Polymers

Long string like molecules give rise to universal properties in dynamics as well as in structure – properties of importance when dealing with:

- Pure polymers and polymer solutions & mixtures
- Composites (reinforced plastics)
- Biological macromolecules (DNA, F-actin, cellulose, natural rubber etc.)

Hevea brasiilensis

Today's content

With simple models we will be able to:

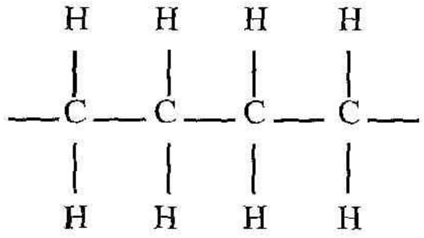
- Define length-scales in polymers (rms end-to-end distance, radius of gyration, Kuhn length, etc).
- Describe dynamic properties (viscosity, rubber elasticity and reptation, etc).

Structure and Chemistry

- Polymers are giant molecules usually with carbons building the backbone – exceptions exist (poly dimethylsiloxane)
- Linear chains, branched chains, ladders, networks, dendrimers
- Homopolymers, copolymers, random copolymers, micro phase separated polymers (like amphiphilic polymers)

Some different polymers

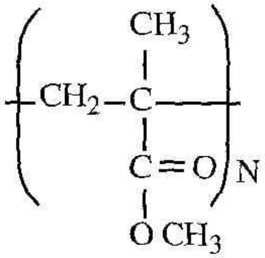
Polyethylene



or $(CH_2)_N$

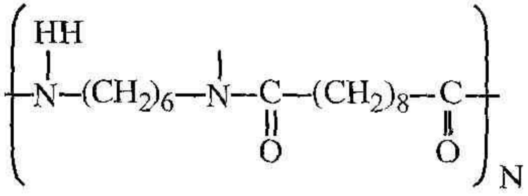
where N = degree of polymerisation

Polymethyl methacrylate

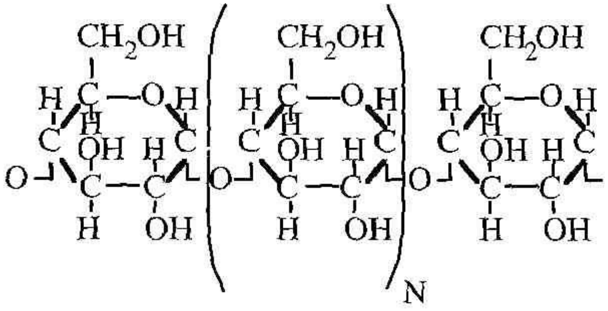


PMMA or Perspex (ICI trade name)

Nylon 6-10

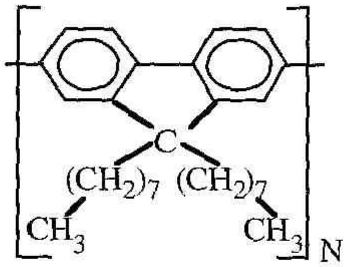


Amylose

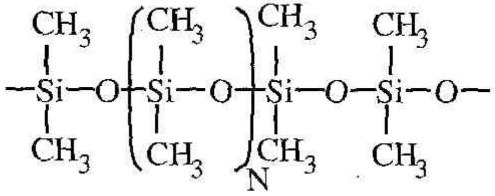


Starch

Poly(di-octyl fluorene)



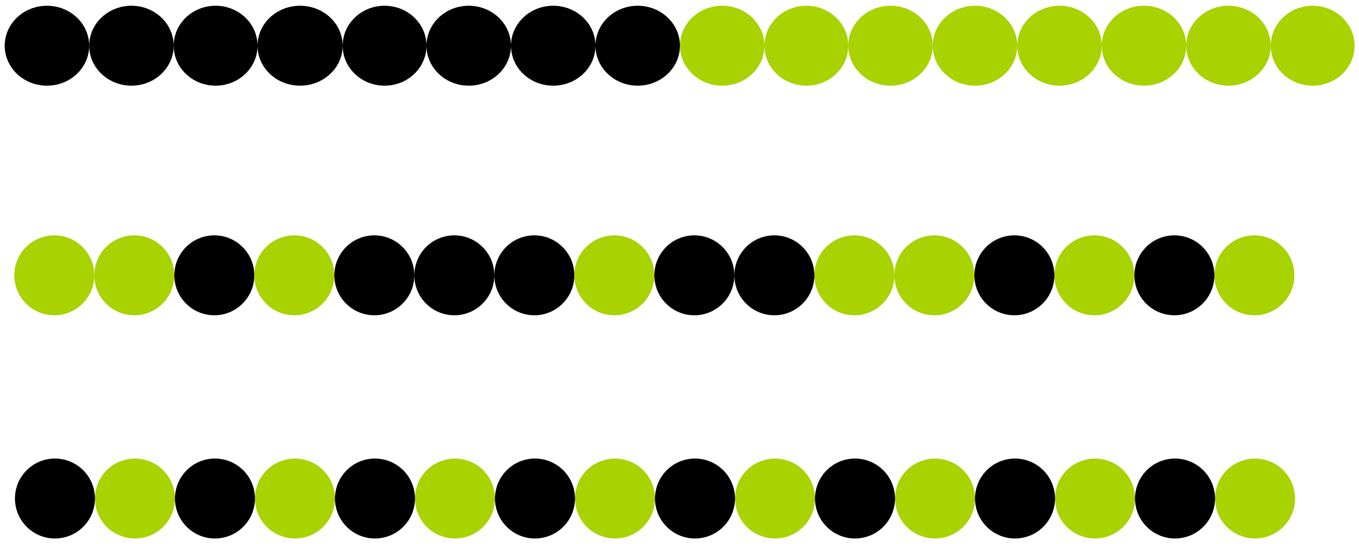
Polydimethyl siloxane



PDMS or silicone oil

Copolymers

In contrast to homo-polymers co-polymers are composed of more than one type of repeat unit



Block copolymer

Random copolymer

Alternating

Repeat units with different properties => self assembly and micro phase separation. Chapter 9

Molecular weight and dispersion

Syntetic polymers always show a distribution in molecular weights.

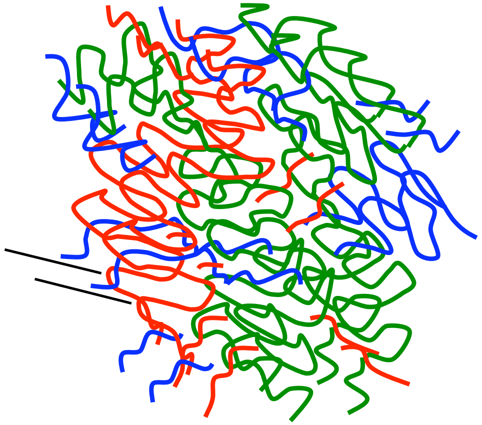
number average : $$M_n = \frac{\sum n_i M_i}{\sum n_i}$$

weight average: $$M_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i M_i}{\sum n_i M_i}$$

(n_i and w_i are number and weight fractions, respectively, of molecules with molar mass M_i)

The polydispersity index is given by M_w / M_n

Molecular weight and dispersion - an example:



Here are:

10 chains of 100 molecular weight

20 chains of 500 molecular weight

40 chains of 1000 molecular weight

5 chains of 10000 molecular weight

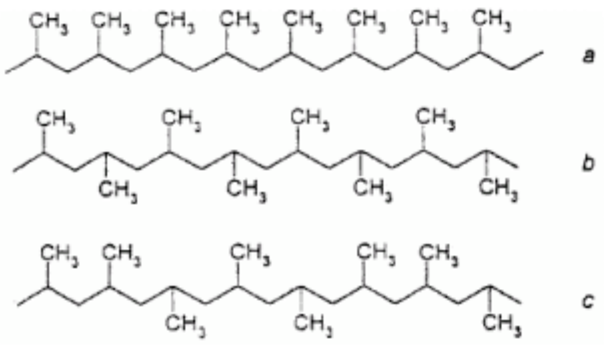
$$\overline{M}_n = \frac{(10 \cdot 100) + (20 \cdot 500) + (40 \cdot 1000) + (5 \cdot 10000)}{10 + 20 + 40 + 5} = 1347$$

$$\overline{M}_w = \frac{(10 \cdot 100^2) + (20 \cdot 500^2) + (40 \cdot 1000^2) + (5 \cdot 10000^2)}{(10 \cdot 100) + (20 \cdot 500) + (40 \cdot 1000) + (5 \cdot 10000)} = 5390$$

$$\text{Polydispersity} = \frac{\overline{M}_w}{\overline{M}_n} \approx 4$$

Stereochemistry

- Isotactic – side groups on the same side of the chain (a)
- Syndiotactic – alternating side groups (b)
- Atactic – random arrangement of side groups (c)



Stereo isomers of poly propylene

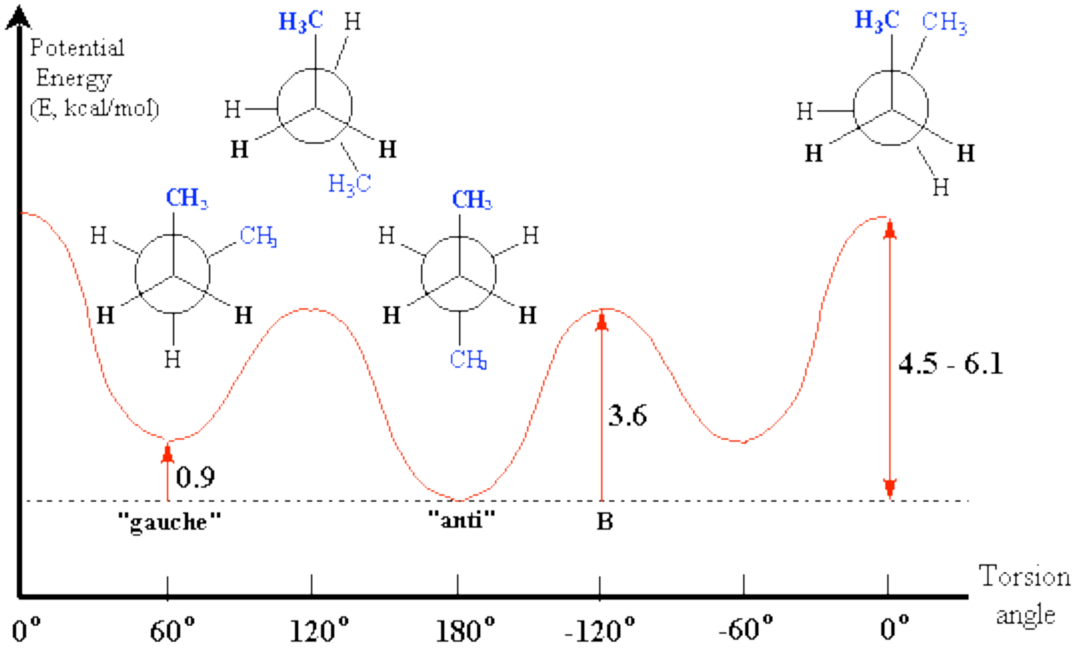
Tacticity determines ability to form crystals: Disordered, atactic polymers form glasses.

Rotational isomers

Newman projections of the C-C bond in the middle of butane.

Rotation about σ bonds is neither completely rigid nor completely free.

A polymer molecule with 10000 carbons have 3^{9997} conformations



Potential energy of butane as a function of the torsion angle.

The energy barrier between gauche and trans is about 2.5 kJ/mol

RT~8.31*300 J/mol~2.5 kJ/mol

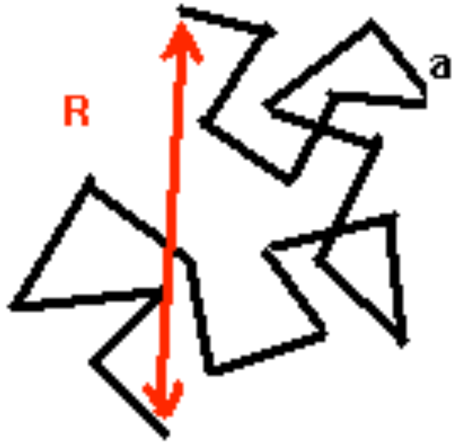
Random walks – a chain model

For a polymer chain model;

- Consider random steps of equal length, **a**, defined by chemical bonds

Complications:

- Excluded volume effects
- Steric limitations



The chain end-to-end vector R “describes” a coil made up of N jump vectors $\mathbf{a}_i$.

Random walk …

$$\overline{R} = \sum_{i=1}^{N} \overline{a}_i$$

R is made up of N jump vectors $\mathbf{a}_i$. The average of all conformational states of the polymer is <**R**>=0

$$\langle \overline{R}^2 \rangle = \langle \sum \sum \overline{a}_i \bullet \overline{a}_j \rangle$$

The simplest non-zero average is the mean-square end to end distance <R^2>

$$\langle \overline{R}^2 \rangle = \underbrace{Na^2}_{i=j} + \left\langle \sum_{i\neq j} \overline{a}_i \bullet \overline{a}_j \right\rangle = \underbrace{Na^2}_{i=j} + 2a^2 \sum_{i\neq j} \cos\theta_{ij}$$

(A matrix of dot-products where the diagonal represents i=j and off axis elements i≠j)

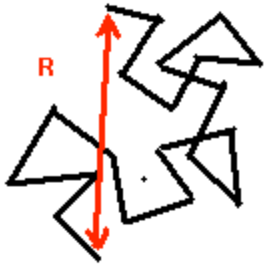
For a freely jointed chain the average of the cross terms above is zero and we recover a classical random walk: <**R**^{2}>=Na^2

The rms end to end distance <**R**^{2}>$^{1/2}$=N$^{1/2}$a

A size example:

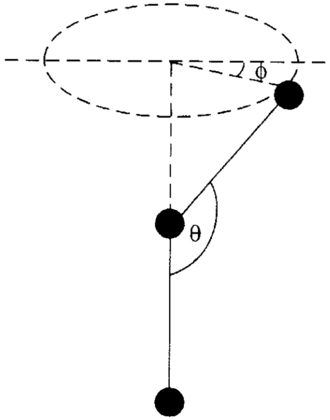
An ideal polymer chain with 10^6 repeat units (not unusual), each unit about 6Å will have:

- a rms end-to-end distance R of 600 nm
- a contour length of 600 μm



The rms end to end distance $\langle \mathbf{R}^2 \rangle^{1/2} = N^{1/2} a$

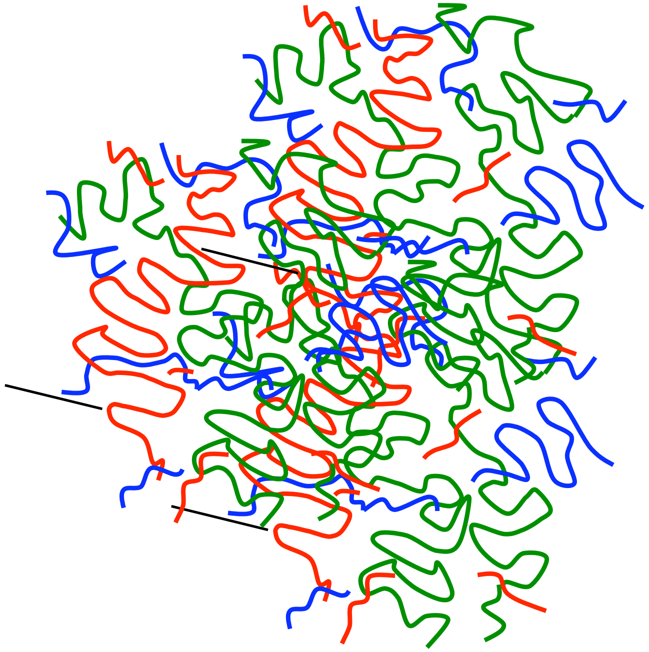
Real chains have steric limitations



$$\langle \overline{R}^{2} \rangle = Na^{2}\sigma^{2}\left(\frac{1-\cos\theta}{1+\cos\theta}\right)$$

- In freely rotating chains Φ can take any value; $\sigma^2=1$. Poly ethylene: $\Theta = 109.5°$ → $<R^2>=2Na^2$
- With hindered rotation σ^2 depends on the average of Φ. σ is experimentally determined.

Space filling?



The random walk and the steric limitations makes the polymer coils in a polymer melt or in a polymer glass “expanded”.

However, the overlap between molecules ensure space filling

Gaussian distribution

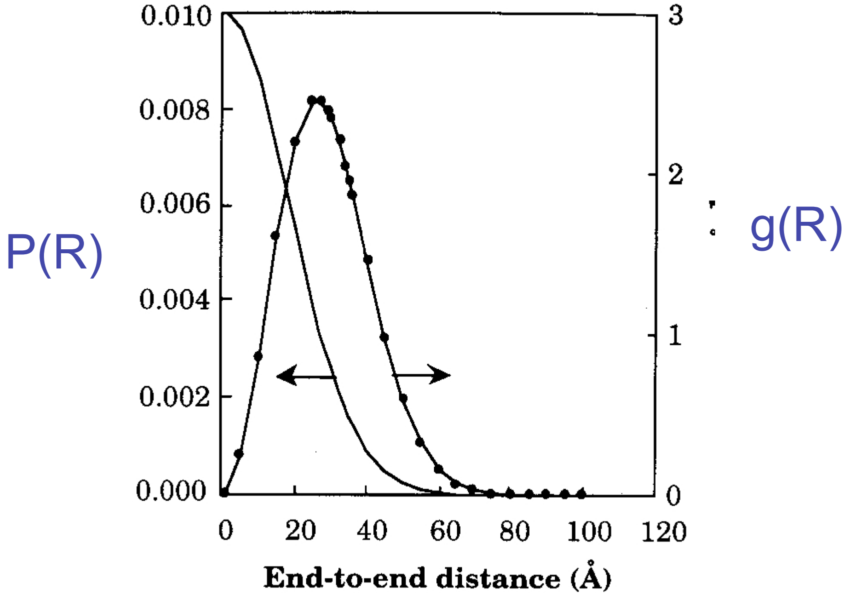
The distribution of end-to-end distances (R) in an ensemble of random polymer coils is Gaussian. The probability function is:

$$P\left(\overline{R}\right)=\left(2\pi Na^{2}/3\right)^{-3/2}\exp\left(\frac{-3\overline{R}^{2}}{2Na^{2}}\right)$$

The probability decreases monotonically with increasing R (one end is attached at origo). The radial distribution g(**R**) is obtained by multiplying with $4\pi R^2$

$$g\left(\overline{R}\right)=4\pi R^{2}\left(2\pi Na^{2}/3\right)^{-3/2}\exp\left(\frac{-3\overline{R}^{2}}{2Na^{2}}\right)$$

The radial distribution function g(R)



Adopted from Gedde; Polymer Physics

Entropic Effects in a Gaussian Coil

From the Boltzmann equation $S=k_b \ln\Omega$ where Ω=statistical weight we have an expression for the entropy of a Gaussian coil: $\ln P(R) = \ln \Omega$;

$$S\left(\overline{R}\right) = -\frac{3k_b R^2}{2Na^2} + \text{const}$$

Entropy decreases with stretching (increasing order)

F=U-TS => The “Entropic Spring” with a spring constant:

$dF/dR=3k_bTR/Na^2$

OBS: dF/dR Increases with T, decreases with N – not like a traditional spring which depends on U!

Homework?

A classic home ‘kissing rubber’ experiment: When we stretch or unstretch a rubber band fast, What happens?

“Real” Polymer Chains

Recall that : $$\left\langle \overline{R}^2 \right\rangle = Na^2 + 2a^2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \cos\theta_{ij}$$

The correlation between bond vectors “dies” with increasing separation: $$\lim_{|i-j|\to\infty} \left\langle \cos\theta_{ij} \right\rangle = 0$$

Thus the sum over bond angles converges to a finite number and we have:

Flory Characteristic Ratio

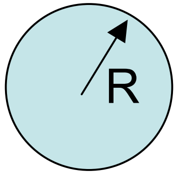
b=Kuhn segment

$$\left\langle R^2 \right\rangle \cong C_\infty N a^2 = N_F b^2 ; \Rightarrow C_\infty = \frac{N_F b^2}{N a^2}$$

After renormalisation this relation holds for all flexible linear polymers!
OBS: Jones uses an oversimplification; $N_F = N$… Valid only for ∞

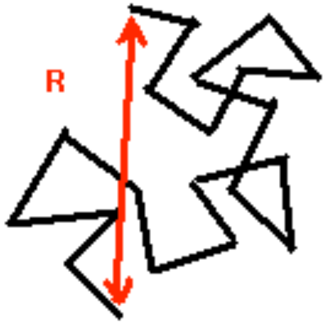
Radius of Gyration of a Polymer Coil

The radius of gyration R_g is defined as the RMS distance of the collection of atoms from their common centre of gravity.



For a solid sphere of radius R;

$$R_g = \sqrt{\frac{2}{5}}R = 0.632R$$



For a polymer coil with rms end-to-end distance R ;

$$R_g = \frac{1}{6}\left\langle \overline{R}^2 \right\rangle^{1/2} = \frac{a}{6}N^{1/2}$$

The excluded volume effect

(in polymer solutions)

- Steric hindrance on short distances limits the number of conformations

- At longer distances we have a topological constraint – the self avoiding walk – or the excluded volume effect:

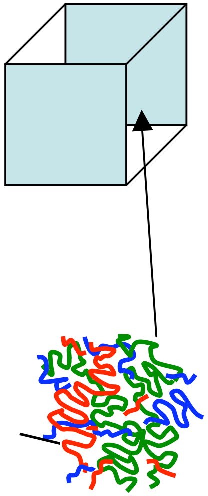
Instead of $<R^2>^{1/2}=aN^{1/2}$ we will have

$<R^2>^{1/2}=aN^{v}$ where $v>0.5$

Experiments tells us that in general: $v \sim 0.6$

Why?

Excluded volume according to Flory



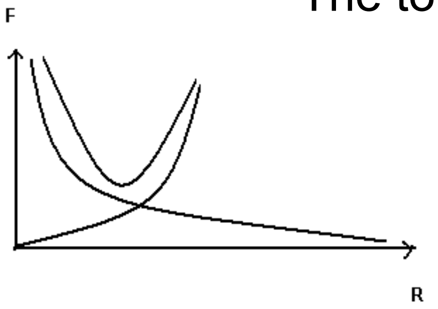
Consider a cube containing N segments of a polymer
$V=r^3$ where r is the radius of gyration.
The concentration of segments is $c \sim N/r^3$

Each segment with volume ν “stuffed” into the cube reduces the entropy with $-k_b \nu N/V = -k_b \nu N/r^3$ (for small x; $\ln(1-x) \sim -x$)

The result is a positive contribution to F; $F_{rep} = k_b \nu T N^2/r^3$ (expansion of the coil)

From before; Coiling reduces the entropy; $F_{el} = k_b T 3R^2/2Na$

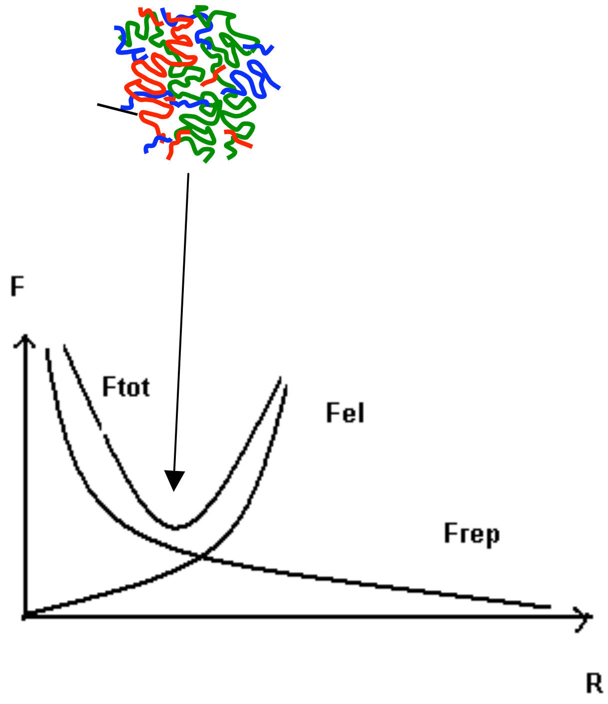
The total free energy F is the sum of the two contributions!



Search for equilibrium!

Flory's result for the swollen coil:

$$F_{tot}(R) = \frac{k_b \nu T N^2}{R^3} + 3\frac{k_b T R^2}{2Na^2} + \text{const}$$



$$\frac{dF_{tot}}{dR} = \frac{-3k_b \nu T N^2}{R^4} + \frac{3k_b T R}{Na^2} = 0$$

$$R^5 = a^2 \nu N^3$$

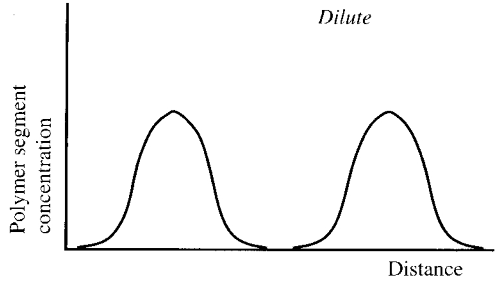
$$\nu \approx a^3$$

$$R^5 \approx a^5 N^3$$

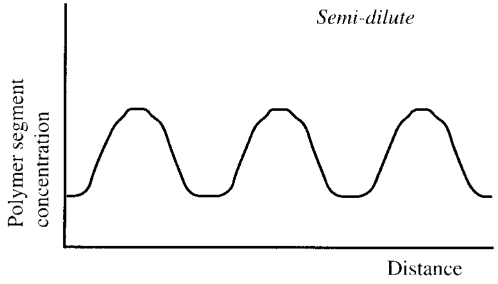
$$R \approx a N^{3/5}$$

Polymer melts – a simpler case

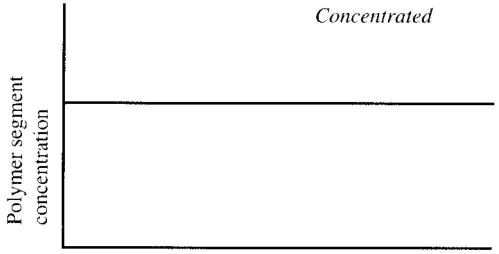
In dilute polymer solutions the excluded volume effect is large. (OBS Theta cond. Later)



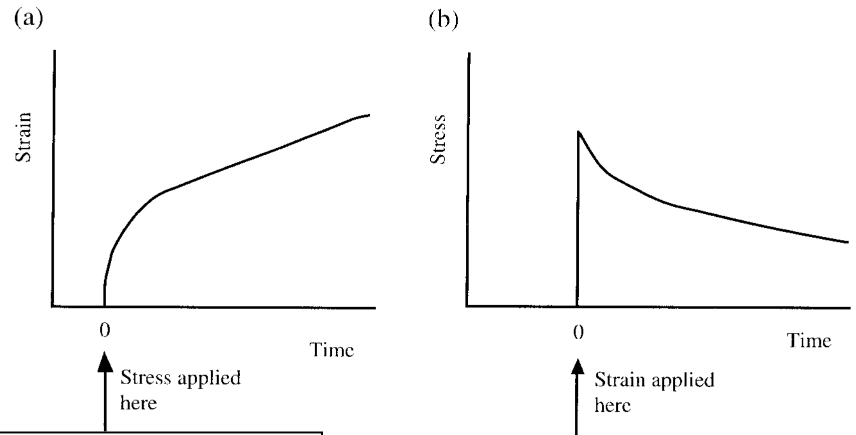
When chains start to overlap the expanding force on a single coil will be reduced



In a polymer melt the concentration of segments is uniform due to space filling. No swelling!



Viscoelastic properties in polymers - characteriscs



A stress σ_0 is applied at time t=0 and held constant. The strain e(t) is followed over time. The creep compliance J(t) is given by:

$$e(t)= \sigma_0\ J(t)$$

A strain e_0 is applied at t=0 and held constant. The stress σ(t) is followed over time. The stress relaxation modulus G(t) is given by:

$$\sigma(t)=e_0 G(t)$$

The complex modulus G*

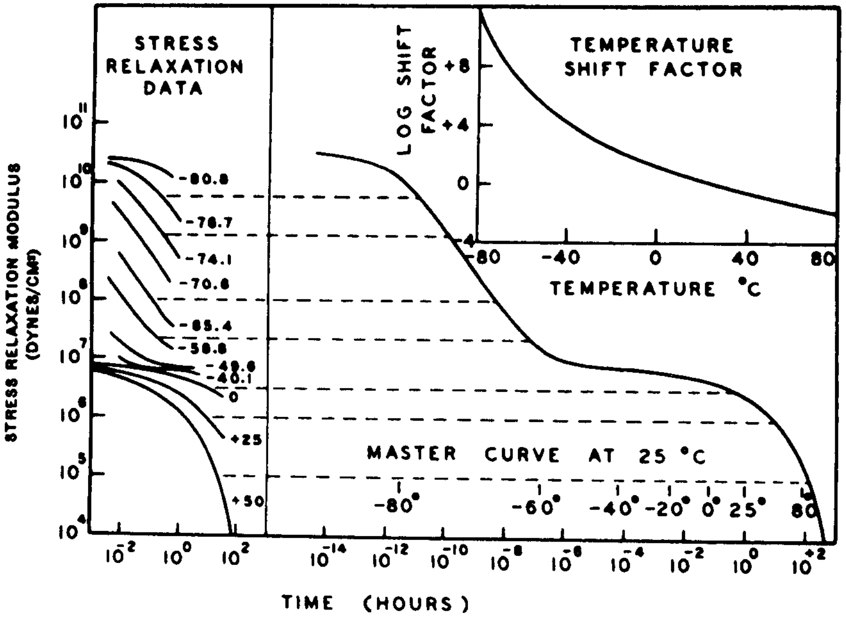
If a sinusoidal strain is applied: $e(t)=e_0\cos(\omega t)$
the resulting stress is given by:

$\sigma(t) = e_0[G'(\omega) \cos(\omega t) - G''(\omega) \sin(\omega t)]$

The complex modulus, $G^* = G'(\omega) + iG''(\omega)$ is given by a Fourier transform of G(t).

G' gives elastic response, G'' the viscous responce

Time-temperature superposition



All relaxing modes in a polymer melt or a solution have the same T-dependence. Therefore:

$$G(t,T) = G(a_T t,\ T_0)$$

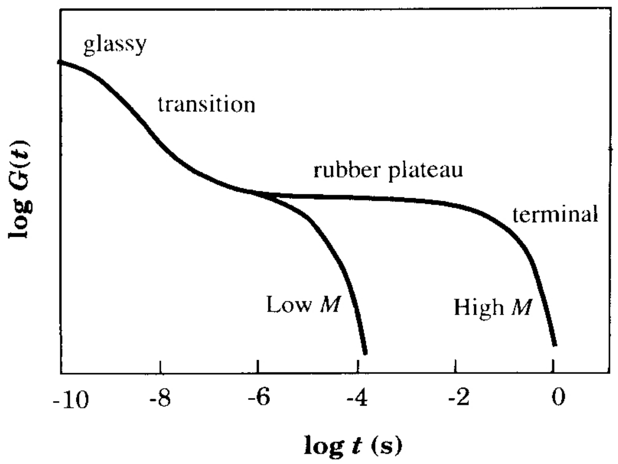
where

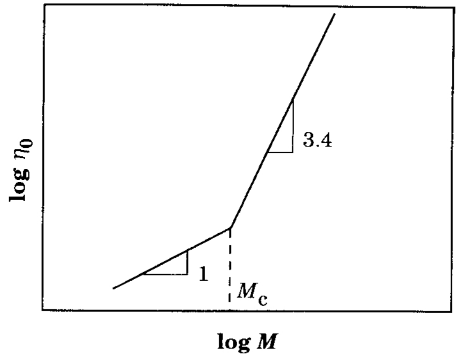
$$\log a_T = -[C_1(T-T_0)]/[C_2+T-T_0]$$

"Quasi-universal" values of C_1 and C_2 are 17.4 and 51.6 K, respectively

The superposition principle help us building larger data set over timescales/temperatures otherwise out of reach

Viscoelasticity





The stress relaxation G(t) for two polymers (homologues) with different molecular weights.

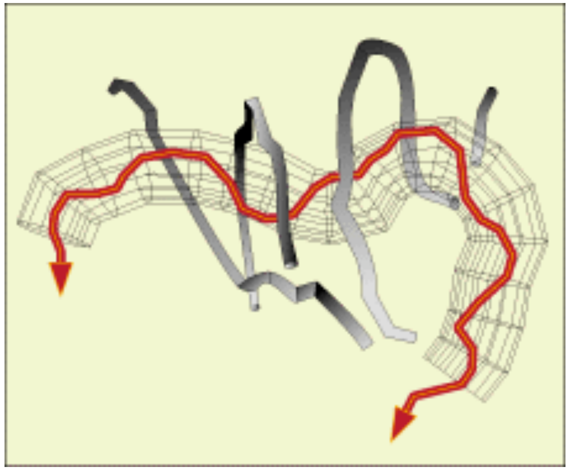
At short time the curves are identical.

At intermediate times we have a plateau with a constant modulus – the plateau modulus.

The plateau ends at a terminal time τ_T which depends strongly on molecular weights (N) according to a power law $\tau_T \sim N^m$ where the exponent $m \approx 3.4$

Two Q's arises: 1) Why is $m \approx 3.4$ almost universal? 2) why do we have an almost purely elastic behaviour at the plateau?

Q1: The tube model and the idea of reptation



A polymer escapes from its own tube of length L after a time τ_T

Every segment in the tube have a mobility, μ_{seg} restricted by the surrounding “resistance”.

The tube with N segments have a mobilty, $\mu_{tube} = \mu_{seg}/N$

Brownian motion within the tubes confinement – use Einstein relation to calculate a Diffusion coefficient =>

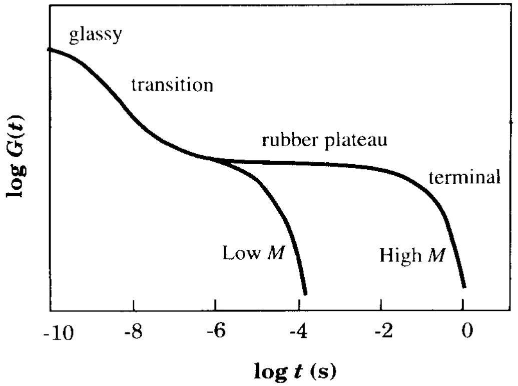
$$\Rightarrow D_{tube} = k_b T \ \mu_{tube} = k_b T \ \mu_{seg}/N$$

$$\tau_T \cdot D_{tube} = L^2$$

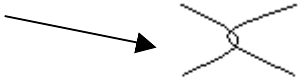
$$\tau_T = \frac{L^2}{D_{tube}} \propto \frac{N^3}{\mathrm{const}}$$

Close to the exp. results!

Q2; The rubber plateau and entanglements



In a similar way as we explained the elastic behaviour at very short times for all simple liquids “as a glassy state” we can explain the rubber plateau in a qualitative way as a signature of entanglements.

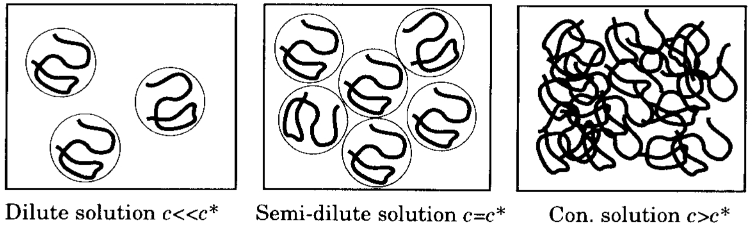


It can be shown that in a rubber, a cross linked polymer (see Ch. 5.4), the elastic modulus depends on the average molecular mass between cross-links M_x, R ,T and the density ρ:

Adopting an identical relation and treating the entanglements as temporary cross-links with a lifetime of the order of τ_T we can calculate an average mass of the molecular mass between the entanglements (M_e).

$$G = \frac{\rho RT}{M_x}$$

Sept 25th: More about solutions and some crystalline stuff…



Remember Thursday Sept 13th at 08.00:

Glasses and glass transition