3.012 Fund of Mat Sci: Structure – Lecture 23

GLASSES

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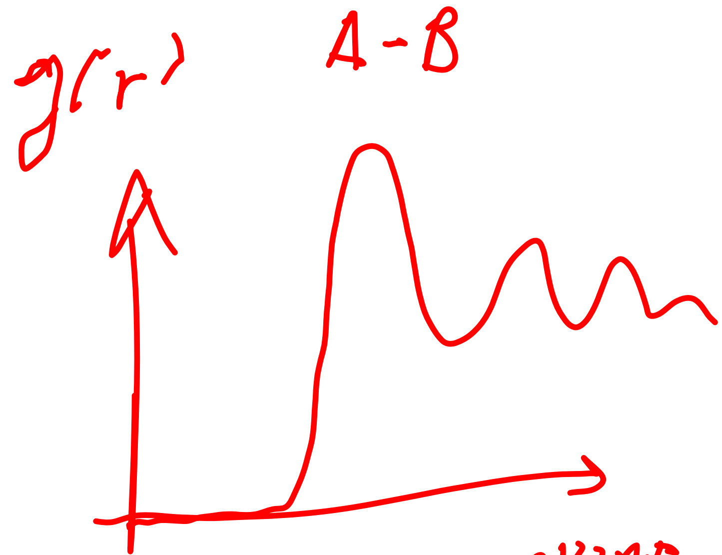
A photonic fiber made from polymeric and chalcogenide glasses (Prof. Fink)

Homework for Fri Dec 2

- Study: Chapter 2 of Allen-Thomas (2.5 excluded)

Last time:



1. Pair correlation functions
2. Bernal's model of hard spheres, Voronoi polyhedra
3. Polymers: homo and co-polymers, tacticity, glass transition, termoplastics-elastomers-thermosets, addition or condensation polymerization, chain or step growth

Glass transition temperature

Free volume, V_F – extra space beyond that is needed to provide an ordered crystalline packing.

$$V_F(T) \equiv V(T) - V_0(T)$$

- V_0 is occupied specific volume of atoms or molecules in the xline state *and* the spaces between them: V_{XL}.
- V_F increases as T increases due to the difference in the thermal expansion coefficients (α_g vs α_l).
- $V_0(T) \approx V_{XL}(T) \quad \leftrightarrow \quad$ take $\alpha_g \approx \alpha_{XL}$
- $V_F(T) = V_F(T_g) + (T-T_g)\dfrac{dV_F}{dT} \qquad T > T_g$
- define <u>fractional free volume, f_F</u>:

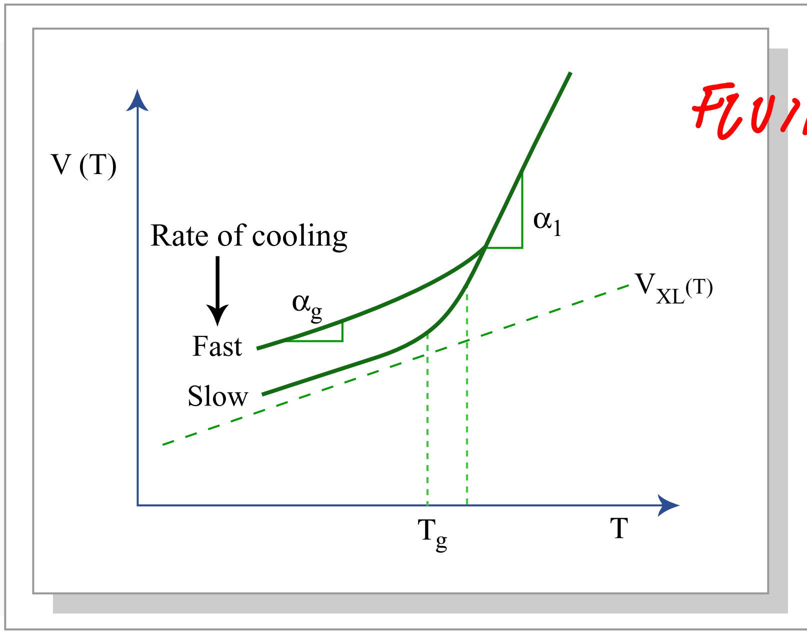


Figure by MIT OCW.

$$f_F(T) = f_F(T_g) + (T-T_g)\alpha_f \qquad \alpha_f = \alpha_l - \alpha_g$$

Viewpoint: T_g occurs when available free volume drops below critical threshold for structural rearrangement [VITRIFICATION POINT], *structure "jams up"*.

Glass transition temperature

Table removed for copyright reasons.

See page 39, Table 2.2 in in Allen, S. M., and E.L. Thomas. *The Structure of Materials.* New York, NY: J. Wiley & Sons, 1999.

Classification: mechanical

- Thermoplastics: (linear, or at most contain branches). Melting temperature, and a glass temperature. Recyclables.

- Elastomers: low degree of cross-linking (rubbers)

- Thermosets: high-degree of cross-linking, structural rigidity

Classification: structure

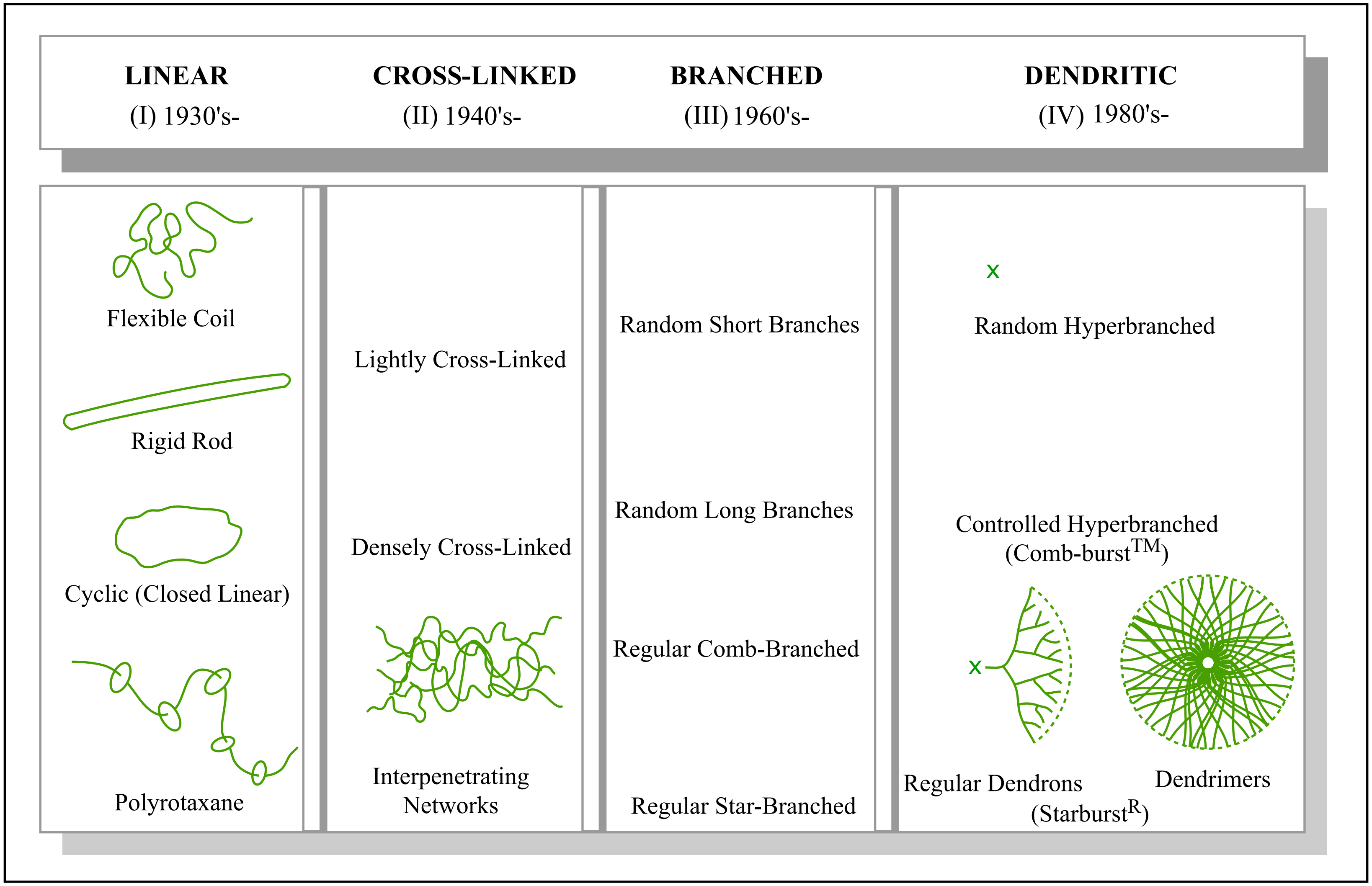
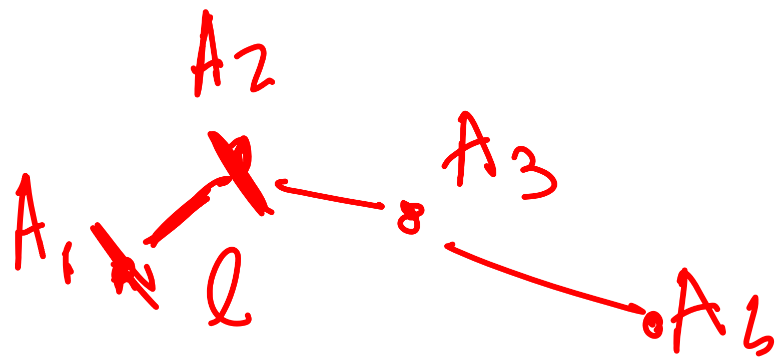
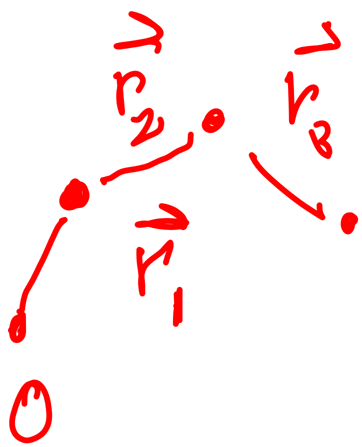


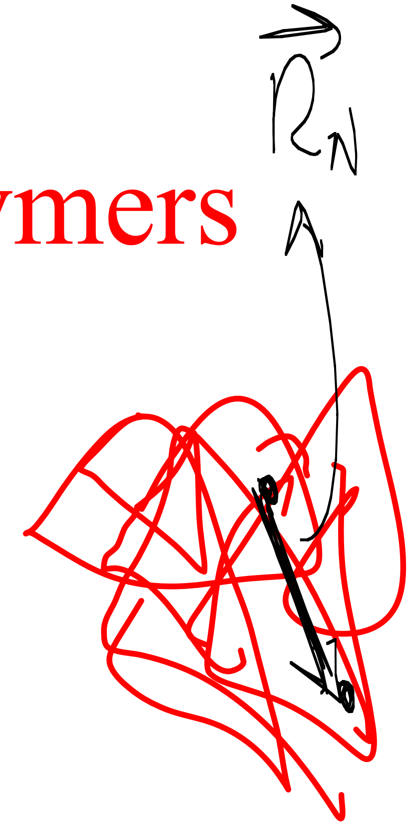
Figure by MIT OCW.

Random walks: size of polymers

N mers







END POINT OF A LINEAR POLYMER WITH N MERS

$$\vec{R}_N = \sum_{i=1}^{N} \vec{r}_i \qquad \|R_N\|^2 = \vec{R}_N \cdot \vec{R}_N$$

$\|R_N\| \propto \sqrt{N}\, \ell \qquad \|R_N\|^2 \propto N \ell^2$

Mean Square Displacements

$$\vec{R}_N \cdot \vec{R}_N = \left(\sum_{i=1}^{N} \vec{r}_i\right) \cdot \left(\sum_{j=1}^{N} \vec{r}_j\right) =$$

$$= \sum_{i,j=1}^{N} \vec{r}_i \cdot \vec{r}_j \Rightarrow \left\langle \sum_{i,j}^{N} \vec{r}_i \cdot \vec{r}_j \right\rangle =$$

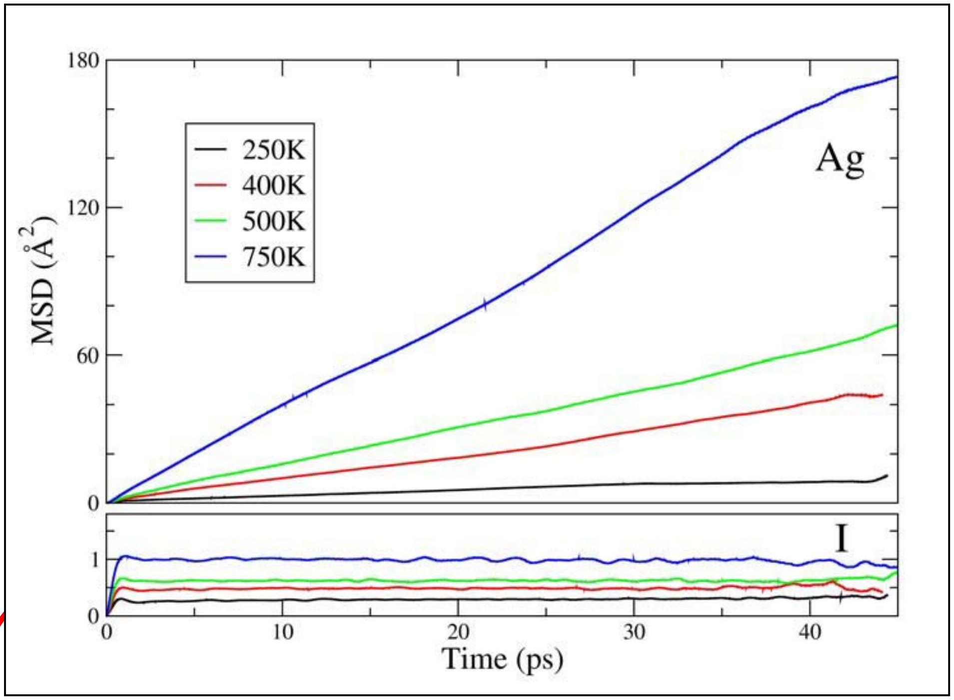
AVERAGE OVER MANY

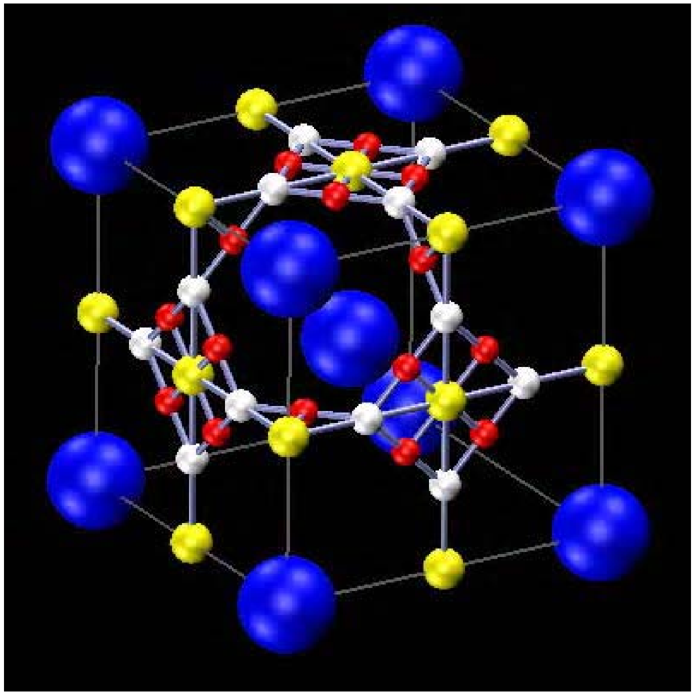
$$= \left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \left(\vec{r}_i + \sum_{\substack{j=1 \\ j \neq i}}^{N} \vec{r}_j \right) \right\rangle = \underbrace{\left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{r}_i \right\rangle}_{N\ell^2} + \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{N} \vec{r}_i \cdot \vec{r}_j \right\rangle = \emptyset$$

$\ell^2 \cos \nu$

RANDOM WALK MODEL $N l^2$

Mean Square Displacements

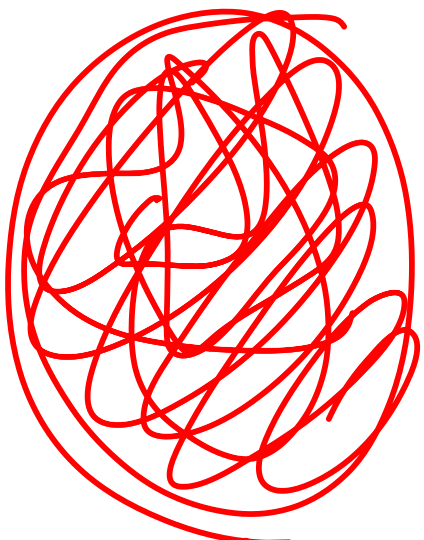




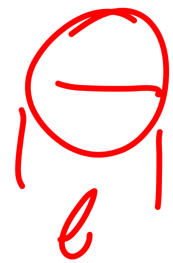
MEAN SQ DIS IODINES

AgI

Packing Fraction in Polymeric Glasses



N MERS



$$N \frac{4}{3}\pi\left(\frac{\ell}{2}\right)^3$$

$$R_N^2 \propto N\ell^2$$

VOLUME OF LINEAR CHAIN $= \frac{4}{3}\pi\left(N^{1/2}\ell\right)^3$

$$= \frac{4}{3}\pi N^{3/2}\ell^3$$

$$\frac{\text{VOL. LIN CHAIN}}{\text{VOL. N UNIT}} \propto \frac{N}{N^{3/2}} = \frac{1}{\sqrt{N}}$$

Solvent quality factor

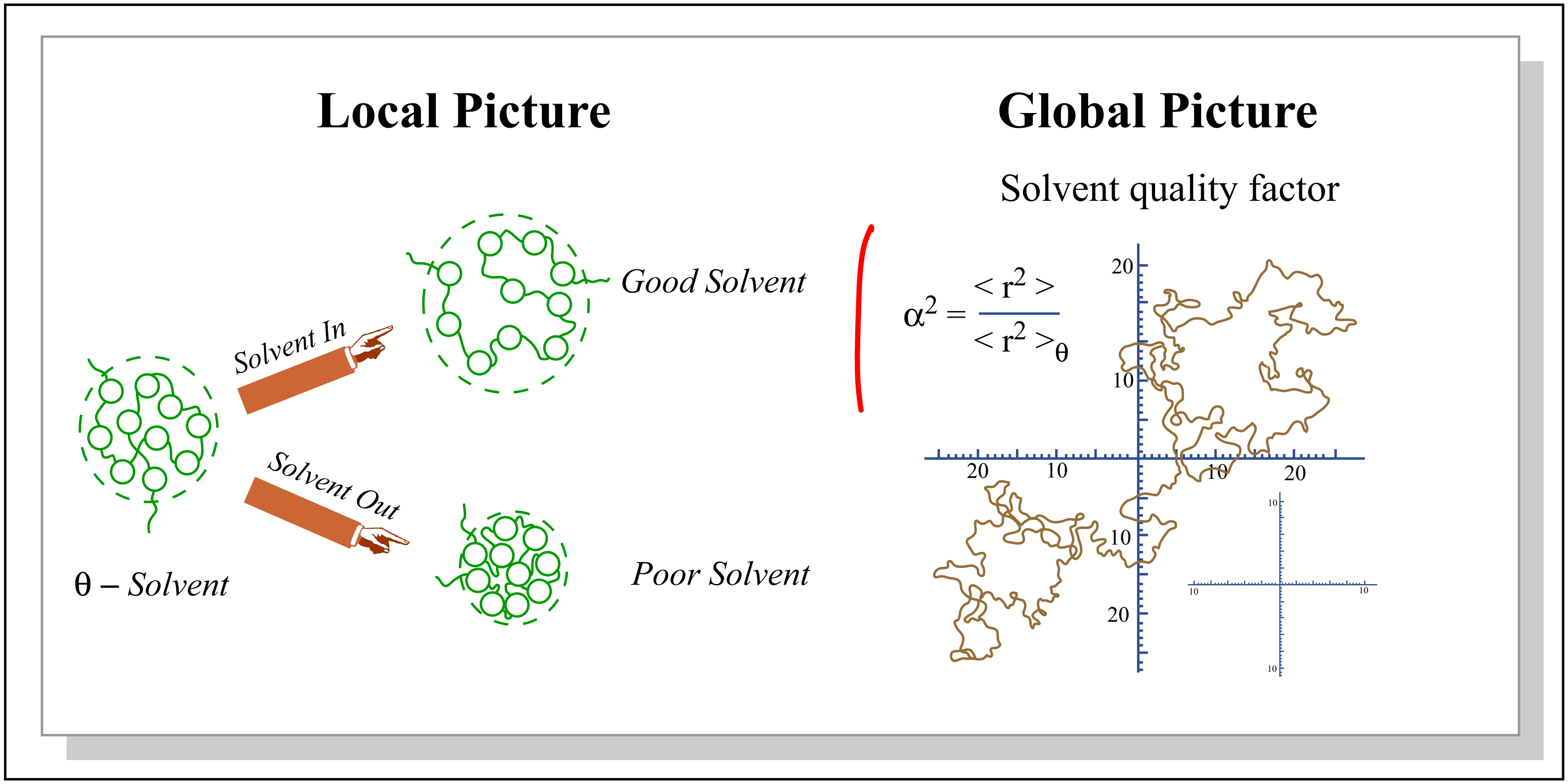


Figure by MIT OCW.

Theta condition

- In a good solvent the chain will expand – interaction between the polymer and the solvent is favored, and solvent-monomer contacts are maximized (and monomer-monomer contacts are minimized).
- In a poor solvent the chain will contract, to reduce interactions with the solvent. In practice, difficult to study (polymer will precipitate away).
- At the theta condition $\alpha=1$

Self-avoiding random walk

Figure by MIT OCW.

$\alpha = 1$, theta solvent

Θ condition: almost poor solvent

$$\langle r^2 \rangle_\theta \sim n l^2$$

$\alpha > 1$, good solvent

Self Avoiding Random Walk (SARW)

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

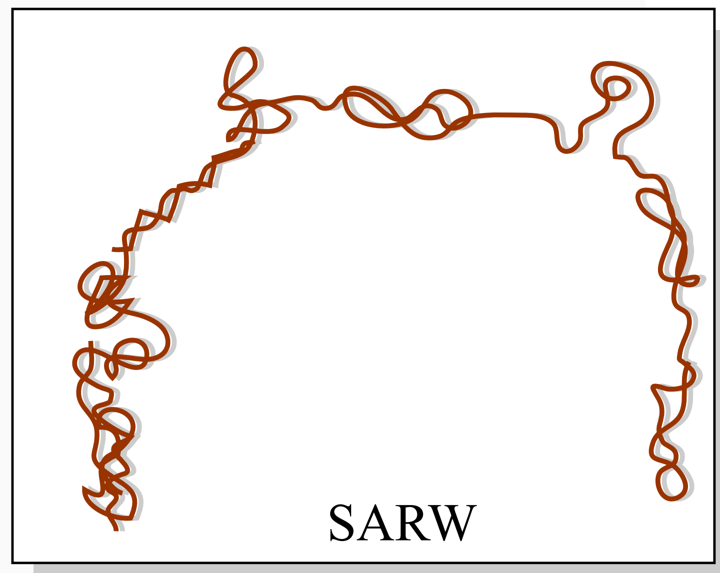


Figure by MIT OCW.

Diffusion: Rouse chain

- Low molecular weight linear polymers:

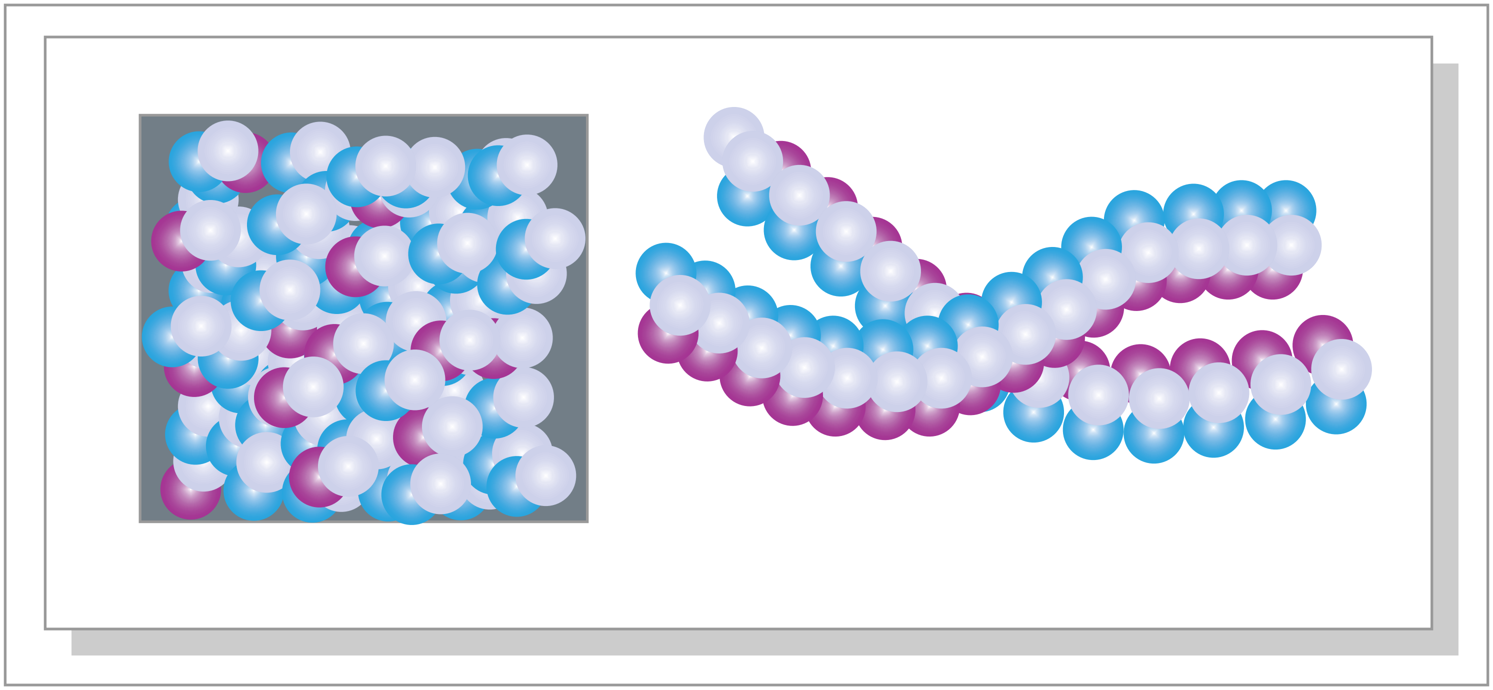
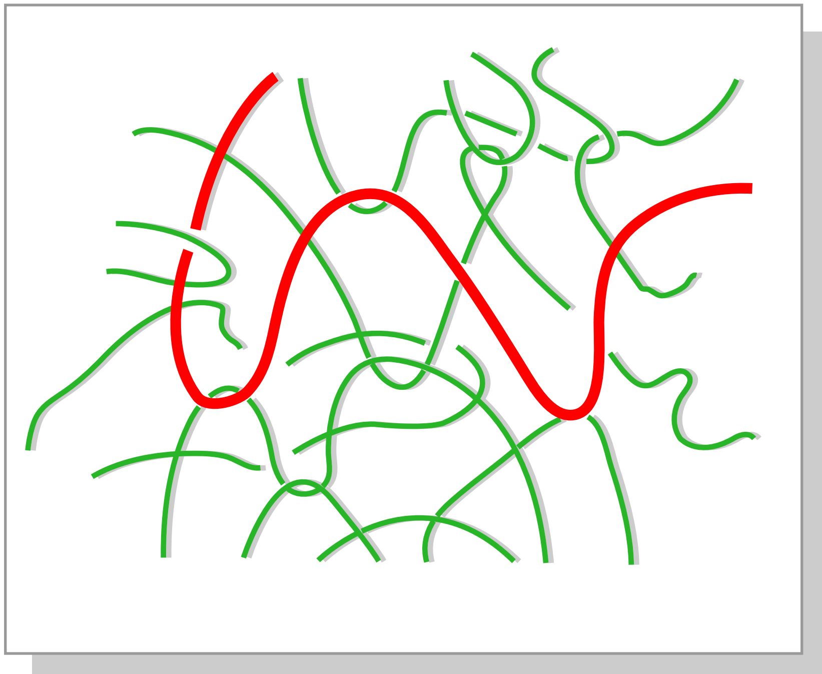


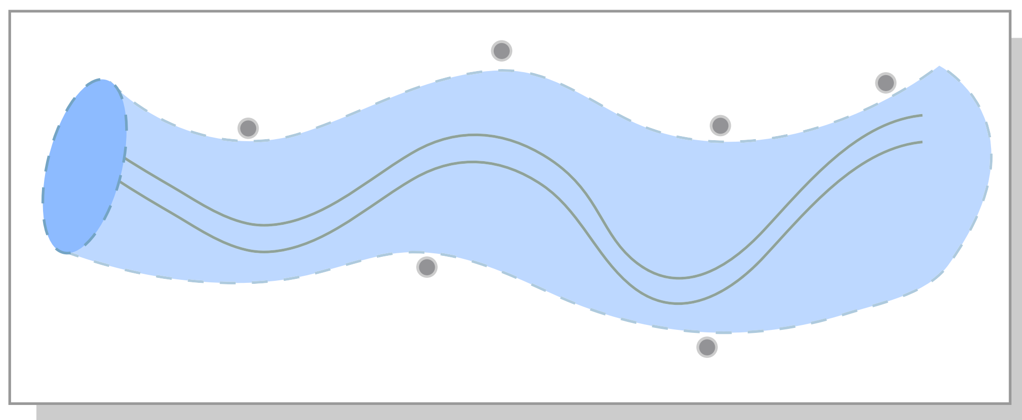
Figure by MIT OCW.

- An elastic string of Brownian particles in a viscous medium: diffusion=1/N

Large molecular weight: Reptation



Reptating chain, entangled



Portion of an effective constraining tube, defined by entanglements ● about a given chain.

- Diffusion=1/N^2

Figure by MIT OCW.

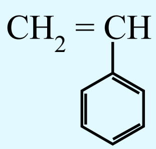
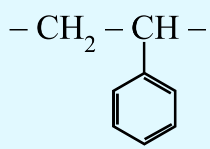
Monomer	Repeating Unit	Polymer Name	Uses
$CH_2 = CH_2$	$- CH_2 - CH_2 -$	Polyethylene	Film, toys, bottles, plastic bags
$CH_2 = CH$ | Cl	$- CH_2 - CH -$ | Cl	Poly(vinyl chloride)	"squeeze" bottles, pipe, siding, flooring
$CH_2 = CH - CH_3$	$- CH_2 - CH -$ | CH_3	Polypropylene	Molded caps, margarine tubs, indoor/outdoor carpeting, upholstery
		Polystyrene	Packaging, toys, clear cups, egg cartons, hot drink cups
$CF_2 = CF_2$	$- CF_2 - CF_2 -$	Poly(tetrafluoroethylene) Teflon®	Nonsticking surfaces, liners, cable insulation
$CH_2 = CH$ | $C \equiv N$	$- CH_2 - CH -$ | $C \equiv N$	Poly(acrylonitrile) Orlon®, Acrilan®	Rugs, blankets, yarn, apparel, simulated fur
$CH_2 = C - CH_3$ | $COCH_3$ ‖ O	CH_3 | $-CH_2-C-$ | $COCH_3$ ‖ O	Poly(methyl methacrylate) Plexiglas®, Lucite®	Lighting fixtures, signs, solar panels, skylights
$CH_2 = CH$ | $OCCH_3$ ‖ O	$-CH_2-CH-$ | $OCCH_3$ ‖ O	Poly(vinyl acetate)	Latex paints, adhesives

Figure by MIT OCW.

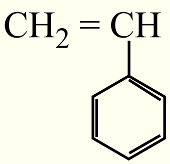
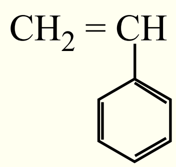
Monomer	Copolymer Name	Uses
$CH_2=CHCl$ + $CH_2=CCl_2$ Vinyl chloride, Vinylidene chloride	Saran	Film for wrapping food.
 + $CH_2=CH{-}C{\equiv}N$ Styrene, Acrylonitrile	SAN	Dishwasher-safe objects, vaccum cleaner parts.
$CH_2=CH{-}C{\equiv}N$ + $CH_2=CH{-}CH=CH_2$ +  Acrylonitrile, 1, 3-butadiene, Styrene	ABS	Bumpers, crash helmets, telephones, luggage.
$CH_2=C(CH_3)CH_3$ + $CH_2=C(CH_3)CH=CH_2$ Isobutylene, Isoprene	Butyl rubber	Inner tubes, balls, inflatable sporting goods.

Figure by MIT OCW.

Network models: Continuous random network

- Monofunctional (dimers), bifunctional (linear chains), trifunctional or more (networks)

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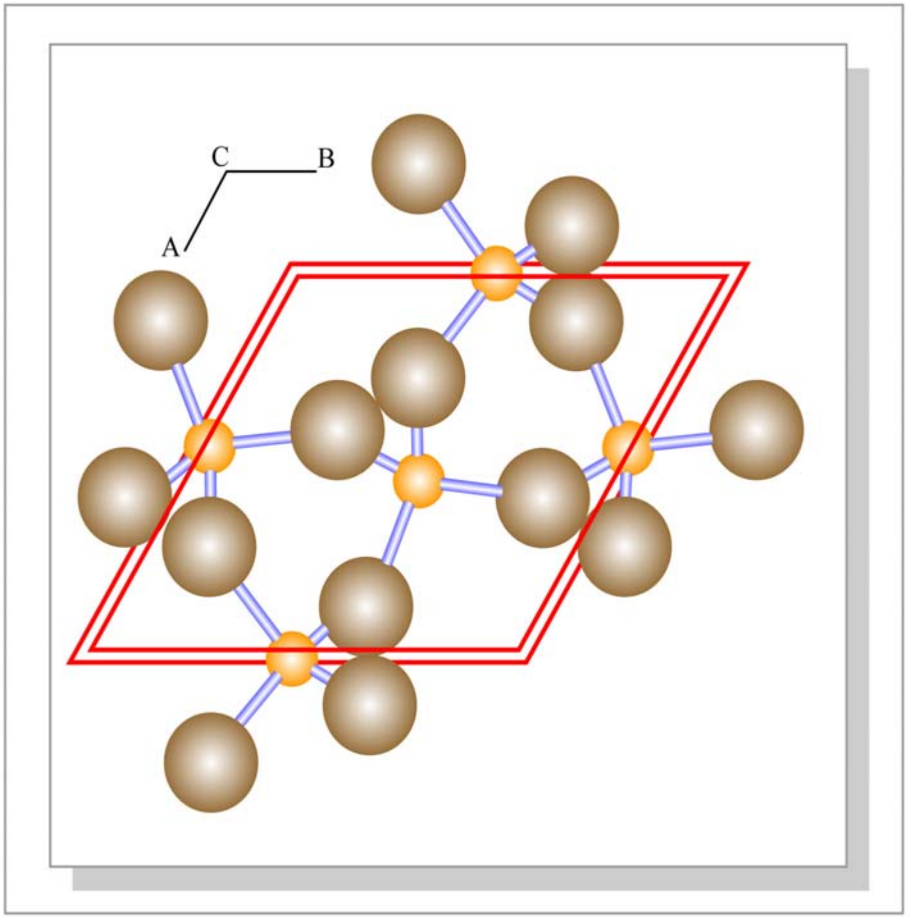
See page 65, Figure 2.20 in Allen, S. M., and E.L. Thomas. *The Structure of Materials*. New York, NY: J. Wiley & Sons, 1999.

Oxide glasses

SiO_2

- Zachariasen constraints: (1932)
  - Each oxygen linked to not more than 2 cations
  - Functionality of central cation small (3-4)
  - Oxygen polyhedra share corners
  - At least three corners of each polyhedron shared

Quartz and silica



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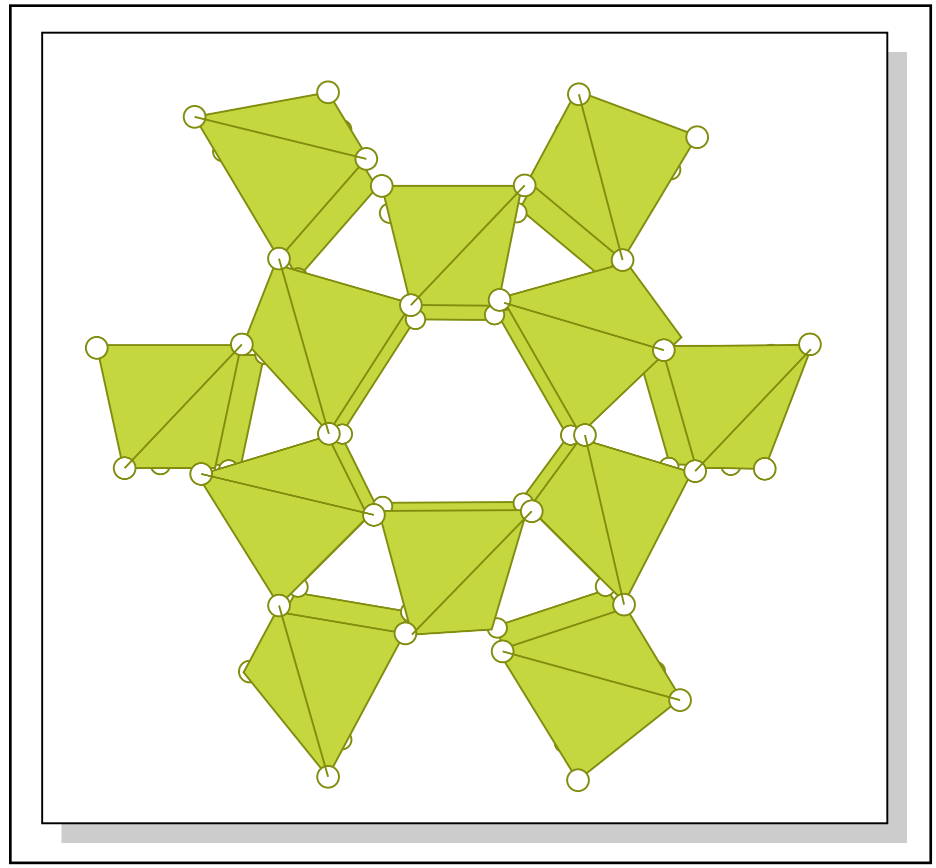

Figure by MIT OCW.

Network modifiers

Diagram of the effect of the lead-to-phosophorus ratio on phosphate glass removed for copyright reasons.
See page 71, Figure 2.25 in Allen, S. M., and E. L. Thomas. *The Structure of Materials*. New York, NY: J. Wiley & Sons, 1999.

Chalcogenide glasses

Diagram of the schematic bonding pattern of a chalcogenide network glass removed for copyright reasons.
See page 72, Figure 2.27 in Allen, S. M., and E. L. Thomas. *The Structure of Materials*. New York, NY: J. Wiley & Sons, 1999.