

Floory theory

Free Energy

chain stretching: $F_{ent} = k_B T \frac{R^3}{N b^2}$

volume interaction: $F_{int} =$

$\frac{N}{R^3}$
 \uparrow
 monomer
 number
 density

v
 \uparrow
 monomer
 volume

N
 \uparrow
 Number

$k_B T$
 \uparrow
 per
 interaction

probability of a monomer interacting

$$F = k_B T \left[v \frac{N^2}{R^3} + \frac{R^3}{N b^2} \right]$$

$$\frac{\partial F}{\partial R} = 0 = k_B T \left[-3v \frac{N^2}{R^4} + 2 \frac{R}{N b^2} \right]$$

$$R^5 = v b^2 N^3$$

$$R \sim N^{3/5}$$

de Gennes: "This is wrong, but gives the right answer miraculously"

The "good" method: renormalization-group theory

$$v = 0.5886$$

instead of 0.6

Polyelectrolytes : - Polymers with charges units
 - electrolytes which are "chain-like"

electrolytes : $U_{\text{Coulomb}} : \frac{e^2 z_i z_j}{4\pi \epsilon_0 \epsilon_r r_{ij}}$

Bjerrum length l_B : when $U_{\text{Coul}} \approx k_B T$

for unit charges $\Rightarrow l_B = \frac{e^2}{4\pi \epsilon_0 \epsilon_r k_B T}$

water at room

temp. : $l_B \approx 7.13 \text{ \AA}$

electrostatic interaction $\frac{U_{\text{Coul}}}{k_B T} = l_B \frac{Q_1 Q_2}{r}$

Flory theory for PE

entropic collapse: $F_{\text{ent}} = k_B T \frac{R^2}{N b^2}$

if there is a charge fraction: f

$F_{\text{Coul}} = k_B T \frac{(Nf)^2}{R} l_B$

$F_{\text{tot}} = k_B T \left(\frac{R^2}{N b^2} + l_B \frac{(Nf)^2}{R} \right)$

$\frac{\partial F}{\partial R} = 0 \Rightarrow \frac{2R}{N b^2} - \frac{(Nf)^2 l_B}{R^2} = 0$

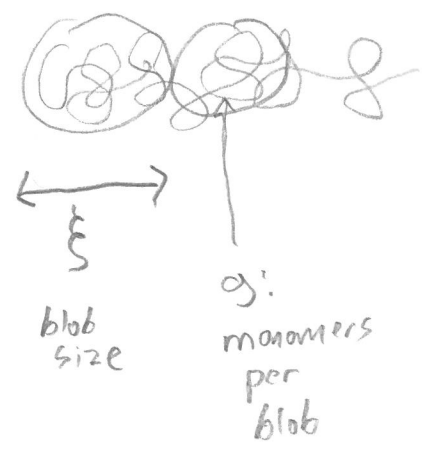
$R^3 \sim N^3 f^2 l_B b^2$

$R \sim N f^{2/3} l_B^{1/3} b^{2/3}$

$R \sim N^{\nu} \quad \nu = 1!$

linear!

Blob theory for polyelectrolytes

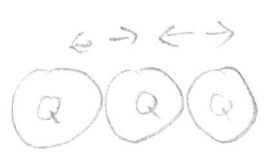


blob length scale
separates the
dominating physics

inside blob:

regular polymer: $R = bN^{1/2}$
 up to $\xi = bg^2$

outside blob:
electrostatics dominate!



linear arrangement of blobs

electrostatics
less than $k_B T$

$$\frac{(Fg)^2 l_B}{\xi} = 1$$

$$R = \frac{N}{g} \xi$$

$$= N \left(\frac{f^2 l_B}{b} \right)^{2/3} \left(\frac{b^4}{f^2 l_B} \right)^{1/3}$$

$$= N l_B^{1/3} f^{2/3} b^{2/3}$$

SAME as Flory theory!

But what about salt/counter ions!?

for a lot of cases they play an important role!

- bridge interactions
- compensate charge

Ex. DNA has $1e^-$ per 0.34 nm , (every base pair)

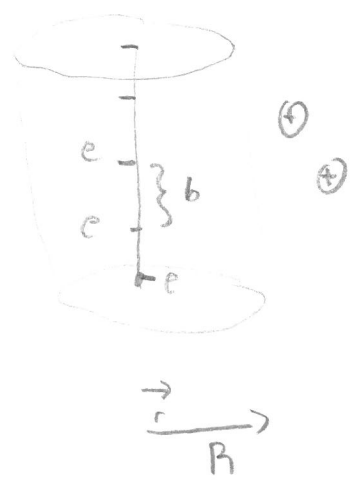
does λ -DNA really behave like

it has a charge of $-48 \times 10^3 e^-$? No!

counter-ions attract, and compensate \rightarrow effective distance between charges is $\approx l_B$

Onsager argument (Manning)

infinite rod with $\lambda = \frac{e}{b}$ charge density



electric potential: $\Phi \approx \frac{\lambda}{2\pi\epsilon_r\epsilon_0} \ln(r)$

Question: where do the counterions go?

Free energy

$$\Delta F = \Delta E - K_B T \Delta S$$

$$\Delta E \sim e \Phi(r) \approx \frac{e\lambda}{2\pi\epsilon_r\epsilon_0} \ln \frac{R}{r}$$

$$\Delta S \sim \ln \frac{V_b}{V_r} \sim 2 \ln \frac{R}{r}$$

$$\Gamma = \frac{l_B}{b}$$

$$\Delta F = \left(\frac{l_B}{b} - 1 \right) 2k_B T \ln \frac{R}{r}$$

$\Gamma < 1$: entropy dominated
 $\Gamma > 1$: energy dominated

planar: $\Phi \sim r$ energy dominated
 sphere: $\Phi \sim \frac{1}{r}$ entropy dominated