

3.063 Polymer Physics

Spring 2007

- Viewpoint: somewhat more general than just polymers:

“Soft Matter”

**Polymers, Colloids, Liquid Crystals,
Nanoparticles and Hybrid Organic-
Inorganic Materials Systems.**

Reference: Young and Lovell, Introduction to Polymer Science

_____ (recommended)

Demos and Lab Experiences:

Molecular Structural Characterization (DSC, GPC, TGA, Xray, AFM, TEM, SEM...) and Mechanical & Optical Characterization

Course Info

eltweb.mit.edu/3.063 - course website: notes, hmwks...

Eric Verploegen

Ms. Juliette Braun

Office hours - How are Wednesdays at 230-330pm?

Mini Assignment

Send Prof. Thomas

- contact info/ name/year/major/email/credit/listener
- and interests relevant to topics in this course
- Any expertise you have on lab demos, characterization tools, cool samples...

Hard vs. Soft Solids

(for $T \sim 300\text{K}$)

- **Hard matter**: metals, ceramics and semiconductors: typically highly crystalline. $U \gg kT$
- **Soft matter**: polymers, organics, liquid crystals, gels, foods, life(!). $U \sim kT$
- Soft matter is therefore sometimes called “delicate material” in that the forces holding the solid together and causing the particular atomic, molecular and mesoscopic arrangements are relatively weak and these forces are easily overcome by thermal or mechanical or other outside influences. Thus, the interplay of several approximately equal types of forces affords the ability to access many approximately equal energy, metastable states. One can also “tune” a structure by application of a relatively weak stimulus. Such strong sensitivity means that soft matter is inherently good for sensing applications.

In 3.063 we aim to understand:

- **The Key Origins of Soft Solid Behavior:**

- relatively weak forces between molecules

- many types of bonding, strong anisotropy of bonding (intra/inter)

- wide range of molecular shapes and sizes, distributions

- large variety of chemistries/functionalities

- fluctuating molecular conformations/positions

- presence of solvent, diluent

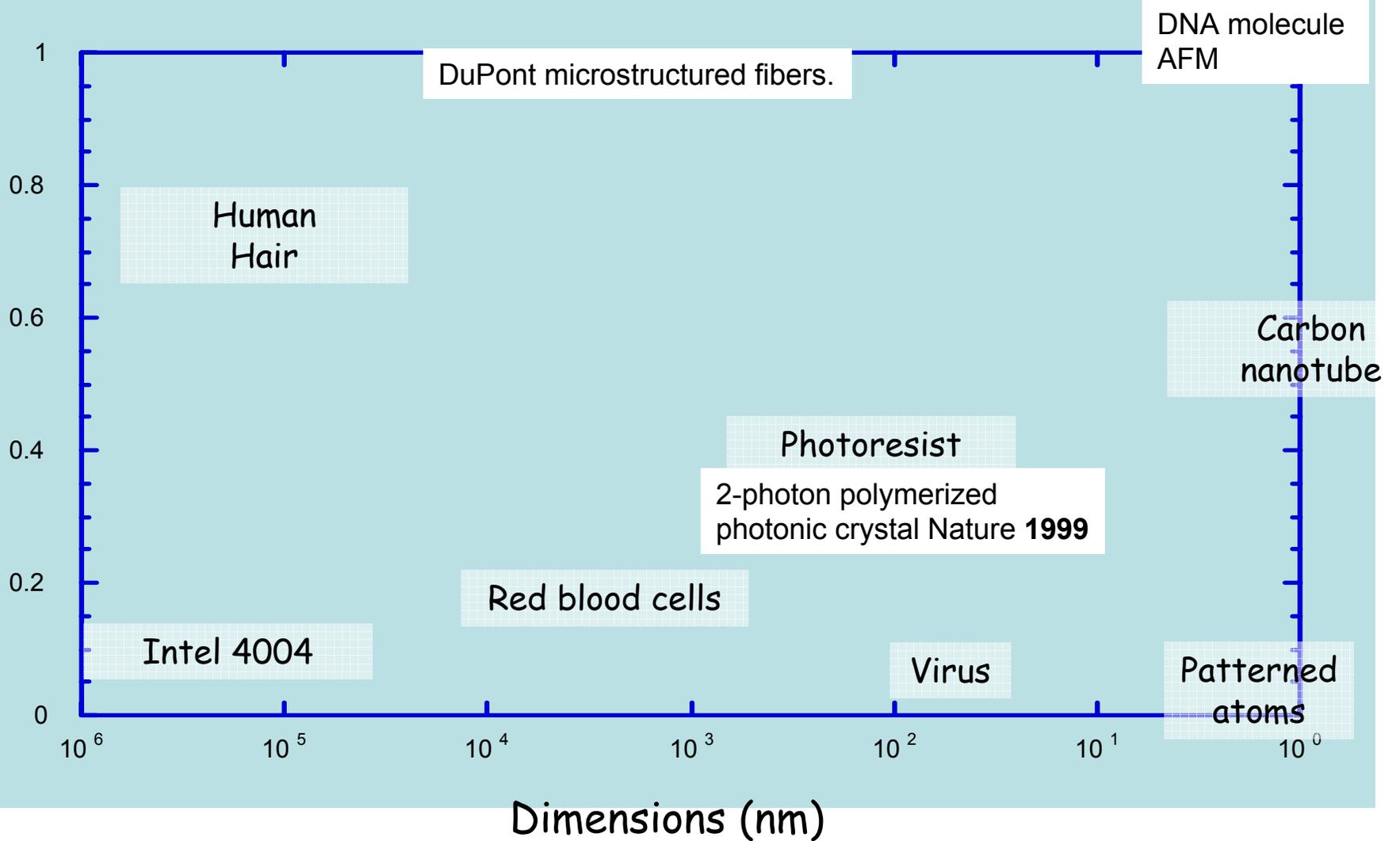
- entanglements

- many types of entropy

- architectures/structural hierarchies over several length scales

- **Characterization of the molecular structures and the properties *of the soft solids comprised of these molecules***

Scale in Soft Matter



Interactions in Soft Solids

- Molecules are predominantly held together by strong covalent bonds.
- Intramolecular - Rotational isomeric states
- Intermolecular potential
 - Hard sphere potential
 - Coulombic interaction
 - Lennard Jones potential (induced dipoles)
 - Hydrogen bonding (net dipoles)
 - “hydrophobic effect” (organics in water)

Polyelectrolyte Domain Spacing Change by e-Field

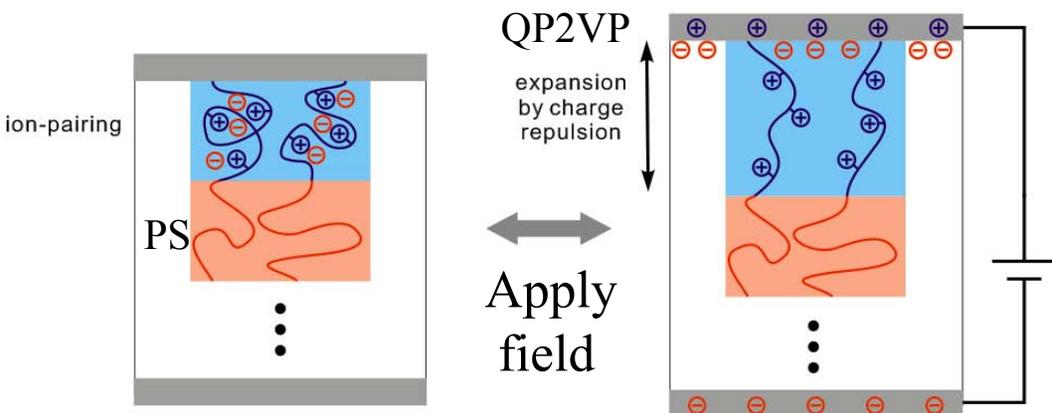
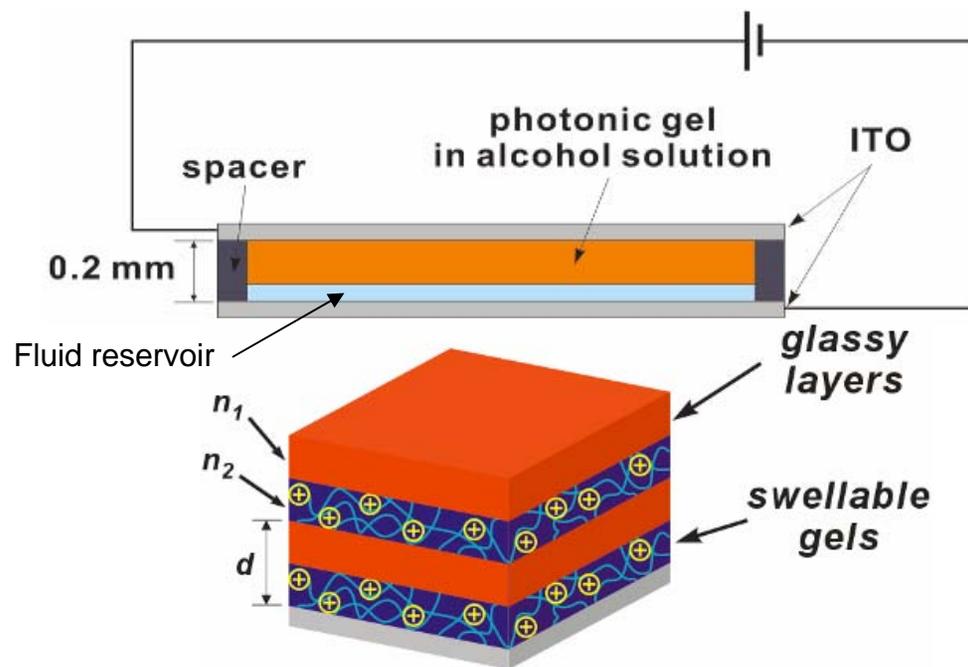


Photo of tunable gels removed due to copyright restrictions. □ □



Initial film thickness: $\sim 3 \mu\text{m}$

Total # of layers: ~ 30 layers

$$n_{\text{PS}} - n_{\text{P2VP}} \sim 1.6$$

$$n_{\text{H}_2\text{O}} = 1.33$$

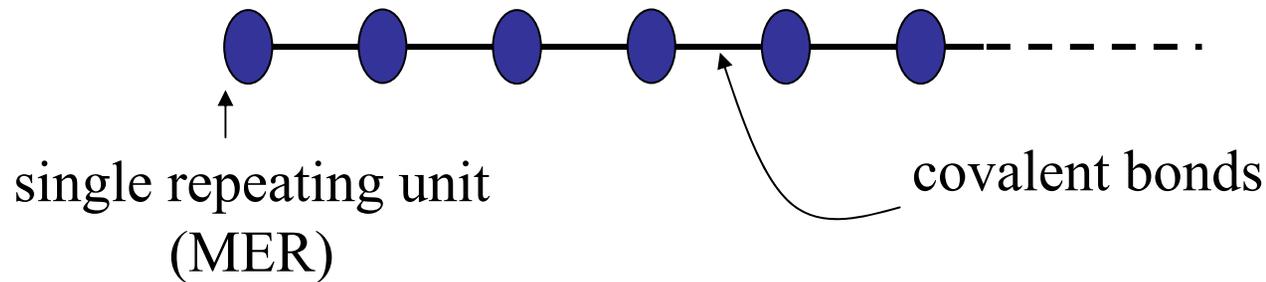
Structure of Soft Solids

- SRO - (always present in condensed phases)
 - intra- and inter-
- LRO - (sometimes present)
 - Spatial: 1D, 2D, 3D periodicities
 - Orientational
- Order parameters (translational, orientational...)
- Defects -
 - influence on properties; at present defects are largely under-appreciated;
 - e.g. transport across membranes...self assembly-nucleation, mutations, diseases
- Manipulation of Orientation and Defects: Develop methods to process polymers/soft solids to create controlled structures/hierarchies and to eliminate undesirable defects

Polymers/Macromolecules

H. Staudinger (1920's) colloidal ass'y vs. molecule

“MACROMOLECULAR HYPOTHESIS”



A SINGLE REPEAT UNIT

→ MONOMER (M)

MANY REPEAT UNITS

→ POLYMER (M)_n

“Macromolecule” - more general term than polymer

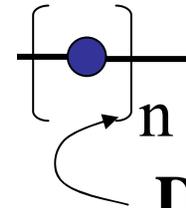
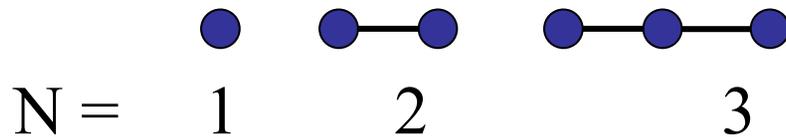
POLYMERIZATION

Common reactions to build polymers:



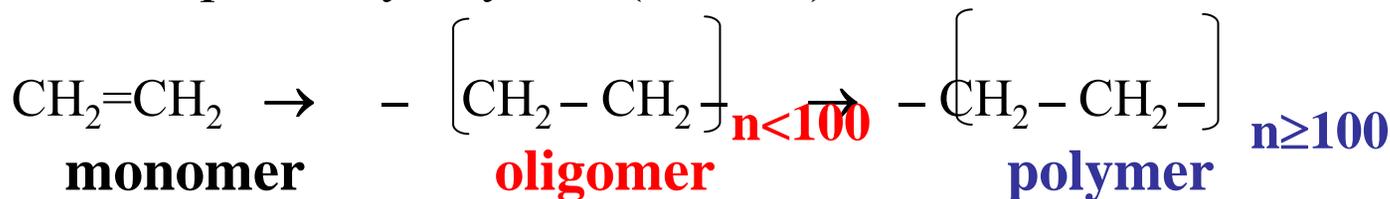
Think of a polymer as the endpoint of a HOMOLOGOUS SERIES:

How do the properties change with n?



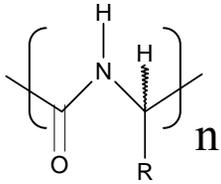
**Degree of
Polymerization**

Example: Polyethylene ($n \approx 10^4$)

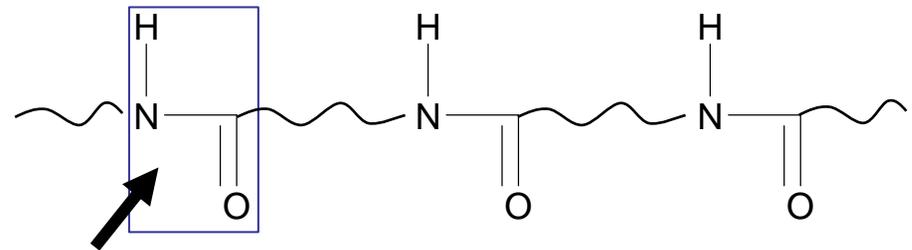


Proteins and Polyamides (Nylons)

Proteins are “decorated nylon 2”

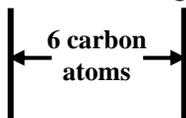
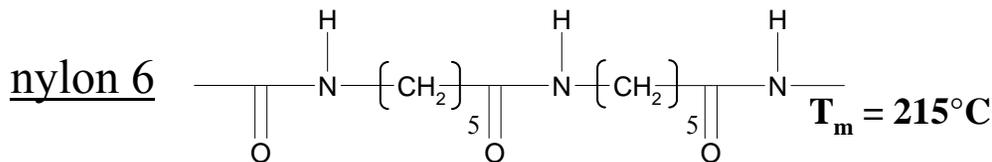
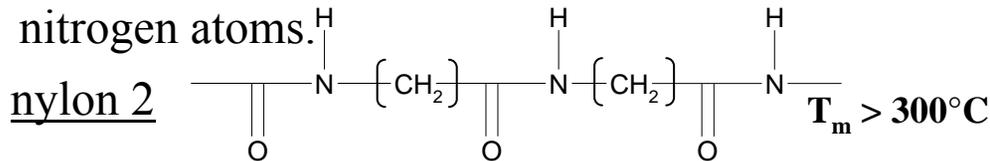


R = various side groups
(20 possible amino acids)
R = H → glycine
R = CH₃ → alanine, etc.



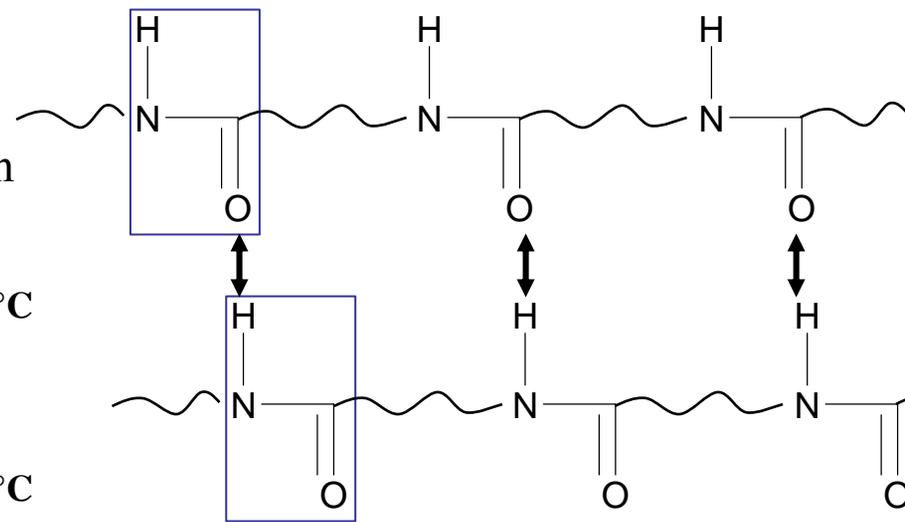
amide linkage

- Members of the nylon family are named by counting the number of carbon atoms in the backbone between nitrogen atoms.



note nylon $n=\infty$ = polyethylene (!)

$T_m \sim 140^\circ\text{C}$



Hydrogen bonds

Characteristic Features of Macromolecules

- **Huge Range of Structures & Physical Properties**

- **Some examples:**

- **Insulating -----> Conducting**
- **Light emitting**
- **Photovoltaic, Piezoelectric**
- **Soft elastic -----> Very stiff plastic**
 - **Ultra large reversible deformation**
 - **Highly T, t dependent mechanical properties**
- **Zero/few crystals -----> High Crystallinity**

- **Readily Tunable Properties:**

Weak interactions between molecules, so chains can be readily reorganized by an outside stimulus

Chain Conformations of Polymers: 2 Extremes

n is the number of links in the chain with each link a step size l so the contour length of the chain L is nl ;

As a measure of size of the chain, we can have two situations:

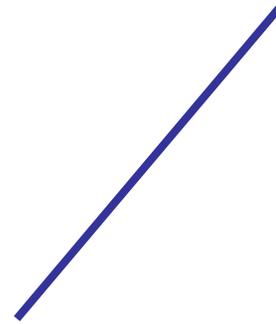
- **1. Rigid rod:** Fully Extended Conformation
 - $\langle r^2 \rangle^{1/2} \approx n l = L$
- **2. Flexible coil:** Random Walk
 - $\langle r^2 \rangle^{1/2} \approx n^{1/2} l$ - note this is *much* smaller than L

Extreme Conformations of (Linear) Polymers

Isolated molecules

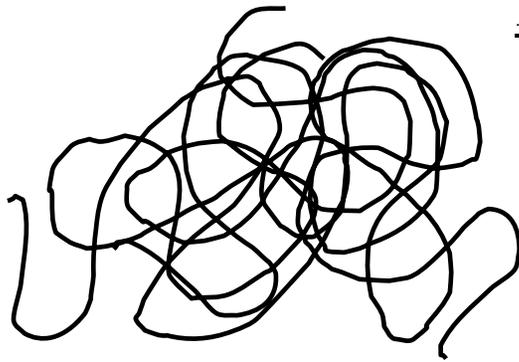


Flexible Coil

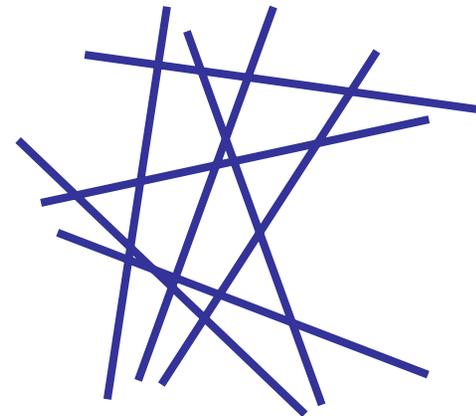


Rigid Rod

Entanglements

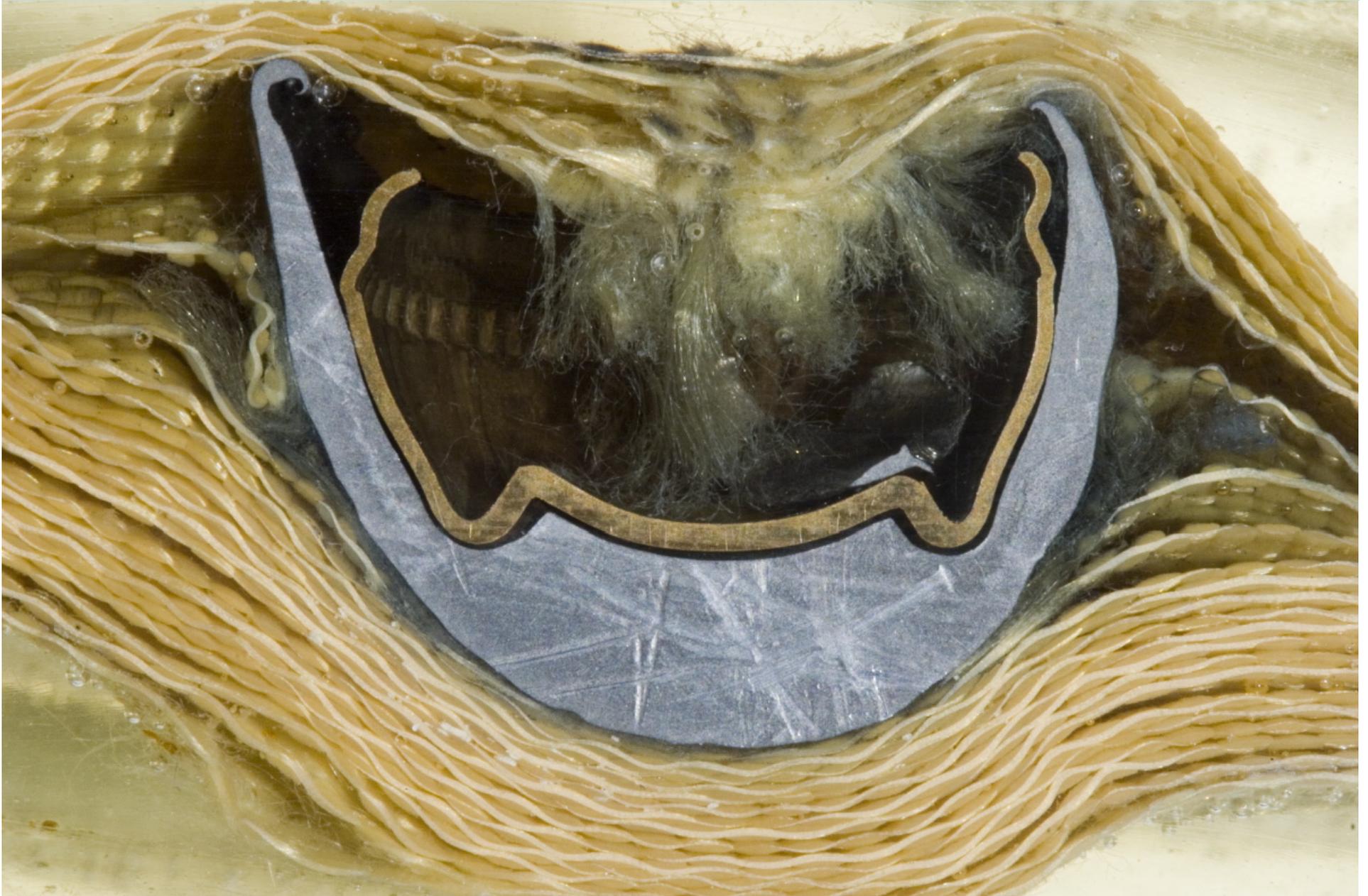


Flexible Coils



Rigid Rods

.357 Magnum, 22 layers of Kevlar



Polymer Architectures

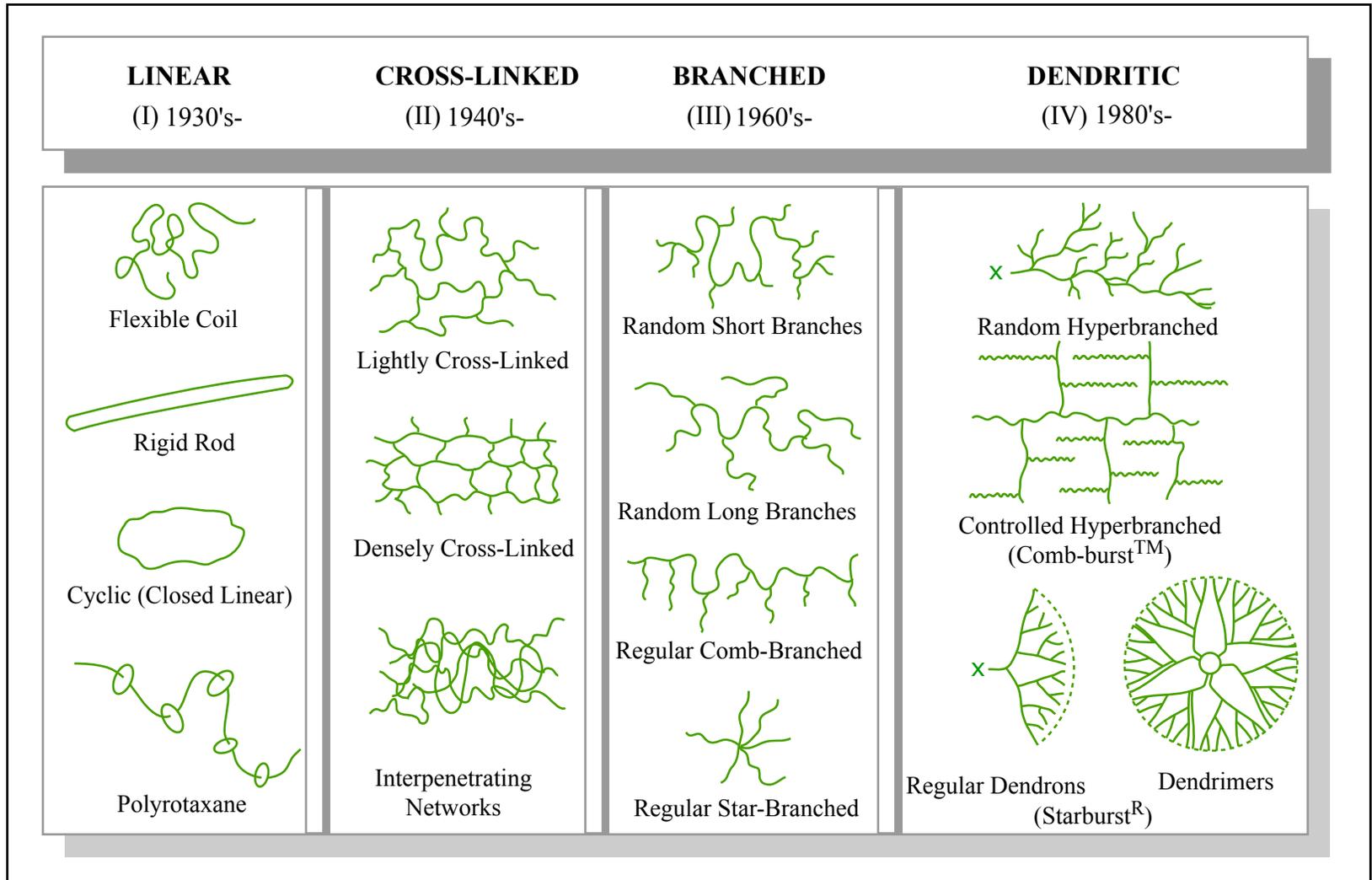
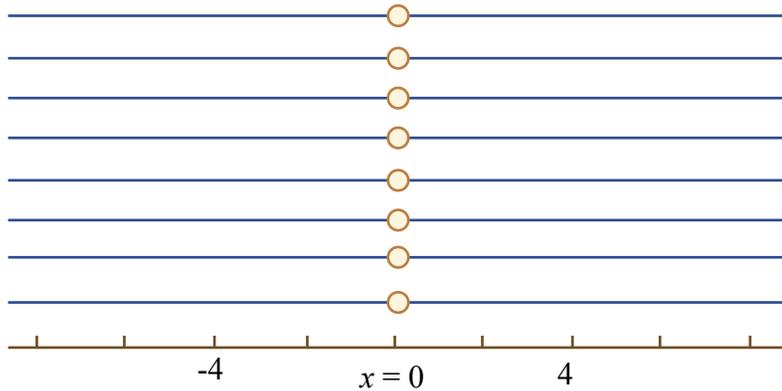


Figure by MIT OCW.

1-D Random Walk

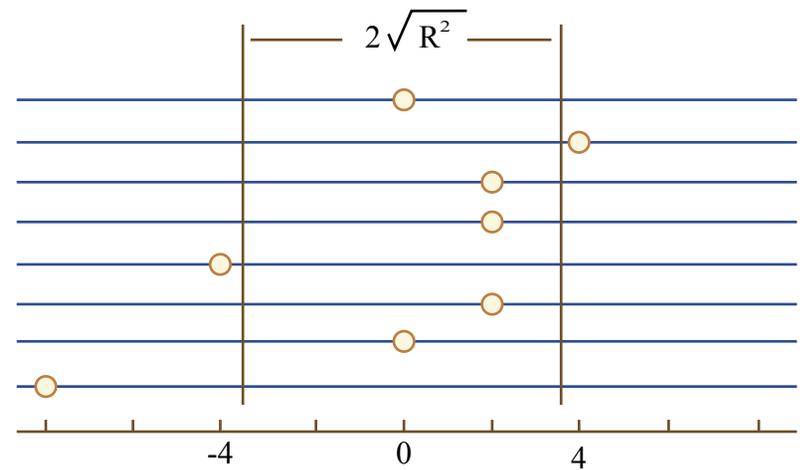
$$\langle R^2 \rangle = N b^2$$

N steps of size b



(a)

(a) Initial distribution of atoms, one to a line.



(b)

(b) Final distribution after each atom took 16 random jumps. $2\sqrt{R^2}$ is the calculated root mean square for the points shown.

Gaussian Distribution

$$P(r,n) = \left(\frac{2\pi n l^2}{3} \right)^{-3/2} \exp\left(-\frac{3r^2}{2nl^2} \right)$$

Note: units are [volume⁻¹]

$$\int_0^\infty P(r,n) 4\pi r^2 dr = 1$$

normalized probability

$$\langle r^2 \rangle = \int r^2 P(r,n) 4\pi r^2 dr$$

Probability of distance r
between 1st and n^{th}
monomer units for an
assembly of polymers
is a Gaussian distribution, here
shown for 3D

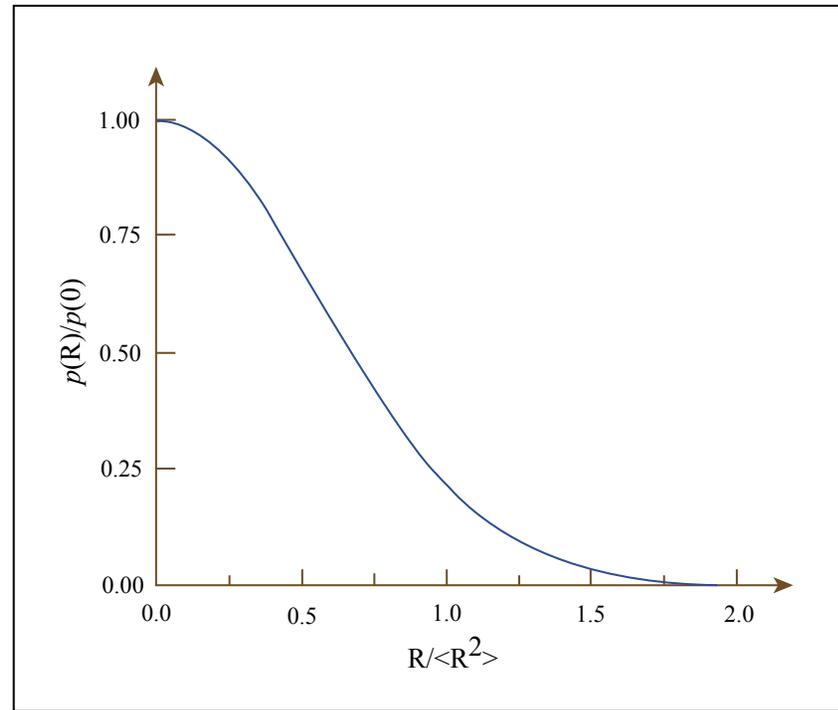


Figure by MIT OCW.

Flexible Coil Chain Dimensions

3 Related Models

- **Mathematician's Ideal Random Walk**

$$\langle r^2 \rangle = n l^2$$

- **Chemist's Chain in Solution and Melt**

$$\langle r^2 \rangle = n l^2 C_{\infty} \alpha^2$$

- **Physicist's Universal Chain**

$$\langle r^2 \rangle = N b^2$$

Mathematician's Ideal Chain

n monomers of length l $|l_i| = l$ *No restrictions on chain passing through itself (excluded volume),
no preferred bond angles*

$$\vec{r}_{l,n} = \vec{l}_1 + \vec{l}_2 + \dots + \vec{l}_n = \sum_{i=1}^n \vec{l}_i$$

$\langle \vec{r}_{l,n} \rangle = 0$ since $\{\vec{r}_{l,n}\}$ are randomly oriented

Consider $\langle r_{l,n}^2 \rangle^{\frac{1}{2}} \neq 0$

Scaling law: $\langle r_{l,n}^2 \rangle^{\frac{1}{2}} \propto n^{\frac{1}{2}}$

$$\langle \vec{r}_{l,n} \cdot \vec{r}_{l,n} \rangle = \langle \sum l_i \cdot \sum l_j \rangle$$

$$= \langle (\vec{l}_1 \cdot (\vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \dots)) + \vec{l}_2 \cdot (\vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \dots) + \dots \rangle$$

$l_1 \cdot l_1$	$l_1 \cdot l_2$	$l_1 \cdot l_3$	\dots	$l_1 \cdot l_n$	l^2	0	0	\dots	0
$l_2 \cdot l_1$	$l_2 \cdot l_2$				\cdot	l^2			\cdot
		\cdot			\cdot		\cdot		\cdot
			\cdot		\cdot		\cdot		\cdot
$l_n \cdot l_1$				$l_n \cdot l_n$	0				l^2

$$\langle \vec{r}_{l,n}^2 \rangle = nl^2 \qquad \langle \vec{r}_{l,n}^2 \rangle^{\frac{1}{2}} = n^{\frac{1}{2}}l$$

Chemists' Chain: Fixed Bond Angle (and Steric Hinderance)

Simpliest case:

*Chain comprised of
carbon-carbon single
bonds*

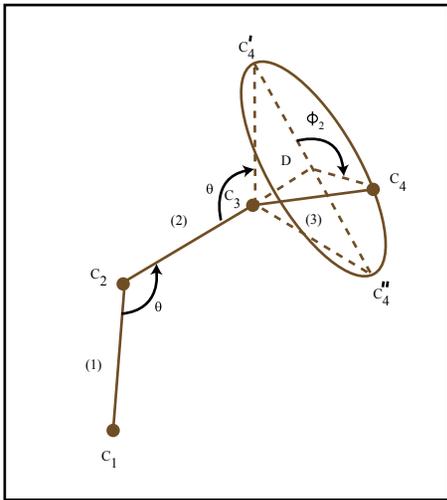


Figure by MIT OCW.

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

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

- projections of bond onto immediate neighbor

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

$$l^2, l^2(-\cos \theta), l^2 \cos^2 \theta, l^2(-\cos^3 \theta), \dots$$

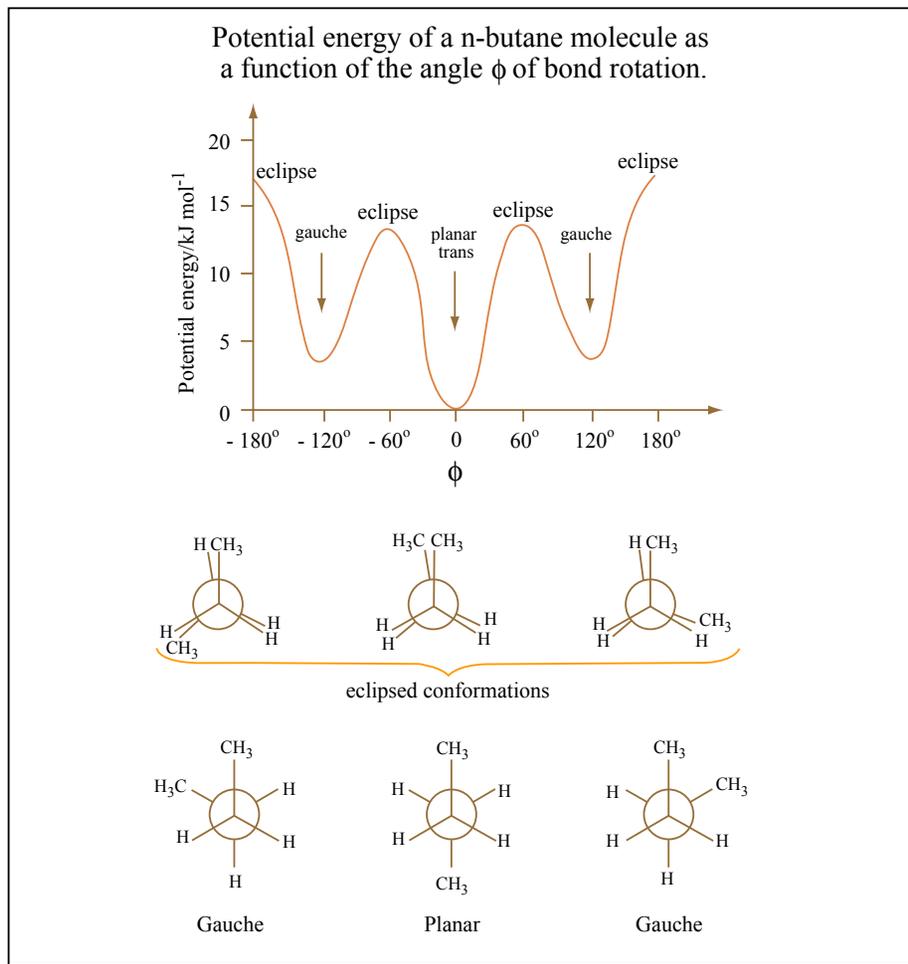
Factor out l^2 :

$$\begin{pmatrix} 1 & -\cos \theta & \cos^2 \theta & -\cos^3 \theta & \dots & (-\cos \theta)^{n-1} \\ -\cos \theta & 1 & -\cos \theta & \cos^2 \theta & \cdot & \\ \cos^2 \theta & -\cos \theta & 1 & -\cos \theta & \cos^2 \theta & \\ & & & 1 & & \\ & & & & \cdot & \\ & & & & & 1 \end{pmatrix}$$

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

Special case: Rotational conformations of n-butane



$$V(\phi)$$


Planar trans conformer is lowest energy

Views along the C2-C3 bond

High energy states

$$V(\phi)$$

Low energy states

Figure by MIT OCW.

Conformers: Rotational Isomeric State Model

- Rotational Potential $V(\phi)$
 - Probability of rotation angle phi $P(\phi) \sim \exp(-V(\phi)/kT)$
- Rotational Isomeric State (RIS) Model
 - e.g. Typical 3 state model : g^-, t, g^+ with weighted probabilities
 - Again need to evaluate $l_i \cdot l_{j+1}$ taking into account probability of a ϕ rotation between adjacent bonds

- This results in a bond angle rotation factor of $\frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle}$

combining

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

where

$$C_\infty = \left(\left(\frac{1 - \cos \theta}{1 + \cos \theta} \right) \left(\frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right) \right)$$

The so called “Characteristic ratio” and is compiled for various polymers

$$\langle \cos \phi \rangle = \frac{\int \cos(\phi) P(\phi) d\phi}{\int P(\phi) d\phi} \quad \text{with } P(\phi) = \exp(-V(\phi)/kT)$$

The Chemist's Real Chain

- Preferred bond angles and rotation angles:
 - θ, ϕ . Specific bond angle θ between mainchain atoms (e.g. C-C bonds) with rotation angle chosen to avoid short range intra-chain interferences. In general, this is called “steric hinderance” and depends strongly on size/shape of set of pendant atoms to the main backbone (F, CH₃, phenyl etc).
- Excluded volume: self-crossing of chain is prohibited (unlike in diffusion or in the mathematician's chain model): Such contacts tend to occur between more remote segments of the chain. The set of allowed conformations thus excludes those where the path crosses and this *forces* $\langle r_{l,n}^2 \rangle^{1/2}$ *to increase*.
- Solvent quality: competition between the interactions of chain segments (monomers) with each other vs. solvent-solvent interactions vs. the interaction between the chain segments with solvent. *Chain can expand or contract.*
 - monomer - monomer
 - solvent - solvent
 - monomer - solvent

$$\epsilon_{M-M} \text{ VS. } \epsilon_{S-S} \text{ VS. } \epsilon_{M-S}$$

Excluded Volume

- **The excluded volume of a particle is that volume for which the center of mass of a 2nd particle is excluded from entering.**
- **Example: interacting hard spheres of radius a**
 - **volume of region denied to sphere A due to presence of sphere B**
 - **$V = 4/3\pi(2a)^3 = 8 V_{\text{sphere}}$**
but the excluded volume is shared by 2 spheres so
 $V_{\text{excluded}} = 4 V_{\text{sphere}}$

Solvent Quality and Chain Dimensions

Theta θ Solvent

Solvent quality factor α

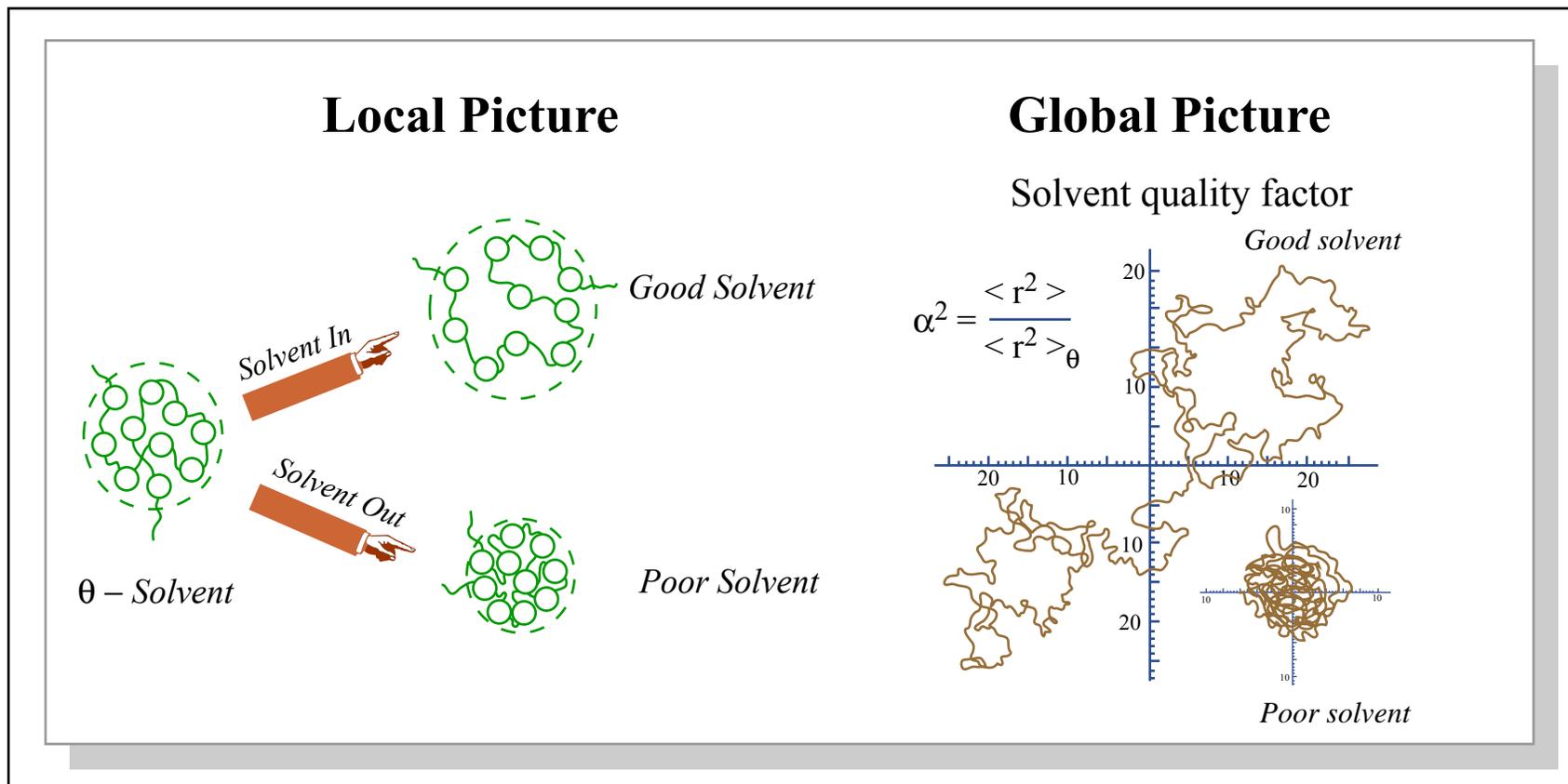


Figure by MIT OCW.

- Solvent quality:
 - M-M, S-S, M-S interactions: ϵ_{M-M} , ϵ_{S-S} , ϵ_{M-S}

Solvent Quality (α)

- **good solvent**: favorable ϵ_{SM} interaction so chain expands to avoid monomer-monomer contacts and to maximize the number of solvent-monomer contacts.

<i>good</i>	<i>poor</i>
$\alpha > 1$	$\alpha < 1$
0	0
$-\epsilon_{SS}$	$-\epsilon_{SM}$
$-\epsilon_{MM}$	$-\epsilon_{SS}$
$-\epsilon_{SM}$	$-\epsilon_{MM}$

- **poor solvent**: unfavorable ϵ_{SM} , therefore monomer-monomer, solvent-solvent interactions preferred so chain contracts.

$$\langle r^2 \rangle = n l^2 C_{\infty} \alpha^2$$

Theta Condition:

Choose a solvent and temperature such that...

- Excluded volume chain expansion is just offset by *somewhat* poor solvent quality and consequent slight chain contraction:

called

⇒ Θ condition ($\alpha = 1$)

$$\langle r^2 \rangle_{\theta} = n l^2 \cdot \left(\frac{\text{local steric influence}}{\text{bond angles, rotation angles}} \right) = n l^2 C_{\infty}$$

$$\alpha^2 = \frac{\langle r^2 \rangle}{\langle r^2 \rangle_{\theta}} \quad \text{“solvent quality factor”}$$

Actually expect a radial dependence to alpha, since segment density is largest at center of “chain segment cloud”.

Random Walks

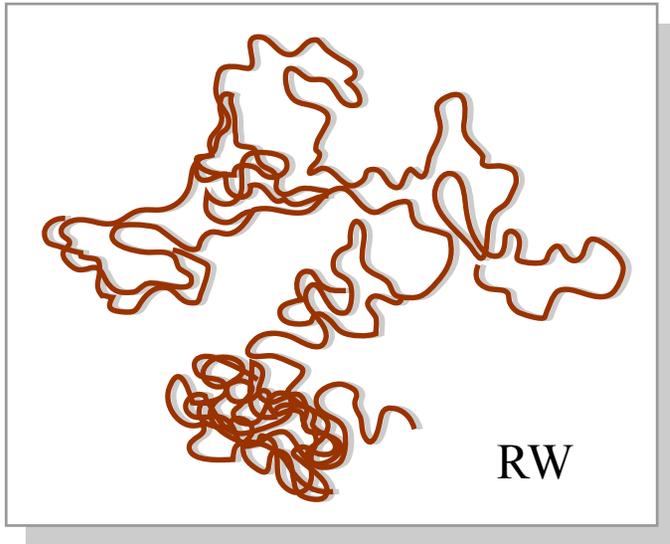
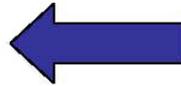


Figure by MIT OCW.

$\alpha = 1$, theta solvent

Θ condition: almost poor solvent

$$\langle r^2 \rangle_{\Theta} \sim nl^2$$



$\alpha > 1$, good solvent

Self Avoiding Random Walk (SARW)

$$\langle r^2 \rangle \sim n^{\frac{6}{5}}l^2$$

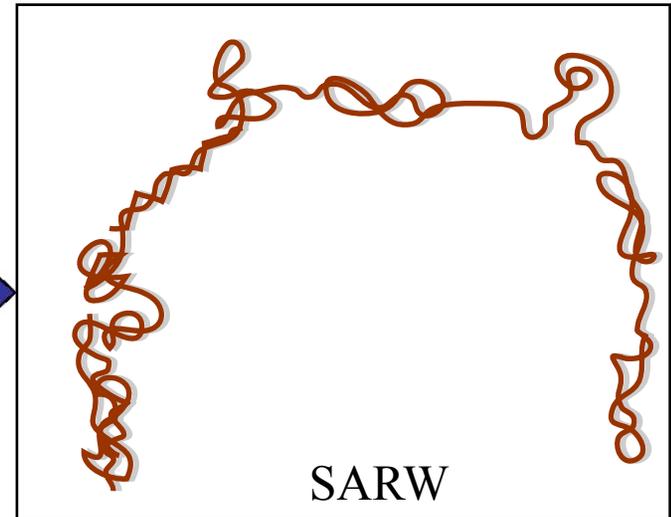


Figure by MIT OCW.