

Chemical Engineering 160/260
Polymer Science and Engineering

Lecture 14:

Amorphous State

February 14, 2001

Objectives

- To provide guidance toward understanding why an amorphous polymer glass may be considered to be a **theta solvent** for an individual polymer chain of the same composition as the matrix polymer
- To provide a molecular basis for the experimental observables of modulus and relaxation time in a dilute solution.

Outline

- Introduction to the Amorphous State
- Dynamic Shear Moduli
- Molecular Theory of Dilute Solution
 - ◆ Friction and Brownian diffusion
 - ◆ Elastic modulus and relaxation time

Polymer Morphology

- **Morphology is the science of form and structure.** It provides the link between the molecular structure and the bulk properties.
- As applied to polymers, morphology involves the study of the arrangement of polymer molecules into **crystalline** and **amorphous** regions.
- Polymers with higher crystallinity are denser, stiffer, harder, tougher and more resistant to solvents.
- Amorphous domains add flexibility and promote ease of processing below the melting temperature.

Introduction to the Amorphous State

The amorphous state is pervasive and of critical importance to the static and dynamic mechanical behavior of:

Polymer melts

Elastomeric networks

Glassy polymers

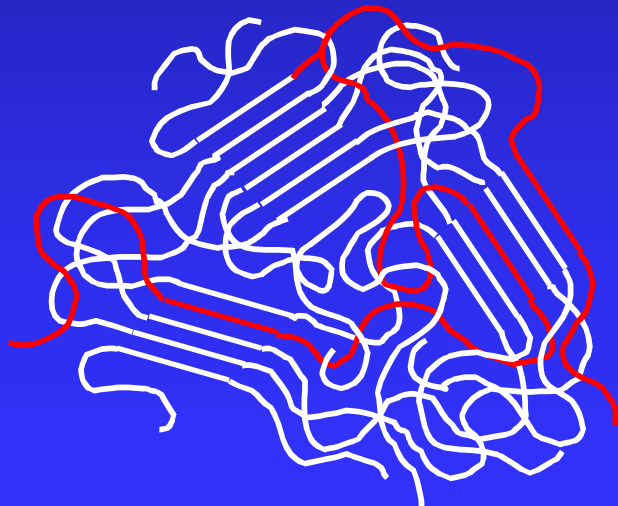
Interlamellar regions of semicrystalline polymers

Fundamental question:

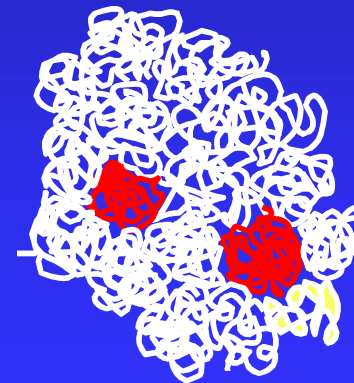
What is the spatial configuration of an individual polymer molecule in the amorphous state?

Chain Configuration in the Amorphous State

- Early workers (Mark, Guth, Flory) all **assumed** that the **random flight model** for polymer conformation applied to flexible polymer chains in the **bulk**. This was the case up to the 50's when the model began to be questioned.
- Alternatives to the random flight model were proposed up through the 70's including quasi-nematic ordering, collapsed chain globules, meandering chains, and nodules.



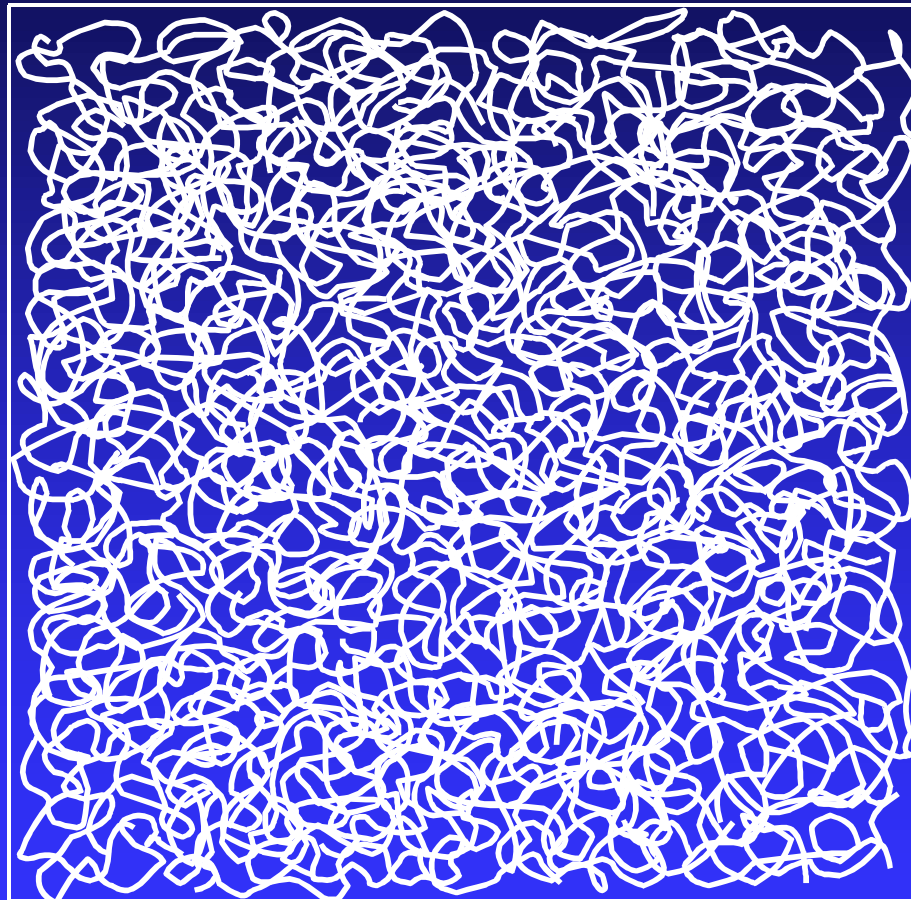
Quasi-nematic ordering



Collapsed chain globules

Random Flight Model for Bulk Polymers

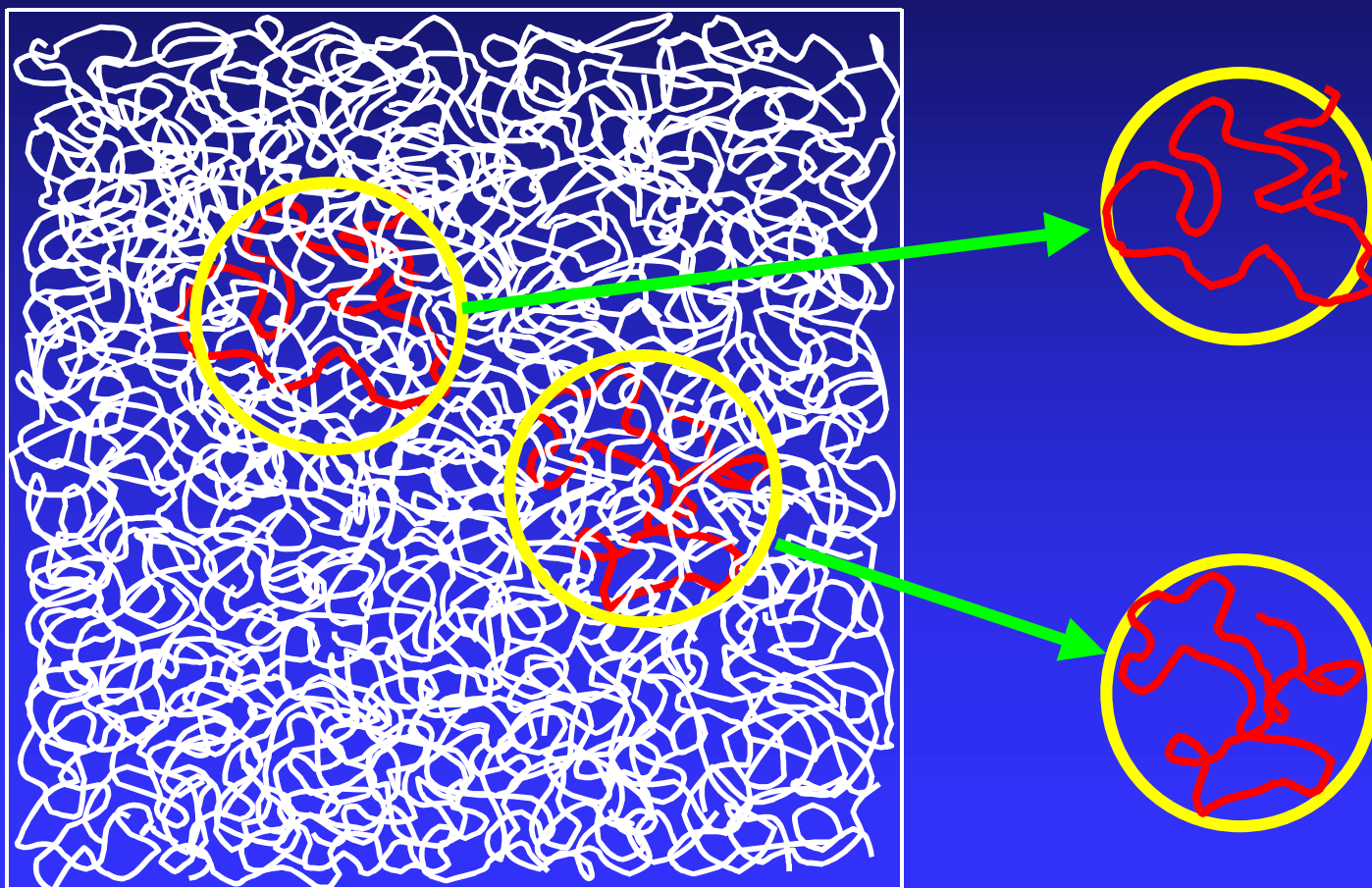
An **amorphous** polymer (melt, glass, etc.) might look like this:



How can we possibly hope to examine individual chains?

Random Flight Model for Bulk Polymers

*We need an **experimental technique** that will permit us “to color a chain red.” - R. Stein*



Neutron Scattering Experiments

Coherent Scattering Lengths for Neutrons (10^{-12} cm)

C ¹²	0.665
H	-0.374
D	0.667

- Neutron scattering arises due to **differences in coherent scattering lengths**, especially for hydrogen and deuterium.
- The **same theory as light scattering** applies, with measurables being the radius of gyration (R_g), weight-average molecular weight (M_w), and second virial coefficient (A_2).

Molecular Dimensions in Amorphous Polymers by Small Angle Neutron Scattering

$$\left(\frac{\langle s^2 \rangle}{M} \right)^{1/2}$$

Angstrom
(Dalton)^{1/2}

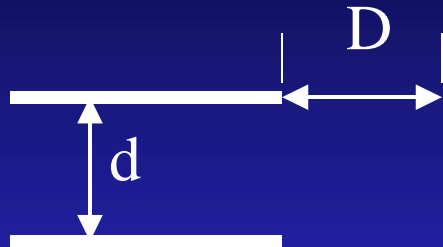
Polymer, bulk state	Dilute Theta Solution	Bulk
Polystyrene, glass	0.275	0.275
Polyethylene, melt	0.45	0.46
Polypropylene, melt	0.33	0.34
Poly(methyl methacrylate), glass	0.30	0.31
Polydimethylsiloxane, melt	0.27	0.25
Poly(vinyl chloride), glass	0.35	0.40
Polyisobutylene, melt	0.305	0.31

D. Y. Yoon, personal communication

Material Functions: Oscillatory Shearing

Assume that there is a periodic, dynamic flow field.

Strain:



$$\gamma = \frac{D}{d}$$

$$\gamma = \gamma_o \sin \omega t$$

Shear rate:

$$\dot{\gamma} = \frac{d\gamma}{dt} = \omega \gamma_o \cos \omega t$$

Modulus:

$$\tau = G' \gamma_o \sin \omega t + G'' \gamma_o \cos \omega t$$

elastic stress

viscous stress

G' = storage modulus, G'' = loss modulus

Dynamic Stress-strain Relationships

Simple elastic material:

$$\tau = G\gamma$$

$$\gamma = \gamma_o \sin \omega t$$

$$G' = G$$

$$\tau = G\gamma_o \sin \omega t$$

$$G'' = 0$$

Simple Newtonian liquid:

$$\tau = \eta\dot{\gamma}$$

$$\dot{\gamma} = \omega\gamma_o \cos \omega t$$

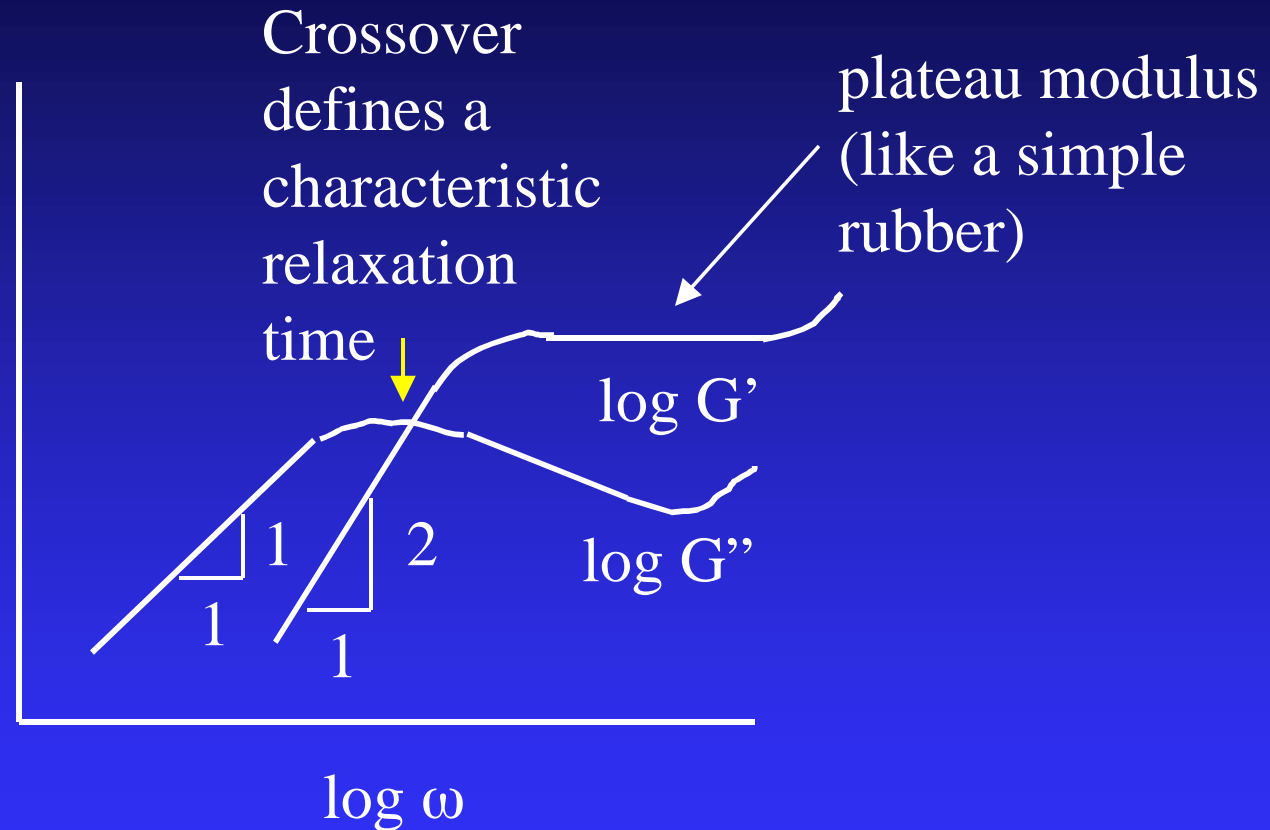
$$G' = 0$$

$$\tau = \eta\omega\gamma_o \cos \omega t$$

$$G'' = \omega\eta$$

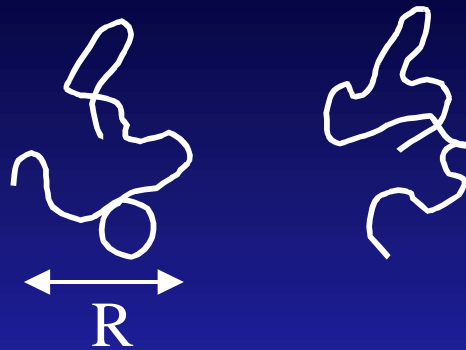
Experimental Results for Shear Moduli

- Assume an entangled polymer melt.



- For very slow frequencies, the molecules have time to rearrange and a simple liquid response is obtained ($G'' > G'$).

Molecular Theories: Dilute Solutions



We will approximate nondraining random coils as spheres with characteristic dimension R .

- Recall the classical Einstein equation:

$$\frac{\eta - \eta_s}{\eta_s} = \frac{5}{2} \phi$$

η_s = solvent viscosity

ϕ = volume fraction of spheres

- Approximate the volume fraction of spheres as:

$$\phi \approx \nu R^3$$

$$\nu = \frac{c}{M}$$

ν = number concentration

c = mass concentration

- We are generally only interested in scaling behavior, so we will drop all numerical coefficients.

Molecular Weight Dependence of Viscosity for Dilute Solution

- Recall the definition of **intrinsic viscosity**:

$$\frac{1}{c} \frac{(\eta - \eta_s)}{\eta_s} = 2.5 \frac{R^3}{M}$$

- For an ideal **Gaussian** chain under **theta** conditions:

$$\langle R^2 \rangle^{1/2} = \sqrt{Nb}$$

N = number of statistical segments
b = statistical segment size

$$\eta \approx \frac{(\sqrt{M})^3}{M} \approx M^{0.5}$$

- For a real chain with excluded volume (self-avoiding walk):

$$\langle R^2 \rangle^{1/2} = N^{0.6} b$$

$$\eta \approx \frac{(M^{0.6})^3}{M} = M^{0.8}$$

Review of Friction and Brownian Diffusion

- **Stokes Law** for flow past a sphere in a Newtonian fluid:

$$F = \zeta U = (6\pi\eta R)U$$

ζ = friction factor

U = velocity of sphere

R = radius of sphere

- **Brownian diffusion** is described by:

$$\langle x^2 \rangle = Dt$$

$\langle x^2 \rangle$ = mean squared distance between origin and position at time t

D = diffusion coefficient

- The **Einstein equation** is:

$$D = \frac{kT}{\zeta}$$

Elastic Modulus and Relaxation Time

Excess viscosity:

$$\eta - \eta_s \approx \nu R^3 \eta_s = (\nu kT) \frac{R^3 \eta_s}{kT}$$

Elastic modulus:

$$G_o = \nu kT = \frac{ckT}{M}$$

Relaxation time:

$$\lambda = \frac{R^3 \eta_s}{kT} = \frac{R \eta_s}{kT} R^2 = \frac{\zeta}{kT} R^2 = \frac{R^2}{D}$$

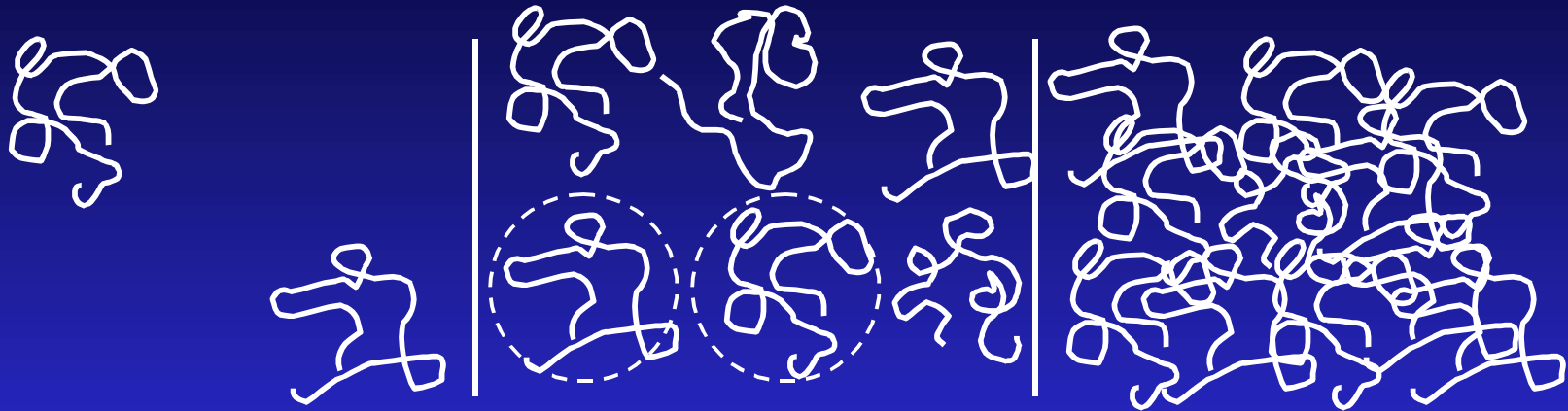
- In general, the viscosity of a dilute solution is given by:

$$\eta \approx G\lambda$$

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 $\nu = \nu^*$ or $c = c^*$, the chains begin to overlap and entangle.

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

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