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III. Assembled Nanostructure of Polymers

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Chapter 5. The Amorphous State

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Chapter 5. The Amorphous State



Introduction – “polymeric glass” and “amorphous”

- ❑ Many of the plastics produced on a large scale for consumer applications exist under application conditions, at least partially, in what is commonly called the *glassy state*.
- ❑ A polymer glass is a solid that has been described as one marked by a relatively random, or amorphous, arrangement of macromolecular chains.
- ❑ All polymers share this definition, but they often have very different properties.
- ❑ **What then is the influence of the molecular structure of the chains on the macroscopic properties of these materials?**
- ❑ **What degree, or level, of structural information is necessary for the prediction of macroscopic properties?**



※ What is amorphous?

- ❑ In general, amorphous species are characterized by **the absence of long range order**; the arrangement of atomic positions is disordered such as in a liquid.
- ❑ What is the difference between an amorphous solid and a liquid, and which of these two states does a polymer fit into?
- ❑ The best known theoretical treatment to describe the glassy state are based upon equilibrium thermodynamics.

“ each microscopic structural unit of the glass must lie at a position of static equilibrium, the totality of which is randomly distributed. If one such exists there must be a large number of similar random structures of equal energy. Nevertheless, the entropy of each is zero, because all the structures are mutually inaccessible. - Cohen, M. H., Turnbull, D. *Nature*, **203** (1964) 964.”

→ The glassy state is viewed as a metastable instead of instable state.

→ The glass is viewed as a solid which has frozen-in liquid-like disorder.



5.1. The Amorphous Polymer State

5.1.1. Solids and Liquids

crystalline polymer	amorphous polymer
regular or ordered	disordered
1st-order melting	no melting
solid becomes liquid-like above T_m	solid becomes liquid-like above T_g

5.1.2. Possible Residual Order in Amorphous Polymers?

The chains appear to lie parallel (i.e. orderly) for short runs because of space-filling requirements, permitting a higher density. \Rightarrow on debating

□ *Questions of interest to amorphous state*

- ① the design of critical experiments concerning the shape of the polymer chain
- ② the estimation of type and extent of order or disorder
- ③ the development of models suitable for physical and mechanical applications.



5.2. Experimental Evidence Regarding Amorphous Polymers

□ Characterize amorphous polymers

- ① in short-range interactions ($< 20 \text{ \AA}$)
- ② in long-range interactions ($> 20 \text{ \AA}$)

Table 5.1 Selected studies of the amorphous state

Methods	Information Obtainable	Principal Findings	Methods	Information Obtainable	Principal Findings
<i>A. Short-Range Interactions</i>			<i>B. Long-Range Interactions</i>		
Stress-optical coefficient	Orientation of segments in isolated chain	Orientation limited to 5–10 Å	Small-angle neutron scattering	Conformation of single chains	Radius of gyration the same in melt as in θ -solvents
Depolarized light-scattering	Segmental orientation correlation	2–3 —CH ₂ — units along chain correlated	Electron microscopy	Surface inhomogeneities	Nodular structures of 50–200 Å in diameter
Magnetic birefringence	Segmental orientation correlation	Orientation correlations very small	Electron diffraction and wide-angle x-ray diffraction	Amorphous halos	Bundles of radial dimension = 25 Å and axial dimension = 50 Å, but order may extend to only one or two adjacent chains
Raman scattering	Trans and gauche populations	Little or no modification in chain conformation initiated by intermolecular forces			
NMR relaxation	Relaxation times	Small fluctuating bundles in the melt			<i>C. General</i>
Small-angle X-ray scattering	Density variations	Amorphous polymers highly homogeneous; thermal fluctuations predominate	Enthalpy relaxation	Deviations from equilibrium state	Changes not related to formation of structure
			Density	Packing of chains	Density in the amorphous state is about 0.9 times the density in the crystalline state

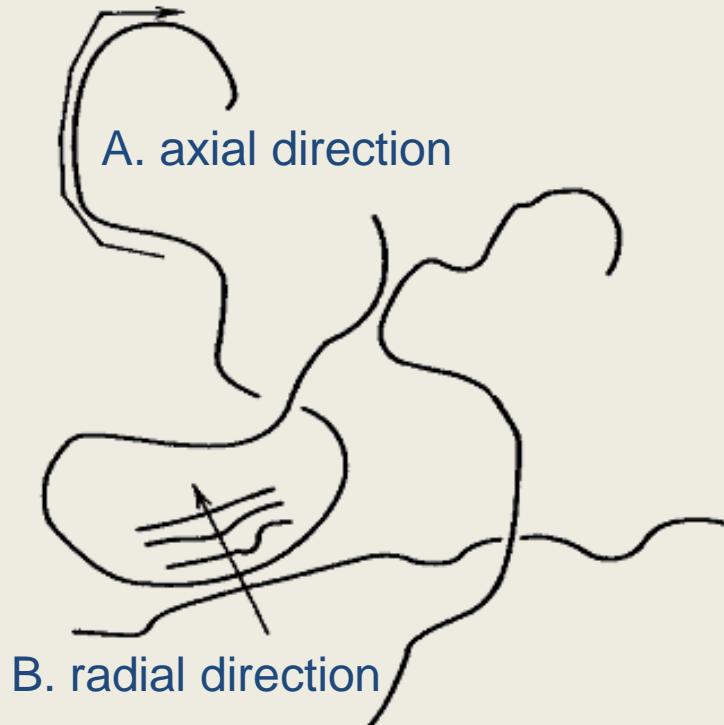


5.2. Experimental Evidence Regarding Amorphous Polymers

5.2.1. Short-range interactions in amorphous in polymers

□ *Short-range Interactions*

- A. Method that measure the orientation or correlation of mers along the *axial direction* of a chain
- B. Method that measure the order between chains in the *radial direction*



❖ Some measurement methods of the orientation in the axial direction

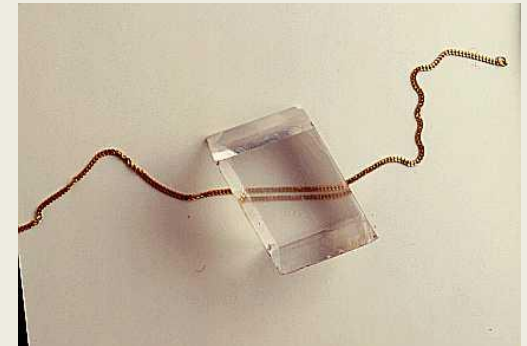
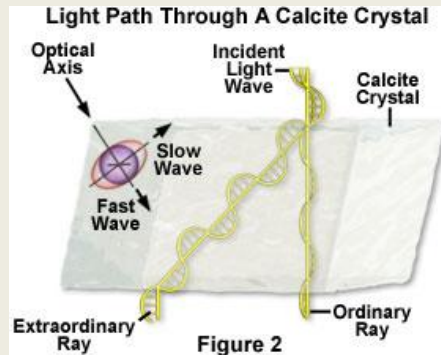
- Kuhn segment length
 - Persistence length
 - Birefringence
- Section 5.3

Fig.5.1 Schematic diagram illustrating the axial and radial correlation direction.

5.2. Experimental Evidence Regarding Amorphous Polymers

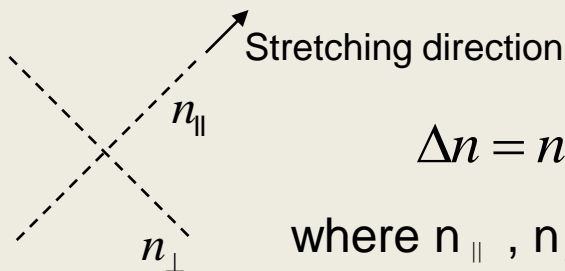
❖ Birefringence

: If a substance is anisotropic, which means that it has different properties in different directions, it will be doubly refracting or birefringent (when transparent).



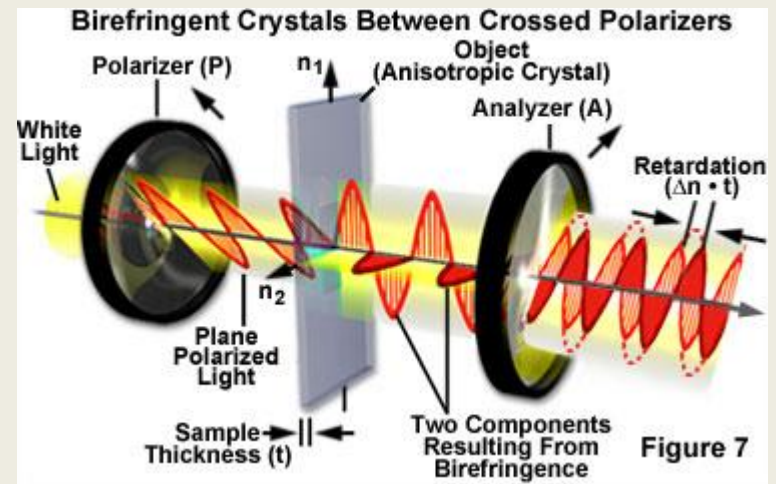
: one of the most powerful experimental method of determining the order in the axial direction

▪ Definition of Birefringence



$$\Delta n = n_{\parallel} - n_{\perp}$$

where n_{\parallel} , n_{\perp} : refractive indices for light polarized in two directions 90° apart.



5.2. Experimental Evidence Regarding Amorphous Polymers

- For stretching at 450 to the polarization directions, the fraction of light transmitted

$$T = \sin^2 \left(\frac{\pi d \Delta n}{\lambda_0} \right) \quad \text{where } d : \text{sample thickness, } \lambda_0 : \text{wavelength of light in vacuum}$$

→ By measuring the transmitted light quantitatively, the birefringence is obtained.

- Relation between the birefringence and the orientation of molecular units such asmers, crystals, or even chemical bonds.

$$\Delta n = \frac{2\pi}{9} \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \sum_i (b_1 - b_2)_i f_i$$

where $b_1 - b_2$: polarizability along and perpendicular to the axes of such units.

\bar{n} : average refractive index

f_i : an orientation function of such units

$$f_i = \frac{3 \cos^2 \theta_i - 1}{2}$$

For Fibers and Films

$\theta = 0^\circ$: perfect orientation

$\theta = 54^\circ$: Zero orientation

e.g. Nylons or Rayons $\theta \approx 5^\circ$

where θ_i is the angle that the symmetry axis of the unit makes w, r, t the stretching direction

5.2. Experimental Evidence Regarding Amorphous Polymers

❖ *Stress-optical coefficient(SOC)*

: the retractive stress is directly proportional to the degree of orientation, which in turn is directly proportional to the birefringence.

: for uniaxial tension, the birefringence and the retractive stress (σ) are related by the simple equation.

$$n_{\parallel} - n_{\perp} = C \sigma$$

C : the stress optical coefficient.
: depends on the chemical structure and temperature

$$C = \frac{2\pi(\alpha_{\parallel} - \alpha_{\perp})}{45} \frac{(\bar{n}^2 + 2)^2}{\bar{n}kT}$$

where $\alpha_{\parallel} - \alpha_{\perp}$: difference in polarizability of a polymer segment
 \bar{n} : average refractive index ($\bar{n} = n$ of the unoriented polymer)

→ The change in birefringence that occurs when an amorphous polymer is deformed yields important information concerning the state of order in the amorphous solid.

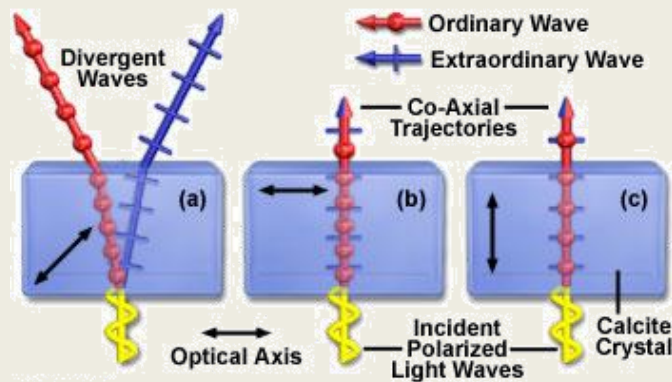


5.2. Experimental Evidence Regarding Amorphous Polymers

❖ *Depolarized light-scattering (DPS)*

: the intensity of scattered light is measured when the sample is irradiated by visible light : the sample is held between crossed Nicols.

N.B. Nicole prism : A prism made of calcite once widely used for polarizing light and analyzing plane-polarized light.



→ Studies on DPS on n-alkane liquids reveals that there is a critical chain length of 8~9 carbons, below which there is no order in the melt.

- For longer chains, only 2~3 $-\text{CH}_2-$ units in one chain are correlated with regard to their orientation, indicating an extremely weak orientational correlation.

5.2. Experimental Evidence Regarding Amorphous Polymers

❖ Other Methods

- 1) Rayleigh Scattering : elastically light-measure scattering angle.
- 2) Brillouin Scattering : a Doppler effect-yields small shift in freq.
- 3) Raman Scattering : inelastic scattering-shift in wavelength



5.2. Experimental Evidence Regarding Amorphous Polymers

5.2.2. Long Range Interactions in Amorphous Polymers

5.2.2.1. Small-Angle Neutron Scattering (Remind Ch 2.2)

$$\frac{Hc}{R(\theta) - R(\text{Solvent})} = \frac{1}{M_w P(\theta)} + 2A_2c \quad \rightarrow \text{See Eqn. 3.44 and Appendix 2.2-4}$$

where $R(\theta) = \frac{I_\theta w^2}{I_0 V_s}$: Rayleigh's ratio

w : the sample-detector distance

V_s : the scattering volume

I_θ/I_0 : the scattering intensity of the solvent or lack initial intensity

(N.B. the scattering intensity of the solvent or background must be subtracted.)

$P(\theta)$: scattering form factor

=1 for very small particles or molecules.



5.2. Experimental Evidence Regarding Amorphous Polymers

- A deuterated polymer is dissolved in an ordinary hydrogen-bearing polymer of the same type
- The background to be subtracted originates from the scattering of the protonated species and the coherent scattering originates from the dissolved deuterated species

$$H : \text{optical const.} = \frac{N_a}{M_p^2} \left[a_s \left(\frac{V_p}{V_s} \right) - a_p \right]^2 \quad \rightarrow \text{See Ch 2.2 eqn. 3.54}$$

M_p : 'mer' molecular weight

a_p, a_s : coherent neutron scattering lengths of the polymer 'mer' and solvent

- the coherent intensity in SANS : described by the cross section, $d\Sigma/d\Omega \rightarrow$ probability that a neutron will be scattered in a solid angle Ω per unit volume of the sample.
- : normally used to express the neutron scattering power of a sample.
- : identical with the quantity $R(\theta)$

$$\frac{C_N}{d\Sigma/d\Omega} = \frac{1}{M_w P(\theta)}$$

$$C_N = \frac{(a_H - a_p)^2 N_p \rho (1-X) X}{M_p^2}$$

a_H, a_D : the scattering length of a normal protonated and deuterated (labeled) structural unit(mer),

: calculated by adding up the scattering lengths of each atom in the mer.

X : the mole fraction of labeled chains

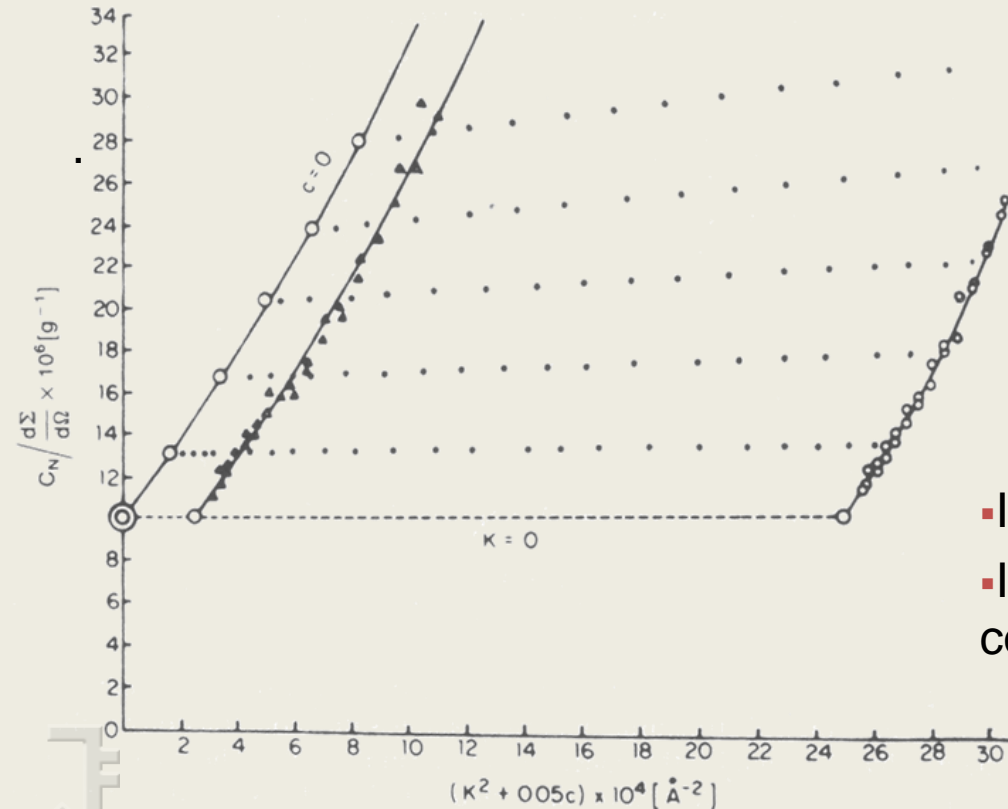
in high dilution-solution, $(1-X)X \approx 0$

5.2. Experimental Evidence Regarding Amorphous Polymers

- By rearrangement of the equation

$$\left(\frac{d\Sigma}{d\Omega}\right)^{-1} = \frac{1}{C_N M_w} \left(1 + \frac{K^2 R_g^2}{3} + \dots\right)$$

- From the Zimm plot of $[d\Sigma/d\Omega]^{-1}$ vs. K^2 ($K = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$: wave vector)



the intercept : $\frac{1}{C_N M_w} \rightarrow M_w$

the slope : $\frac{R_g^2}{3} \rightarrow R_g^2$

- If $A_2 = 0$ the above result is satisfactory.
- If $A_2 \neq 0$ a second extrapolation to zero concentration is required

5.2. Experimental Evidence Regarding Amorphous Polymers

Table 5.4 Molecular dimensions in bulk polymer samples.

Polymer	State of Bulk	$(R_g^2/M_w)^{1/2} \frac{\text{\AA} \cdot \text{mol}^{1/2}}{\text{g}^{1/2}}$		
		SANS Bulk	Light-Scattering θ -Solvent	SAX
Polystyrene	Glass	0.275	0.275	0.27 (i)
Polystyrene	Glass	0.28	0.275	—
Polyethylene	Melt	0.46	0.45	—
Polyethylene	Melt	0.45	0.45	—
Poly(methyl methacrylate)	Glass	0.31	0.30	—
Poly(ethylene oxide)	Melt	0.45	—	—
Poly(vinyl chloride)	Glass	0.30	0.37	—
Polycarbonate	Glass	0.457	—	—



5.2. Experimental Evidence Regarding Amorphous Polymers

$\left(\frac{R_g^2}{M_w}\right)^{\frac{1}{2}}$: values in θ -solvent and in the bulk state
: are identical within experimental error.

↳ theoretically this should be true since under these conditions the polymer chain in the form of random coils is unable to distinguish between a solvent molecule and a polymer segment with which it may be in contact.

→ random coils can also exist in the bulk amorphous state.

(θ -solvent : the conformation of the chain is unperturbed because the $\Delta G(P-S)$ and the $\Delta G(P-P)$ are all the same.)

→ See Ch 2.2.2.5



5.2. Experimental Evidence Regarding Amorphous Polymers

5.2.2.2. Electron and X-ray Diffraction

- ❖ Amorphous materials, including ordinary liquids, gives much more diffuse (or halos) diffraction.
 - : For low-molecular-weight liquids, the diffuse halos → the nearest-neighbor spacings are slightly irregular, and after two or three molecular spacings all sense of order is lost.

 - : For polymers having long chains, questions to be resolved center about
 - ① Whether or not chains lie parallel for some distance,
 - ② If so, to what extent.

- ❖ X-ray diffraction studies (wide-angle X-ray scattering, or WAXS)
 - : The analysis is made by comparing experimental and calculated scattering by means of reduced intensity function, $s_i(s)$, rather than total intensity, since the features are more evenly weighted in the former.



5.2. Experimental Evidence Regarding Amorphous Polymers

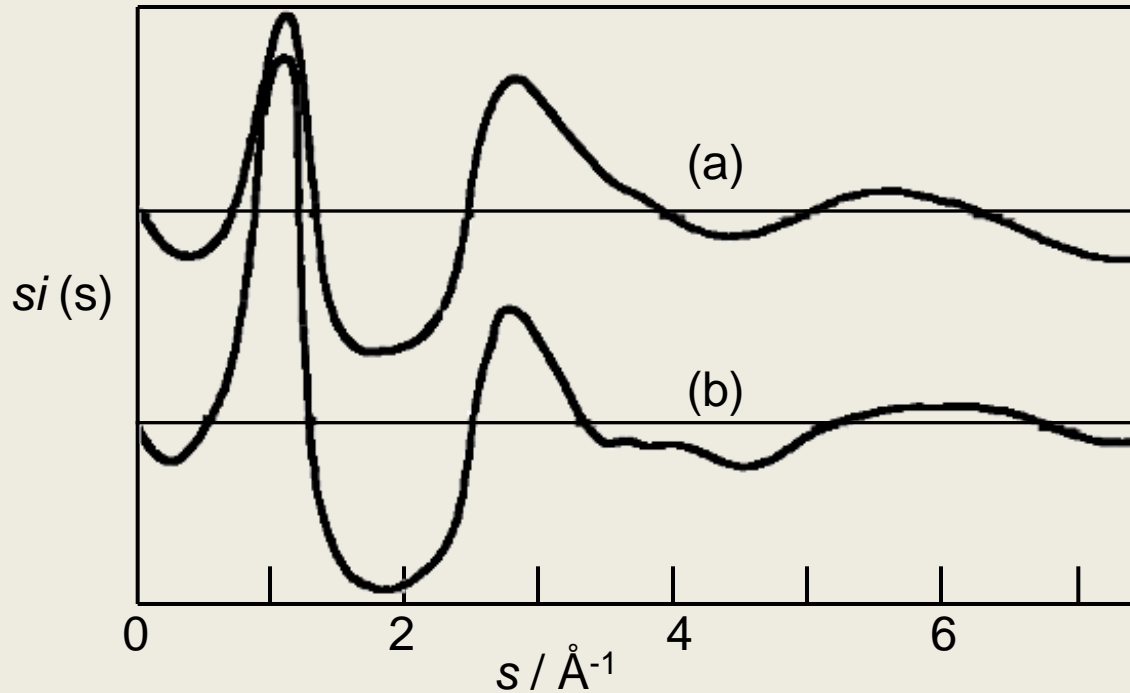


Fig.5.3 WAXS data on polytetrafluorethylene:

(a) experimental data and (b) theory.

Model is based on a disordered helix arranged with fivefold packing in a 24- \AA diameter cylinder.

- $si(s) = kI(s) - \Sigma f^2(s)$

where $s = 4\pi\sin\theta/\lambda$,

k : scaling factor to electron units,
 Σf^2 : independent scattering from a repeat unit

→ Refer to *Faraday Discuss. Chem. Soc.*, 1979, 68, 46

- The 1st scattering maximum
→ chain spacing distance

$s = 4\pi\sin\theta/\lambda$

$n\lambda = 2d\sin\theta$ (Bragg's law)

→ We can obtain the d spacing of polymer chains

5.2. Experimental Evidence Regarding Amorphous Polymers

- The triangular nature of the peak at $\approx 3.0 \text{ \AA}^{-1}$ is indicative of long segments in a *trans*-type conformation. → [Appendix 5.1](#)
 - The semi-empirical energy calculations and evaluation of solution properties predict a chain based on four states (t^+ , t^- , g^+ , g^-) which has a weighted average aspect ratio of all-*trans* segments of ≈ 3 . [*Macromolecules*, **1** (1968) 12]
 - The packing density of a cylinder to enclose such an all-*trans* disordered segment is ≈ 0.8
 - The two dimensional packing fraction of the cylinders of course depends on the "softness" assumed, but a reasonable value, taking the packing density of the melt as ≈ 0.52 , would be $0.52/0.8 (= 0.65)$.
 - A comparison of this with values derived from the computer simulations of disc packing, indicates a **non-crystalline structure**. [*J. Colloid Interface Sci.*, **56** (1976) 483]
 - For PE, the two-dimensional packing fraction required is ≈ 0.87 , which could only be accounted for by some form of defective crystalline packing.
- ❖ In analyzing WAXS data, two different molecular directions must be borne in mind
- (a) Conformational orientation in the axial direction, which is a measure of how ordered or straight a given chain might be
 - (b) organization in the radial direction, which is a direct measure of intermolecular order.

5.2. Experimental Evidence Regarding Amorphous Polymers

5.2.2.3. General Properties

- ❖ Two of the most important general properties of the amorphous polymers
 - ① Density : approximately 0.85~0.95 that of crystalline phase.
 - ② The excess free ϵ due to non-attainment of equilibrium.
: mostly smooth changes on relaxation and annealing

Table 5.6 Major order-disorder arguments in amorphous polymers

Order	Disorder
Conceptual difficulties in dense packing without order (a, b) Appearance of nodules (b, c)	Rubber elasticity of polymer networks (e, f) Absence of anomalous thermodynamic dilution effects (g)
Amorphous halos intensifying on equatorial plane during extension (d) Nonzero Mooney–Rivlin C_2 constants (a)	Radii of gyration the same in bulk as in θ -solvents (h) Fit of $P(\theta)$ for random coil model to scattering data (i)
Electron diffraction (l) lateral order to 15–20 Å	Rayleigh–Brillouin scattering, X-ray diffraction (j, k), stress–optical coefficient, etc. studies showing only modest (if any) short-range order (j, k, m, n)

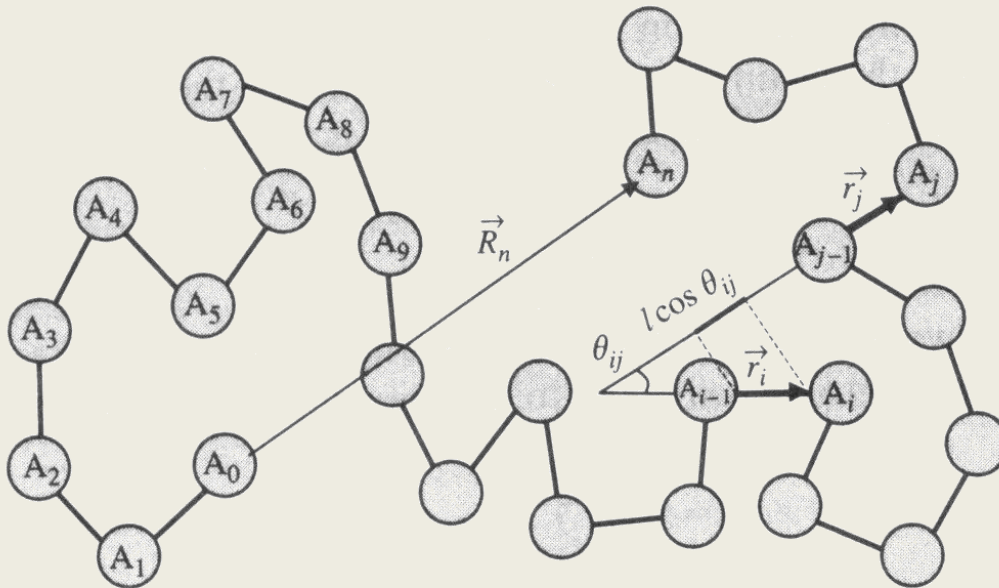


5.3. Conformation of the Polymer Chain

- ❖ One of the great classic problem in polymer science has been determination of the conformation of the polymer chain in space
- ❖ The resulting models are important in deriving equations for viscosity , diffusion, rubbery elasticity, and mechanical behavior.

5.3.1. The Freely Jointed Chain

- ❖ Consider a flexible polymer of $n+1$ backbone atoms A_i (with $0 \leq i \leq n$)



- The end-to-end vector is the sum of all n bond vectors in the chain

$$\vec{R}_n = \sum_{i=1}^n \vec{r}_i$$

- The average end-to-end vector

$$\langle \vec{R}_n \rangle = 0$$

- ※ The ensemble average $\langle \rangle$ denotes an average over all possible states of the system



5.3. Conformation of the Polymer Chain

- The simplest non-zero average is the mean-square end-to-end distance

$$\langle R^2 \rangle \equiv \langle \vec{R}_n^2 \rangle = \langle \vec{R}_n \cdot \vec{R}_n \rangle = \left\langle \left(\sum_{i=1}^n \vec{r}_i \right) \cdot \left(\sum_{i=1}^n \vec{r}_i \right) \right\rangle = \sum_{i=1}^n \sum_{j=1}^n \langle \vec{r}_i \cdot \vec{r}_j \rangle$$

- If all bond vectors have the same length $l = |\vec{r}_i|$, the scalar product can be represented in terms of the angle θ_{ij} between bond vector \vec{r}_i and \vec{r}_j

$$\vec{r}_i \cdot \vec{r}_j = l^2 \cos \theta_{ij}$$

- The mean-square end-to-end distance becomes a double sum of average cosines

$$\langle R^2 \rangle = \sum_{i=1}^n \sum_{j=1}^n \langle \vec{r}_i \cdot \vec{r}_j \rangle = l^2 \sum_{i=1}^n \sum_{j=1}^n \langle \cos \theta_{ij} \rangle$$

- In the **freely jointed chain model**, $l = |\vec{r}_i|$ and $\langle \cos \theta_{ij} \rangle = 0$

$$\langle R^2 \rangle = nl^2$$

- For any bond vector i , the sum over all other bond vector j converges to a finite number, denote by C'_i

$$C'_i \equiv \sum_{j=1}^n \langle \cos \theta_{ij} \rangle$$



5.3. Conformation of the Polymer Chain

$$\langle R^2 \rangle = l^2 \sum_{i=1}^n \sum_{j=1}^n \langle \cos \theta_{ij} \rangle = l^2 \sum_{i=1}^n C'_i = C_n n l^2$$

- The coefficient C_n , called *Flory's characteristic ratio*, is the average value of the constant C'_i over all main-chain bonds of the polymer

$$C_n = \frac{1}{n} \sum_{i=1}^n C'_i \rightarrow \text{An infinite chain : } C_\infty$$

- The equivalent freely jointed chain has the same mean-square end-to-end distance $\langle R^2 \rangle$ and same maximum end-to-end distance R_{\max} , but has N freely jointed effective bonds of length b (called the *Kuhn length*).

- The contour length : $Nb = R_{\max}$
- The mean-square end-to-end distance

$$\langle R^2 \rangle = Nb^2 = bR_{\max} = C_\infty n l^2$$

- The degree of polymerization : $N = \frac{R_{\max}^2}{C_\infty n l^2}$

- Equivalent bonds (Kuhn monomers) of length

$$b = \frac{\langle R^2 \rangle}{R_{\max}} = \frac{C_\infty n l^2}{R_{\max}}$$



5.3. Conformation of the Polymer Chain

❖ Example :

Calculate the Kuhn length b of a polyethylene chain with $C_\infty=7.4$, main- chain bond length $l=1.54 \text{ \AA}$, and bond angle $\Theta=68^\circ$.

Substituting the maximum end-to-end distance from $R_{\max} = nl \cos \frac{\theta}{2}$ determines the Kuhn length

$$b = \frac{C_\infty l^2 n}{nl \cos(\theta/2)} = \frac{C_\infty n l^2}{\cos(\theta/2)}$$

$$R_0 = \sqrt{\langle R^2 \rangle} = bN^{1/2} \quad : \text{ The root mean-square end-to-end distance}$$



5.3. Conformation of the Polymer Chain

5.3.2. The Random Coil (remember that of Ch.2.2)

: the unperturbed shape of the polymer chain in both dilute solutions and in the bulk amorphous state.

In dilute solutions

: under Flory θ -solvent conditions, the polymer-solvent interactions and the excluded volume terms just cancel each other.

In the bulk amorphous state

: the mers are surrounded entirely by identical mers, and the sum of all the interactions is zero.

- The end-to-end distances for random coils : $r^2 = 6R_g^2$ (See Ch.2.2 Radius of Gyration)
- The most important result is that, for random coils, there is a well-defined maximum in the frequency of the end-to-end distances $\rightarrow r_0$





Appendix

Various Models for Defining Polymer Chains



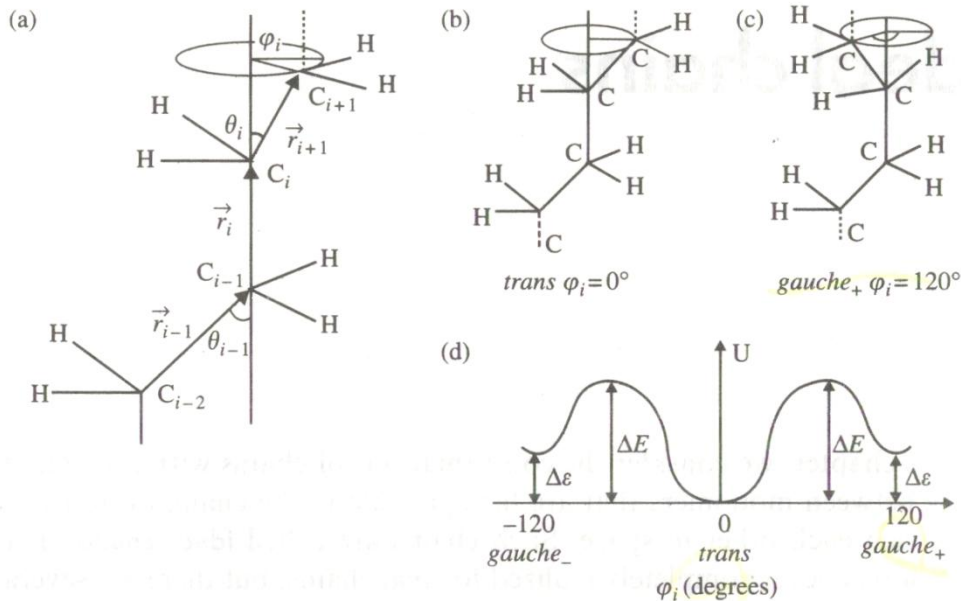
Models for Flexible Polymer Chains



Model	$\langle r^2 \rangle$	Comments
Mathematician's Ideal Random Coil	$\langle r^2 \rangle = nl^2$	Freely jointed chain model n bonds each of length l
Chemist's Real Chain θ : fixed	$\langle r^2 \rangle = nl^2 \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right) \left(\frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right)$ $\langle r^2 \rangle_{\theta} = nl^2 C_{\infty}$ $\langle r^2 \rangle = nl^2 C_{\infty} \alpha^2$ $\alpha^2 = \frac{\langle r^2 \rangle}{\langle r^2 \rangle_{\theta}}$	<p>RIS (Rotational Isomeric State) model</p> <p>Allow preferred bond angles and preferred rotation angles about main chain bonds</p> <p>Characteristic ratio takes into account all local steric interactions</p> <p>Factor α takes into account solvent quality and long range chain self-intersections</p>
Physicist's Universal Chain	$\langle r^2 \rangle = Nb^2$ N: # of statistical segments, b: statistical segment length, $b = lC_{\infty}$	C_{∞} is incorporated into Kuhn length b.



Models for Flexible Polymer Chains



FJC: Freely Jointed Chain
 FRC: Freely Rotating Chain
 HR: Hindered Rotation
 RIS: Rotational Isomeric State

Models	FJC	FRC	HR	RIS
Bond length l	Fixed	Fixed	Fixed	Fixed
Bond angle θ	Free	Fixed	Fixed	Fixed
Torsion angle Φ	Free	Free	Controlled by $V(\Phi)$	t, g+, g-
Next Φ independent?	Yes	Yes	Yes	No
C_∞	1	$\left(\frac{1 - \cos \theta}{1 + \cos \theta}\right)$	$\left(\frac{1 - \cos \theta}{1 + \cos \theta}\right) \left(\frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle}\right)$	$\left(\frac{1 - \cos \theta}{1 + \cos \theta}\right) \left(\frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle}\right)$

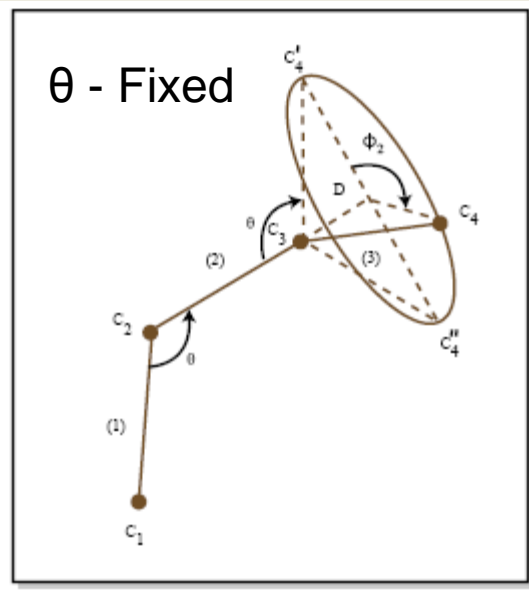
FJC (Freely Jointed Chain)



$$\begin{aligned}\langle r^2 \rangle &= \langle \vec{r}_{1,n} \cdot \vec{r}_{1,n} \rangle = \left\langle \sum_{i=1}^n l_i \cdot \sum_{j=1}^n l_j \right\rangle \\ &= \langle (l_1 \cdot (l_1 + l_2 + l_3 + \dots)) + l_2 \cdot (l_1 + l_2 + l_3 + \dots) + \dots \rangle \\ &= \left\langle \begin{vmatrix} l_1 \cdot l_1 & l_1 \cdot l_2 & l_1 \cdot l_3 & \dots & l_1 \cdot l_n \\ l_2 \cdot l_2 & l_2 \cdot l_2 & & & \\ & & \cdot & & \\ & & & \cdot & \\ l_n \cdot l_2 & & & & l_n \cdot l_n \end{vmatrix} \right\rangle \\ &= \left\langle \begin{vmatrix} l^2 & 0 & 0 & \dots & 0 \\ 0 & l^2 & & & \cdot \\ 0 & & \cdot & & \cdot \\ 0 & & & \cdot & \cdot \\ 0 & & & & l^2 \end{vmatrix} \right\rangle = nl^2\end{aligned}$$



FRC (Freely Rotating Chain)



$$l_i \cdot l_{i+1} = l^2 (-\cos \theta)$$

$$l_i \cdot l_{i+2} = l^2 (-\cos \theta)^2$$

\vdots

$$l_i \cdot l_{i+m} = l^2 (-\cos \theta)^m$$

$$\langle r^2 \rangle = l^2 \begin{pmatrix} 1 & -\cos \theta & (-\cos \theta)^2 & \dots & (-\cos \theta)^{n-1} \\ -\cos \theta & 1 & -\cos \theta & & \\ (-\cos \theta)^2 & -\cos \theta & 1 & & \\ & & & \ddots & \\ & & & & 1 \end{pmatrix}$$

$$= nl^2 \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right)$$



HC (Hindered Rotation)

bond length l , bond angle θ : fixed

torsion angles rotation is taken to be hindered by a potential $U(\Phi)$

The probability of any value of the torsion angle Φ is taken to be proportional to the Boltzmann factor $\exp(-U(\Phi)/kT)$

$$\langle r^2 \rangle = nl^2 \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right) \left(\frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right)$$

$$\langle \cos \phi \rangle = \frac{\int \cos \phi \exp(-U(\phi) / kT) d\phi}{\int \exp(-U(\phi) / kT) d\phi}$$



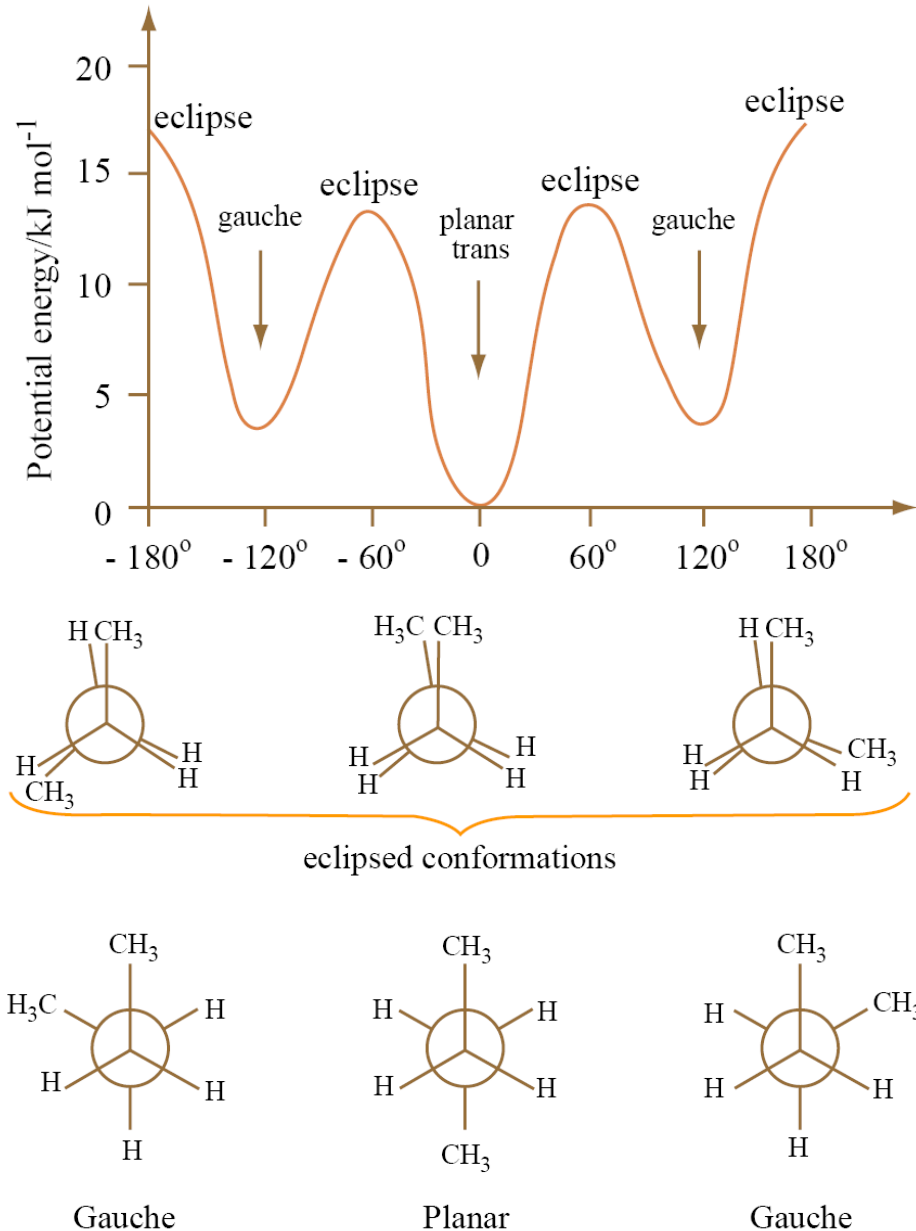
RIS (Rotational Isomeric State)

bond length l , bond angle θ : fixed

For relatively high barrier b/n *trans* and *gauche* states, the value of the torsion angles Φ are close to the minima.

(t, g+, g-)

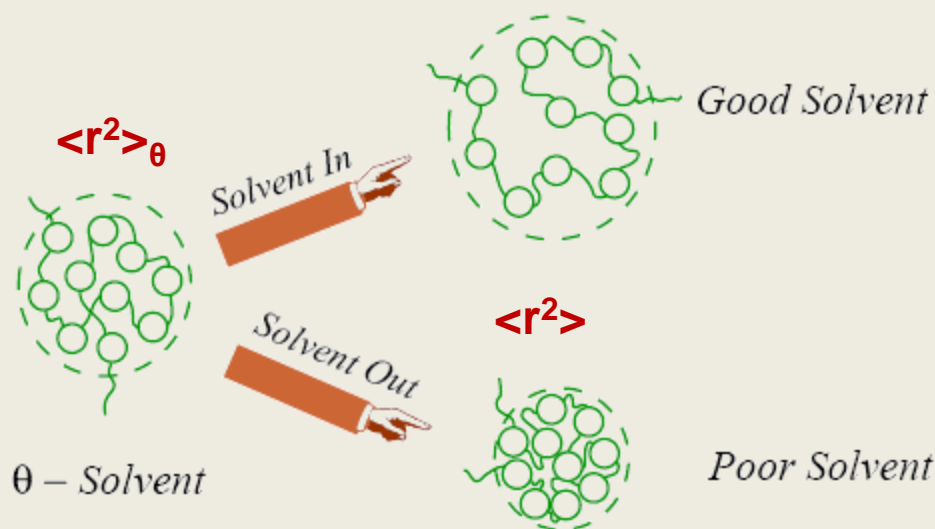
In RIS model, each molecule is assumed to exist only in discrete torsional states corresponding to the potential energy minima.



RIS (Rotational Isomeric State)

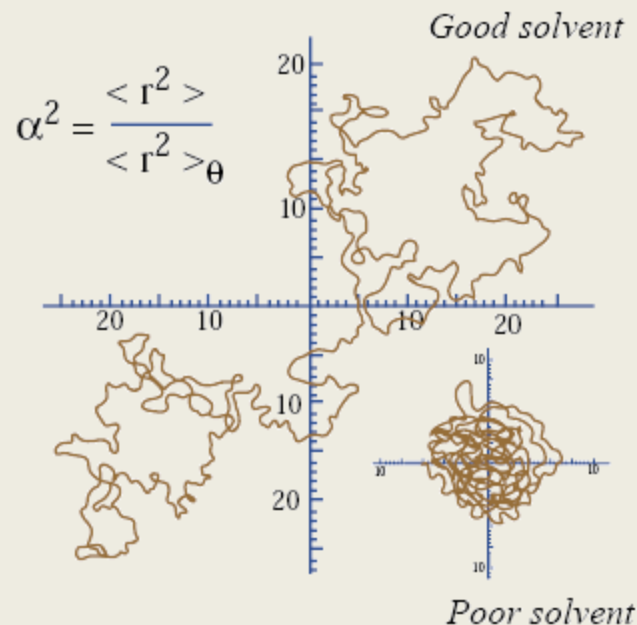
Solvent Quality and Chain Dimensions

Local Picture



Global Picture

Solvent quality factor



$$\alpha^2 = \frac{\langle r^2 \rangle}{\langle r^2 \rangle_\theta}$$

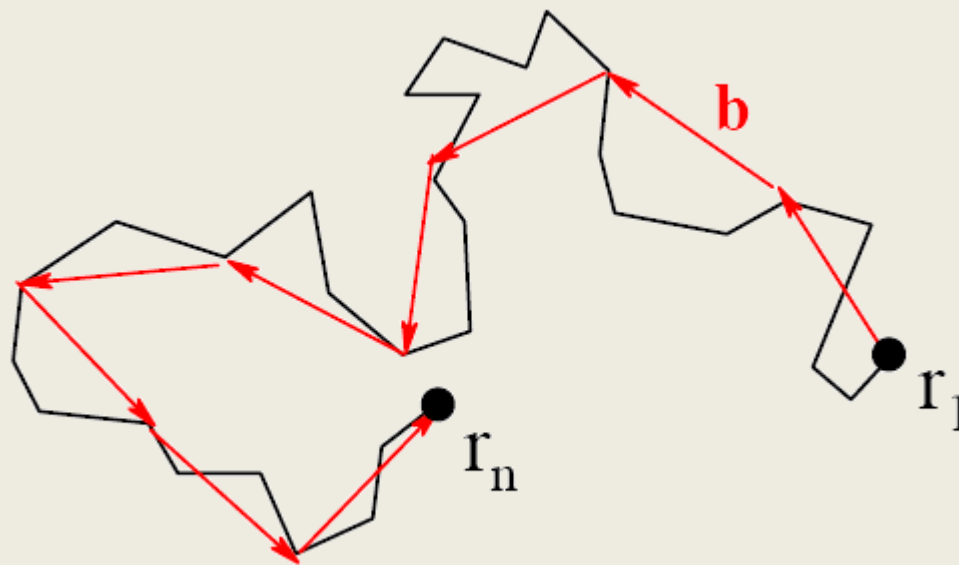
Solvent Quality Factor



Physicist's Universal Chain



Coarse grained model of N Kuhn steps



Fewer and larger steps

$$\langle r^2 \rangle = Nb^2$$



5.3. Conformation of the Polymer Chain

5.3.3. Models of Polymer Chains in the Bulk Amorphous State

Fig 5.5 Models of the amorphous state in pictorial form.



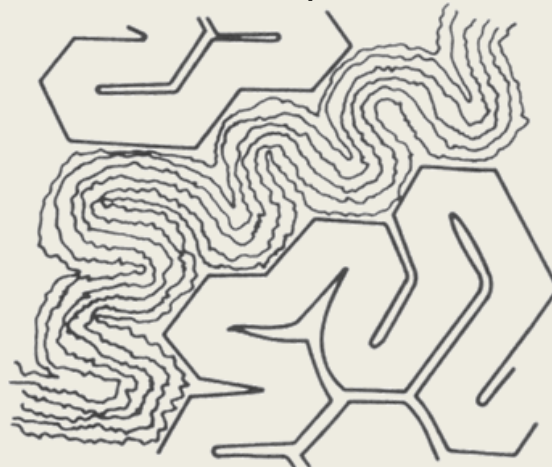
(a) P. J. Flory



(b) V. P. Privalko and
Y. S. Lipatov



(c) G. S. Y. Yeh



(d) W. Pechhold

- (a) Flory's random coil model
- (b) Privalko and Lipatov randomly folded chain conformation
- (c) Yeh's folded-chain fringed micellar model
- (d) Pechhold's meander model

→ For details, see Appendix 5.1
in the text book

5.4. Macromolecular Dynamics



- ❖ Polymer motion can take two forms :
 - (a) the chain can change its overall conformation, as in relaxation after strain,
or
 - (b) it can move relative to its neighbors.
- Self-Diffusion = subcase of Brownian motion, being induced by random thermal processes.
- ❖ For center-of-mass distance diffused $\propto t^{1/2}$



5.4. Macromolecular Dynamics

5.4.1. The Rouse-Bueche Theory

- ❖ a polymer chain : a succession of equal submolecules, each long enough to obey the Gaussian distribution function.
- ⇒ submolecules are replaced by a series of beads connected by springs with the proper Hooke's force constant.

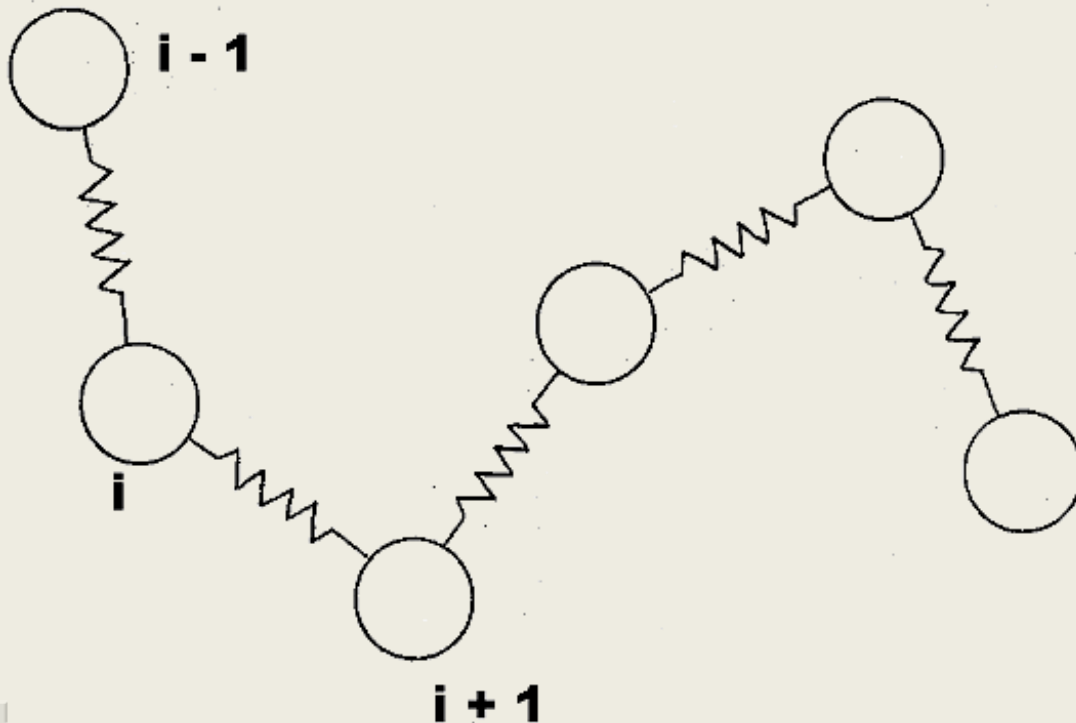


Fig.5.6 Rouse-Bueche bead and spring model of a polymer chain



5.4. Macromolecular Dynamics

- For this kind of molecular model, the restoring force f on a chain or chain portion

$$f = \frac{3kT\Delta x}{\bar{r}^2} \quad \text{where } \Delta x : \text{ the displacement} \\ r : \text{ the end-to-end distance}$$

- the restoring force on the i th bead

$$f_i = \frac{-3kT}{a^2}(x_{i-1} + 2x_i - x_{i+1}) \quad 1 \leq i \leq z-1 \quad \rightarrow \text{Appendix 5.2}$$

- It is assumed that the force is proportional to the velocity of the beads, which is equivalent to assuming that the beads behaves exactly as if it were a macroscopic bead in a continuous medium.
- The viscous force on the i th bead is given by

$$f_i = \rho \left(\frac{dx_i}{dt} \right) = \rho X_i \quad \text{where } \rho \text{ is the segmental frictional factor}$$

- The solution of the above matrix algebra yields the relaxation time τ

$$\tau_{p,i} = \frac{6\eta_0 M_i^2}{\pi^2 c R T M_w p^2} \quad \text{where } \eta_0 : \text{ the bulk-melt viscosity} \\ p : \text{ a running index} \\ c : \text{ the polymer concentration} \quad \rightarrow \text{Appendix 5.3}$$



5.4. Macromolecular Dynamics

- ❖ Rouse-Bueche theory is highly successful in establishing the idea that chain motion is responsible for creep, relaxation, and viscosity, although quantitative agreement with experiment was generally unsatisfactory.
- ❖ Rouse-Bueche theory is useful especially below 1% concentration.
- ❖ While it does not speak about the center-of-mass diffusional motions of the polymer chains, the theory is important because it serves as a precursor to the de Gennes reptation theory.

❖ Example:

For polyisobutylene at 25°C, τ_1 is about $10^{2.5}$ hr. Use above eqns. to estimate the viscosity of this polymer, remembering that $M = 1.56 \times 10^6$. As a check on the value obtained, use the Debye viscosity equation (refer to Appendix 5-3), to evaluate M_c , that threshold for entanglements, if it is known that $\rho = 4.47 \times 10^{-8}$ kgs⁻¹ at this temperature. As a semi-empirical correction, multiply ρ by $(M/M_c)^{2.4}$ to account for entanglements.

density : 1.0 gcm⁻³

unperturbed bond length l_0 : 5.9×10^{-10} m

5.4. Macromolecular Dynamics

5.4.2. The Reptation and Chain Motion

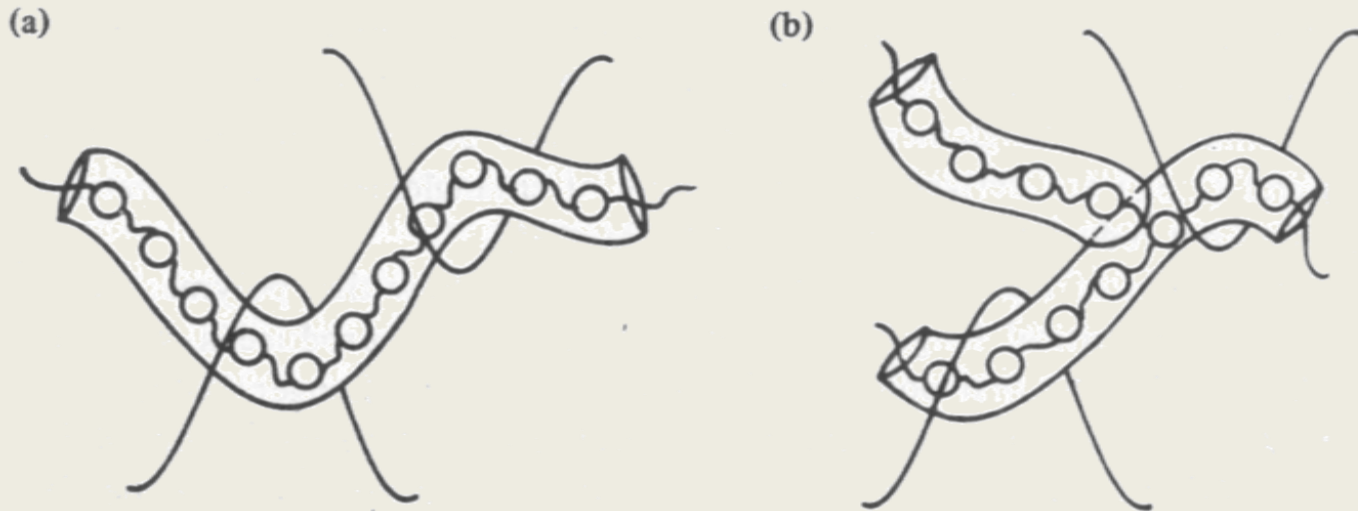


Fig. Reptation model for entanglement for (a) a linear molecule and (b) a branched molecule

→ Refer to Appendix 5.4

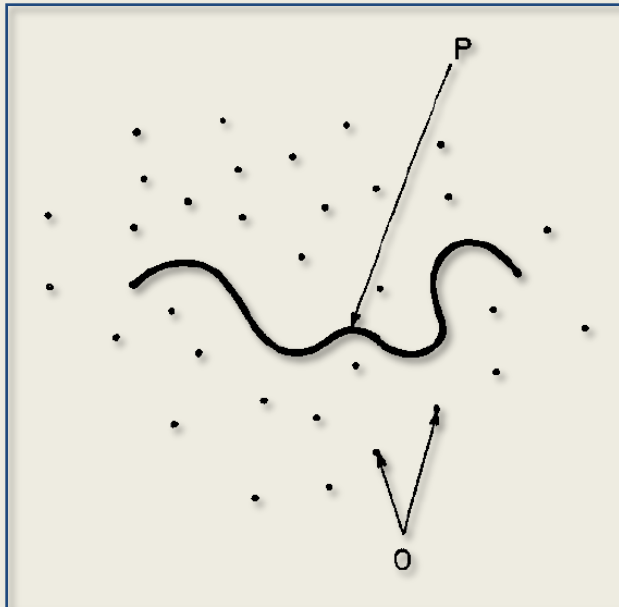


5.4. Macromolecular Dynamics

5.4.2. The Reptation and Chain Motion

5.4.2.1. The de Gennes Reptation Theory

- ❖ Rouse-Bueche theory is highly successful in establishing the idea that chain motion is responsible for creep, relaxation, and viscosity, although quantitative agreement with experiment was generally unsatisfactory.
- ❖ In 1971, de Gennes introduced the reptation theory of polymer chains that consisted of a single polymeric chain (P), trapped inside a 3-dimensional network (G) such as a polymeric gel. (*J. Chem. Phys.* **55**, 572 (1971))



- The chain P is not allowed to cross any of the obstacles O; however, it may move in a snake-like fashion among them.
- The snake-like motion is called “reptation”.

5.4. Macromolecular Dynamics

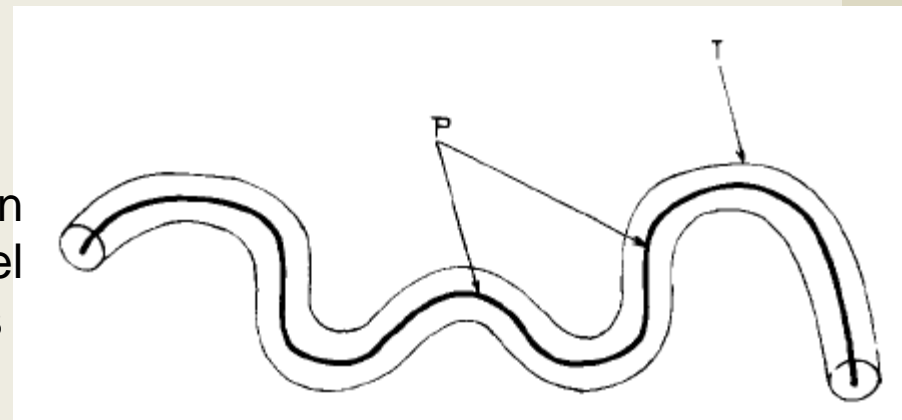
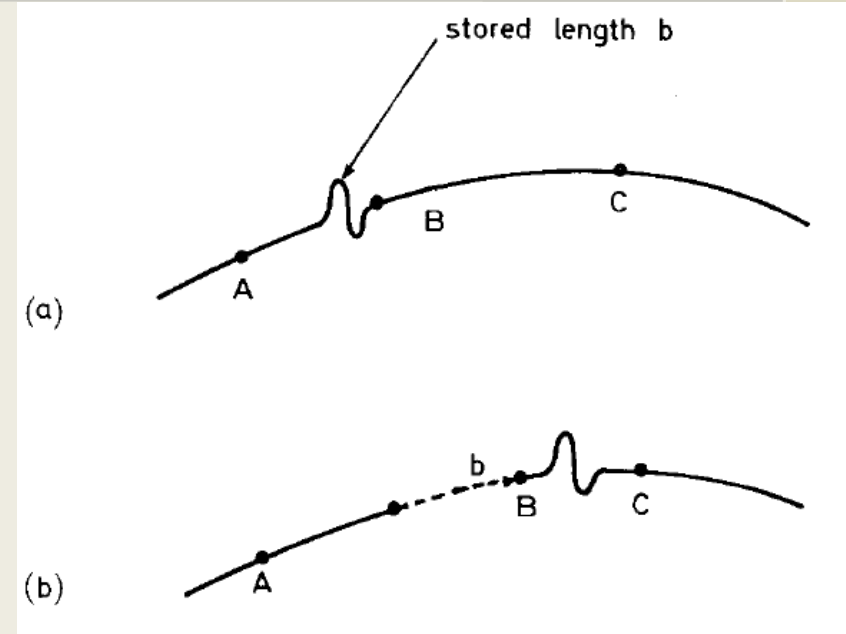
- The chain is assumed to have certain defects, each with stored length b .
- These defects migrate along the chain in a type of defect current.
- When the defects move, the chain progresses, as shown in Fig. 5.9
- The velocity of the n th mer is related to the defect current J_n by

$$\frac{d\vec{r}_n}{dt} = bJ_n$$

- It is found that the self-diffusion coefficient, D , of a chain in the gel depends on the molecular weight M as

$$D \propto M^{-2}$$

→ Appendix 4.1 in Text book



An infinitely long chain P cannot move sideways: It is trapped in a thin tube T.

5.4. Macromolecular Dynamics

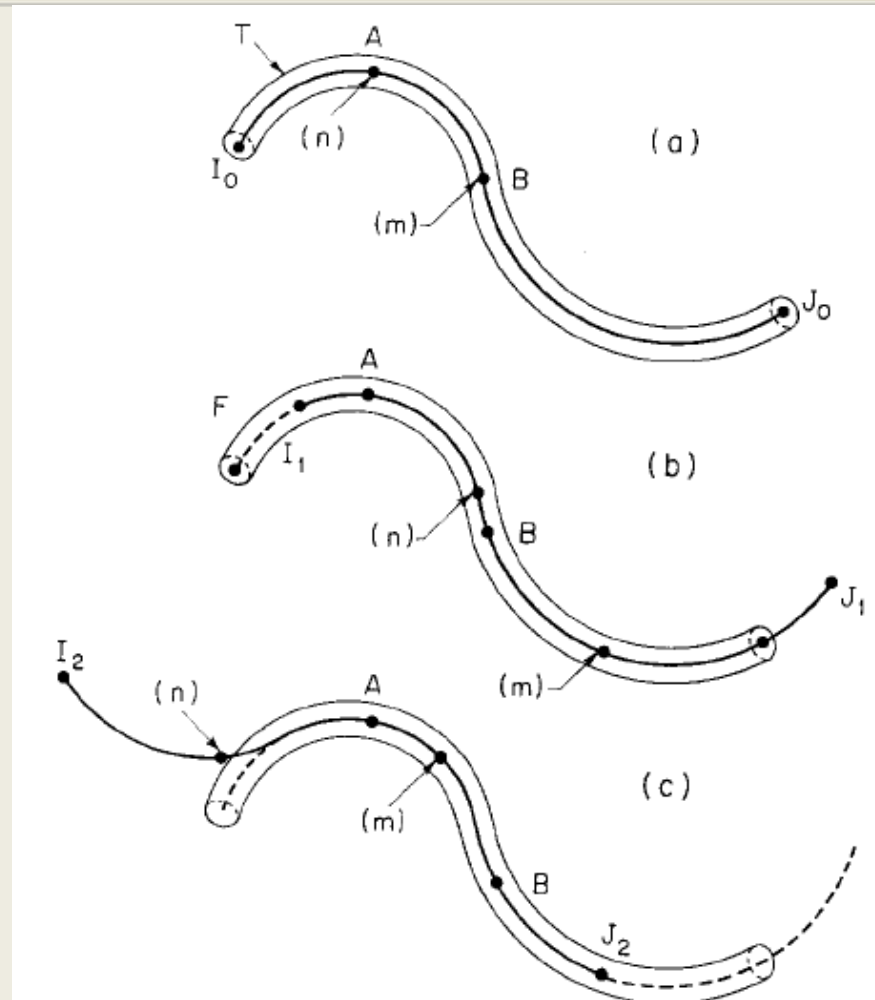


Fig. 5.9 Successive steps of a chain inside a gel.

- (a) Initial position: the chain is restricted to a certain tube T
- (b) First stage: the chain has moved to the right by reptation
- (c) Second state: the chain has moved to the left

5.4. Macromolecular Dynamics

- ❖ The de Gennes theory of reptation as a mechanism for diffusion has also seen applications in the dissolution of polymers, termination by combination in free radical polymerizations, and polymer-polymer welding.
- ❖ Dr. Pierre de Gennes was awarded the 1991 Nobel Prize in Physics for his work in polymers and liquids crystals.

Nobel Prize winners for advances in polymer science and engineering

Scientist	Year	Field	Research and Discovery
Hermann Staudinger	1953	Chemistry	Macromolecular Hypothesis
Karl Ziegler and Giulio Natta	1963	Chemistry	Ziegler-Natta catalysts and resulting stereospecific polymers like isotactic PP
Paul J. Flory	1974	Chemistry	Random coil and organization of polymer chain
Pierre de Gennes	1991	Physics	Reptation in polymers and polymer structures at interface
A.J. Heeger, A.G. MacDiarmid and H. Shirakawa	2000	Chemistry	Discovery and development of conductive polymers

5.4. Macromolecular Dynamics

5.4.3. Nonlinear Chains

: *How do branched, star, and cyclic polymers diffuse?*

- Two possibilities for translational motion
- ① One end way move forward, pulling the other end and the branch into the same tube.
 - ⇒ This process is strongly resisted by the chains as it requires a considerable decrease in entropy to cause a substantial portion of a branch to lie parallel to the main chain in an adjacent tube.
- ② Renew its conformation by retracting a branch so that it retraces its path along the confining tube to the position of the center mer. Then, it may extend outward again, adopting a new conformation at random
 - ⇒ energetically much feasible process

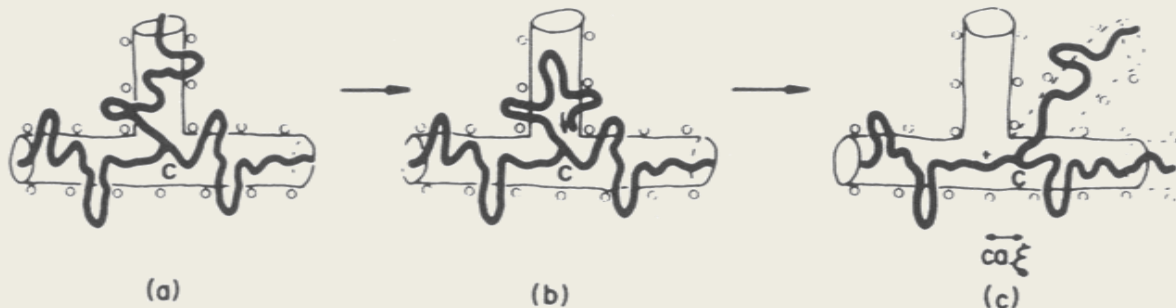


Fig. 5.10 The basic diffusion steps for a branched polymer. Note motion of mer C, which requires a fully retracted branch before it can take a step into a new topological environment.

5.4. Macromolecular Dynamics

- ❖ The probability P_1 of an arm of n -mers folding back on itself

$$P_1 = \exp(-\alpha n/n_c) \quad \text{where } n_c : \text{the critical No. of mers between physical entanglements}$$

α : a constant.

⇒ diffusion in branched-chain polymers is much lower than in linear chains

- ❖ Cyclic polymers are even more sluggish, because the ring is forced to collapse into a quasilinear conformation in order to have center-of-mass motion.

5.4.4. Experimental Methods of Determining Diffusion Coefficients

- by measuring the broadening of concentration gradients as a function of time
- by measuring the translation of molecules directly using local probes such as NMR





Keywords in Chapter 6

- The Fringed Micelle Model
 - Spherulite Formation
- The Avrami Equation, Keith-Padden Kinetics, Hoffman's theory
 - Extended Chain Crystallization

