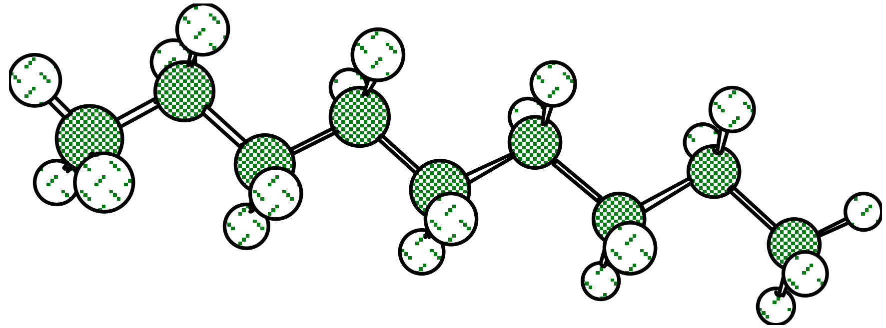
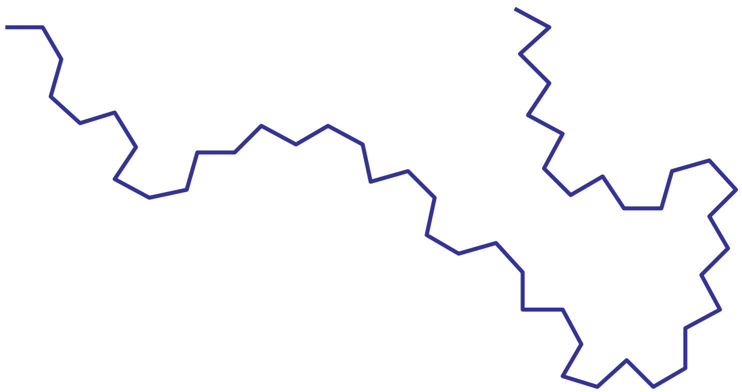
A typical simple polymer: polyethylene

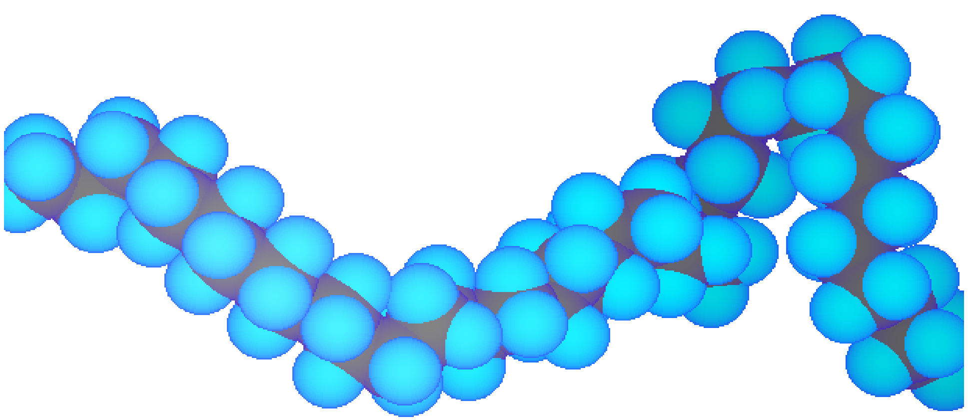
$-CH_2-CH_2-$

← ~0.1 nm →





← ~10 nm →



What is the size of a polymer?

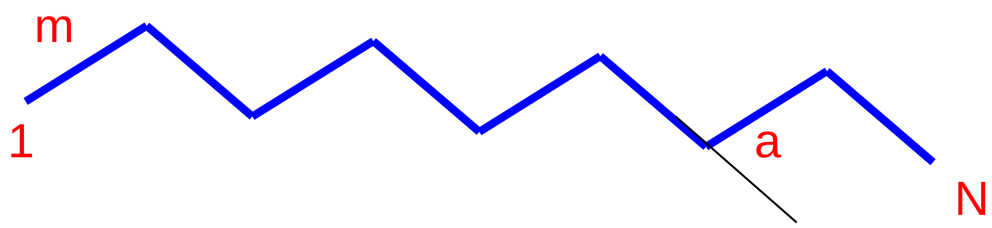
First (simplistic approach):

We know the size of monomer m, and the degree of polymerization N

Hence, contour length is L=mN

But this is rather the maximum length which cannot be ever realized.
Polymer has a lot of degrees of freedom

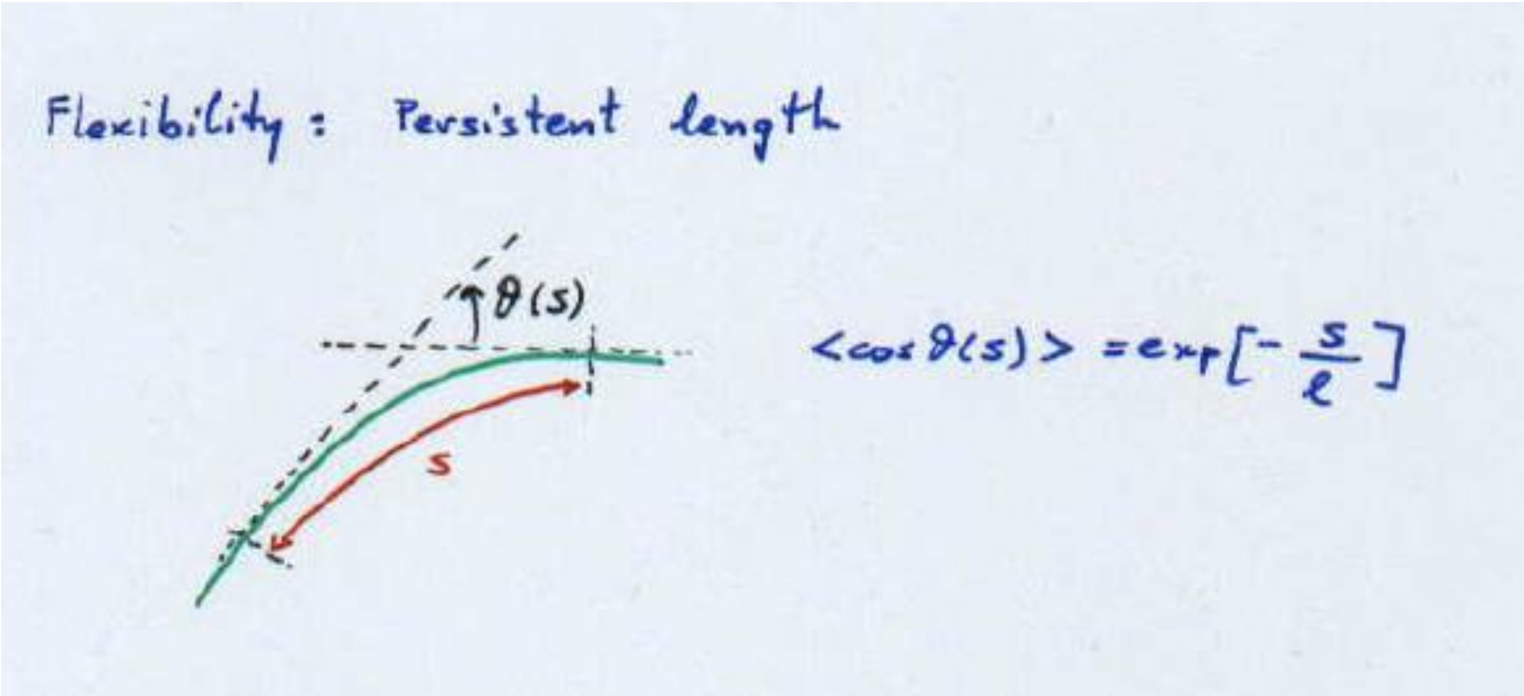
Also, stereochemical considerations suggest and average bond angle a



Hence, L_{max}=mN cos(a/2)

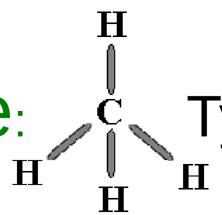
To get reasonable statistical averages, account to chain conformation
(here consider flexible chains)

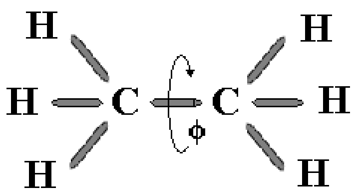
A measure of (static) flexibility: persistence length

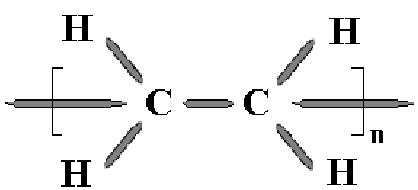


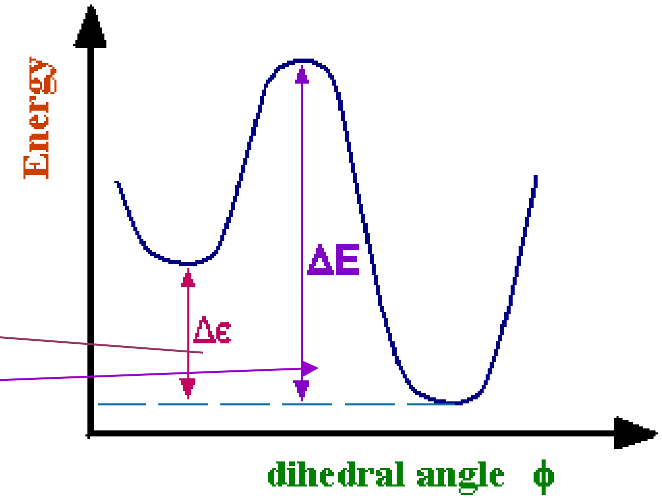
Note: what matters is the ratio l/L, with L the contour length
(e.g., DNA is semiflexible)
Indirect link to ability of chain to entangle

Dynamic flexibility and glass transition temperature Tg

Methane:  Typical fluctuations 3% in $r_{C\text{-}H}$ and 3° in ∠ HCH

Ethane:  Almost free rotation around C-C: 3 conformations

Polyethylene:  3^n possible conformations ($n \simeq 10^4$): **Statistics**

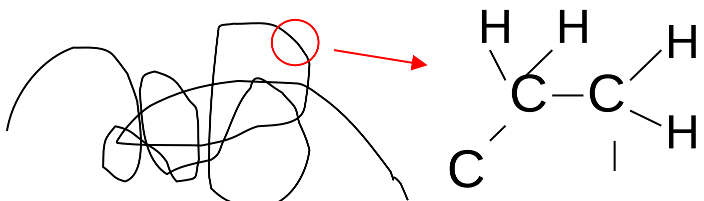


Static flexibility (PE, DNA)
(persistence length)

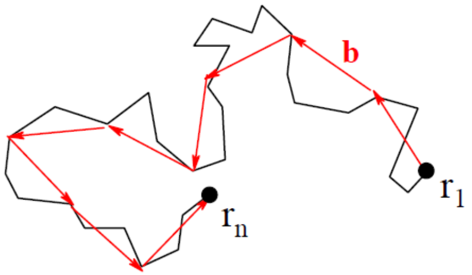
Dynamic flexibility
(structure in motion - T_g)

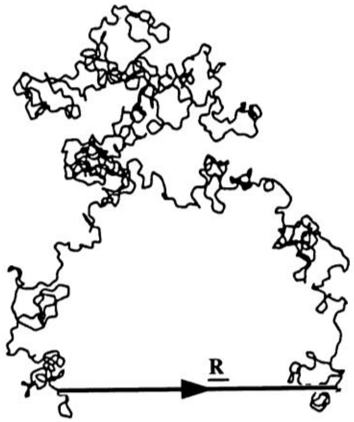
Molecular models of polymer chains: Ideal chain (non-interacting, 'fantom' solvent)

Definition of the chain configuration:

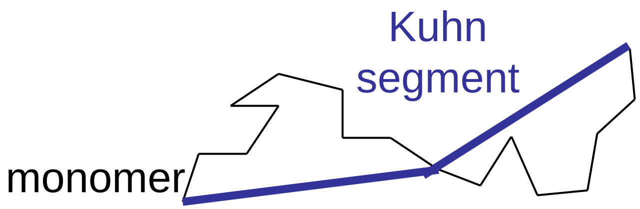


Example: polyethylene $(CH_2)_n$





Approximation: the Kuhn segment (and equivalent chain)

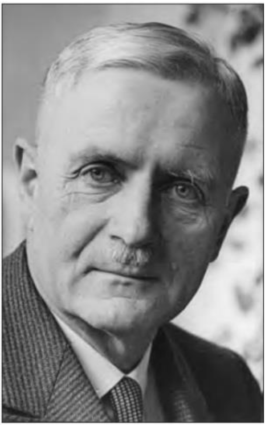


- No volume, no interaction between the segments

- equivalent chain with N Kuhn segments

- each with fixed length (=b)

- Bond between two monomers requires specific angle. Bond between two Kuhn segments can take any angle value (freely joint).

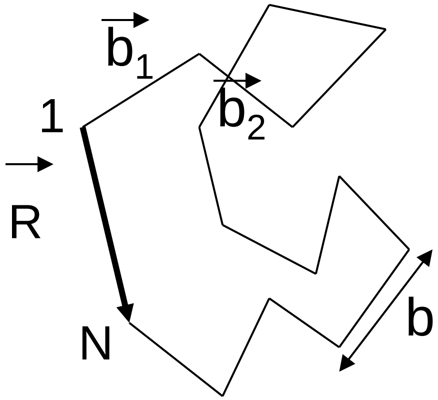


W. Kuhn 1899-1963

This approximation allows us to use the so-called Random walk model

Molecular models of polymer chains: **average end-to-end distance**

Random walk model:



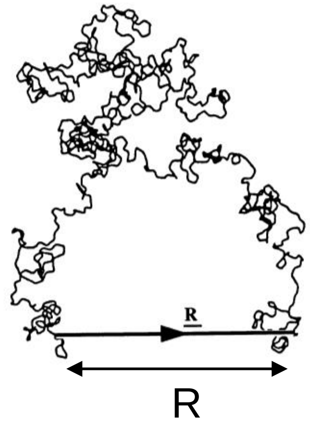
$$\vec{R} = \sum_{i=1}^{N} \vec{b}_i$$

$$\langle \vec{R} \rangle = \sum_{i=1}^{N} \langle \vec{b}_i \rangle = 0$$

$$\langle \vec{R}^2 \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \vec{b}_i \vec{b}_j \rangle = Nb^2$$

$$R^2 = C_\infty N b^2$$

$$\langle |\underline{R}|^2 \rangle = R^2 = Nb^2$$



Quadratic distance R^2:

$$\langle \vec{R}^2 \rangle = \langle R^2 \rangle = \frac{1}{p} \sum_{i=1}^{p} \vec{R}_i^{\,2}$$

p: all possible configurations

For each configuration:

$$\vec{R}_i = \sum_{j=1}^{N} \vec{b}_j \Rightarrow R_i^{\,2} = \sum_{j=1}^{N} \vec{b}_j \vec{b}_j + 2 \sum_{j<k} \vec{b}_j \vec{b}_k = \sum_{j=1}^{N} \vec{b}_j \vec{b}_j + 2 \sum_{j<k} b^2 \cos(\theta_{jk})$$

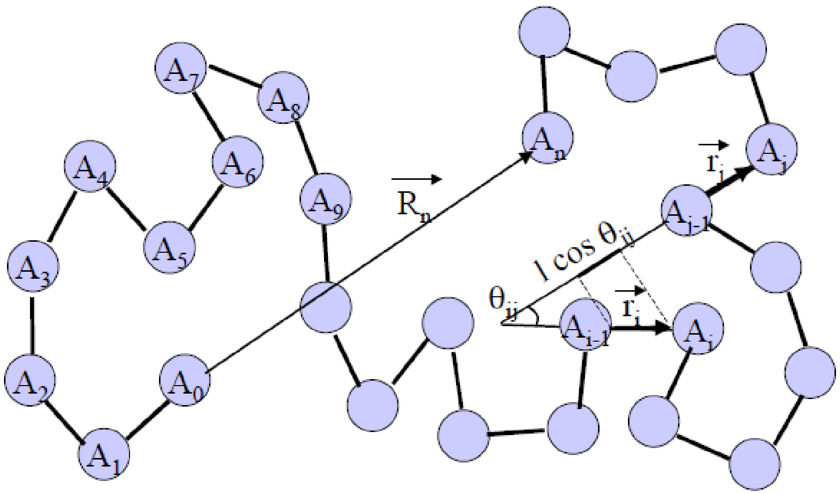
$$\vec{R}_i^{\,2} = R_i^{\,2} = \vec{R}_i \bullet \vec{R}_i$$

$= Nb^2$

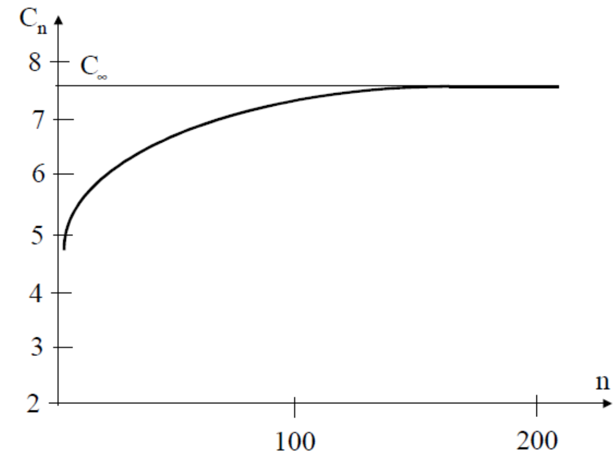
= 0

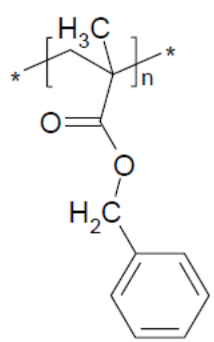
Chemical chain with N_m monomers, each of size m, or N Kuhn segments each of b

Flory's characteristic ratio

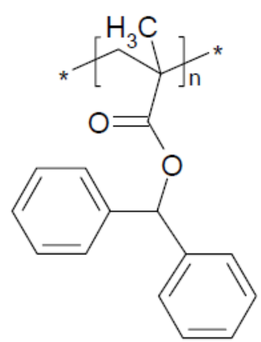


$$C_n = \frac{1}{n}\sum_{i=1}^{n} C_i' \qquad C_i' \equiv \sum_{j=1}^{n} \langle \cos\theta_{ij} \rangle$$

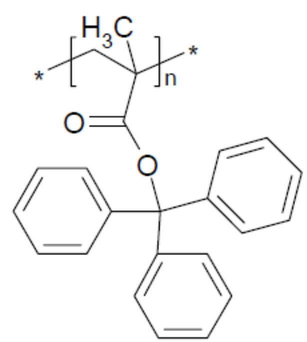




$C_\infty = 10$

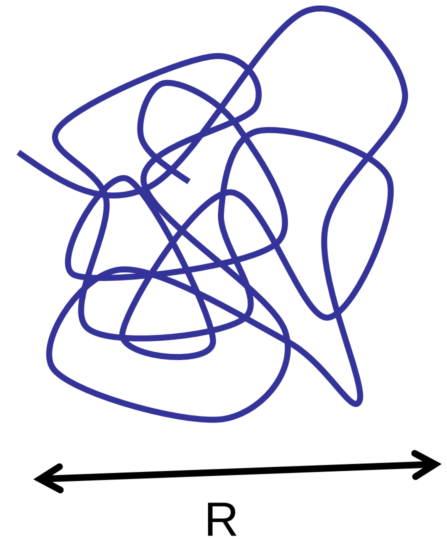


$C_\infty = 14$



$C_\infty = 20.3$

Single Gaussian chain (conformation): Size distribution

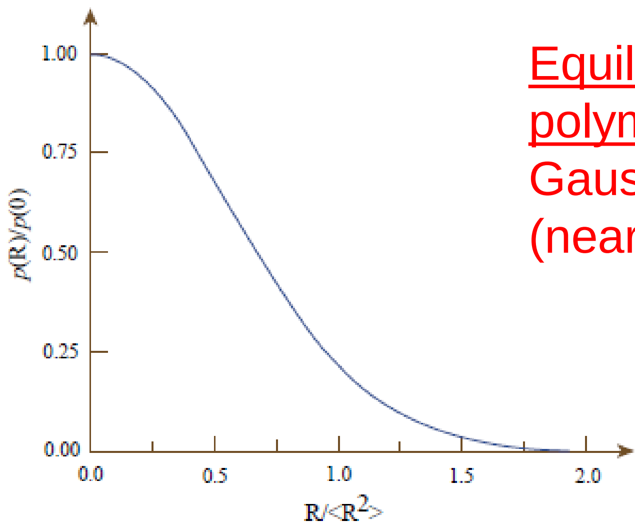


Random walk statistics (same step R)

Probability density function (for end-end distance):

$$P(\underline{R}_0 = \underline{R}) \propto \exp\left(\frac{-3|\underline{R}|^2}{2Nb^2}\right)$$

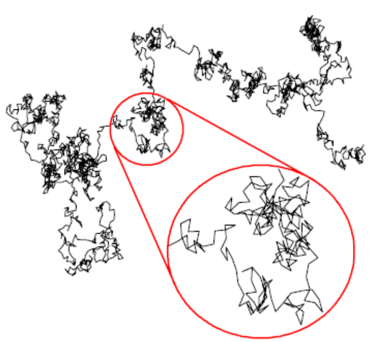
(Gaussian)



Equilibrium form of polymer chain: Gaussian coil (nearly spherical)

Compare:

$V=Nb^3$ vs. $V=R^3=N^{3/2}b^3$

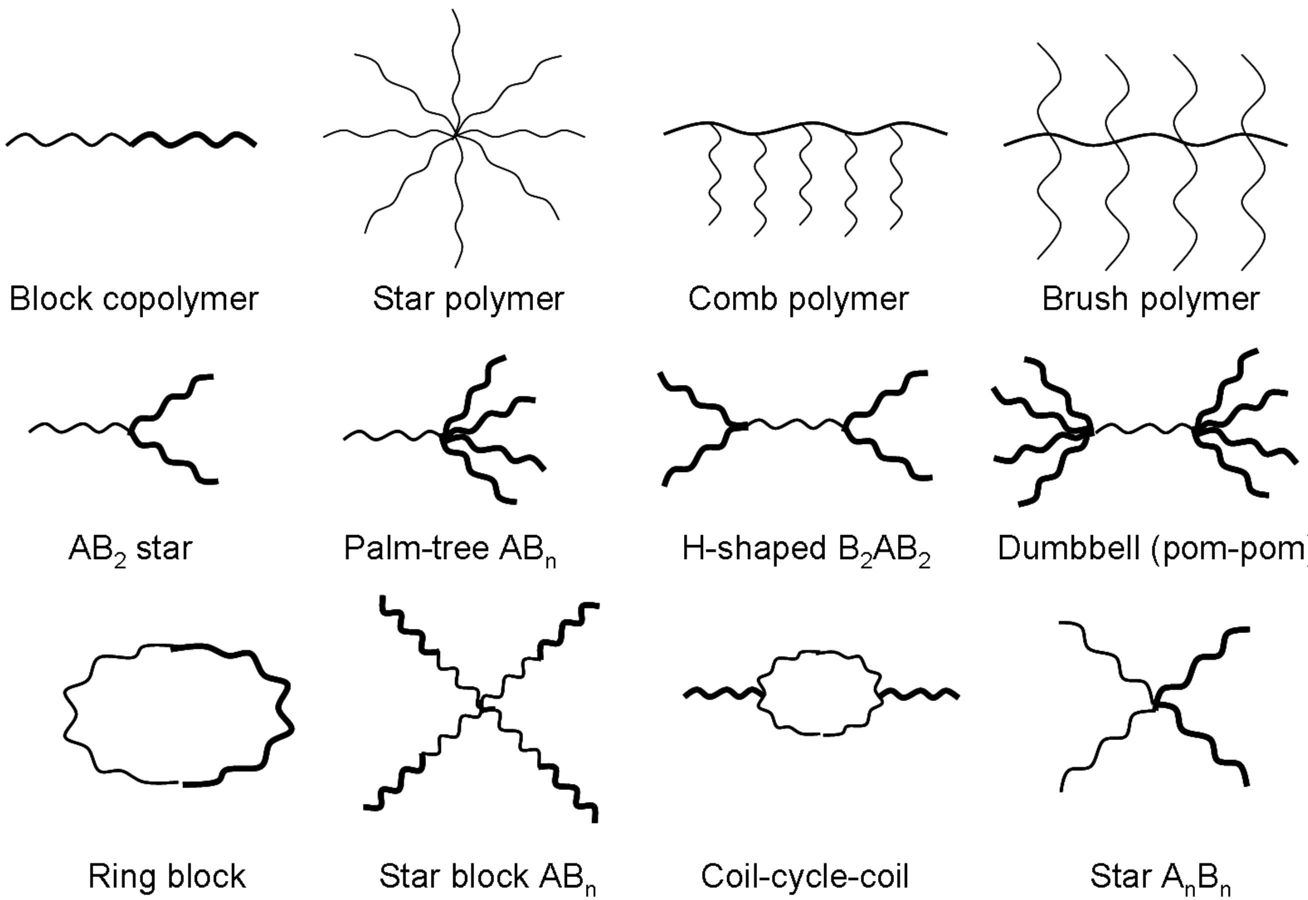


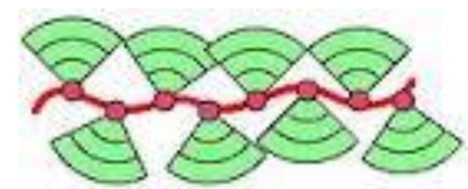
Polymers are fractal objects (here for ideal chain, $d_f=2$)

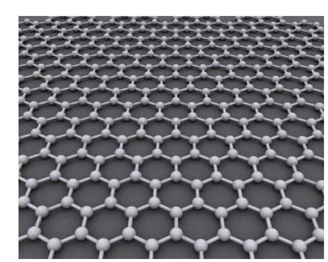
Question:

Can I define the end-to-end distance of any polymer unambiguously?

Do I need another measure of length?



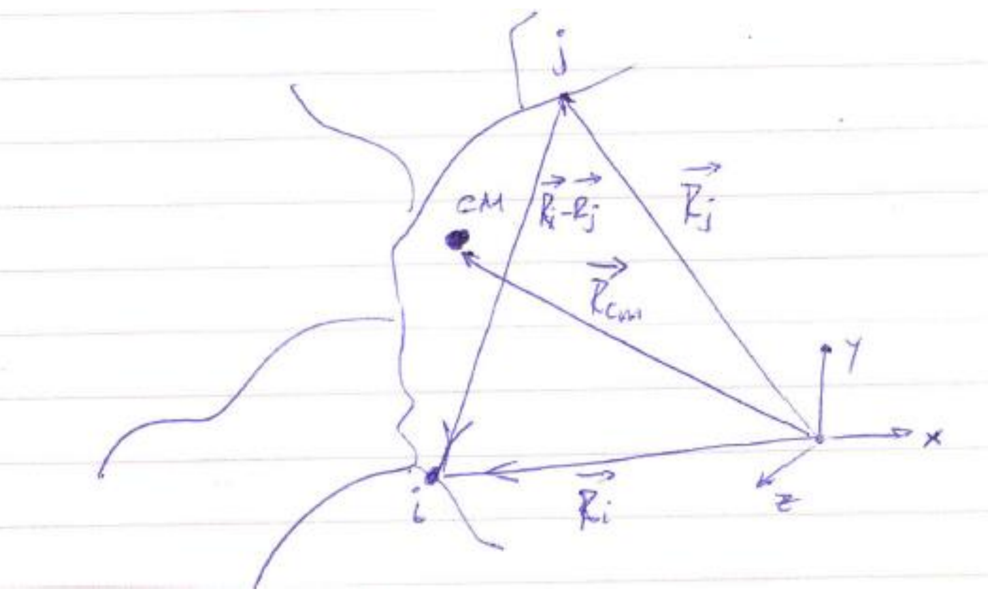




Radius of gyration

(also for nonlinear polymers)

$$R_g^2 \equiv \frac{1}{N}\sum_{i=1}^{N}(\vec{R}_i - \vec{R}_{cm})^2$$



$$< R_g^2 >= \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N} < (R_i - R_j) >^2$$

Ideal

$$< R_g^2 >= \frac{1}{N^2}\int_0^N\int_u^N < (R(u) - R(v))^2 > dvdu = Nb^2/6$$

$$< R_g^2 >= \frac{< R^2 >}{6}$$

Debye

Rod: L=Nb $<R_g^2>=L^2/12$

Question:

How many characteristic lengths exist in a polymer?

Why?

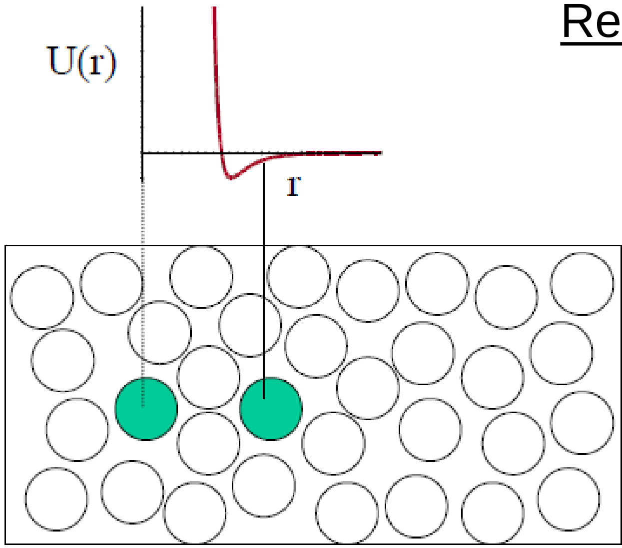
What dictates the form (shape) of a flexible chain?

Think of degrees of freedom

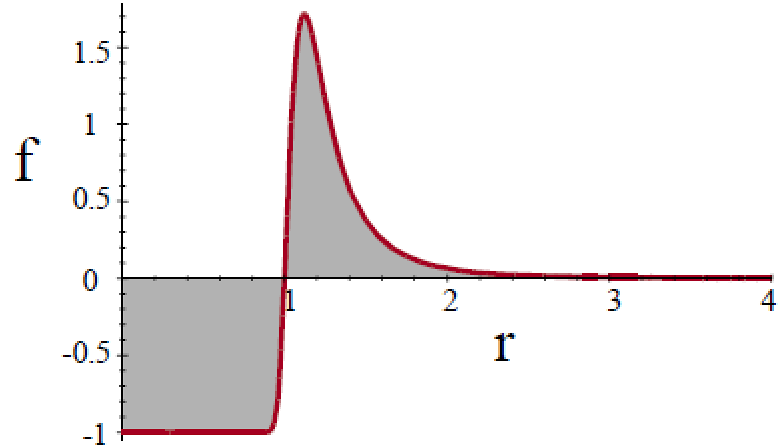
What is the effect of solvent?

The effects of solvent quality (temperature)

Monomer pair interaction potential in solution; Boltzmann factor; f-Meyer function; excluded volume



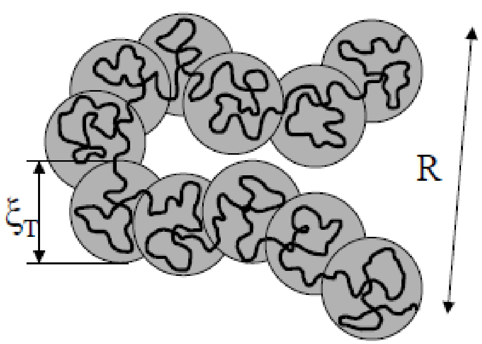
Real chains



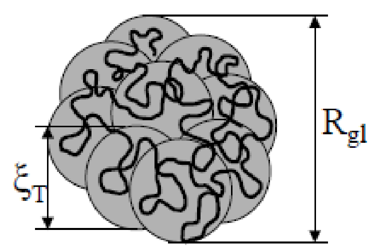
$$v = -\int f\left(\overrightarrow{r}\right) d^3 r = \int \left(1 - \exp\left[-U(r)/(kT)\right]\right) d^3 r$$

Athermal, good: $v>0$; theta: $v=0$; bad, non-solvent: $v<0$

Athemal: $v_{max}=b^3$ non-solvent: $v_{min}=-b^3$



Good solvent

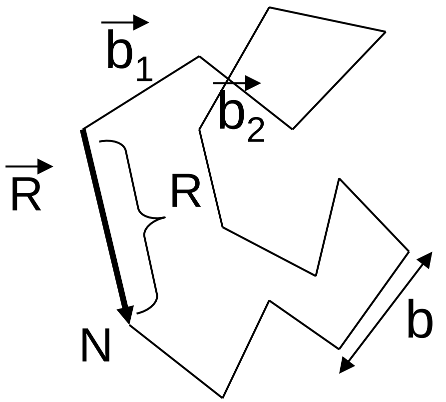


Poor solvent

Thermal blob $\xi_T \approx b g_T^{1/2}$

Rubinstein, Colby, Polymer Physics 2003

The effects of solvent quality (temperature)



Theta solvent (T_θ): $R \sim N^{1/2}$

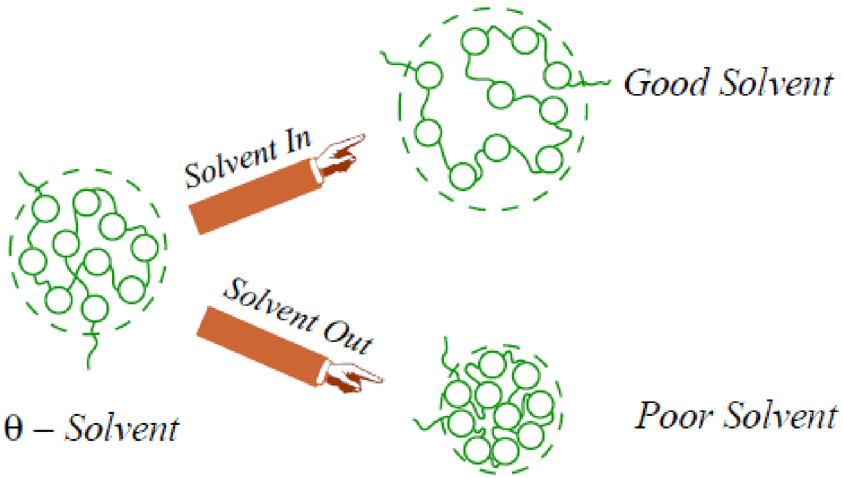
P. J. Flory
1910-1985

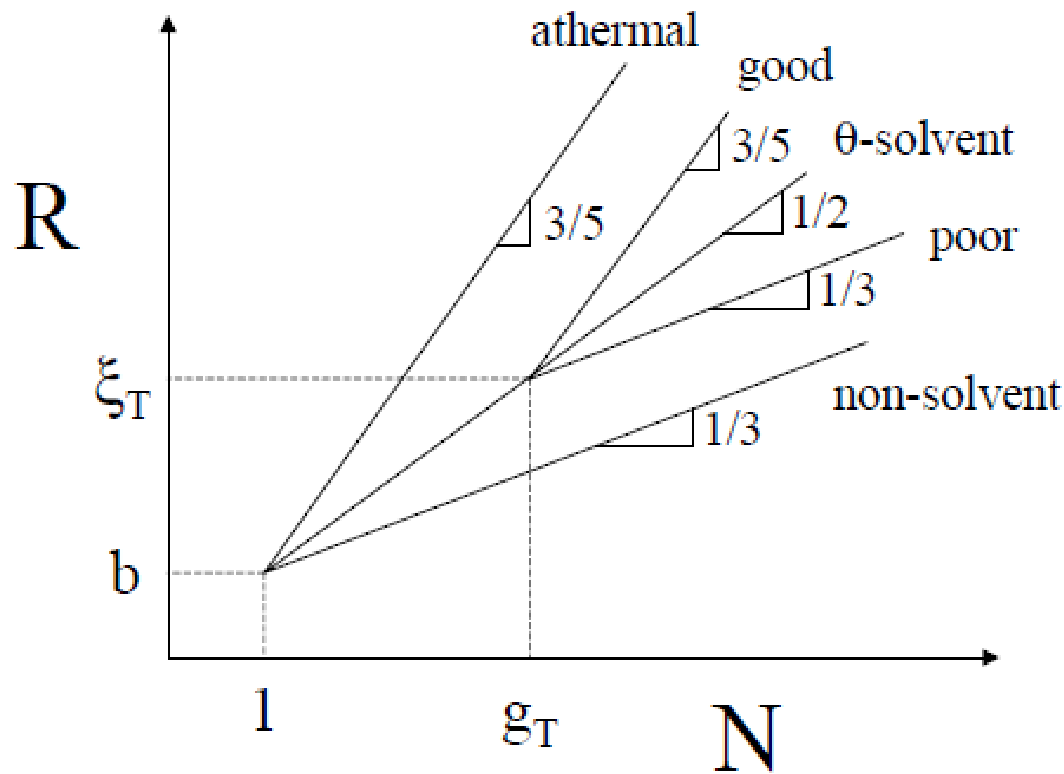
Interactions:

- Good solvent: $T > T_\theta$, $R \sim N^{3/5}$ swelling
- Poor solvent: $T < T_\theta$, shrinkage (phase separation)
- Range: Athermal, good, theta, bad, non-solvent

Key idea: blobs, excluded volume
Approach: minimize free energy to get size

$$F = F_{int} + F_{ent} \approx kT\left(v\frac{N^2}{R^3} + \frac{R^2}{Nb^2}\right) \qquad \frac{\partial \Delta F}{\partial R} = 0 \qquad R_F \approx v^{1/5} b^{2/5} N^{3/5}$$

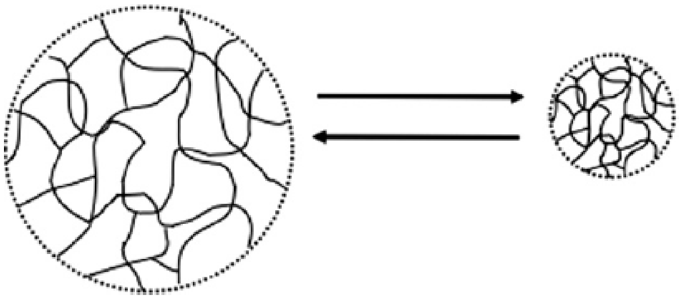




Rubinstein, Colby, Polymer Physics 2003

Application:

thermoresponsive polymers (e.g., PNIPAM microgels)



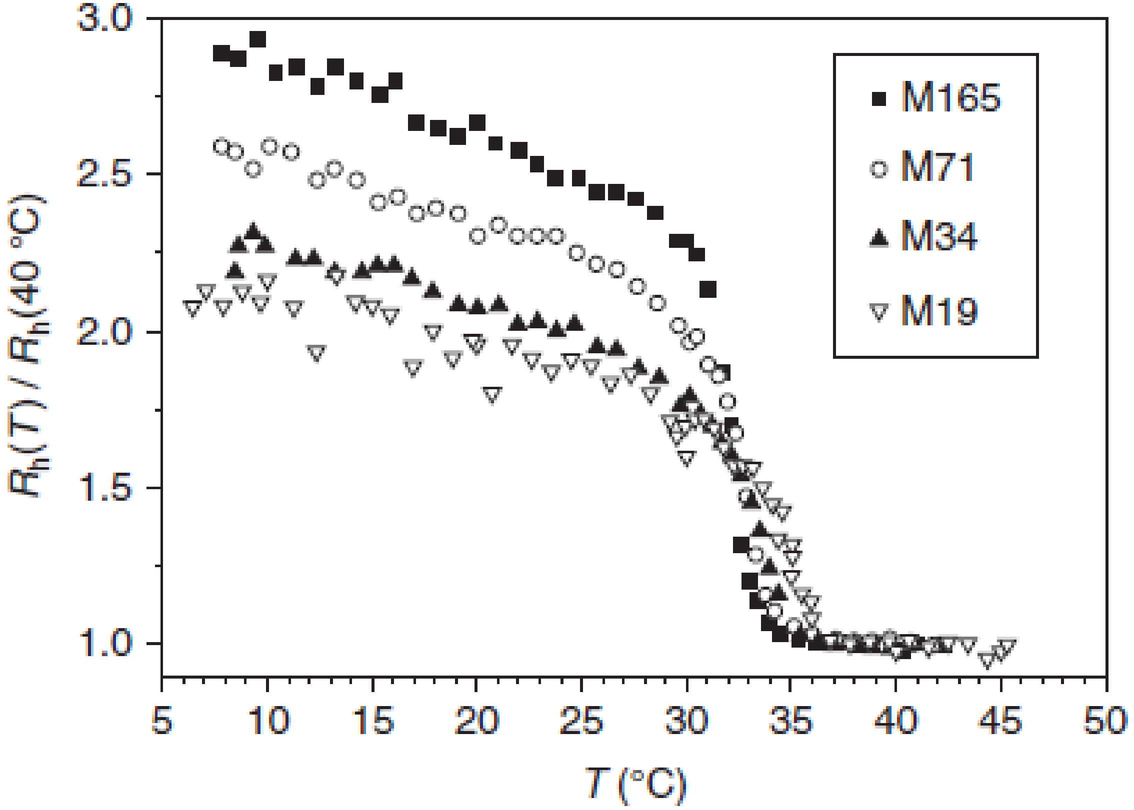
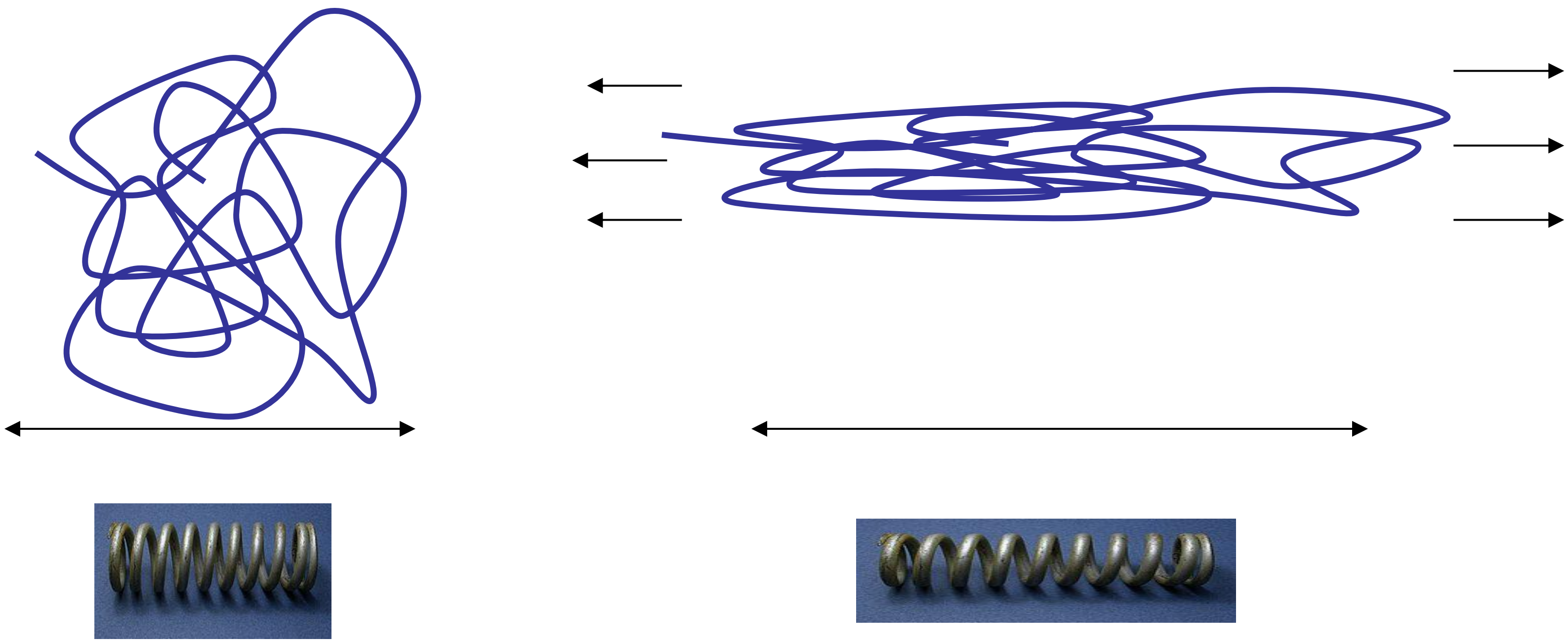


Figure 18 Size of PNIPAM microgels with different cross-linker content (increasing from top to bottom) vs. temperature. Reproduced with permission from Figure 1 in Senff, H.; Richtering, W. *Colloid Polym. Sci.* **2000**, *278*, 830.[141]

Chain elasticity:

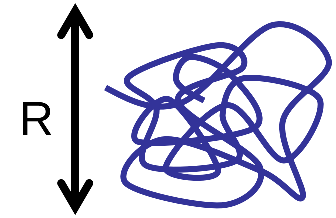
"Gedankenexperiment":



Pull the chain with hands by exerting a force *f*.
The chain deforms due to its elasticity – it changes conformation
It exerts on hands a force –*f*.
This force relates to the change of conformation (thermodynamics)
Force is derivative of (free) energy to distance
Relate force to deformation via Hooke's law

Chain elasticity

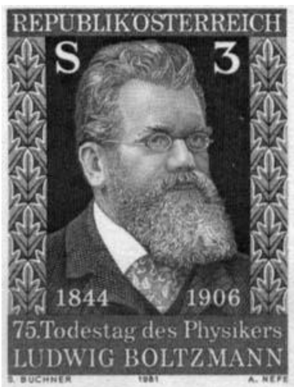
$$P(R) \propto \exp\left(\frac{-3R^2}{2Nb^2}\right)$$



$R=bN^{1/2}$

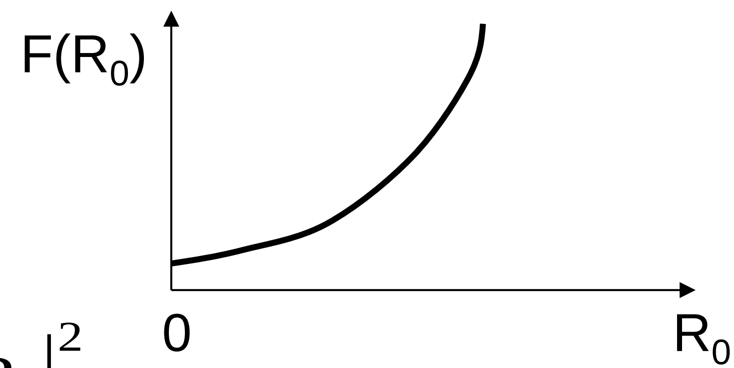
Free energy: $\Delta F = \Delta U - T\Delta S = -T\Delta S$

0 (ideal polymer)



Boltzmann:

$$S = k \ln P$$



$$\frac{F(\underline{R}_0)}{kT} = const + \frac{3}{2Nb^2}\left|\underline{R}_0\right|^2$$

$$f = \frac{\Delta F}{\Delta R} \Rightarrow \sigma = \frac{3kT}{Nb^2}R$$

$$G = \frac{3kT}{Nb^2}$$

Entropy elasticity

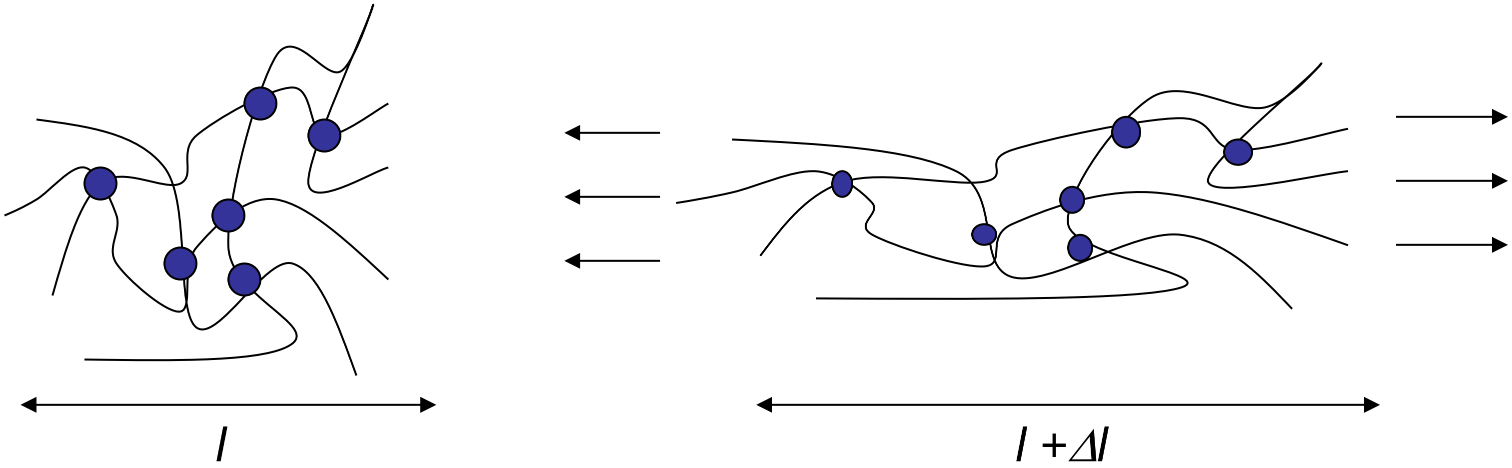
Question:

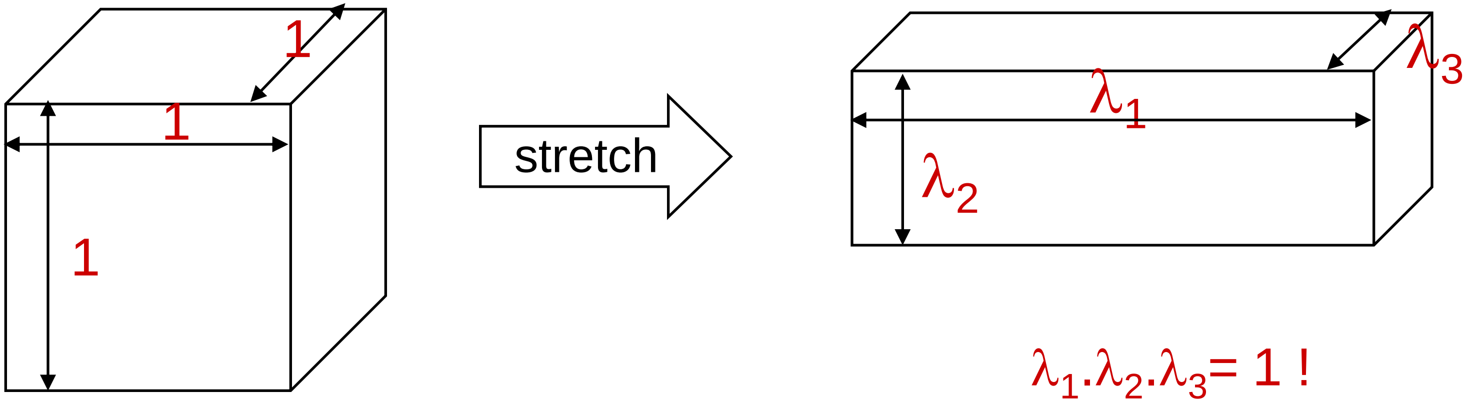
Why we call the chain elasticity “entropy” elasticity?

Explain why, for the same applied stress, a metal deforms far less than a polymer

Under a certain applied load (weight), a polymer chain deforms. We then increase the temperature. Is the (fractional) deformation going to change and how?

Rubber elasticity (main chains, crosslinked):





We consider an affine deformation with the principal directions aligned with the coordinate system and principal deformations λ_1 λ_2 λ_3

Use Flory's conjecture (ideal chain statistics in melt)

Rubber elasticity (main chains, crosslinked):

$$\sigma = 3kT\nu \frac{\Delta l}{l}$$

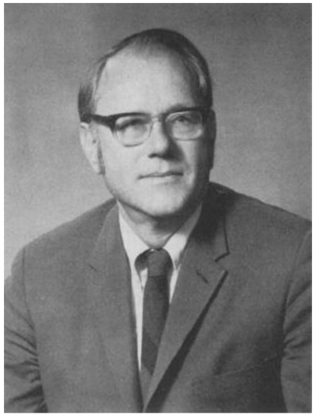
ν = number concentration of elastically active elements

$$G \approx \nu kT$$

$\nu \sim 1/\xi^3$

$$G \approx \frac{kT}{\xi^3}$$

Relates modulus to size



Green and Tobolsky (1919-1972)

Question:

Can I probe the concentration of junctions in an associating polymer or a crosslinked rubber? How?

Can I probe characteristic length scales in polymers? How?
What is their meaning?