Chemical Engineering 160/260
Polymer Science and Engineering

Lecture 15:
Molecular Aspects of
Polymer Rheology

February 21, 2001

Objectives

- To introduce the concept of **scaling analysis** to account for the concentration and molecular weight dependence of modulus, relaxation time, and viscosity.
- To illustrate the concept of **screening** that arises from chain interactions in concentrated solutions and show how this allows simplification of the analysis.
- To introduce the concept of **reptation** for diffusion in highly concentrated solutions and melts.

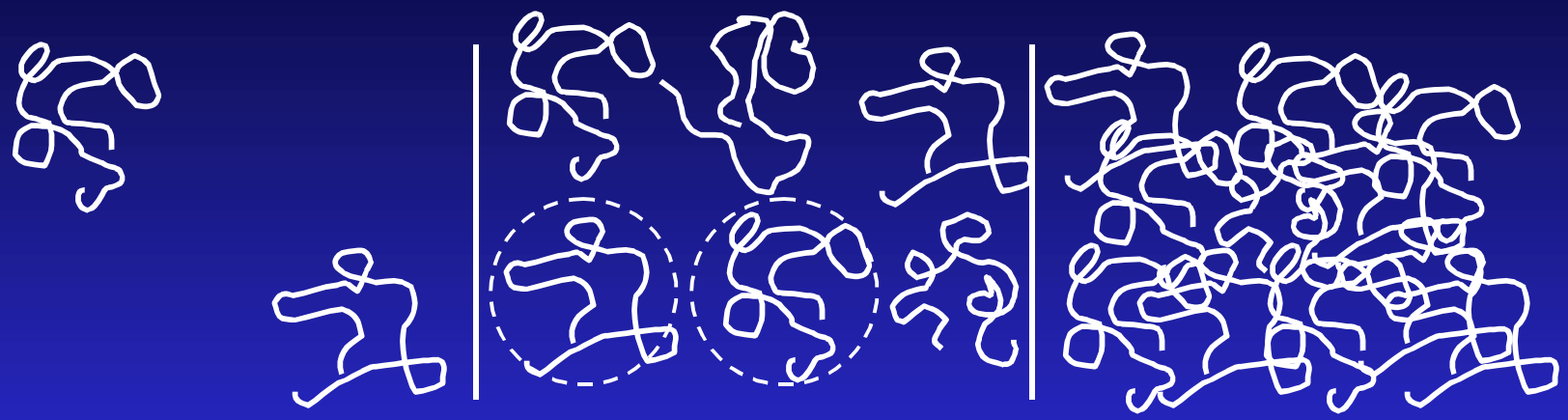
Outline

- Molecular Theory of Semi-dilute Solution
  - Overlap concentration
  - Blobs
  - Screening
- Molecular Theory of Concentrated Solution and Melts
  - Reptation

Summary of Dilute Solution Results

	Concentration dependence	Molecular weight dependence
Modulus	$G_o \propto c$	$G_o \propto \frac{1}{M}$
Relaxation time	c-independent	$\lambda \propto M^{1.8}$
Viscosity	$\eta_{polymer} \propto c$	$\eta_{polymer} \propto M^{0.8}$

Semi-dilute and Concentrated Solutions in Good Solvents



Dilute $c < c^*$

Semi-dilute $c \cong c^*$

Concentrated $c > c^*$

At ν = ν* or c = c*, the chains begin to overlap and entangle.

$$\nu^* \approx \frac{1}{R_o^3}$$

$$c^* \approx \frac{M}{R_o^3} = \frac{1}{[\eta]}$$

Scaling Concept due to DeGennes

- The governing idea is that when c > c*, the modulus must be independent of the molecular weight, i.e., the mechanical interactions are **screened** from each other and the polymer does not "know" how big it is.

$$G = G_o f\left(\frac{c}{c^*}\right) \qquad G_o = \nu kT$$

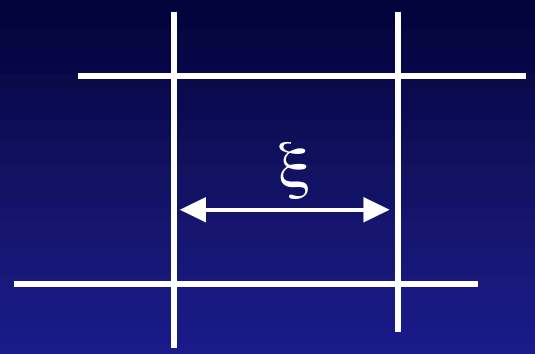
- The measurement of the modulus simply involves local "jiggling" of the chain, not center-of-mass movement.

$$f\left(\frac{c}{c^*}\right) \rightarrow 1 \text{ as } \frac{c}{c^*} > 1$$

Modulus in Semi-dilute Solution

- For $\frac{c}{c^*} > 1$ the modulus must be independent of molecular weight.
- Propose that $G = G_o \left(\frac{c}{c^*} \right)^{\alpha}$ and determine α.
- We know that $G_o \propto \frac{1}{M}$ $\quad c^* = \frac{1}{[\eta]} \propto M^{-0.8}$
- Thus, $G = G_o \left(\frac{c}{c^*} \right)^{1.25} \propto c^{2.25}$

The "Blob" Size: a Simple View



ξ is the **"screening length"** or **"correlation length"**

- In the scaling analysis, the screening length also cannot be a function of molecular weight. Dimensional analysis gives

$$\xi = R_o f\left(\frac{c}{c^*}\right) = R_o\left(\frac{c}{c^*}\right)^{\beta}$$

- In a good solvent

$$R_o \propto M^{0.6}$$

$$c^* \propto M^{-0.8}$$

$$\xi = R_o\left(\frac{c}{c^*}\right)^{-0.75}$$

$$0.6 + 0.8\beta = 0$$

Relation Between Modulus and Blob Size

- The modulus may be written as

$$G = \frac{kT}{\xi^3} \Leftarrow \xi = R_o\left(\frac{c}{c^*}\right)^{-0.75}$$

$$\Downarrow$$

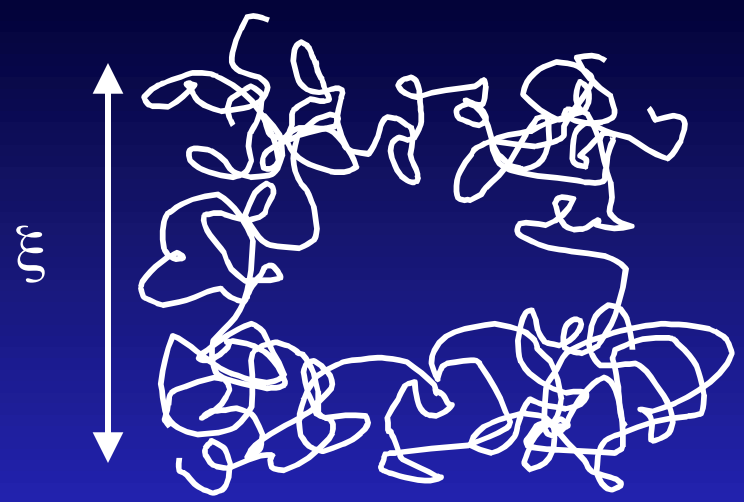
$$G = \frac{kT}{R_o^3}\left(\frac{c}{c^*}\right)^{2.25} = \frac{kTc}{R_o c^*}\left(\frac{c}{c^*}\right)^{1.25} = \frac{kTc}{M}\left(\frac{c}{c^*}\right)^{1.25} = \nu kT\left(\frac{c}{c^*}\right)^{1.25}$$

- This is the same result as before: $G = G_o\left(\frac{c}{c^*}\right)^{1.25} \propto c^{2.25}$

- This suggests that $G = \nu_{network} kT$ (for concentrated systems)

- By analogy to the ideal gas law, G is the isotropic "pressure" generated by the solution.

A More Realistic Picture of the Blob



A strand is any length of polymer between two contact points; these are really random walk coils (or blobs).

- If the polymer itself consists of N statistical subunits, how many such units (call this number g) make up the blob of polymer that forms the strands?
- Because $R_o = bN^{0.6}$ we propose that $\xi = bg^{0.6}$

$$\xi = R_o\left(\frac{c}{c^*}\right)^{-0.75} \Rightarrow g = N\left(\frac{c}{c^*}\right)^{\frac{-0.75}{0.6}} = N\left(\frac{c}{c^*}\right)^{-1.25}$$

Screening

- The number of blobs per chain is obtained from:

$$N_{blob} = \frac{N}{g} = \left(\frac{c}{c^*}\right)^{1.25}$$

- The excluded volume interaction that swells the chain in good solvents is now screened for distances larger than ξ and the chain becomes a random walk with step length ξ.
- In concentrated solution, the blob is now the statistical unit, and the radius of gyration then becomes:

$$R = \xi\sqrt{N_{blob}} = R_o\left(\frac{c}{c^*}\right)^{-0.75}\left(\frac{c}{c^*}\right)^{0.625} = R_o\left(\frac{c}{c^*}\right)^{-0.125}$$

- Thus, the chain **shrinks** with increasing concentration. (In the bulk solid, the chain will exhibit theta dimensions.)

Friction Factor of a Blob

- The close proximity of the chains also screens hydrodynamic interactions between the chains. This means that the friction factor of a chain is simply given by

$$\zeta = N_{blob}\zeta_{blob}$$

- A single blob can then be treated by the dilute solution case:

$$\zeta_{blob} = \eta_s \xi = \eta_s R_o \left(\frac{c}{c^*}\right)^{-0.75}$$

$$\zeta = \eta_s R_o \left(\frac{c}{c^*}\right)^{0.5}$$

- Even though the friction experienced by the chains only comes from the solvent, screening causes an enhancement of friction with increasing concentration.

Summary of Results for Semi-dilute Solutions

Diffusion coefficient:

$$D = \frac{kT}{\zeta} = \frac{kT}{\eta_s R_o}\left(\frac{c}{c^*}\right)^{-0.5}$$

Relaxation time:

$$\lambda = \frac{R^2}{D} = \frac{R^2\zeta}{kT} = \left(\frac{R_o^3\eta_s}{kT}\right)\left(\frac{c}{c^*}\right)^{0.25} = \lambda_o\left(\frac{c}{c^*}\right)^{0.25}$$

Recall that $c^* = \frac{M}{R_o^3} = \frac{1}{[\eta]} \propto M^{-0.8}$

Thus, $\lambda \propto R_o^3[\eta]^{0.25} \propto M^{1.8}(M^{0.8})^{0.25} = M^2$

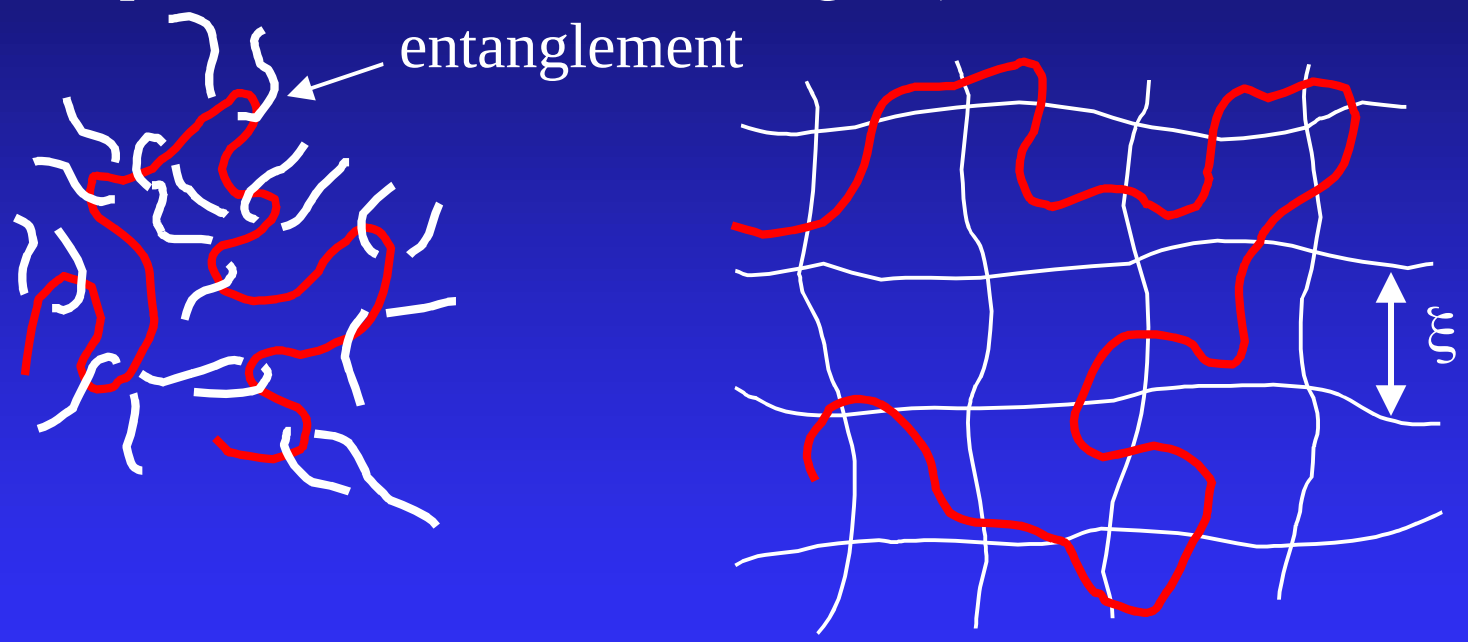
For dilute solution, $\lambda \propto M^{1.8}$

Viscosity:

$$\eta = G\lambda = G_o\lambda_o\left(\frac{c}{c^*}\right)^{1.5} \propto c^{2.5}$$

Highly Concentrated Solutions and Melts

- In this regime we consider the long polymer chains to be fully **entangled**, which leads to a fundamental change in how the system relaxes. (In the semi-dilute case, the chains may interpenetrate, but are not entangled.)



- In the **reptation** model of polymer dynamics, the chain can relax its conformations and diffuse along its contour by slipping through the entanglements.

New Length Scale for Reptation

- In the reptation model a new length scale becomes important because friction occurs all along the chain contour.

Contour length: $L = N_{blob}\xi$

- The time scale, λ, is now calculated differently in that the contour length, L, is used instead of the radius of gyration, R, as the characteristic length.

$$\lambda = \frac{L^2}{D} = \frac{L^2\zeta}{kT} = \frac{\eta_s N_{blob}^3 \xi^3}{kT} = \left(\frac{\eta_s R_o^3}{kT}\right)\left(\frac{c}{c^*}\right)^{1.5} = \lambda_o\left(\frac{c}{c^*}\right)^{1.5}$$

- Note that this is a much stronger concentration dependence than for the semi-dilute solution.

Scaling Results for Reptation

Relaxation time:

$$\lambda = \lambda_o \left(\frac{c}{c^*} \right)^{1.5}$$

Semi-dilute: $\lambda \propto M^{1.8}$

$$c^* = \frac{M}{R_o^3} = \frac{1}{[\eta]} \propto M^{-0.8}$$

$$\lambda \propto M^{1.8} (M^{0.8})^{1.5} = M^3$$

Viscosity:

$$\eta = G\lambda = G_o \lambda_o \left(\frac{c}{c^*} \right)^{2.75} \propto c^{3.75}$$

$$\eta \propto M^3$$

Experiment yields an exponent of 3.4

Scaling Results for Reptation

Center of mass diffusion:

- Since the polymer chain will eventually diffuse through the tube, the relevant length scale is R, not L.

$$D_M \approx \frac{R^2}{\lambda} = D\frac{R^2}{L^2} = \frac{D}{N_{blob}} \propto M^{-2}$$

Agrees with experiment

- The reptation model is still the best molecular picture today.