11. Polyelectrolyte Conformations III:

Poor-Solvent Chain with Charges

Consider first an uncharged chain & its Θ transition

$$R \propto \begin{cases} N^{\nu} \quad (\nu \simeq 0.6) & T \gg \Theta \quad \text{SAW} \\ N^{1/2} & T \simeq \Theta \left(\pm O(N^{-1/2})\right) \quad \text{RW} \\ N^{1/3} & T \ll \Theta \quad \text{globule} \end{cases}$$

effective (T-dependent) interaction energy v

between monomers (attractive)

$$v = k_B \theta - k_B T = k_B \theta \underbrace{\left(1 - \frac{T}{\theta}\right)}_{=: \tau > 0} = k_B \theta \tau$$

A N-monomer RW chain in 3d has $O(N^{1/2})$

intrachain contacts

thermal blob size ξ_t

length scale $\begin{cases} \ll \xi_t & \text{Gaussian} \\ \gg \xi_t & \text{globule} \end{cases}$

# of monomers in ξ_t : g_t $\qquad \xi_t \sim b\, g_t^{1/2}$

$$\underbrace{k_B \Theta \tau}_{\text{interaction energy}} \; \underbrace{g_t^{1/2}}_{\text{\# contacts in blob}} \overset{!}{\simeq} k_B T \simeq k_B \Theta$$

$$\boxed{g_t \sim \frac{1}{\tau^2}} \qquad \boxed{\xi_t \sim \frac{b}{\tau}}$$

\# blobs: $\frac{N}{g_t} \sim N\tau^2$

density: $\rho \sim \frac{g_t}{\xi_t^3} \sim \frac{g_t}{b^3 g_t^{3/2}} \sim$

$$\sim g_t^{-1/2} b^{-3} \sim b^{-3}\tau \sim \frac{\tau}{b^3}$$

$$R^3 \sim \xi_t^3 N \tau^2$$

$$\sim N b^3 \frac{1}{\tau^3} \tau^2 \sim N b^3 \frac{1}{\tau}$$

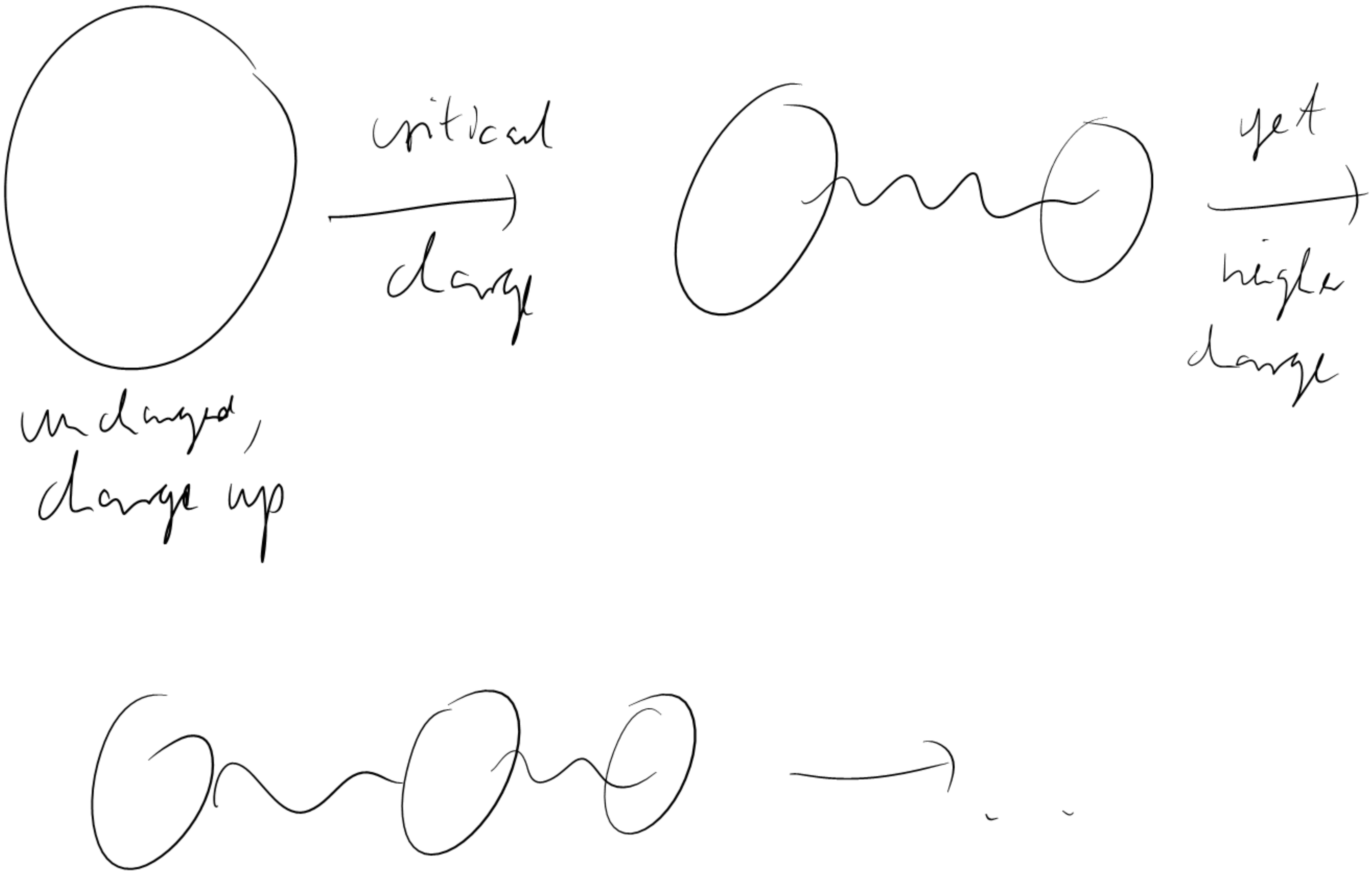
charged RW: $\xi_{el} \sim b\left(f^2 u\right)^{-1/3}$

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

charged globule: interplay between

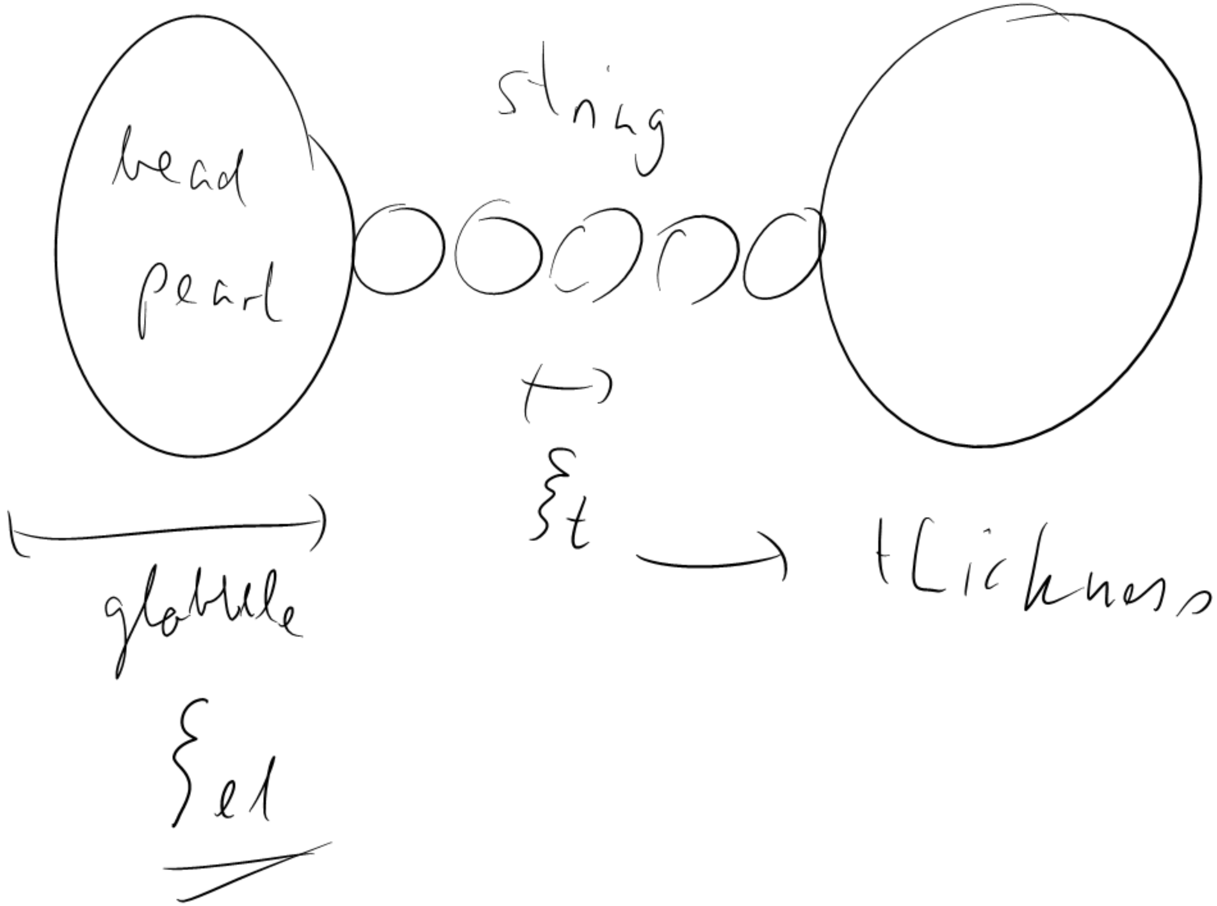
ξ_t and ξ_d

analogy to Rayleigh instability



"pearl-necklace structures"

balance between electrostatics and surface tension



thickness of strings

back to Rayleigh instability,

dimensionless parameter that controls the transition

$$q \equiv \frac{Q^2}{4\pi\varepsilon} \frac{1}{V} \frac{1}{\sigma}$$ (numerical prefactors ignored)

Q = charge

V = volume

σ = surface tension

$$Q \simeq N f e$$

$$V \simeq R^3 \sim N b^3 \frac{1}{\tau}$$

$$\sigma \simeq \frac{k_B T}{\xi_t^2} \sim \frac{k_B \theta}{b^2} \tau^2$$

$$q \sim \frac{N^2 f^2 e^2}{4\pi \varepsilon} \frac{\tau}{N b^3} \frac{b^2}{\tau^2} \frac{1}{k_B \theta} \sim N f^2 l_B \frac{1}{b} \frac{1}{\tau}$$

$$\boxed{q \sim N \frac{f^2 u}{\tau}}$$

Split-up occurs when $q = N\frac{f^2 u}{\tau}$ exceeds a critical value (of order unity)

What is globule size at criticality?

$$R \sim N^{1/3} b \tau^{-1/3}$$

$$N\frac{f^2 u}{\tau} \sim 1 \qquad \frac{N}{\tau} \sim (f^2 u)^{-1}, \quad \left(\frac{N}{\tau}\right)^{1/3} \sim (f^2 u)^{-1/3}$$

$$R \sim b (f^2 u)^{-1/3} \rightarrow \boxed{R_{crit} \sim \xi_{el}}$$

geometry & energetics of the

DRO pearl-necklace structure

→ Dobrynin, Rubinstein, Obukhov

$$\xi_{el} \gg \xi_t = b\left(f^2 u\right)^{-1/3} \gg \frac{b}{\tau}$$

$$\tau^3 \gg f^2 u$$

assume: practically all mass is stored in the pearls!

$n_b \equiv$ # of beads $\Rightarrow$ $\dfrac{N}{n_b} \equiv$ # of monomers in one bead

$n_{str} \equiv$ # of thermal blobs in one string

<u>bead radius</u> : R_b , $\rho \sim \dfrac{\tau}{b^3} \sim \dfrac{N/n_b}{R_b^3}$

$$R_b \sim b\,\tau^{-1/3}\left(\frac{N}{n_b}\right)^{1/3}$$

Surface energy of a bead:

$$F_b^s \sim R_b^2 \sigma \sim \left(\frac{N}{n_b}\right)^{2/3} b^2 \tau^{-2/3} \frac{k_B \theta}{b^2} \tau^2$$

$$\frac{F_b^s}{k_B T} \sim \tau^{4/3} \left(\frac{N}{n_b}\right)^{2/3}$$

electrostatic energy of a bead:

$$F_b^{el} \sim \frac{1}{4\pi\varepsilon R_b} \left(\frac{N}{n_b} f e\right)^2$$

$$\frac{F_b^{el}}{k_B T} \sim \left(\frac{N}{n_b}\right)^2 f^2 l_B \frac{1}{R_b} \sim \left(\frac{N}{n_b}\right)^2 f^2 l_B \frac{1}{b} \tau^{+1/3} \left(\frac{N}{n_b}\right)^{-1/3}$$

$$\sim \left(\frac{N}{n_b}\right)^{5/3} f^2 u \, \tau^{1/3}$$

total energy of a bead (in units of $k_B T$):

$$\tau^{4/3} \left(\frac{N}{n_b}\right)^{2/3} + \left(\frac{N}{n_b}\right)^{5/3} f^2 u \, \tau^{1/3} =$$

$$= \tau^{4/3} \left(\frac{N}{n_b}\right)^{2/3} \left[1 + \frac{N}{n_b} f^2 u \frac{1}{\tau} \right]$$

$\left\{ \text{recall} \quad N f^2 u \frac{1}{\tau} = q \quad (\text{Rayleigh parameter}) \right\}$

$$= \tau^{4/3} \left(\frac{N}{n_b}\right)^{2/3} \left[1 + \frac{q}{n_b} \right]$$

total energy of all beads is

$$\tau^{4/3} N^{2/3} n_b^{1/3} \left(1 + \frac{q}{n_b} \right)$$

length of a string:

$$l_{str} = \xi_t \, n_{str} = \frac{b}{\tau} \, n_{str}$$

surface energy of <u>all</u> strings:

$$F^s_{str} \sim k_B T \, n_b \, n_{str} \Rightarrow \frac{F^s_{str}}{k_B T} \sim n_b \, n_{str}$$

electrostatic energy from repulsion between the beads ("shish-kebap"):

$$F^{el}_{str} \sim \frac{N^2 f^2 e^2}{4\pi \varepsilon n_b l_{str}} \ln n_b$$

$$\frac{F^{el}_{str}}{k_B T} \sim \frac{N^2 f^2 l_B}{n_b l_{str}} \ln n_b \sim \frac{N^2 f^2 l_B}{n_b b n_{str}} \tau \ln n_b \sim$$

$$\sim \frac{N^2 f^2 u}{n_b n_{str}} \tau \ln n_b \sim N \frac{q\tau^2}{n_b n_{str}} \ln n_b$$

total String energy (in units of $k_B T$)

$$n_b n_{str} + N \left[q\tau^2 / (n_b n_{str}) \right] \ln n_b$$

grand total

$$\tau^{4/3} N^{2/3} n_b^{1/3} \left(1 + \frac{9}{n_b}\right) + n_b n_{str} + \frac{N q \tau^2}{n_b n_{str}} \ln n_b$$

minimize wrt n_b, n_{str}

optimize n_{str} $\Rightarrow$

$$0 = n_b + \frac{N q \tau^2}{n_b} \ln n_b \left(-\frac{1}{n_{str}^2}\right) \quad \Big| \cdot \frac{n_{str}^2}{n_b}$$

$$0 = n_{str}^2 - \frac{N q \tau^2}{n_b^2} \ln n_b$$

$$n_{str} \sim \frac{\tau}{n_b} \left(Nq\right)^{1/2} \left(\ln n_b\right)^{1/2}$$

$$\rightsquigarrow \quad l_{str} \sim n_{str}\, \xi_t \sim \frac{b}{n_b} \left(Nq\right)^{1/2} \left(\ln n_b\right)^{1/2}$$

Optimized string energy:

$$n_b n_{str} + \frac{Nq\tau^2}{n_b n_{str}} \ln n_b \sim \tau \left(Nq\right)^{1/2} \left(\ln n_b\right)^{1/2}$$

$$+ \frac{Nq\,\tau^2}{\tau \left(Nq\right)^{1/2} \left(\ln n_b\right)^{1/2}} \ln n_b \sim \tau \left(Nq\right)^{1/2} \left(\ln n_b\right)^{1/2}$$

energy as a whole:

$$\tau^{4/3} N^{2/3} n_b^{1/3} \left(1 + \frac{q}{n_b}\right) + \underbrace{\tau (Nq)^{1/2} \left(\ln n_b\right)^{1/2}}_{\text{neglect for optimization of } n_b}$$

(i) dependence is only log

(ii) $N^{2/3} \gg N^{1/2}$

$$\Rightarrow n_b^{1/3}\left(1+\frac{q}{n_b}\right) \overset{!}{=} \text{Min.}$$

$$n_b^{1/3} + q\, n_b^{-2/3} \overset{!}{=} \text{Min}$$

$$n_b^{-2/3} - q\, n_b^{-5/3} = 0 \quad \Big|\, n_b^{+5/3}$$

$$n_b - q = 0 \quad \Rightarrow \quad \boxed{n_b \sim q}$$

Size of the bead

$$R_b \sim b\, t^{-1/3} \left(\frac{N}{n_b}\right)^{1/3}$$

$$\leftarrow\; q \simeq N \frac{f^2 u}{\tau}$$

$$\sim b\, N^{1/3} (\tau q)^{-1/3}$$

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

length of a string

$$l_{str} \sim \frac{b}{n_b} (N q)^{1/2} (\ln n_b)^{1/2} \simeq \frac{b}{q} (N q)^{1/2} (\ln q)^{1/2}$$

$$l_{str} \sim b N^{1/2} \left(\frac{\ln q}{q} \right)^{1/2} \sim$$

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

$$\sim b \left(\frac{\tau}{f^2 u} \right)^{1/2} \left(\ln \left[\frac{N f^2 u}{\tau} \right] \right)^{1/2}$$

$$\frac{\xi_{el}^{3/2}}{\xi_t^{1/2}} \sim \frac{b^{3/2}\left(f^2 u\right)^{-1/2}}{\left(\frac{b}{\tau}\right)^{1/2}} \sim b\left(\frac{\tau}{f^2 u}\right)^{1/2}$$

$$\Rightarrow l_{str} \sim \frac{\xi_{el}^{3/2}}{\xi_t^{1/2}} \cdot \text{log-correction}$$

$$l_{str} \gg R_b$$

$$\frac{\xi_{el}^{3/2}}{\xi_t^{1/2}} \approx \underbrace{\xi_{el}}_{R_b} \underbrace{\left(\frac{\xi_{el}}{\xi_t}\right)^{1/2}}_{\gg 1}$$

Size of necklace:

$$L_{nec} \sim l_{str} n_b \sim \xi_{el} \left(\frac{\xi_{el}}{\xi_T} \right)^{1/2} \cdot q \cdot \text{log-correction}$$

$q \propto N$ stretched

volume of string

$$\sim l_{str} \cdot \xi_t^2 \sim \frac{\xi_{el}^{3/2}}{\xi_t^{1/2}} \xi_t^2 \sim (\xi_{el} \, \xi_t)^{3/2}$$

volume of bead $\sim \xi_{el}^3$

$$\frac{V_{string}}{V_{bead}} \sim \frac{\xi_{el}^{3/2} \, \xi_t^{3/2}}{\xi_{el}^3} = \left(\frac{\xi_t}{\xi_{el}} \right)^{3/2} << 1$$

indeed all mass is in the beads !