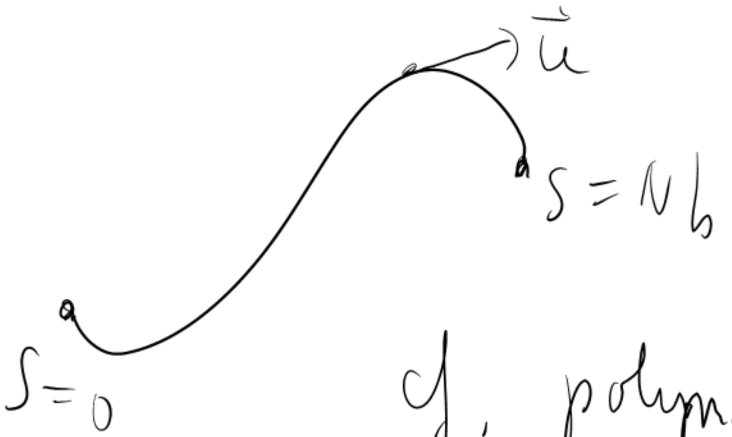
$$\simeq \frac{1}{\mu^2}\int_{0}^{\infty} dy\, e^{-y}\left[y^2-\mu^2+y\right] = \frac{1}{\mu^2}\left(2-\mu^2+1\right) = \frac{3}{\mu^2}-1$$

$$\frac{\beta \Delta \mathcal{H}}{f^2 n} = \frac{\alpha^2 N}{6} \left\{ \frac{3}{\mu^2} \underbrace{- 1 + \gamma - \ln\left(\frac{2}{\mu}\right)}_{\text{neglect for } \mu \to 0} \right\}$$

$$= \frac{\alpha^2 N}{2} \frac{1}{\mu^2} = \left(\frac{\theta}{2N}\right)^2 \frac{N}{2} \frac{1}{\kappa^2 b^2}$$

$$\boxed{\beta \Delta \mathcal{H} = \frac{f^2 n}{8} \frac{\theta^2}{N b^2} \ell_D^2}$$

Now, consider a worm-like chain model (stiff polymer chain)



s contour length

$\vec{u}$ unit tangent vector

cf. polymer physics lecture

$$\mathcal{H}_{WLC} \propto \int_0^{Nb} ds \left(\frac{\partial \vec{u}}{\partial s} \right)^2$$

define the persistence length l_p via the relation

$$\mathcal{H}_{WLC} = \frac{1}{2} k_B T \, l_p \int_0^{Nb} ds \left(\frac{\partial \vec{u}}{\partial s} \right)^2$$

$$\beta \mathcal{H}_{WLC} = \frac{l_p}{2} \int_0^{Nb} ds \left(\frac{\partial \vec{u}}{\partial s} \right)^2$$

for our arc: angle $\varphi \in [0, \Theta]$

contour length $s \in [0, Nb]$

$$s = \frac{Nb}{\Theta}\varphi \qquad \varphi = \frac{\Theta}{Nb} s$$

$$\vec{u} = \begin{pmatrix} -\sin\varphi \\ \cos\varphi \\ 0 \end{pmatrix} \qquad \frac{\partial \vec{u}}{\partial \varphi} = \begin{pmatrix} -\cos\varphi \\ -\sin\varphi \\ 0 \end{pmatrix}$$

$$\left(\frac{\partial \vec{u}}{\partial \varphi}\right)^2 = 1 \qquad \frac{\partial \vec{u}}{\partial s} = \frac{\partial \vec{u}}{\partial \varphi} \frac{\Theta}{Nb} \Rightarrow \left(\frac{\partial \vec{u}}{\partial s}\right)^2 = \frac{\Theta^2}{N^2 b^2}$$

$$\beta \mathcal{H}_{WLC} = \frac{l_p}{2} N b \frac{\theta^2}{N^2 b^2} = \frac{l_p}{2} \frac{\theta^2}{N b}$$

this must be equal to

$$\beta \Delta \mathcal{H}_{DH} = \frac{f^2 u}{8} \frac{\theta^2}{N b^2} l_D^2$$

$$\boxed{l_p = \frac{f^2 u}{4} \frac{l_D^2}{b}} \gg l_D$$

typically

OSF theory

Odijk, Skolnick, Fixman

1977

13. Polyelectrolyte Conformations V:

Weakly Charged Gaussian Debye-Hückel Chains

$$\mathcal{H} = \mathcal{H}_{RW} + \mathcal{H}_{DH}$$

assume $f^2 N \ll 1$ no Manning condensation

want to analyze: Start with salt-free case ($l_D = \infty$), add salt ($l_D \downarrow$), and look at R_E

combine $\xi_{el} \sim b\,(f^2 u)^{-1/3}$

OSF persistence length $\quad l_{p\,OSF} \sim f^2 u \dfrac{l_D^2}{b}$

$$b \ll l_D \ll Nb$$

$l_D = 0 \quad \sim$ blob pole

$$R_E \sim Nb\,(f^2 u)^{1/3} \sim \frac{N}{g_{el}}\,\xi_{el}$$

$l_D \downarrow$ blob pole becomes less stiff

Khokhlov & Khatchaturian 1982

new effective monomers : electrostatic blobs!!

$$l_p \sim f_{eff}^2 \, l_B \, \frac{l_D^2}{b_{eff}^2}$$

$$\xi_{el}^2 = b^2 g_{el}$$

$$b_{eff} = \xi_{el} \sim b \, (f^2 n)^{-1/3}$$

$$f_{eff} = f \, g_{el} \sim f \, (f^2 n)^{-2/3}$$

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

$$= \frac{l_D^2}{b} \left(f^2 n\right)^{1-4/3+2/3} = \frac{l_D^2}{b} \left(f^2 n\right)^{1/3} \sim \frac{l_D^2}{\xi_{el}}$$

end of blob-pole regime

$$l_p \sim R_E \text{ (blob pole)}$$

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

$$l_D^2 \sim Nb^2$$

$$\boxed{l_D \sim bN^{1/2}}$$

for smaller l_D is semiflexible chain of electrostatic blobs

$$R_E^2 \sim \frac{N}{g_{el}} \quad \xi_{el} \quad l_p$$

$$\sim N g_{el}^{-1} \xi_{el} \frac{l_D^2}{\xi_{el}} \sim N g_{el}^{-1} l_D^2$$

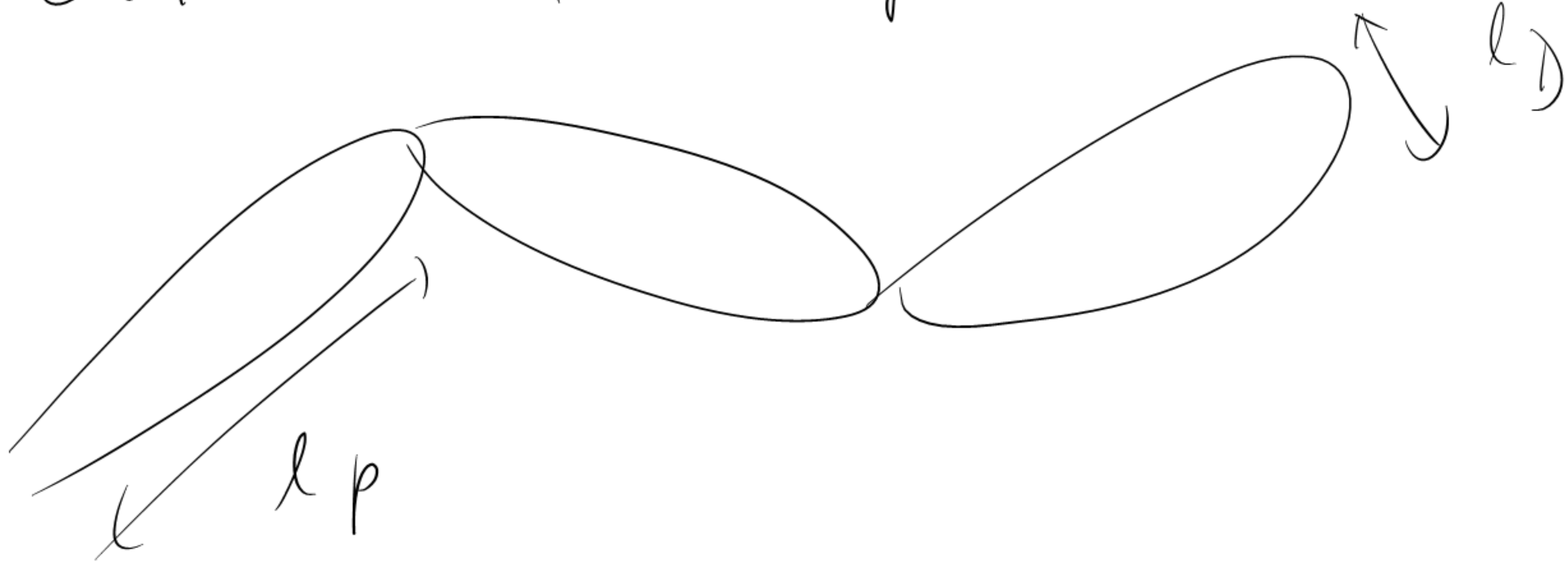
$$R_E \sim N^{1/2} g_{el}^{-1/2} l_D \sim N^{1/2} l_D \left(f^2 u\right)^{1/3} \sim R_E$$

$$g_{el} \sim \left(f^2 u\right)^{-2/3} \Rightarrow g_{el}^{-1/2} \sim \left(f^2 u\right)^{1/3}$$

decrease l_D further $\Rightarrow$ at some point excluded-volume effects become important

$\hookrightarrow$ strength of this excluded volume?

chain = sequence of rods



excluded volume between two rods ?

Onsager : excluded volume $\sim \underline{\underline{l_p^2 \, l_D}}$

number of rods : $\dfrac{R_E(\text{blob pole})}{l_p} \sim$

$$\frac{N}{g_{el}} \xi_{el} \frac{\xi_{el}}{l_D^2} \sim \frac{N}{l_D^2} \frac{\xi_{el}^2}{g_{el}} \sim \frac{N b^2}{l_D^2}$$