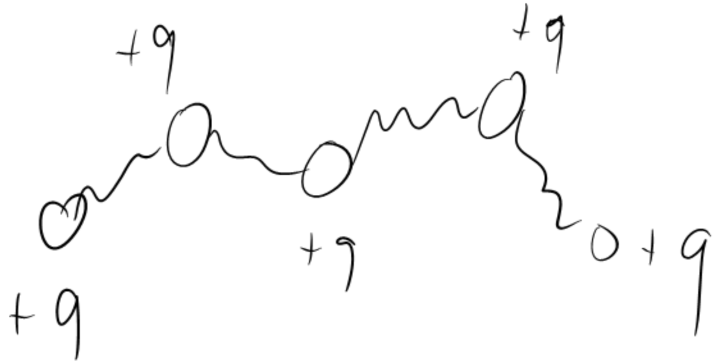
9. Polyelectrolyte Conformations I:

Gaussian Chain + Charges



ions and other polymers infinitely far away

$$\mathcal{H} = \underbrace{\frac{3 k_B T}{2 b^2} \sum_{i=1}^{N-1} \left(\vec{r}_{i+1} - \vec{r}_i \right)^2}_{\text{bead-spring model}} + \frac{q^2}{4\pi\varepsilon} \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

coulomb repulsion

Set $q = fe$ $\quad f$: "fraction"

weak charging: $\boxed{f^2 u \ll 1}$

$$u = \frac{l_B}{b} \quad \text{coupling parameter}$$

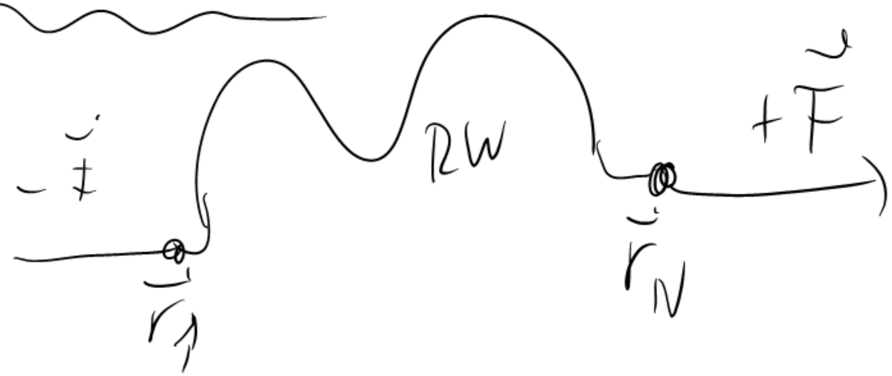
$$\beta \mathcal{H} = \frac{3}{2b^2} \sum_{i=1}^{N-1} (\vec{r}_{i+1} - \vec{r}_i)^2 + f^2 l_B \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

uncharged $\quad \vec{R}_E \equiv \vec{r}_N - \vec{r}_1$

$$\langle \vec{R}_E^2 \rangle = b^2 (N-1) \simeq b^2 N$$

charged: chain strongly stretched in some direction, due to electrostatic repulsion

intermission:



→ "Pincus blobs"

stretching by an external force

$$\mathcal{H} = \frac{3 k_B T}{2 b^2} \sum_{i=1}^{N-1} \left(\vec{r}_{i+1} - \vec{r}_i \right)^2 \underbrace{- \vec{F} \cdot \vec{r}_N + \vec{F} \cdot \vec{r}_1}_{- \vec{F} \cdot \left(\vec{r}_N - \vec{r}_1 \right)}$$

$$\begin{aligned} \vec{r}_N - \vec{r}_1 &= \left(\vec{r}_N - \vec{r}_{N-1} \right) + \left(\vec{r}_{N-1} - \vec{r}_{N-2} \right) + \ldots + \left(\vec{r}_2 - \vec{r}_1 \right) \\ &= \sum_{i=1}^{N-1} \left(\vec{r}_{i+1} - \vec{r}_i \right) \end{aligned}$$

$$\mathcal{H} = \frac{3 k_B T}{2 b^2} \sum_{i=1}^{N-1} \left\{ \left(\vec{r}_{i+1} - \vec{r}_i \right)^2 - \frac{2 b^2}{3 k_B T} \vec{F} \cdot \left(\vec{r}_{i+1} - \vec{r}_i \right) \right\} =$$

$$= \frac{3k_BT}{2b^2} \sum_{i=1}^{N-1} \left\{ \left(\vec{r}_{i+1} - \vec{r}_i - \frac{b^2 \vec{F}}{3k_BT} \right)^2 - \underbrace{\left(\frac{b^2 \vec{F}}{3k_BT} \right)^2}_{=\text{const., discard}} \right\}$$

$$\rightarrow \frac{3k_BT}{2b^2} \sum_{i=1}^{N-1} \left(\vec{r}_{i+1} - \vec{r}_i - \frac{b^2 \vec{F}}{3k_BT} \right)^2$$

$$\langle \vec{r}_{i+1} - \vec{r}_i \rangle = \frac{b^2 \vec{F}}{3k_B T}$$; equipartition theorem $\Rightarrow$

$$\frac{3k_B T}{2b^2} \left\langle \left(\vec{r}_{i+1} - \vec{r}_i - \frac{b^2 \vec{F}}{3k_B T} \right)^2 \right\rangle = \frac{3}{2} k_B T$$

$$\left\langle \left(\vec{r}_{i+1} - \vec{r}_i - \frac{b^2 \vec{F}}{3k_B T} \right)^2 \right\rangle = b^2$$

$$\vec{r}_{i+1} - \vec{r}_i = \frac{b^2 \vec{F}}{3 k_B T} + \frac{1}{\sqrt{3}} b \vec{q}_i$$

Gaussian random vector

$$\langle \vec{q}_i \rangle = 0$$

$$\langle q_{i\alpha} q_{j\beta} \rangle = \delta_{ij} \delta_{\alpha\beta}$$

$$\vec{R}_{EE} = \vec{r}_N - \vec{r}_1 = \sum_{i=1}^{N-1} (\vec{r}_{i+1} - \vec{r}_i) =$$

$$= \underbrace{(N-1) \frac{b^2 \vec{F}}{3 k_B T}}_{O(N)} + \frac{b}{\sqrt{3}} \underbrace{\sum_{i=1}^{N-1} \vec{q}_i}_{O(N^{1/2})}$$

extension of chain: $R_{F\parallel} \sim N \dfrac{b^2 F}{3 k_B T}$

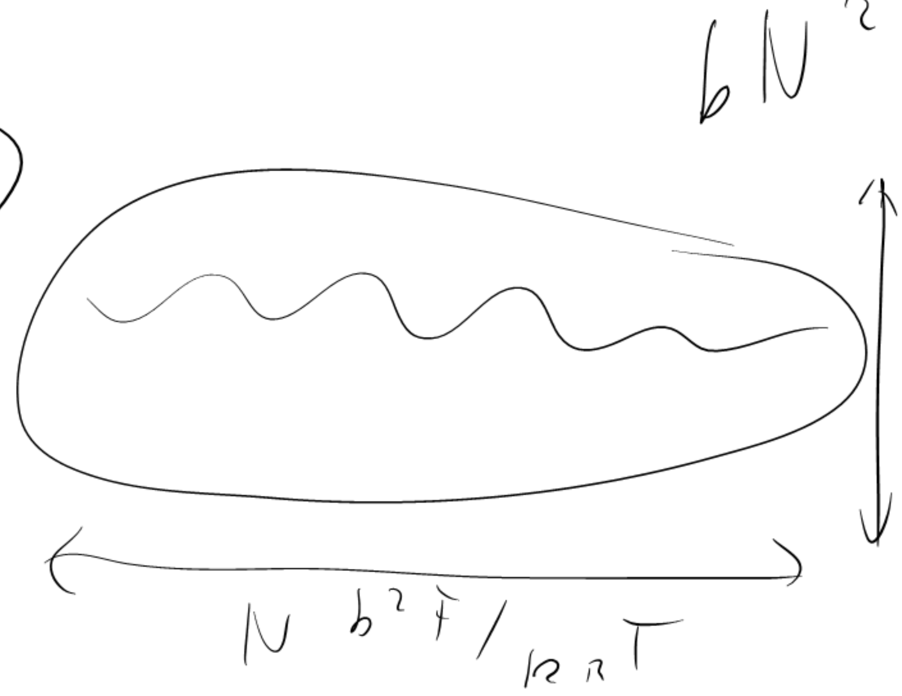
$R_{F\perp} \sim \sqrt{\dfrac{2}{3}}\, N^{1/2} b$

$\sqrt{\langle R_{F\parallel}^2 \rangle}$

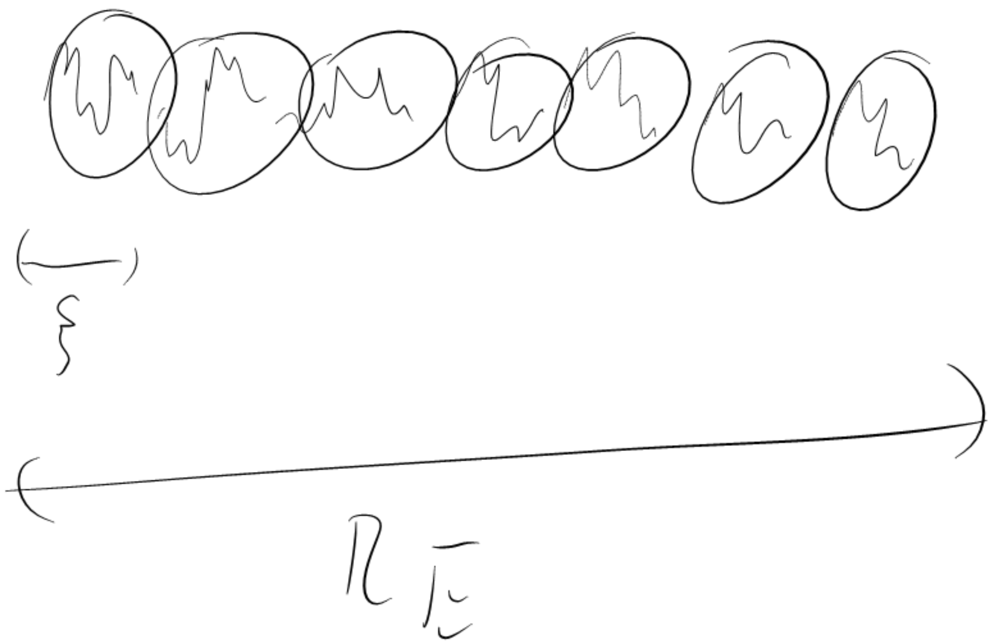
$\sqrt{\langle R_{F\perp}^2 \rangle}$

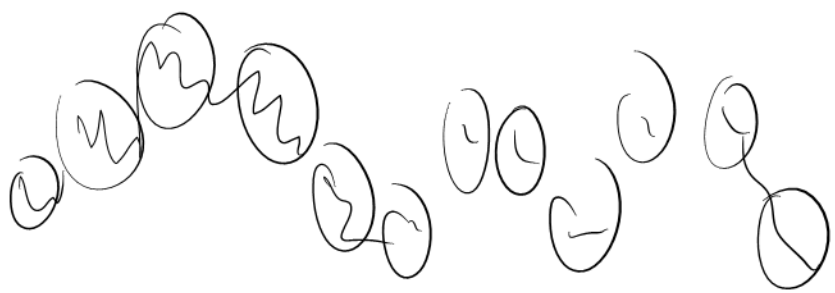
$b^2 = \langle (\vec{r}_{i+1} - \vec{r}_i)^2 \rangle$

$\vec{F} = 0$



"Pincus blobs"





one blob: n monomers

blobs: $\dfrac{N}{n}$

within a blob: RW $\Rightarrow$ $\xi \sim b n^{1/2}$

$$F \xi \overset{!}{\sim} k_B T \qquad \xi \sim \frac{k_B T}{F} \qquad b n^{1/2} \sim \frac{k_B T}{F}$$

$$n \sim \left(\frac{k_B T}{F b} \right)^2 ,$$ number of blobs $\sim \dfrac{N}{n} \sim$

$$\sim N \left(\frac{F b}{k_B T} \right)^2$$

$$R_{E\parallel} \sim \frac{N}{n}\xi \sim N\left(\frac{Fb}{k_BT}\right)^2 \frac{k_BT}{F} \sim N\,\frac{b^2F}{k_BT}$$

end of intermission. back to the charged chain.

<u>assume</u> a stretched conformation,

extension R_E in one direction,

" $bN^{1/2}$ perpendicular

aspect ratio $\frac{R_E}{bN^{1/2}}$

for electrostatics: assume geometry of an ellipsoid

$\curvearrowright$ electrostatic energy $\sim \dfrac{(Nfe)^2}{4\pi\varepsilon R_E} \ln\left(\dfrac{R_E}{bN^{1/2}}\right)$

entropic elastic energy $\sim k_B T \dfrac{R_E^2}{Nb^2}$

"Flory theory"

$$k_B T \frac{R_E^2}{Nb^2} + \frac{(Nfe)^2}{4\pi\varepsilon R_E} \ln\left(R_E / bN^{1/2}\right) \overset{!}{=} \text{Min. wrt } R_E$$

$$\frac{R_E^2}{Nb^2} + \frac{N^2 f^2 l_B}{R_E} \ln\left(\frac{R_E}{bN^{1/2}}\right) \stackrel{!}{=} \mathrm{Min.}$$

first ignore log correction $\Rightarrow$

$$\frac{R_E^2}{Nb^2} + \frac{N^2 f^2 l_B}{R_E} \stackrel{!}{=} \mathrm{Min}$$

$$\frac{R_E}{Nb^2} - \frac{1}{R_E^2} N^2 f^2 l_B = 0 \quad \Big| \; R_E^2 \cdot Nb^2$$

$$R_E^3 = N^3 b^2 f^2 l_B$$

coupling parameter $u = \frac{l_B}{b}$

$$R_E^3 = N^3 b^3 f^2 u$$

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

result for neglected log-correction

now, take log-correction into account

Write: $R_E = Nb\,(f^2 n)^{1/3}\,x$ ← determine x

$$\frac{R_E^2}{N b^2} \sim N\,(f^2 n)^{2/3}\,x^2$$

$$\frac{N^2 f^2 l_B}{R_E} \sim N \underbrace{f^2 \frac{l_B}{b}}_{f^2 n} (f^2 n)^{-1/3} \frac{1}{x} = N\,(f^2 n)^{2/3}\,\frac{1}{x}$$

$$\frac{R_E}{b N^{1/2}} \sim N^{1/2} \left(f^2 n\right)^{1/3} x$$

$$x^2 + \frac{1}{x} \ln\left[N^{1/2} \left(f^2 n\right)^{1/3} x\right] \overset{!}{=} \text{Min.}$$

$$x - \frac{1}{x^2} \ln\left[N^{1/2} \left(f^2 n\right)^{1/3} x\right] + \frac{1}{x}\frac{1}{x} = 0 \quad \Big| \, x^2$$

$$x^3 = \ln\left[N^{1/2} \left(f^2 n\right)^{1/3}\right] + \ln x - 1$$

N large $\Rightarrow$ $\ln[\ldots]$ large $\Rightarrow$ x large

$x^3 \gg \ln x \qquad x^3 \gg 1$

$$\rightsquigarrow \; x \sim \left\{ \ln\left[N^{1/2} (f^2 u)^{1/3} \right] \right\}^{1/3}$$

$$\underbrace{R_E \sim N b \,(f^2 u)^{1/3} \left\{ \ln\left[N^{1/2} (f^2 u)^{1/3} \right] \right\}^{1/3}}$$

with log-correction

"electrostatic blobs"

blob size ξ , # monomers in the blob: n

$\xi \sim b\, n^{1/2}$

electrostatic energy in one blob

$$k_B T \sim \frac{(nfe)^2}{4\pi\varepsilon\,\xi} \Rightarrow 1 \sim \frac{n^2 f^2 l_B}{\xi} \sim \frac{n^2 f^2 l_B}{b\, n^{1/2}}$$

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

$$\boxed{n \sim \left(f^2 u\right)^{-2/3}}$$

$$\boxed{\xi \sim b\, n^{1/2} \sim b \left(f^2 u\right)^{-1/3}}$$

electrostatic blob size

$$\#\text{ of blobs: } \frac{N}{n} \sim N \left(f^2 u\right)^{+2/3} \longrightarrow$$

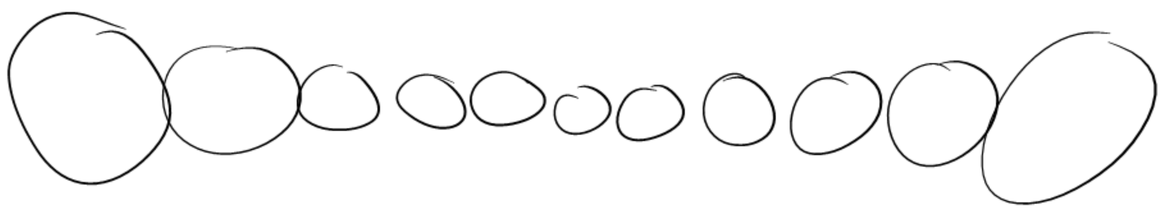
$$R_E \sim \frac{N}{n}\, \xi \sim N \left(f^2 u\right)^{2/3} b \left(f^2 u\right)^{-1/3}$$

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

1 right answer, except log!

Simple blob picture ignores mutual repulsion of blobs and hence does not get the log-correction!

improvement: "inhomogeneous blobs"



much more complicated

Dobrynin & Rubinstein 2005

Typically, log-corrections are simply ignored!

10. Polyelectrolyte Conformations II:

Excluded-Volume Chain with Charges

blob picture: blobsize ξ, n: # monomers in a blob: $\xi \sim b n^{\nu}$ $\quad \nu \simeq 0{,}588$

$$k_B T \sim \frac{(n f e)^2}{4 \pi \varepsilon \xi} \Rightarrow 1 \sim \frac{n^2 f^2 l_B}{\xi} \sim \frac{n^2 f^2 l_B}{b\, n^{\nu}}$$

$$\sim n^{2-\nu} f^2 u \Rightarrow 1 \sim n \left(f^2 u\right)^{1/(2-\nu)}$$

$$\boxed{n \sim (f^2 u)^{-1/(2-\nu)}}$$

$$\xi \sim b\, n^\nu \sim b\, (f^2 u)^{-\nu/(2-\nu)}$$

$$\#\text{ of blobs} \sim \frac{N}{n} \sim N (f^2 u)^{+1/(2-\nu)}$$

$$R_E \sim \frac{N}{n}\xi \sim N (f^2 u)^{1/(2-\nu)}\, b\, (f^2 u)^{-\nu/(2-\nu)}$$

$$\boxed{R_E \sim N b\, (f^2 u)^{(1-\nu)/(2-\nu)}}$$

+ log corrections