CHARGED POLYMERS
THE STORY SO FAR…

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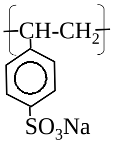
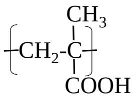
What are polyelectrolytes?

Poly(styrene sulfonate)

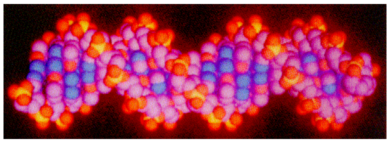


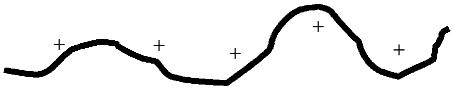
Poly(methacrylic acid)



$$\left[CH_2\text{-}\overset{CH_3}{\underset{COOH}{C}} \right]$$

DNA

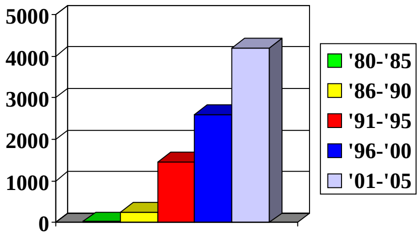




Half a Century of Polyelectrolytes

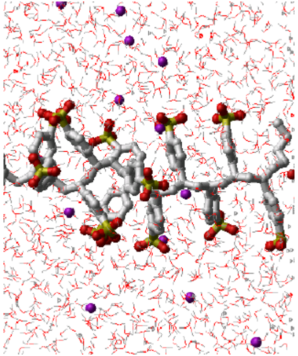
40-50's Fuoss, Katchalsky, Morawetz, Flory..

60-70's Oosawa, deGennes, Odijk, Manning, Fixman…

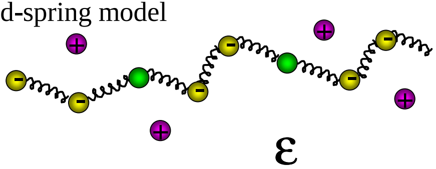


Number of publications in scientific journals on topic POLYELECTROLYTES

Physical model of polyelectrolyte chain



Bead-spring model



ε

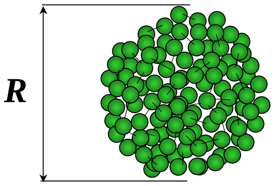
$f=N_{charg}/N$ – fraction of the charged monomers

Pearl-Necklace Story
of
Hydrophobic Polyelectrolytes

Dilute solutions
- Necklace globule
- Counterion condensation

Semidilute solutions

Polymers in poor solvent Uncharged globule



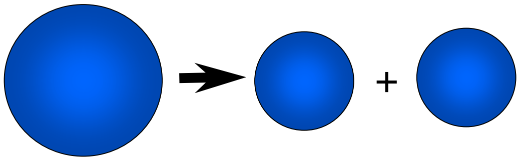
Globule is densely packed by attraction between monomers

The average monomer density inside globule is
$\rho \sim a^{-3}$

Globule size $R \sim a N^{1/3}$

Instability of a charged liquid droplet

Lord Rayleigh 82

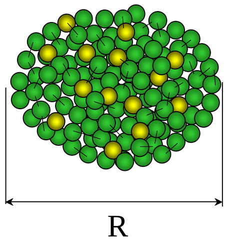


$Q < Q_{crit}$ $Q > Q_{crit}$

For the surface charge larger than the critical value charged liquid droplet splits into two smaller droplets.

$$\gamma R^2 \approx \frac{Q_{crit}^2}{\varepsilon R}$$

Charged globule



Rayleigh's stability condition:

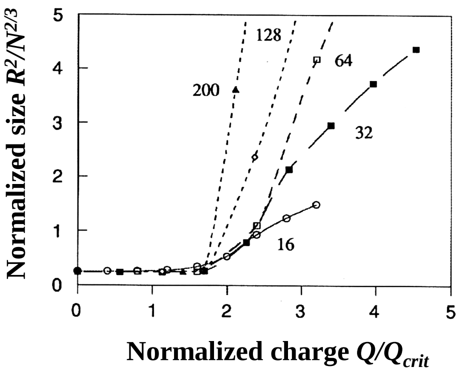
electrostatic repulsion is balanced by surface energy

$$\frac{(efN)^2}{\varepsilon R} \approx \gamma R^2$$

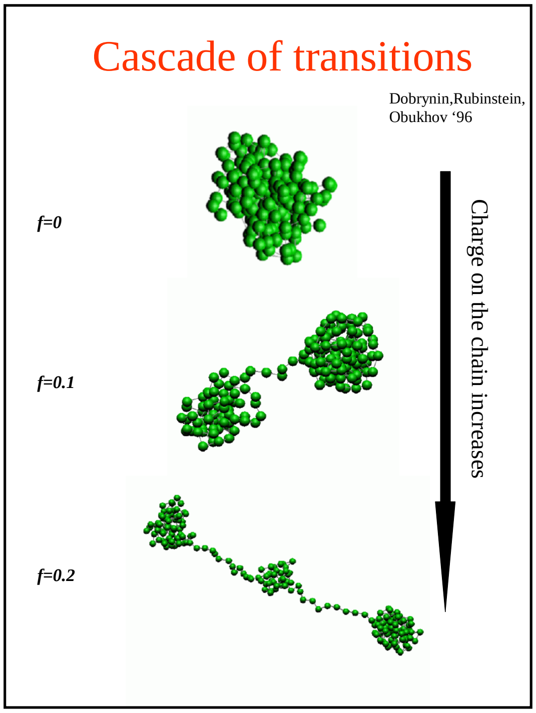
Critical fraction of charged monomers

$f_{crit} \sim N^{-1/2}$

Chain size vs charge

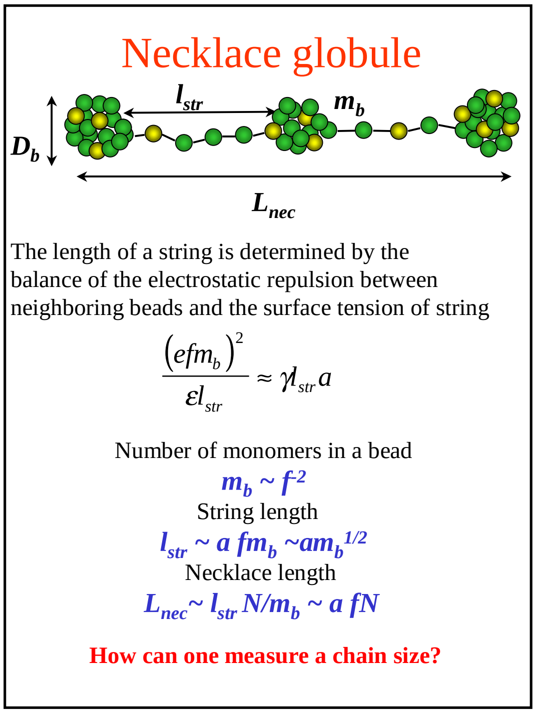


$u=2,\ \varepsilon_{LJ}=1.5$



Cascade of transitions

Dobrynin,Rubinstein, Obukhov ‘96



Necklace globule

The length of a string is determined by the balance of the electrostatic repulsion between neighboring beads and the surface tension of string

$$\frac{(efm_b)^2}{\varepsilon l_{str}} \approx \gamma l_{str} a$$

Number of monomers in a bead

$m_b \sim f^{-2}$

String length

$l_{str} \sim a\, f m_b \sim a m_b^{1/2}$

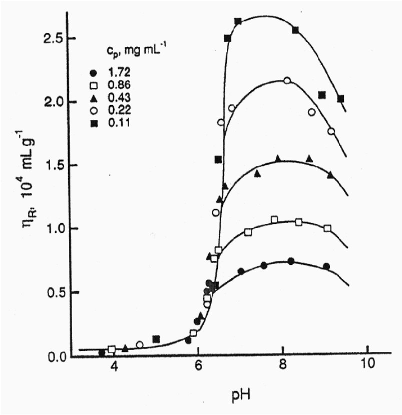
Necklace length

$L_{nec} \sim l_{str} N/m_b \sim a\, fN$

How can one measure a chain size?

pH dependence of the reduced viscosity for poly(methyacrylic acid)

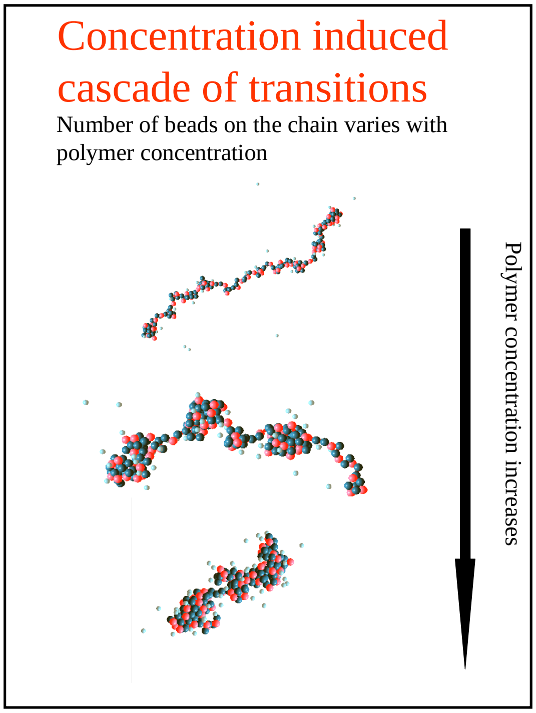
**Katchalsky&
Eisenberg ‘51**



$$\eta_R \approx L_{nec}^3$$

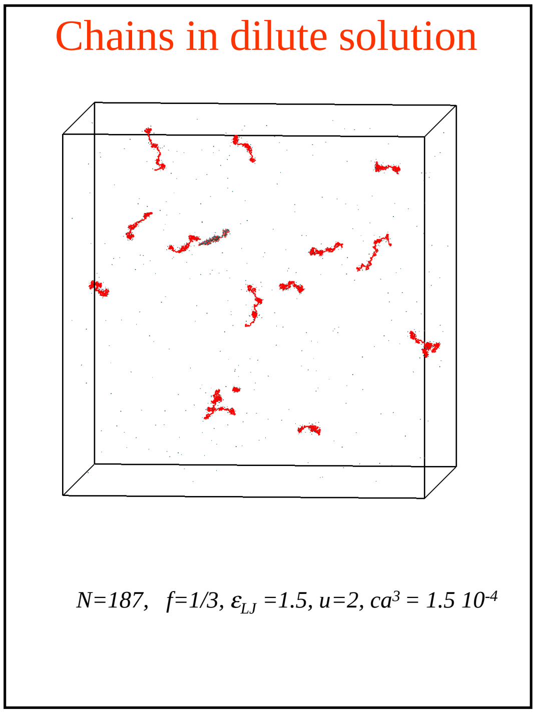
Dilute solutions
- Necklace globule
- Counterion condensation

Semidilute solutions



Concentration induced cascade of transitions

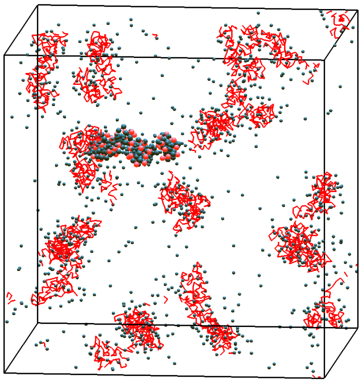
Number of beads on the chain varies with polymer concentration



Chains in dilute solution

$N=187$, $f=1/3$, $\varepsilon_{LJ}=1.5$, $u=2$, $ca^3 = 1.5\ 10^{-4}$

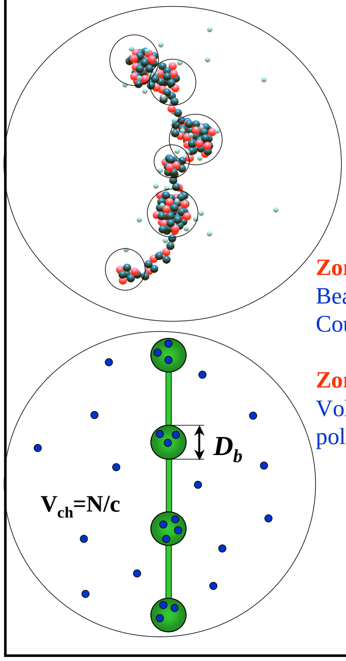
Chains in dilute solution



$N=187$, $f=1/3$, $\varepsilon_{LJ}=1.5$, $u=2$, $ca^3 = 1.5\ 10^{-2}$

Two-zone model

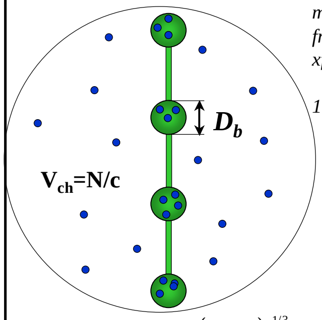
Oosawa '68



Zone I
Beads with condensed Counterions

Zone II
Volume free of the polymer

Counterion condensation



m_b – monomers per bead
fm_b – original charge
xfm_b – effective charge of a bead
1-x – fraction of condensed counterions

Rayleigh stability condition

$$\frac{l_B\left(fxm_b\right)^2}{D_b} \approx \frac{D_b^2}{a^2}$$

Bead size $D_b \approx a\left(uf^2x^2\right)^{-1/3}$ $m_b \approx \left(uf^2x^2\right)^{-1}$

Total free energy of the necklace

$$\frac{F}{kT} \approx Nf\left[\varepsilon_c x^{2/3} + x\ln\frac{xfNa^3}{D_b^3} + (1-x)\ln\frac{(1-x)fNa^3}{V_{ch} - D_b^3 N/m_b}\right]$$

Electrostatic energy

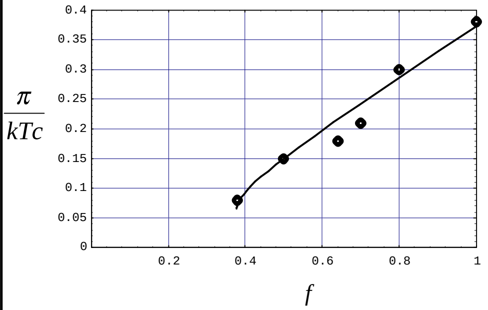
Counterion entropy

$\varepsilon_c \approx (u/f)^{1/3}$ -attraction of counterion to a fully charged bead

Effective charge of PSS

Osmotic pressure measurements in dilute solution

Williams et al ‘01



Best fit with the parameters ε_c*=4.3* and $ca^3=10^{-3}$

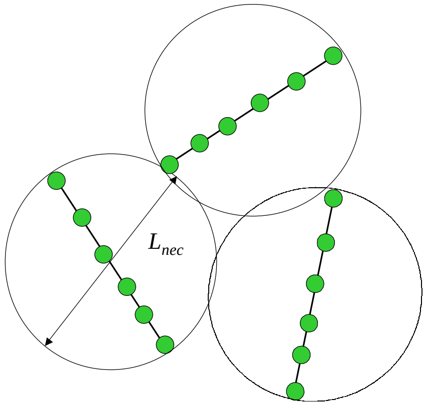
Osmotic coefficient for two-zone model

$$\frac{\pi}{kTc} = fx + f(1-x)\exp\left(\frac{2\varepsilon_c}{3x^{1/3}}\right)$$

Dilute solutions
- Necklace globule
- Counterion condensation

Semidilute solutions

Overlap concentration

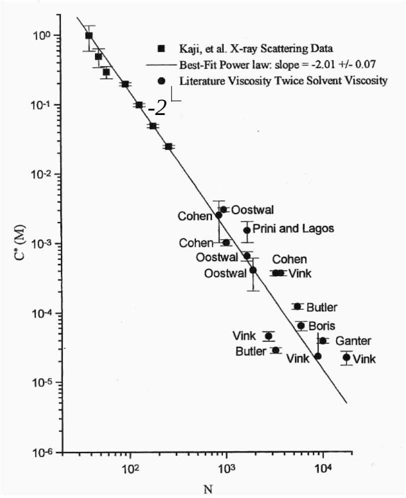


$$C^* \approx \frac{N}{L_{nec}^3} \approx N^{-2}$$

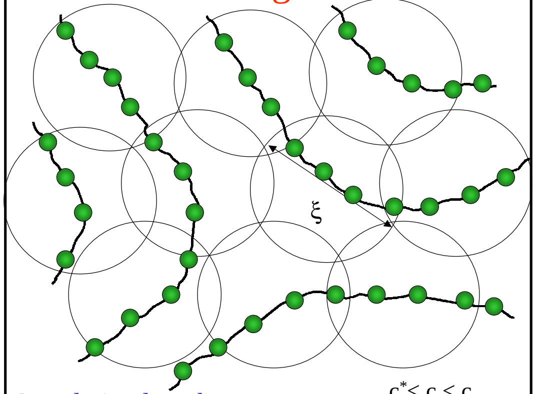
For c < c* - dilute solution of necklaces

For c > c* - sedilute solution of necklaces

Dependence of overlap concentration on degree of polymerization



Semidilute string controlled regime



$c^* < c < c_{str}$

Correlation length

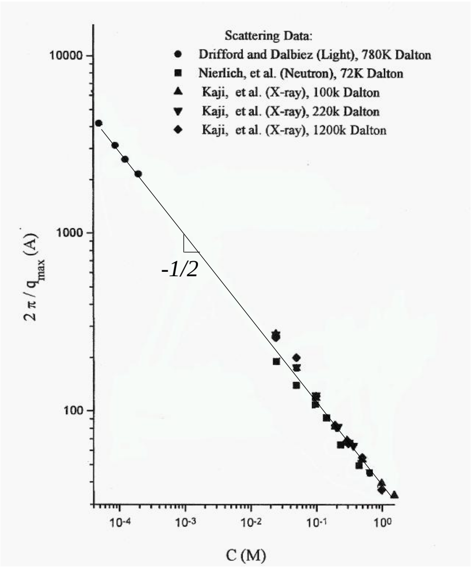
Chain is strongly stretched on the length scales smaller than correlation length

de Gennes et al 76

$$\xi \sim c^{-1/2}$$

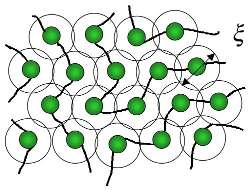
Chain size: $R \sim N^{1/2} c^{-1/4}$

Concentration dependence of the correlation length



Semidilute Bead Controlled Regime

Dobrynin& Rubinstein 99



$D_b < \xi$

$c_{str} < c < c_b$

Colloidal fluid of beads

Beads on neighboring chains screen electrostatic repulsion of beads on the same chain reducing the length of strings to the distance between beads ξ.

Correlation length

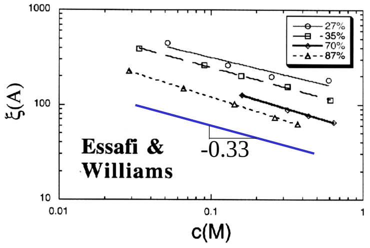
$$m_b \approx c\xi^3 \quad \Rightarrow \quad \xi \approx m_b^{1/3} c^{-1/3}$$

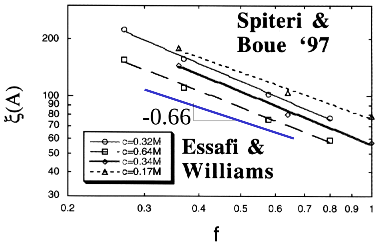
$$\xi \sim c^{-1/3} f^{-2/3}$$

Chain size: $R \approx \xi\sqrt{N/m_b} \approx N^{1/2} c^{-1/3}$

Correlation Length

$\xi \sim c^{-1/3} f^{-2/3}$





NaPSS, M_W(PS)=68 000

Single Chain Form Factor

Spiteri & Boue '97

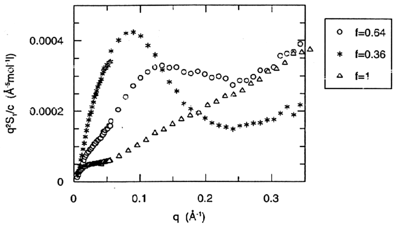


Fig. IV-4: Facteur de forme des polyions de taux de charge variable à la concentration c=0.34M. Représentation de Kratky.

(NaPSS, $M_W(PS_H)$=68 000, $M_W(PS_D)$=73 000)

Bead size vs fraction of charged monomers

Theory: $D_b \sim f^{-2/3}$ Experiment: $D_b \sim f^{-0.7}$

Effect of Added Salt

Spitery & Boue '97

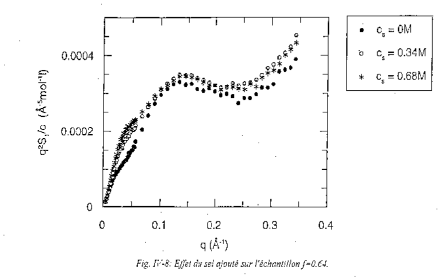
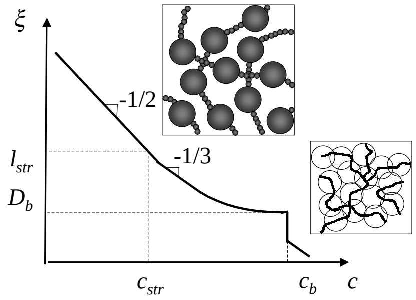


Fig. IV-8: Effet du sel ajouté sur l'échantillon f=0.64.

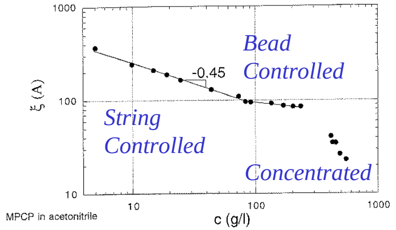
For charge fraction *f*=0.64
at polymer concentration *C* = 0.34 M

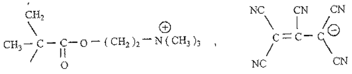
$$R_g(c_s = 0M) = 97 \pm 5A$$
$$R_g(c_s = 0.34M) = 73 \pm 8A$$
$$R_g(c_s = 0.68M) = 66 \pm 5A$$

Correlation length



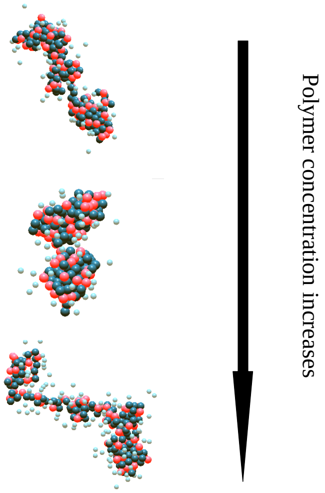
Waig, Ober, Williams, and Galin



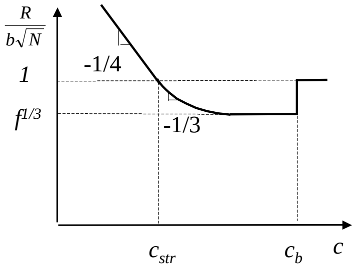


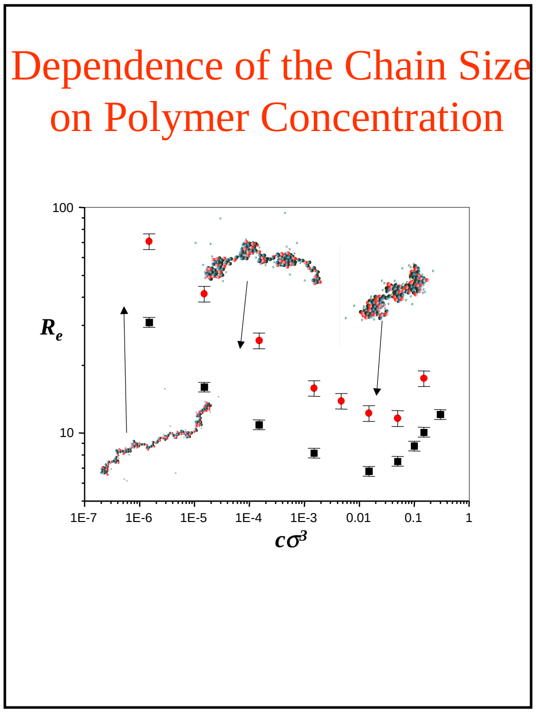
Polyelectrolyte MPCP

Nonmonotonic Dependence of the Chain Size on Polymer Concentration

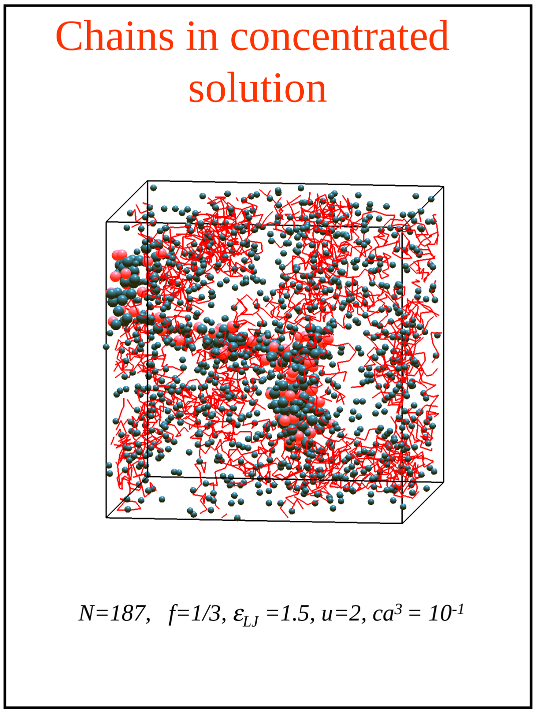


Dependence of the Chain Size on Polymer Concentration



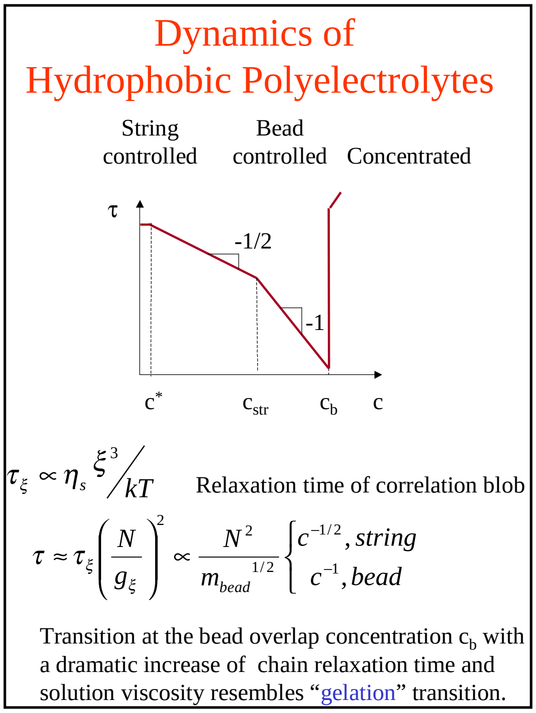


Dependence of the Chain Size on Polymer Concentration



Chains in concentrated solution

$N=187$, $f=1/3$, $\varepsilon_{LJ}=1.5$, $u=2$, $ca^3 = 10^{-1}$

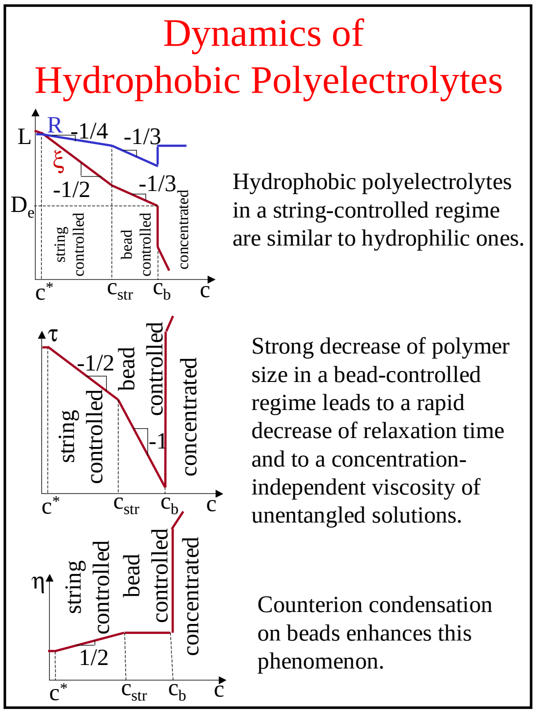


Dynamics of Hydrophobic Polyelectrolytes

$$\tau_\xi \propto \eta_s \, {\xi^3}/{kT}$$ Relaxation time of correlation blob

$$\tau \approx \tau_\xi \left(\frac{N}{g_\xi}\right)^2 \propto \frac{N^2}{m_{bead}^{1/2}} \begin{cases} c^{-1/2}, string \\ c^{-1}, bead \end{cases}$$

Transition at the bead overlap concentration c_b with a dramatic increase of chain relaxation time and solution viscosity resembles “gelation” transition.

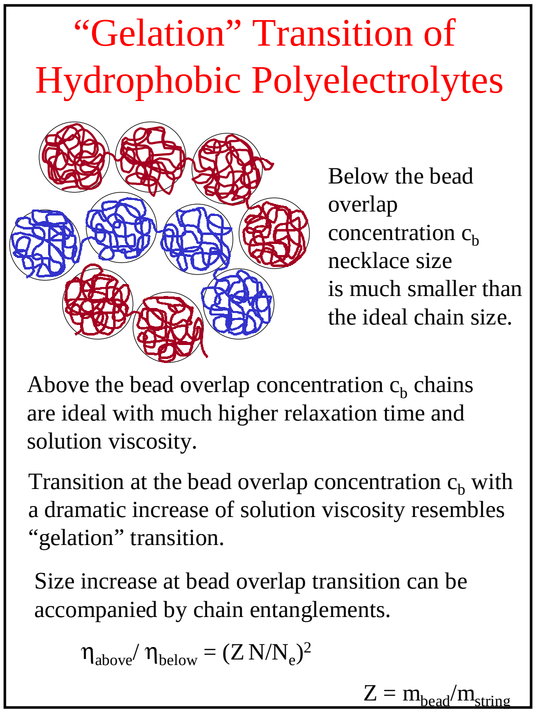


Dynamics of Hydrophobic Polyelectrolytes

Hydrophobic polyelectrolytes in a string-controlled regime are similar to hydrophilic ones.

Strong decrease of polymer size in a bead-controlled regime leads to a rapid decrease of relaxation time and to a concentration-independent viscosity of unentangled solutions.

Counterion condensation on beads enhances this phenomenon.



“Gelation” Transition of Hydrophobic Polyelectrolytes

Below the bead overlap concentration c_b necklace size is much smaller than the ideal chain size.

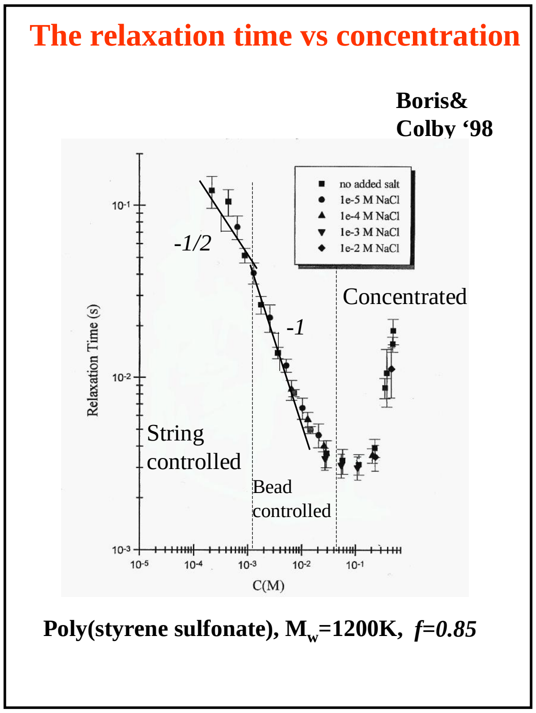
Above the bead overlap concentration c_b chains are ideal with much higher relaxation time and solution viscosity.

Transition at the bead overlap concentration c_b with a dramatic increase of solution viscosity resembles “gelation” transition.

Size increase at bead overlap transition can be accompanied by chain entanglements.

$$\eta_{above}/\eta_{below} = (Z\,N/N_e)^2$$

$Z = m_{bead}/m_{string}$

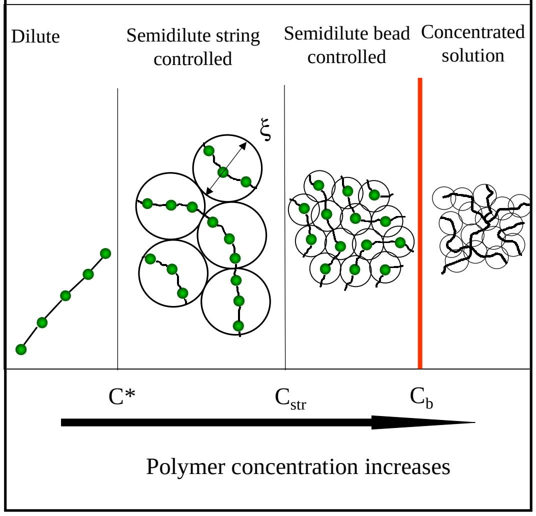


The relaxation time vs concentration

Boris& Colby ‘98

Poly(styrene sulfonate), M_w=1200K, *f=0.85*

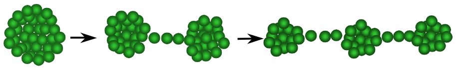
Diagram of regimes for solutions of hydrophobic polyelectrolytes



Polymer concentration increases

Conclusions

- Polyelectrolyte chain with short-range attraction and long-range repulsion forms a necklace globule.
- With changing charge on the chain or polymer concentration there exists cascade of transitions between necklaces with different number of beads.



- Conformational transition in solutions of hydrophobic polyelectrolytes leads to a sharp increase of viscosity - an “apparent gelation”.
- The predictions of the model are confirmed by recent experiments.

Acknowledgments

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