Lecture 2

Dilute Polyelectrolyte Solutions

Polymer Size

Typical segment length $b \sim 1nm$ Consider a chain with $N = 10^3$ segments

Polymer size depends on solvent quality.

Poor solvent

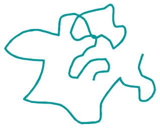
globular state

$R = bN^{1/3} \sim 10\ nm$

Theta solvent

“ideal” coil

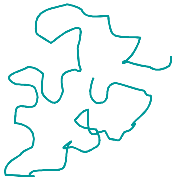
$R = bN^{1/2} \sim 30\ nm$



Good solvent

$R = bN^{3/5} \sim 60\ nm$

swollen coil



Long-range repulsion

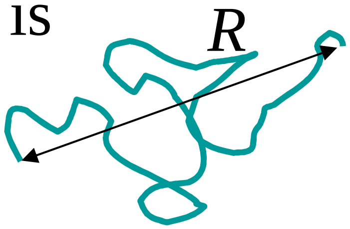
$R \sim L = bN \sim 1\ \mu m$

stretched chain

Things to Remember about Uncharged Polymers

Polymer size in a solvent is determined by the balance of interaction energy and conformational entropy.

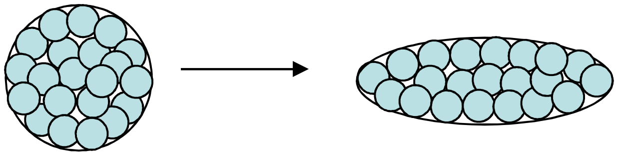
Entropic elasticity of a polymer in a solvent is



$$F \approx kT \frac{R^2}{b^2 N}$$

Entropic free energy cost for doubling chain size is ~ kT

Polymer size in a non-solvent is controlled by the surface energy, while the volume of the globule is almost constant determined by the balance of 2-body attraction and 3-body repulsion.



Free energy cost for deforming the globule is >> kT

Flory Theory of Polyelectrolytes

(not done by Flory)

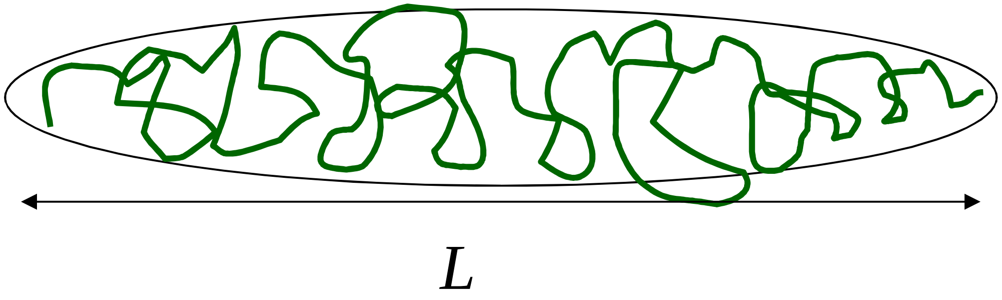
Kuhn, Kunzle, Katchalsky, 1948

f – fraction of charged monomers of an N-mer of size L

$\frac{(efN)^2}{\varepsilon L}$ – electrostatic energy $kT\frac{L^2}{Nb^2}$ – entropic elasticity

Balance of electrostatic and entropic parts of free energy

$$L \approx bN\left(uf^2\right)^{1/3} \qquad u = l_B/b$$

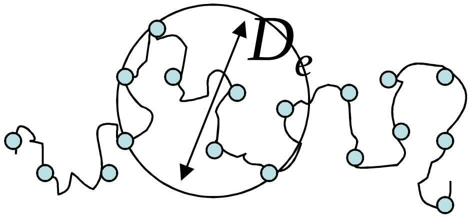


e.g. $N \approx 10^3$, $b = 2.5Å$, $f = 0.2$ ⟶ $L = 120\ nm$

What is the typical polyelectrolyte conformation?

Scaling Theory

de Gennes et al '76



D_e – size of an **electrostatic blob** with g_e monomers

θ – solvent for uncharged backbone

fg_e – charges in an electrostatic blob

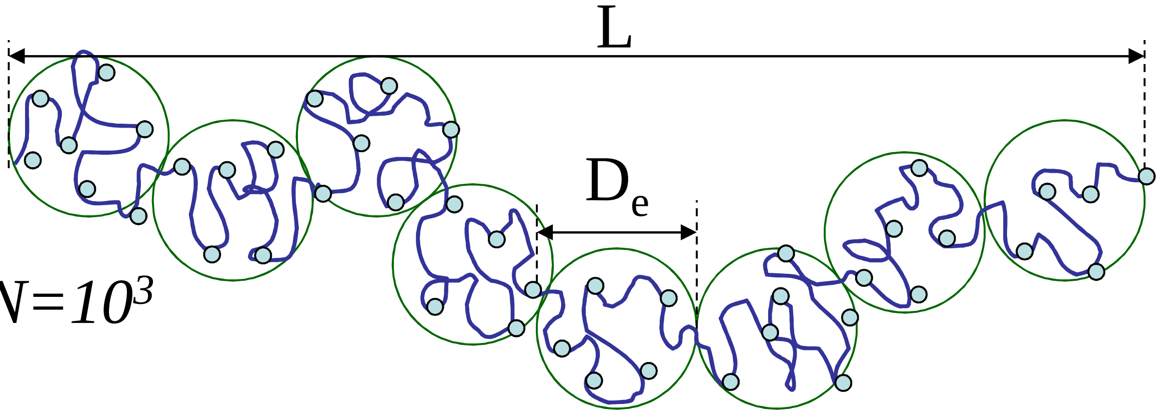
$$D_e \approx b g_e^{1/2}$$

$$\frac{(fg_e e)^2}{\varepsilon D_e} \approx kT$$ – electrostatic energy of a blob is ~ thermal energy

$$D_e \approx b(uf^2)^{-1/3}$$ – size of an electrostatic blob $u = l_B/b$

$$g_e \approx (uf^2)^{-2/3}$$ – number of monomers in an electrostatic blob

$$L \approx D_e \frac{N}{g_e} \approx bN\left(uf^2\right)^{1/3}$$ – end-to-end distance of a chain in dilute solution

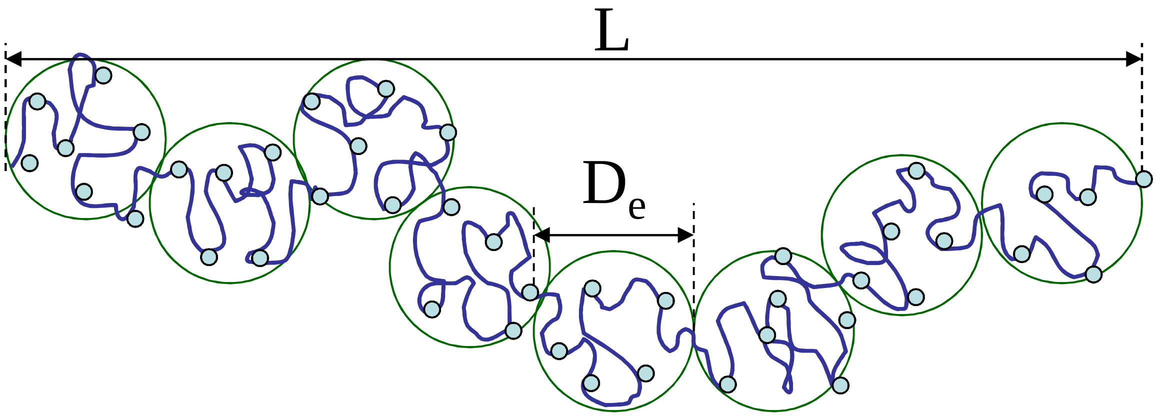


e.g. $u=2$, $f=0.2$, $b \approx 2.5$Å, $N=10^3$

$g_e \approx 5$, $D_e \approx 6$Å, $L \approx 120nm$

Hydrophilic Polyelectrolytes

de Gennes et al '76



Chain conformation – balance of electrostatics and entropy.

Electrostatic blob D_e – electrostatic energy is of order thermal energy kT.

At length scales < D_e – chain conformation is unperturbed by electrostatics.

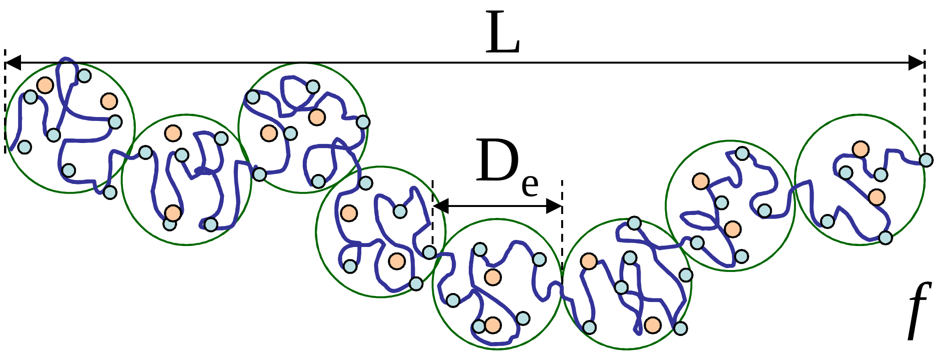
At length scales > D_e – long-range electrostatic repulsion forces the chain into a stretched array of electrostatic blobs.

$$L \approx D_e \frac{N}{g_e}$$

g_e – number of monomers in an electrostatic blob

Condensed counterions reduce chain charge and electrostatic repulsion.

Counterion Condensation



Electrostatic blob

$D_e \approx b(uf^2)^{-1/3}$ $\quad u = l_B/b$

$g_e \approx (uf^2)^{-2/3}$

f – fraction of charged monomers

Number of charges per Bjerrum length along the end-to-end direction

$$(fg_e/D_e)l_B \approx (u^2f)^{1/3}$$

$u^2f < 1$ – counterions are free to “escape” from the chain

$u^2f > 1$ – Onsager-Manning condensation of counterions onto the chain

$u^2f\beta \rightarrow 1$ ($f \rightarrow \beta f = 1/u^2$) fraction of free counterions $\rightarrow \beta \approx 1/(u^2f)$

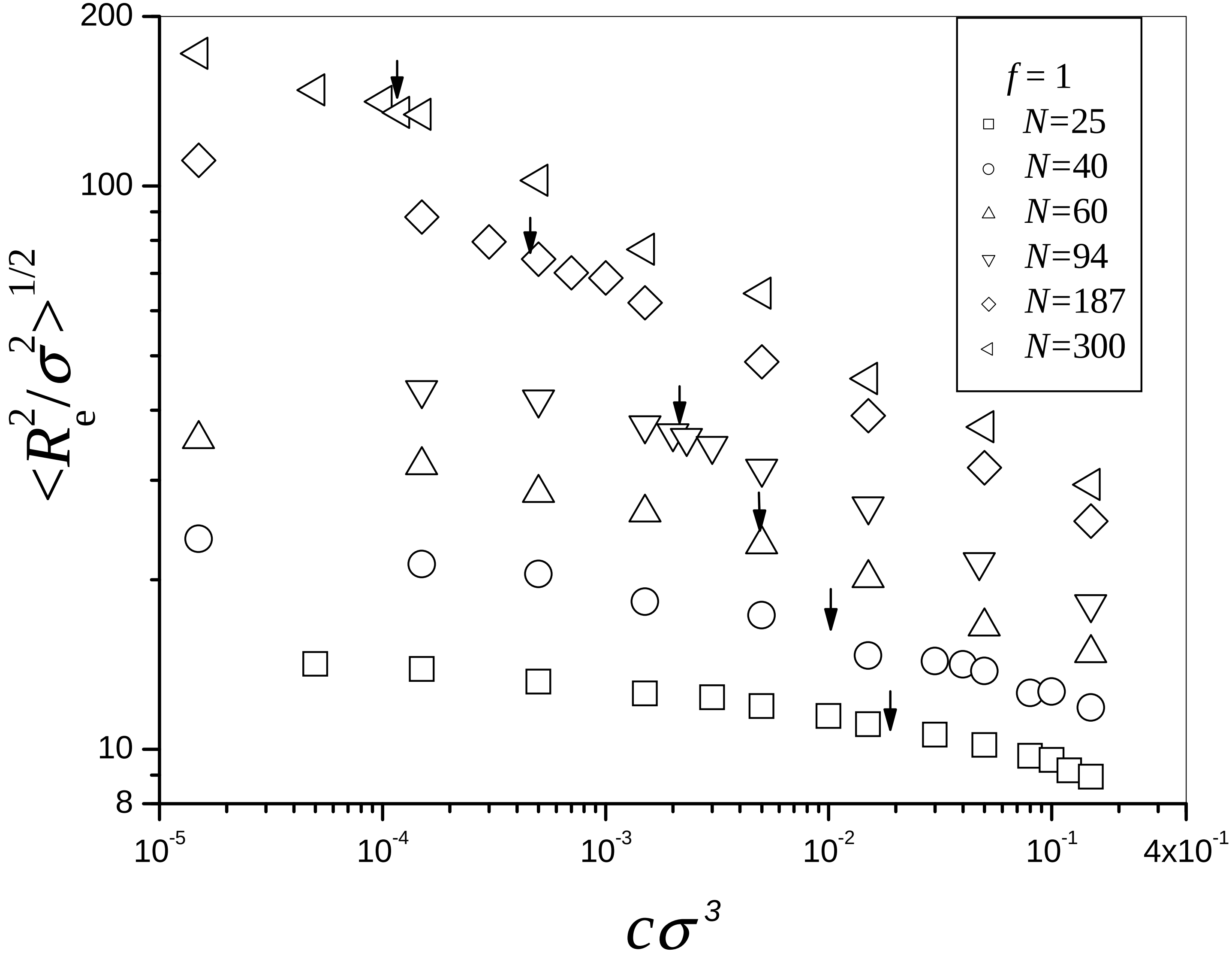
$D_e \approx l_B$ – electrostatic blob is equal to Bjerrum length ($g_e \approx u^2$)

($n_e \approx \beta f g_e \approx 1$)

$L \approx D_e N/g_e \approx bN/u \approx l_B N/u^2$ – chain size is independent of charge fraction f

e.g. 200K PSS with $N \approx 10^3$, $b \approx 3Å$, $f = 1$ → $\beta \approx$ 0.2, $L \approx 100\ nm$

Concentration Dependence of Chain Size



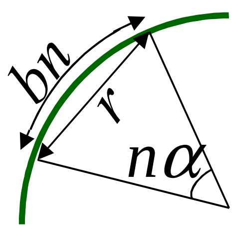
Salt Dependence of Chain Size

$r_D > L$ – chain size is unaffected by added salt r_D – Debye length

$r_D < L$ – electrostatic interactions are screened at r_D by salt ions.

Electrostatic Persistence Length

I. Odijk-Skolnick-Fixman Theory 1977



Electrostatic energy increases upon bending charged rod because distance between charges decreases

$$r(n) \approx bn(1-n^2\alpha^2/24) < bn$$

$$\frac{\Delta U}{kT} = l_B \sum_n \left(\frac{\exp\left(-r(n)/r_D\right)}{r(n)} - \frac{\exp\left(-bn/r_D\right)}{bn} \right) \approx \frac{l_B r_D^2}{8b^3}\alpha^2$$ – per monomer

$\alpha = b/l_{OSF}$ – angle per monomer

Electrostatic persistence length l_{OSF} for semiflexible polymers (e.g. DNA) $\Delta U\, l_{OSF}/b \sim kT$ $\boldsymbol{l_{OSF} \approx l_B r_D^2/b^2}$

Khokhlov & Khachaturian generalized OSF to flexible polyelectrolytes $\boldsymbol{l_{KK} \approx r_D^2/D_e}$ 1982

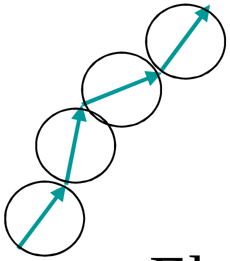
Electrostatic Persistence Length

$l_{OSF} \approx l_B r_D^2/b^2 \sim 1/c_s$ $l_{KK} \approx r_D^2/D_e \sim 1/c_s$

Example: in 10^{-3} M salt solution $r_D=10$ nm and $l_{OSF} \sim l_{KK} \approx 200$ nm

Electrostatic persistence length in both OSF and KK models is $>> r_D$

II. Joanny-Dobrynin Model



Flexible chains can bend much easier than semiflexible ones

$$l_{JD} \approx u\, r_D$$

Electrostatic persistence length is proportional to Debye length.

The issue is still controversial and we will assume that

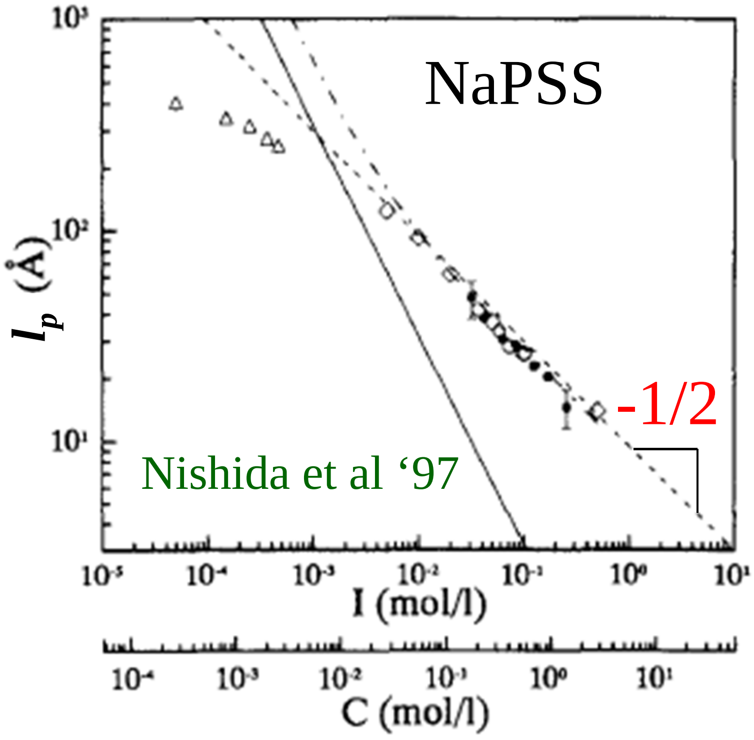
Odijk-Skolnick-Fixman theory is valid for **semiflexible** chains $l_{OSF} \sim r_D^2$

Joanny-Dobrynin model is correct for **flexible** polymers $l_{JD} \sim r_D$

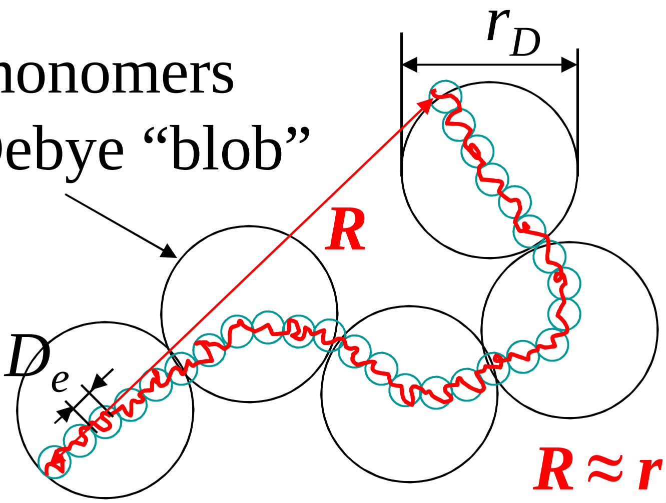
Salt Dependence of Chain Size

Electrostatic persistence length of flexible polymers is proportional to Debye length.

$l_p \sim r_D \sim c_s^{-1/2}$



Chain is elongated & electrostatic repulsion is strong on length scales $D_e < r < r_D$



g_D monomers in Debye "blob"

$R \approx r_D\,(N/g_D)^{3/5}$

Polyelectrolyte forms a "self-avoiding chain" of Debye blobs of size $\sim r_D$

In the case of counterion condensation on chain $r_D \approx bg_D/u$

Polyelectrolyte size is $R \approx r_D^{2/5}(bN/u)^{3/5}$

$R \approx bN^{3/5}(u^4b^3c_s)^{-1/5}$

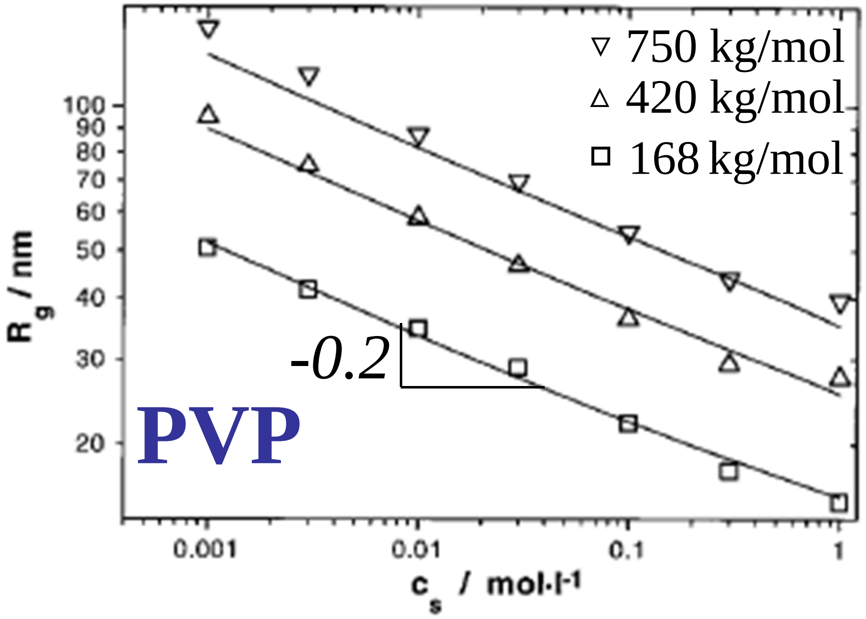
$R \approx v_{el}^{1/5}b^{2/5}N^{3/5}$ Electrostatic excluded volume $v_{el} \approx 1/(u^4c_s)$

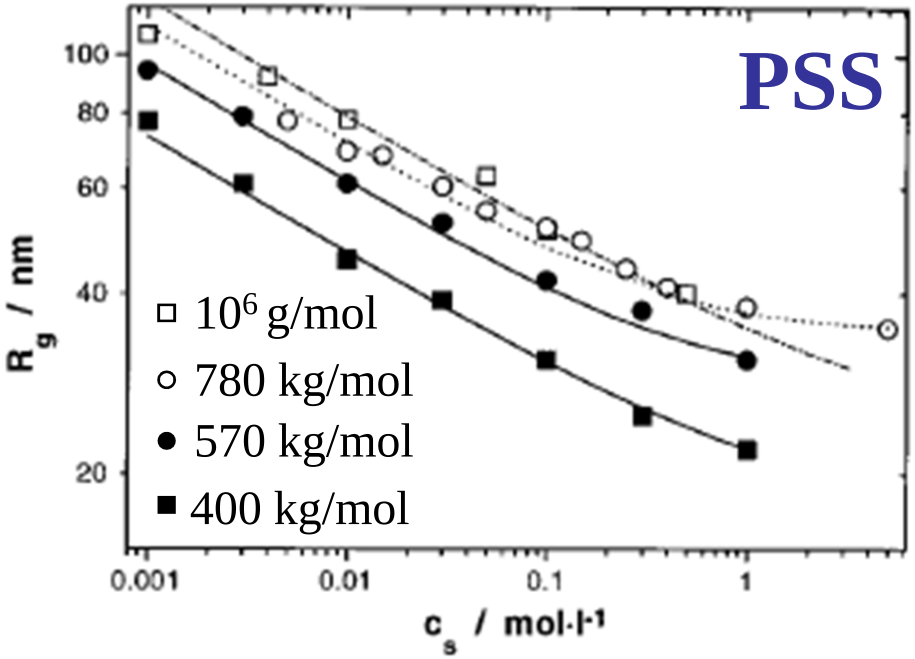
Salt Dependence of Chain Size

$$R \approx bN^{3/5}(u^4b^3c_s)^{-1/5}$$

E.g. 400kg/mol PSS, $N \approx 2{,}000$; $u=2$, $c_s = 10^{-2}$ M; $r_D \approx 3$ nm; $b \approx 0.3\ nm$

$$R \approx bN^{3/5}(r_D{}^2/ul_B{}^2)^{1/5} \approx 45\ nm$$





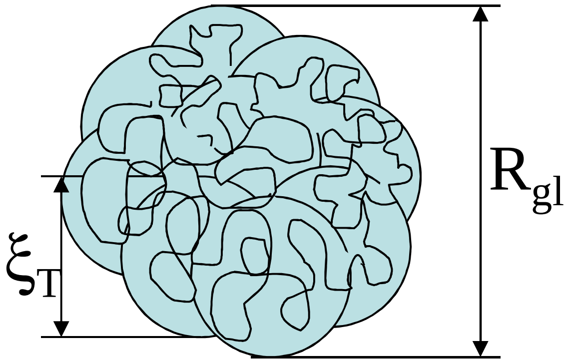
$$R \sim c_s^{-1/5}$$

Beer et. al. '97

Polymer in a Poor Solvent

Thermal blob - length scale ξ_T at which short range attractions are of order *kT*

Globule is a dense packing of thermal blobs



$$R_{gl} \sim N^{1/3}$$

Cohesive energy density inside the globule is *kT* per thermal blob volume.

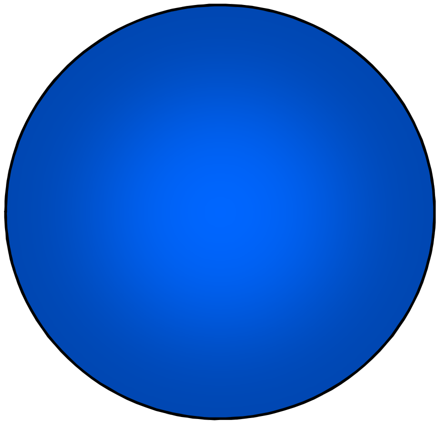
Surface tension is *kT* per thermal blob area at the surface of the globule.

$$\gamma \sim kT/\xi_T^{\,2}$$

Polymer globule is analogous to a liquid droplet.

Instability of a charged liquid droplet

Lord Rayleigh ‘82

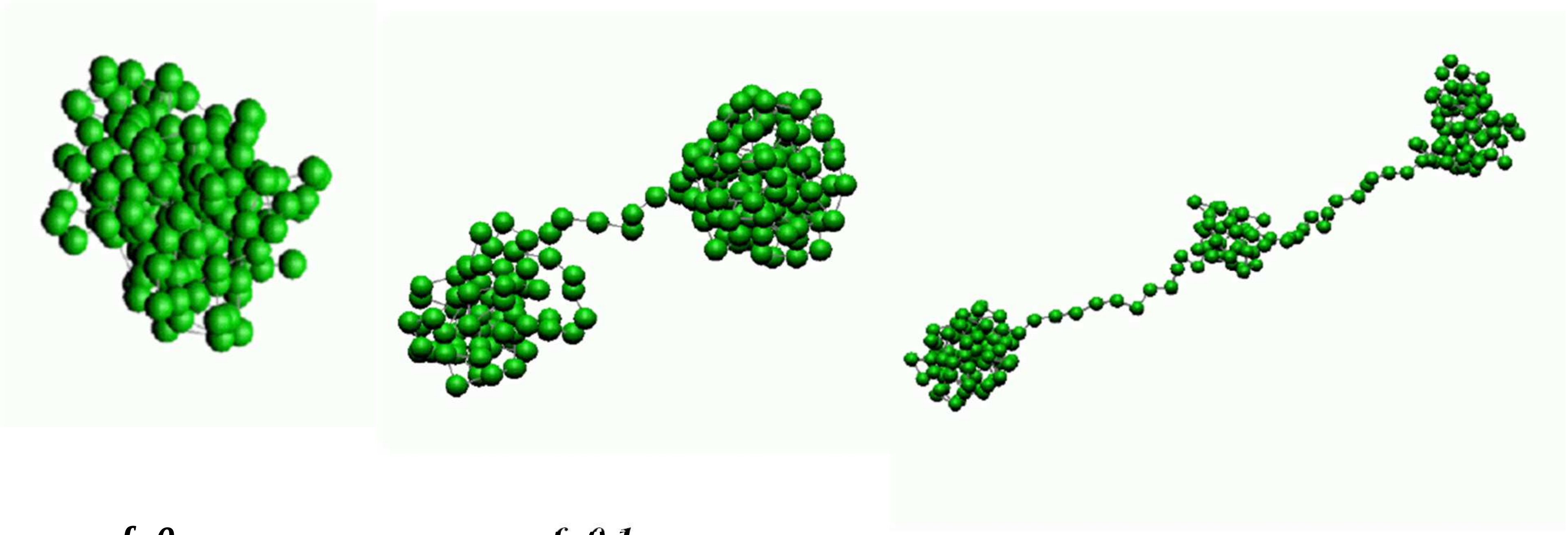


$Q < Q_{crit}$

Cascade of Necklace Transitions

Charge on the chain increases

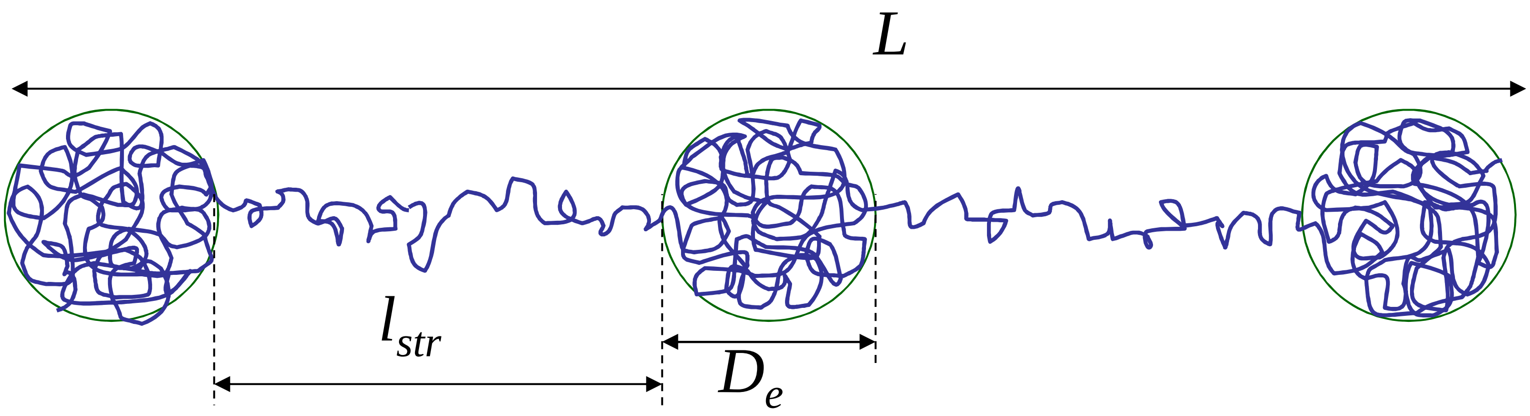
Dobrynin, Rubinstein,
Obukhov ‘96



$f=0$ **$f=0.1$** **$f=0.2$**

Hydrophobic Polyelectrolytes

Necklace Conformation



Short-range hydrophobic attraction vs. long-range electrostatic repulsion leads to a necklace of beads (globules) connected by strings.

Bead size D_e is determined by the Rayleigh stability condition – balance of surface tension due to hydrophobicity and electrostatic self-energy of a bead.

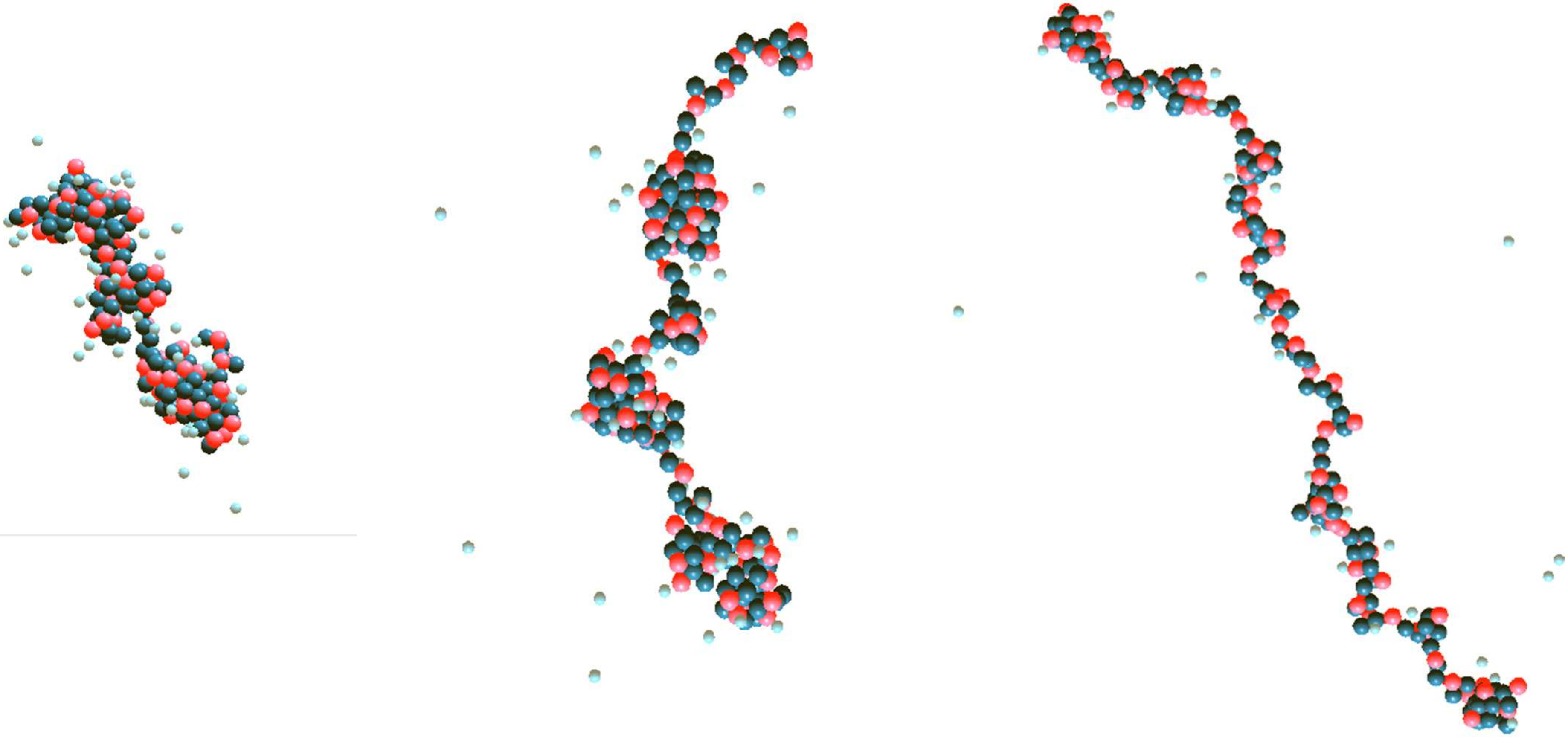
String length l_{str} is determined by the balance of the electrostatic repulsion between beads and hydrophobicity of the strings.

Concentration Induced Cascade

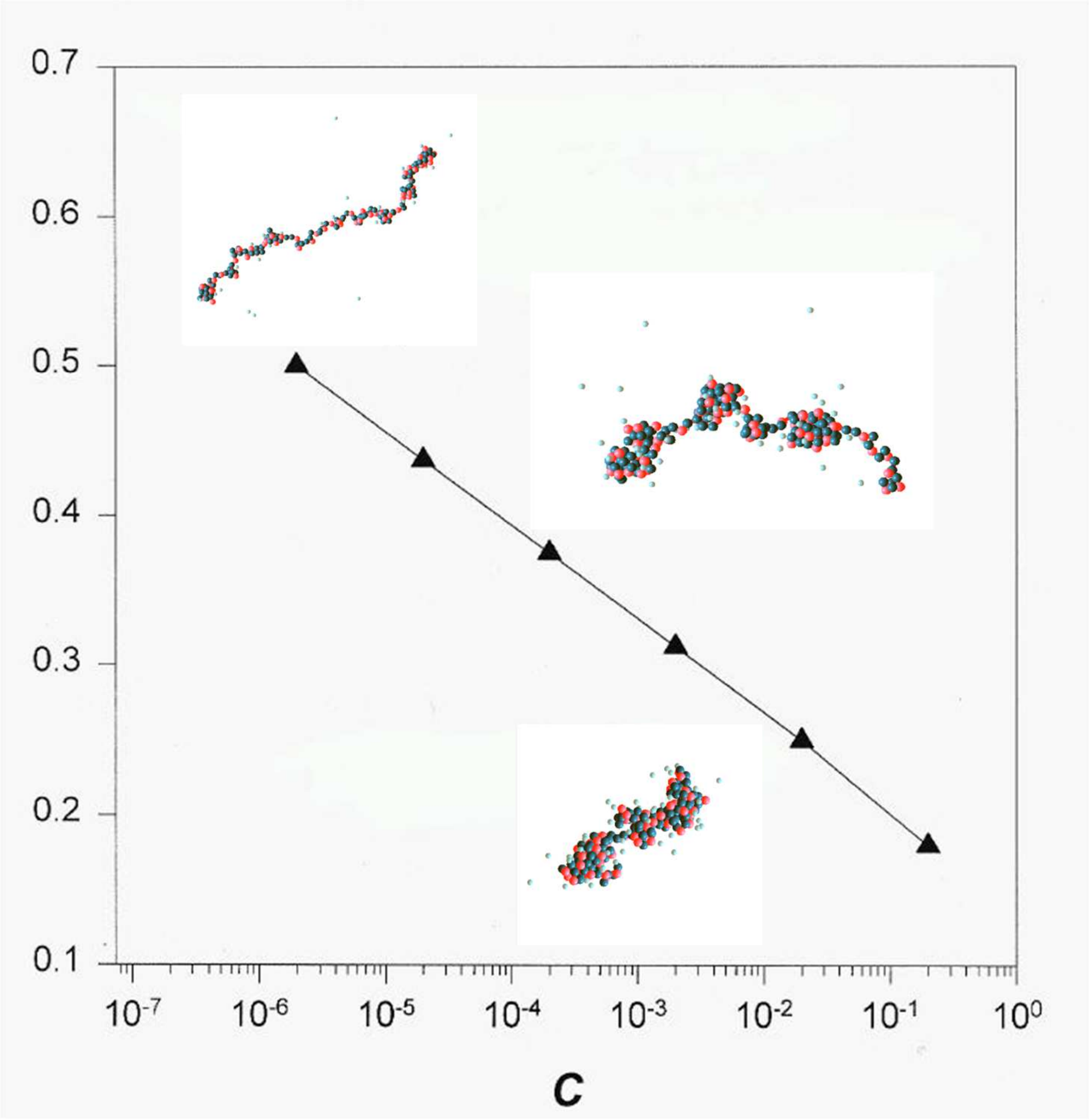
Number of beads on the chain varies with polymer concentration

Effective charge increases

Polymer concentration decreases



Chain Size vs Concentration



Qi Liao

AFM Image of a Necklace

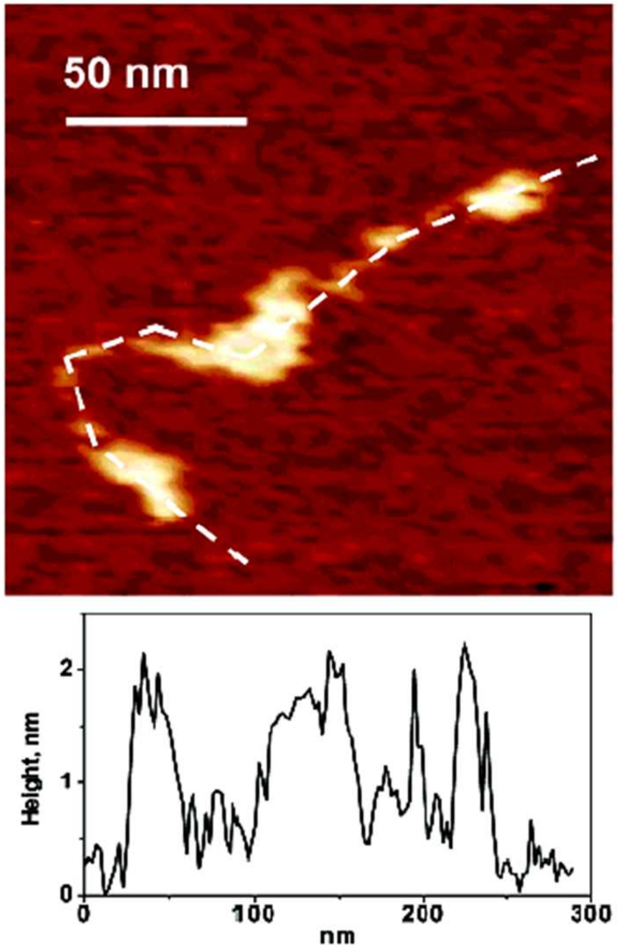
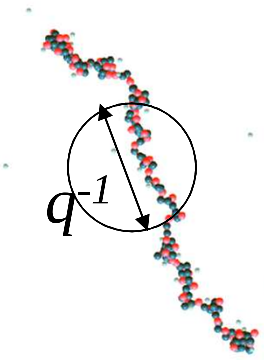
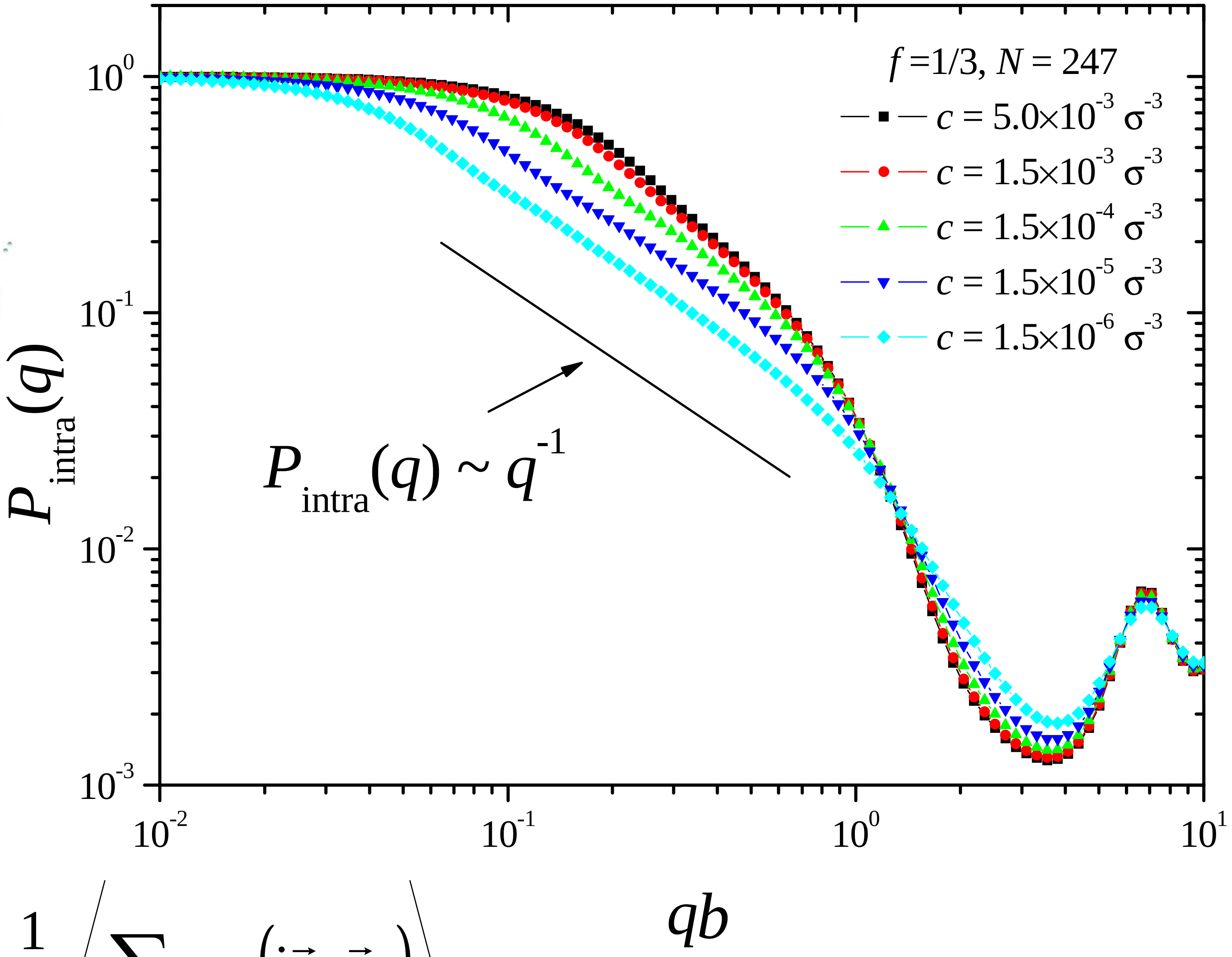


Figure 10. AFM image of P2VP-*co*-PS single molecules deposited from aqueous solution at pH 2.

Kiriy, Gorodyska, Minko, Jaeger, Stepanek, & Stamm JACS 2002

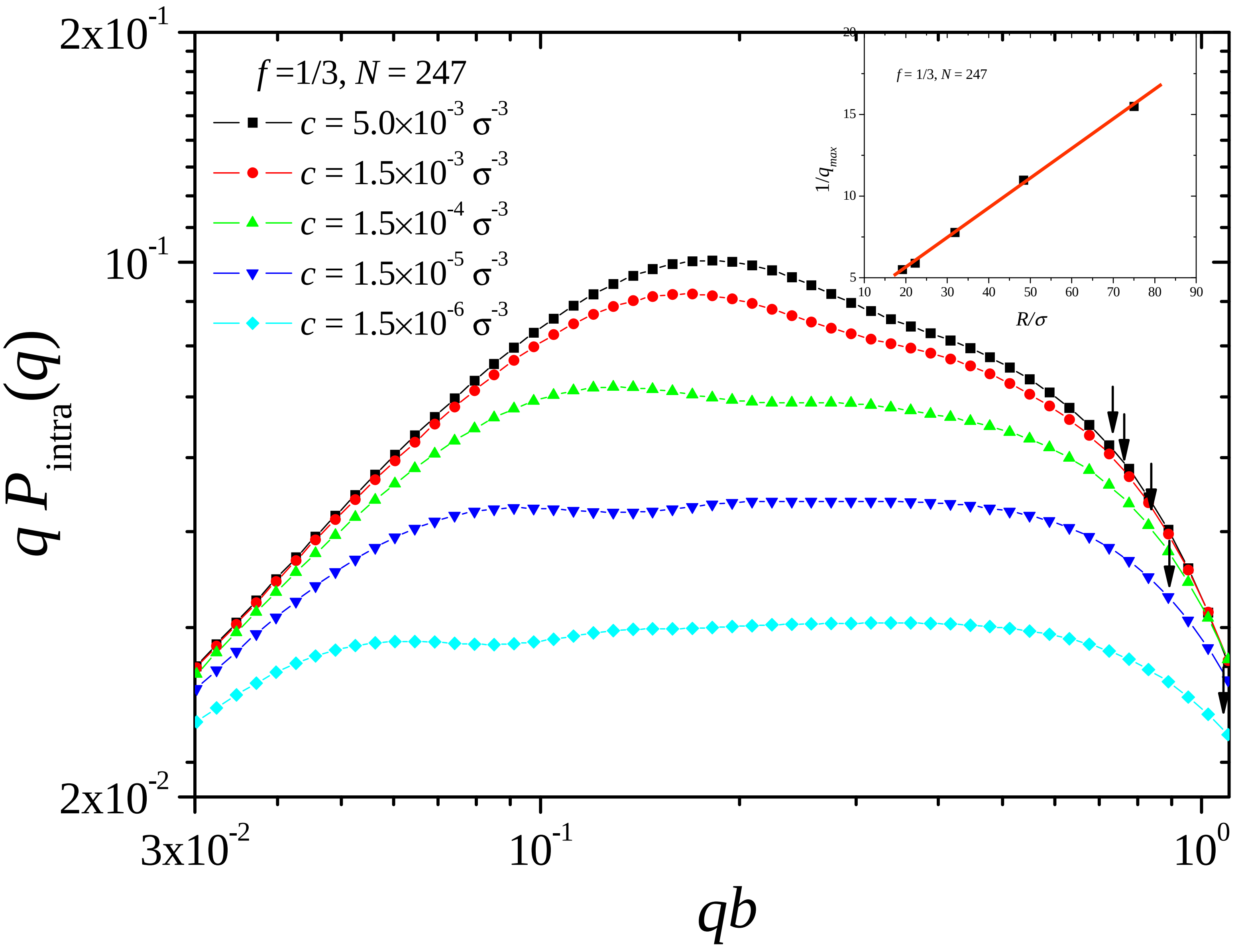
Form Factor of a Polyelectrolyte Chain

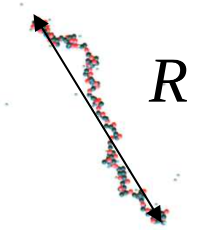




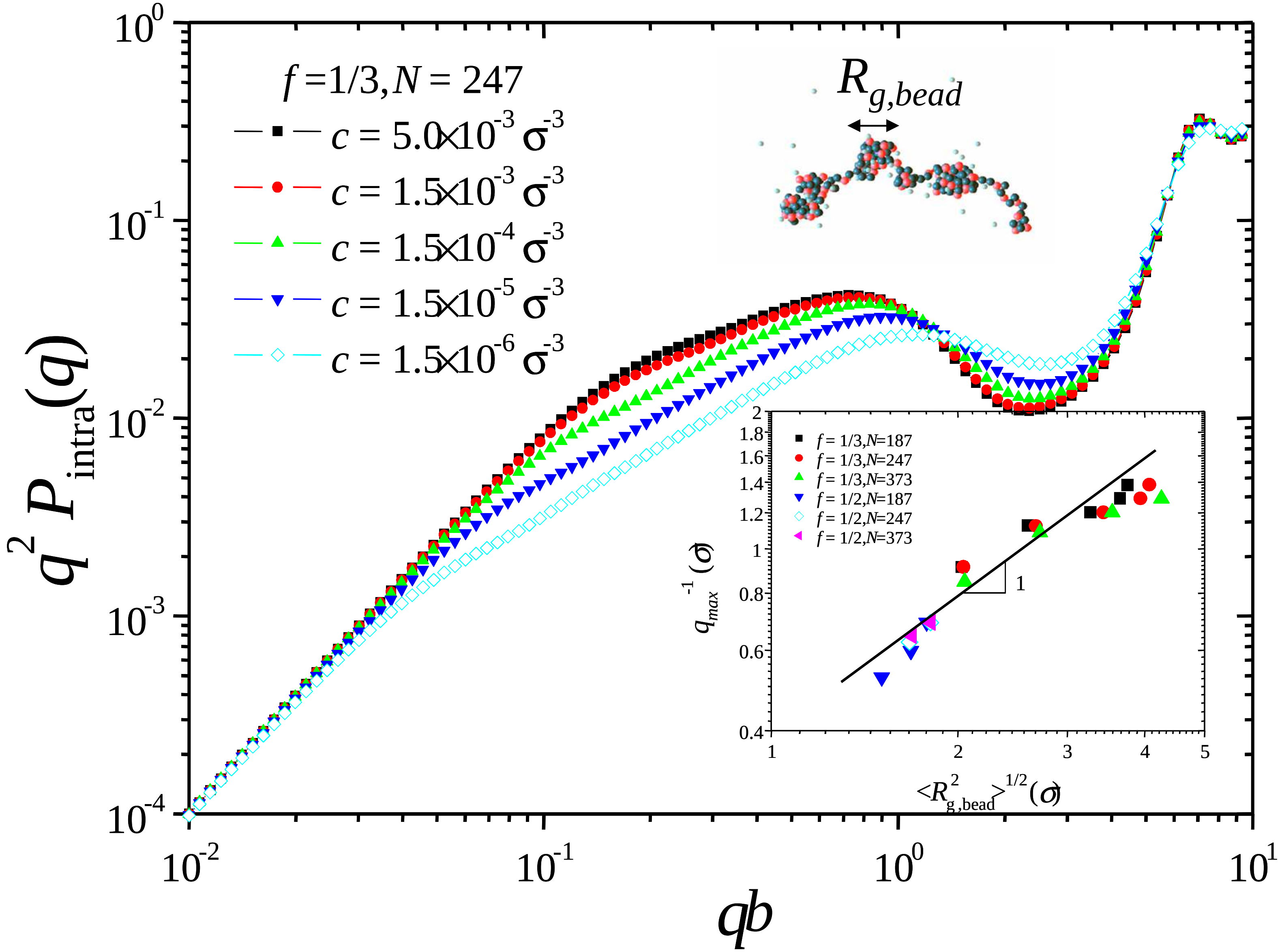
$$P_{\text{int}\,ra}(q)=\frac{1}{N^2}\left\langle \sum_{i,j}\exp\left(i\vec{q}\cdot\vec{r}_{ij}\right)\right\rangle$$

Holtzer Plot

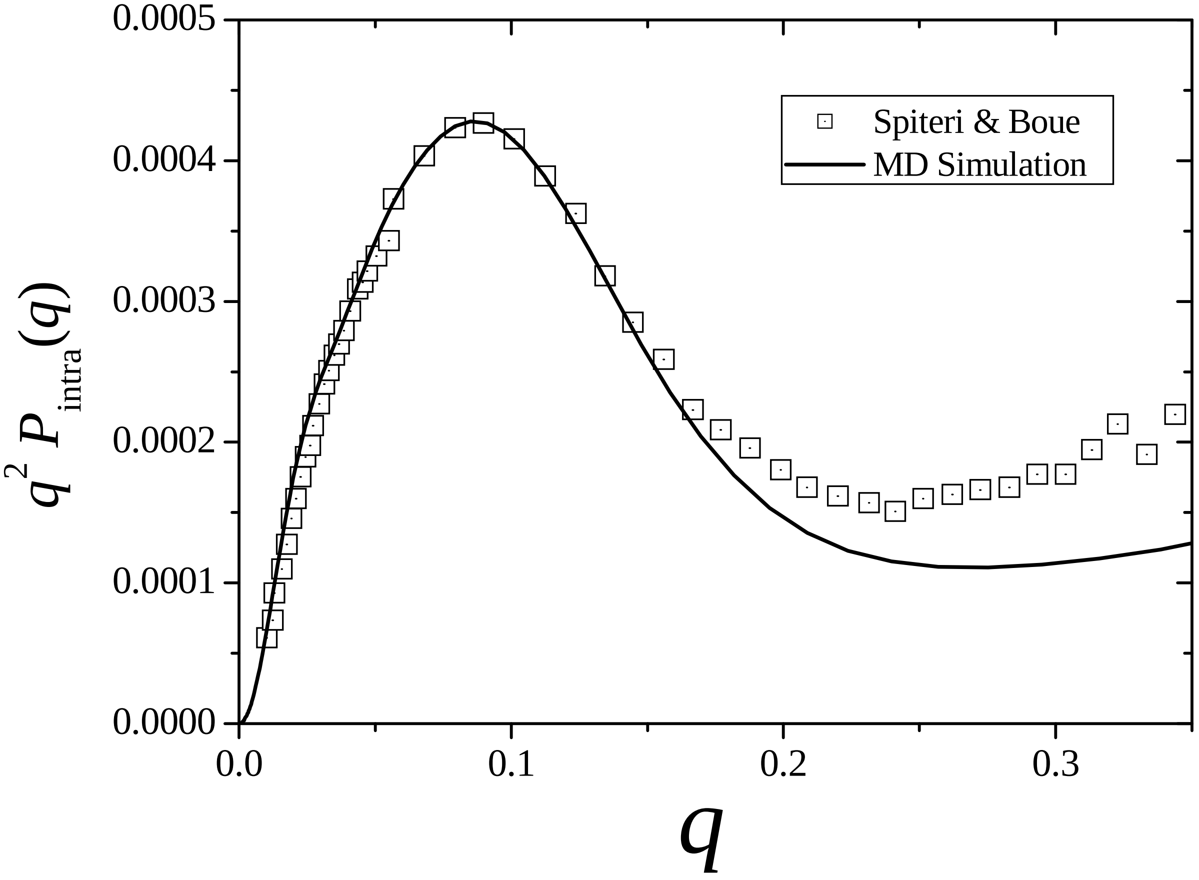


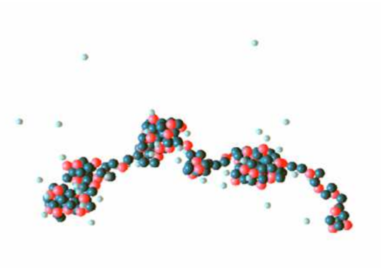


Kratky Plot


f =1/3, N = 247
c = 5.0×10^-3 σ^-3
c = 1.5×10^-3 σ^-3
c = 1.5×10^-4 σ^-3
c = 1.5×10^-5 σ^-3
c = 1.5×10^-6 σ^-3
R_g,bead
q^2 P_intra(q)
qb
10^0
10^-1
10^-2
10^-3
10^-4
10^-2
10^-1
10^0
10^1
f = 1/3,N=187
f = 1/3,N=247
f = 1/3,N=373
f = 1/2,N=187
f = 1/2,N=247
f = 1/2,N=373
q_max^-1 (σ)
<R_g,bead^2>^1/2 (σ)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
1
2
3
4
5
1

Experimental Kratky Plot





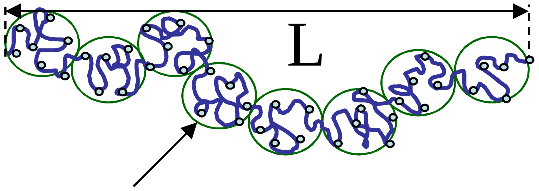
□ - data of Spiteri & Boue on 36% sulfonated NaPSS

contrast matched $M_W(PS_H)=68\,000$, $M_W(PS_D)=73\,000$

— - MD simulations of $c=5\times10^{-3}b^{-3}$ polyelectrolyte solution with $N=247$ and $f=1/3$

Things to Remember about Dilute Solutions

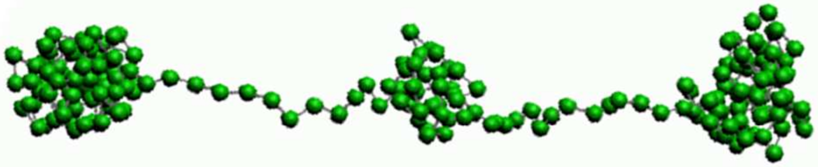
Polyelectrolyte in dilute no-salt solutions are strongly stretched.



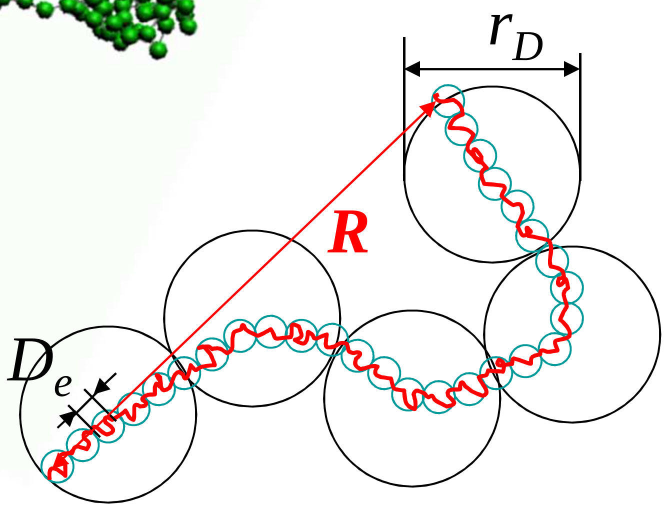
$L \approx L_{max}/u$ $u = l_B/b$

Hydrophilic polyelectrolytes - stretched arrays of electrostatic blobs

Hydrophobic polyelectrolytes – necklace with beads and strings



Salt screens electrostatic repulsion



Persistence length ~ Debye screening length for flexible polyelectrolytes

$l_p \sim r_D \sim c_s^{-1/2}$

Chain size $R \sim c_s^{-1/5}$