Lecture 3

Semidilute Polyelectrolyte Solutions
Overlap Concentration $c^*$

$$c^* \approx \frac{N}{L^3} \approx N^{-2}$$

$L \sim N$

$c^*$ is very low

e.g. 200k PSS
$N \approx 10^3$
$L \approx 100 \text{ nm}$
$c^* \approx 10^{-3} \text{ M}$

For $c < c^*$ - dilute solution
For $c > c^*$ - semidilute solution
Overlap Concentration

\[ c^* \sim 1/N^2 \]

D. Boris
Semidilute Solutions

d e Gennes et al ‘76

Correlation length $\xi$ – distance between neighboring chains

- $r < \xi$ – strong electrostatic repulsion
dilute-like behavior chains are strongly stretched
- $r > \xi$ – interactions are screened by neighboring chainschains are random walks of correlations “blobs” of size $\xi$

Chain size $R \approx \xi (N/g)^{1/2}$

Contour length is still $L$

$R^2 \approx L \xi$
Scattered Intensity

Correlation peak is one of the distinguishing properties of polyelectrolyte solutions.

Intensity growth with decreasing $q$ for $q > 1/\xi$ is due to scattering from larger sections ($1/q$) of the chain.

Intensity decrease with decreasing $q$ for $q < 1/\xi$ is due to electrostatically induced suppression of density fluctuations.

High osmotic compressibility $\sim 1/S(0)$. 

SANS of NaPSS
Nierlich et al. ‘79
Scattering Data:
- Drifford and Dalbiez (Light), 780K Dalton
- Nierlich, et al. (Neutron), 72K Dalton
- Kaji, et al. (X-ray), 100k Dalton
- Kaji, et al. (X-ray), 220k Dalton
- Kaji, et al. (X-ray), 1200k Dalton

Correlation Length

NaPSS

$2\pi/q_{max} (\AA) \propto C (M)^{-1/2}$
Dynamics of Polymer Solutions

A. Likhtman
Self-Similar Dynamics

Chains are fractal – they look the same on different length scales and move in the same way on different time scales.

Relaxation Time of Entangled Solutions of Uncharged Polymers

Relaxation of a strand between entanglements

Relaxation of correlation blob

\[ \tau_{\text{rep}} = \tau_{\xi} \left( \frac{N_e}{g} \right)^2 \left( \frac{N}{N_e} \right)^3 \]
Dynamics of Polyelectrolytes

Semidilute Unentangled Solutions

Chain sections of size $\xi$ are hydrodynamically coupled to solvent inside correlation volume.

Friction coefficient of correlation strand $\xi$

$$\zeta_\xi \approx \eta_s \xi$$

$\eta_s$ – solvent viscosity

Friction coefficient of a chain

$$\zeta \approx \zeta_\xi (L/\xi) \approx \eta_s L$$

is independent of concentration.

Self-diffusion coefficient

$$D \approx kT/\zeta \approx kT/(\eta_s L)$$

is independent of concentration.

Relaxation time

$$\tau \approx R^2/D \sim \xi \sim c^{-1/2}$$

$R^2 \approx L\xi$

decreases with increasing concentration!!!
Concentration Dependence of Diffusion Coefficient

Self-diffusion coefficient is independent of concentration and reciprocally proportional to degree of polymerization.

\[ D \sim c^0/N \]

Oostwal et al. ‘93

Pulsed field gradient NMR

NaPSS

c = 2 × 10^{-2} \text{ M}
Concentration Dependence of Relaxation Time

Relaxation time decreases with increasing concentration.

$M_w = 1200K$ PSS, $f = 0.85$

Boris & Colby ‘98
Viscosity of Semidilute Unentangled Solutions

Modulus $G \approx kTc/N$

Relaxation time $\tau \sim c^{-1/2}N^2(uf^2)^{1/2}$

Viscosity $\eta \sim c^{1/2}N(uf^2)^{1/2}$

**Fuoss Law**

$\eta_{red} = (\eta/\eta_s - 1)/c \sim c^{-1/2}$

Reduced viscosity grows with decreasing concentration – another distinguishing property of polyelectrolyte solutions.

Figure 3 Concentration dependence of zero-shear reduced viscosity: O, HPSS$_{po}$; ●, NaPSS$_{po}$
Concentration Dependence of Viscosity

Viscosity $\eta \sim c^{1/2} N(uf^2)^{1/2}$

- 1200k (Boris & Colby)
- 398k (Oostwal)
- 300k (Prini & Lagos)
- 199k (Oostwal)
Unentangled Polyelectrolytes – Rouse Dynamics

Oscillatory shear data for solutions of poly(2-vinyl pyridine) in 0.0023 M HCl in water. Open symbols are the storage modulus $G'$ and filled symbols are the loss modulus $G''$. Squares have $c = 0.5 \text{ g L}^{-1}$, triangles have $c = 1.0 \text{ g L}^{-1}$, and circles have $c = 2.0 \text{ g L}^{-1}$. The curves are the predictions of the Rouse model [Eqs (8.49) and (8.50)]. Data from D. F. Hodgson and E. J. Amis, *J. Chem. Phys.* 94, 4581 (1991).
## Dynamics of Unentangled Polymers

<table>
<thead>
<tr>
<th>Property</th>
<th>General Equation</th>
<th>Neutral in Θ-solvent</th>
<th>Neutral in good solvent</th>
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<td><strong>Scaling Exponent</strong></td>
<td>$\nu = \frac{\partial (\log R_{dilute})}{\partial (\log N)}$</td>
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<td>$\xi \sim N^0 c^{-\nu/(3\nu-1)}$</td>
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<td><strong>Chain Relaxation Time</strong></td>
<td>$\tau_{\text{chain}} \sim N^2 c^{(2-3\nu)/(3\nu-1)}$</td>
<td>$\tau_{\text{chain}} \sim N^2 c$</td>
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<td>$G = N^{-1} c_n kT$</td>
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<td><strong>Polymer Contribution to Viscosity</strong></td>
<td>$\eta - \eta_s \approx G \tau \sim N c^{1/(3\nu-1)}$</td>
<td>$\eta - \eta_s \sim N c^2$</td>
<td>$\eta - \eta_s \sim N c^{1.3}$</td>
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<td><strong>Diffusion Coefficient</strong></td>
<td>$D \approx R^2 / \tau \sim N^{-1} c^{-(1-\nu)/(3\nu-1)}$</td>
<td>$D \sim N^{-1} c^{-1}$</td>
<td>$D \sim N^{-1} c^{-0.54}$</td>
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Entanglement Onset

In semidilute regime \( c > c^* \)

\[ d \sim c^{-1/3} \quad R \sim c^{-1/4} \]

Number of overlapping chains

\[ n \approx cR^3/N \approx (c/c^*)^{1/4} \]

\( n_e = 5 – 10 \) chains per entanglement volume

(Kavassalis & Noolandi ’87)

Entanglement onset \( c_e \approx c^*n_e^4 \)

3 – 4 decades of unentangled semidilute regime

– unique feature of polyelectrolyte solutions

In entangled regime \( c > c_e \)

\[ c \approx n_eN_e/a^3 \]

\[ a \approx n_e \xi \] – tube diameter

\[ N_e \approx n_e^2 g \] – number of monomers between entanglements
Semidilute Entangled Solutions

\[ \tau \approx \tau_\xi (N_e/g)^2 (N/N_e)^3 \sim c^0 N^3 \]

Relaxation time is c-independent!

Plateau modulus \( G_e \approx kT \frac{c}{N_e} \sim c^{3/2} \)

Viscosity \( \eta \approx \tau G_e \sim c^{3/2} N^3 \)
Relaxation Time and Modulus of Entangled Polyelectrolyte Solutions

Boris & Colby '98

NaPSS

$\tau \sim c^0$

Dou & Colby

$G_e \sim c^{3/2}$

Random copolymer 2-vinyl pyridine and N-methyl-2-vinyl pyridinium chloride in ethylene glycol
Viscosity of Entangled Solutions

\[ \eta \sim c^{3/2} N^3 \]

Dou & Colby

300k NaPSS

\[ \eta \sim c^{1/2} N \]

Prini & Lagos ‘64

Random copolymer 2-vinyl pyridine and N-methyl-2vinyl pyridinium chloride in ethylene glycol

"uncharged"
## Dynamics of Entangled Polymers

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Polyelectrolyte Entanglement Mystery

R. Colby
Things to Remember about Semidilute “Hydrophilic” Polyelectrolytes

Overlap concentration is very low \((c^* \sim 1/N^2)\).

Characteristic scattering peak at \(q \sim 1/\xi \sim c^{1/2}\).

Osmotic pressure is controlled by counterions.

Unentangled Solutions

Diffusion coefficient is concentration–independent.

Relaxation time decreases with concentration.

Viscosity \(\eta \sim c^{1/2}\) – Fuoss Law.

Very wide unentangled semidilute regime \((3 – 4\) decades of \(c\)).

Entangled Solutions

Relaxation time is concentration–independent.
Hydrophobic Polyelectrolytes

If correlation length $\xi$ is larger than distance between beads $l_{str}$, the string-controlled regime is similar to semidilute “hydrophilic” regime.

$$l_{str} < \xi < L$$  \hspace{1cm}  $$c^* < c < c_{str}$$

Correlation length

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

Hydrophobic Polyelectrolytes

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Hydrophobic Polyelectrolytes

Bead-controlled regime

As soon as $\xi$ decreases down to $l_{str}$, beads on neighboring chains screen electrostatic repulsion of beads on the same chain reducing the length of strings to the distance between beads $\xi$.

Correlation length $\xi \sim c^{-1/3}$

$c_{str} < c < c_b$

$l_{str} \equiv \xi > D_e$
Correlation Length $\xi = 2\pi/q^*$

SAXS of PSS by Baigl, Ober, Qu, Fery, & Williams
Europhysics Letters 2003
Correlation Length Exponent

\[ \xi \sim c^{-\alpha} \]

PSS data by Baigl, Ober, Qu, Fery, & Williams
Europhysics Letters 2003
Single Chain Form Factor

\[ D_b \sim f^{-2/3} \]

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

For charge fraction $f=0.64$

at polymer concentration $c = 0.34$ M

$$R_g (c_s = 0 M) = 97 \pm 5 \text{Å}$$

$$R_g (c_s = 0.34 M) = 73 \pm 8 \text{Å}$$

$$R_g (c_s = 0.68 M) = 66 \pm 5 \text{Å}$$
Necklace size in bead-controlled regime ($c_{str} < c < c_b$) is much smaller than the ideal chain size.

Above the bead overlap concentration $c_b$ chains are ideal.
Correlation Length

\[ \xi = l_{str}^{1/3} D_b^{-1/3} \]

- Bead Controlled
- String Controlled
- Concentrated

Waig, Ober, Williams, and Galin

MPCP in acetonitrile
Figure 2. Small-angle X-ray scattering curves from MPAC in AC at a series of different concentrations (9.9–169 g/L). The scattered intensity in relative units is shown as a function of the momentum transfer ($q$). (a) Lower concentrations: • 9.6 g/L; ×, 43.5 g/L; ○, 169 g/L. (b) Higher concentrations: ×, 260 g/L; ●, 340 g/L; ○, 414 g/L; ○, 546.7 g/L. Note the sharp decrease in intensity between 404 and 422 g/L followed by the reappearance of a peak.
“Gelling” Transition of Hydrophobic Polyelectrolytes

Conformational transition from a pearl necklace below the bead overlap concentration \( c_b \) to an ideal chain above the overlap with a sharp size increase leads to a \textbf{dramatic increase} of relaxation time and solution viscosity.

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

\[
\eta_{\text{above}} / \eta_{\text{below}} = (Z N/N_e)^2
\]

\[Z = M_{\text{bead}}/M_{\text{string}}\]
Summary of Hydrophobic Polyelectrolytes

Hydrophobic polyelectrolytes at low concentrations are similar to hydrophilic ones. Properties of hydrophobic polyelectrolytes at concentrations higher than string overlap are even more unusual. In the bead-controlled regime correlation length $\xi \sim R \sim c^{-1/3}$ and relaxation time $\tau \sim c^{-1}$.

“Gelling transition” at bead overlap with a sharp increase of chain size, relaxation time, and solution viscosity.

Things to Remember about Semidilute “Hydrophilic” Polyelectrolytes

Overlap concentration is very low ($c^* \sim 1/N^2$). Characteristic scattering peak at $q \sim 1/\xi \sim c^{1/2}$. Osmotic pressure is controlled by counterions.
Open Questions

1. Effect of local fields on dissociation of “weak” charged groups
   (local shift of pKa)
2. Dielectric constant and ion binding in regions with high local $c$
3. Effect of screening by chains on Debye length
4. Entanglement onset in PSS solutions has weak $c$-dependence
   - Effect of electrostatic repulsion on tube diameter
5. Ionic strength dependence of electrostatic persistence length
Dozen of Length Scales

1. Bjerrum length $l_B = \frac{e^2}{(\varepsilon kT)} \approx 7\ \text{Å}$ in water at room $T$.
2. Debye screening length $r_D = (8\pi l_B c_s)^{-1/2} \approx 1\text{nm}$ in $0.1 M$ 1-1 salt.
3. Gouy-Chapman length $\lambda = 1/(2\pi l_B \sigma) \approx 2.3\text{nm}$ for $\sigma = 0.1\ \text{nm}^{-2}$
4. Monomer size $b \approx 2.5\ \text{Å}$ for chemical and $b \approx 1\ \text{nm}$ for Kuhn.
5. Contour length between charges $b/f \approx 1\text{nm}$ for $f = 0.25$, $b \approx 2.5\text{Å}$
6. Persistence length $l_p \sim 1\text{nm}$ for flexible chains
7. Contour length $Nb \approx 250\ \text{nm}$ for $N=10^3$ and $b \approx 2.5\text{Å}$
8. Electrostatic blob $D_e \approx b(uf^2)^{-1/3} \approx 9\text{Å}$ for $u=2$, $f=0.1$, $b \approx 2.5\text{Å}$
9. Dilute no-salt chain size $L \approx D_e N/g \approx 70\text{nm}$
10. Correlation length in semidilute solutions $\xi$
11. Chain size $R$
12. Tube diameter $a$