Section 5 Polymer chain configuration and chain entropy

5.1 The overall picture

Polymer Chain Configuration

The physical configuration of a polymer chain is important in relation to many **process** and end user **properties.**

Key Temperatures **T_d = dissolution Temp.**

often room temp $\rightarrow$ 150°C

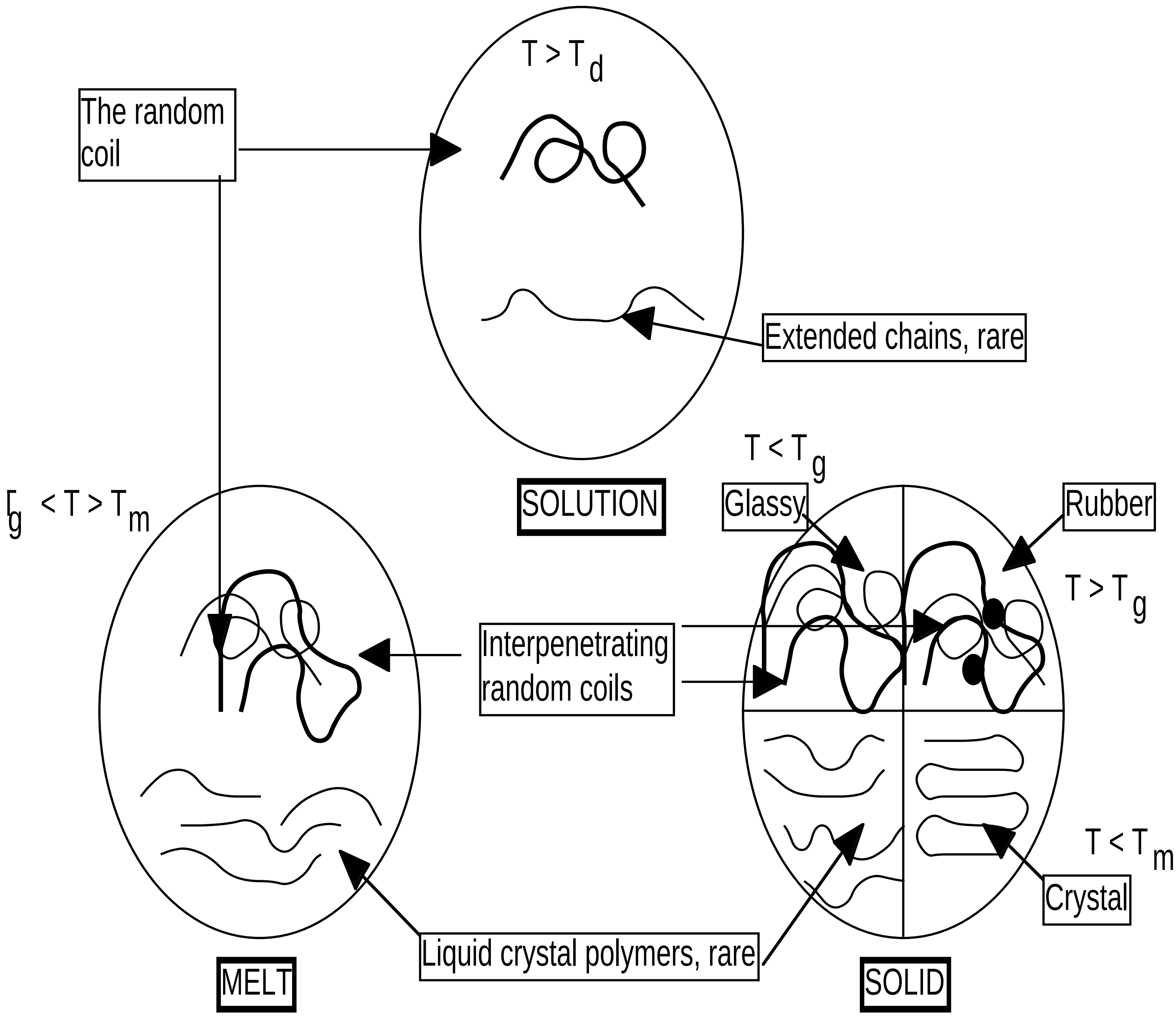
T_g = Glass transition Temperature

$\approx$ -80°C $\rightarrow$ 300°C

T_m = melting temperature (if crystalline)

$\approx$ RT $\rightarrow$ 350°C

Schematic of chain configuration in different phases



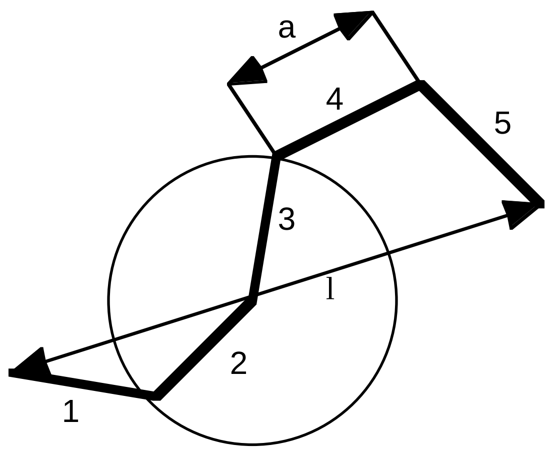
The polymer can be in a random coil configuration when the chain is **in solution, in the melt or in the solid state**.

5.2 The random walk of a single polymer chain

We wish to establish the chain configuration of polymer chains.

Reading. Treloar, Tanford, Flory.

Assume a chain consists of r links each of length a. Let each link take a random configuration wrt adjacent link.



We are interested in determining the characteristic dimensions of the chain and we will show, route mean square end to end distance is given

by, $$\langle r^2 \rangle^{1/2} = l_o = ar^{1/2}$$

Typical example $a = 1$ nm $\left(10\,\dot{A}\right)$

$r = 10^4$

RMS end-to-end dist $l_o = 10^2$ nm $\left(1{,}000\,\dot{A}\right)$

Extended length $ar = 10^4$ nm , 10 μm, $10^5\,\dot{A}$

Polymer random coils occupy dimensions typically

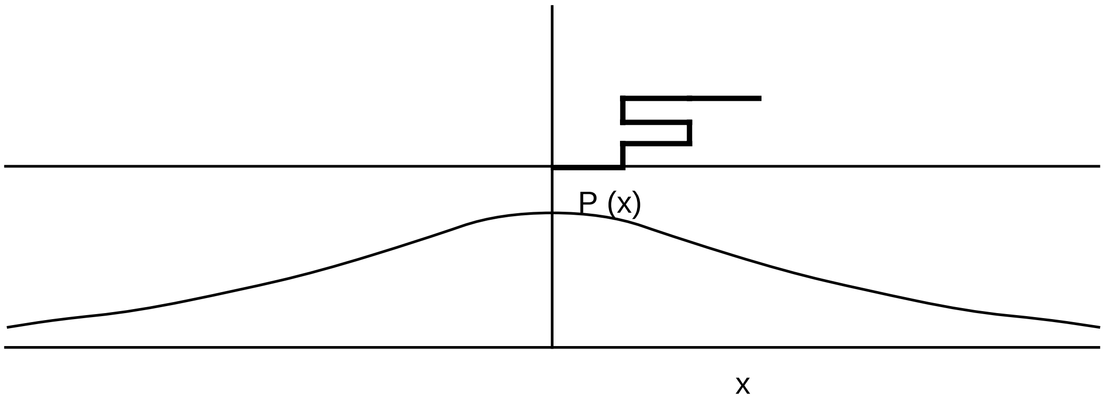
$l_o \sim 10\ nm\ 100\,\dot{A}\ -\ 100\ nm,\ 1000\,\dot{A}$

Note:- **very much less than extended length**.

The one dimensional random walk

Lord Rayleigh (1919) Sci Papers Vol VI, 604 - 627

r steps at random
each of length **a**



P(x) is probability that after r random steps each of length a that end of chain is at a position x from origin.

Start at origin, r steps each of length a.

Forward and backward steps equally likely.

In order to get to x we make

r_f = number of forward steps
r_b = number of backward steps
total $r = r_f + r_b$

$x = ar_f + (-a)r_b$

So

$$\mathbf{r_f = \frac{1}{2}\left(r + \frac{x}{a}\right), \quad r_b = \frac{1}{2}\left(r - \frac{x}{a}\right)}$$

A displacement + x results from r_f forward steps and r_b backward steps in any order.

Number of ways displacement can be made

$$\left[\mathbf{{}_n c_m = \frac{n!}{m!(n - m)!}}\right]$$

number of ways m can be selected from n things.

W_x = Nos ways displacement x can be made.

$$= \frac{r!}{r_f!\,r_b!} = \frac{r!}{\left(\frac{1}{2}\left(r + \frac{x}{a}\right)\right)!\left(\frac{1}{2}\left(r - \frac{x}{a}\right)\right)!}$$

note r typically 10^2 - 10^4 i.e., large

Use Stirlings Approx 1n r! = rlnr - r

$$\ln W_x = r\ln r - \frac{1}{2}\left(r + \frac{x}{a}\right)\ln\frac{1}{2}\left(r + \frac{x}{a}\right) - \frac{1}{2}\left(r - \frac{x}{a}\right)\ln\frac{1}{2}\left(r - \frac{x}{a}\right)$$

(other terms cancel out) Now, $\ln\frac{1}{2}\left(r + \frac{x}{a}\right) = \ln\frac{r}{2}\left(1 + \frac{x}{ra}\right)$

rearrange

$$\ln W_x = r\ln r - \frac{1}{2}\left(r + \frac{x}{a}\right)\ln\frac{r}{2} - \frac{1}{2}\left(r - \frac{x}{a}\right)\ln\frac{r}{2}$$
$$-\frac{1}{2}\left(r + \frac{x}{a}\right)\ln\left(1 + \frac{x}{ra}\right) - \frac{1}{2}\left(r - \frac{x}{a}\right)\ln\left(1 - \frac{x}{ra}\right)$$

if x << ra then $\ln\left(1 + \frac{x}{ra}\right) = \frac{x}{ra} - \frac{x^2}{2r^2a^2}$ ....

$$\ln W_x = r\ln 2 - \frac{1}{2}\left(r + \frac{x}{a}\right)\left(\frac{x}{ra} - \frac{x^2}{2r^2a^2}\right) \;.......$$

$$-\frac{1}{2}\left(r - \frac{x}{a}\right)\left(-\frac{x}{ra} - \frac{x^2}{2r^2a^2}\right)........$$

assume x/ra << 1, 1st terms only

$$\left[\ln W_x = r\ln 2 - \frac{r}{2}\left[\frac{x}{ra} + \frac{x^2}{r^2a^2} - \frac{x^2}{2r^2a^2} - \frac{x}{ra} + \frac{x^2}{r^2a^2} - \frac{x^2}{2r^2a^2}\right.\right.$$

$$\ln W_x = r\ln 2 - \frac{x^2}{2ra^2}$$

$$W_x = e^{r\ln 2}e^{-x^2/2ra^2}$$

Now Probability of displ x is proportional to the number of ways displ can be made

$$P_x \propto W_x$$

$$\underline{\mathbf{P_x = A\,e^{-\frac{x^2}{2ra^2}}}}$$

where A is a constant for a given r

Determine A from BC

$$\sum_{-ra}^{ra} P_x = 1 \approx \int_{-\infty}^{\infty} A e^{-x^2 / 2ra^2} dx = 1$$

Discreet Continuous

$$\left[\int_{-\infty}^{\infty} e^{-bx^2} dx = \left[\frac{\Pi}{b} \right]^{1/2} \right]$$

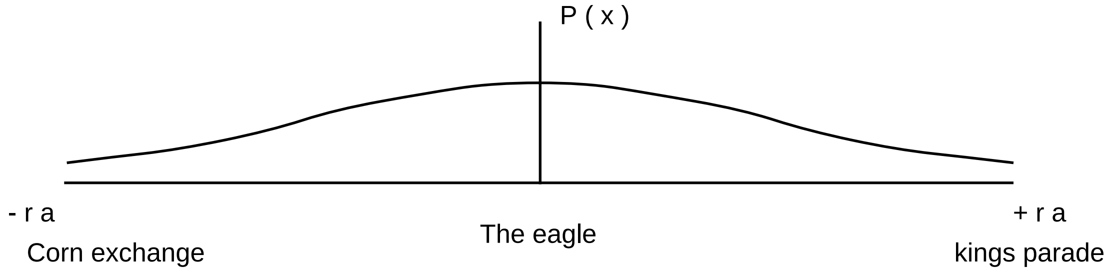
Yields $A = \dfrac{1}{a(2\Pi r)^{1/2}}$

Then $P_x = \dfrac{\beta^{©}}{\pi^{1/2}} e^{-\beta^{©2} x^2} dx$ .... (1)

P_x prob of finding and end between x and x + dx.

where $\beta^{©2} = \dfrac{1}{2ra^2}$

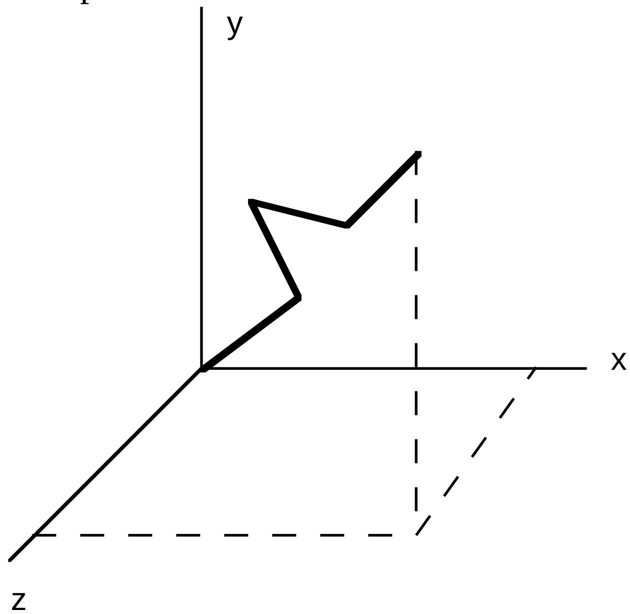
Gaussian Probability



Magnitude and width of probability distribution controlled by number of repeat units (steps) and length of step (ra^2) term.

5.2. 3 Dimensional random flight

Fix one end at origin, Probability (x) with be less than 1D problem as total path will involve movements in x and y.



Given without proof.

Mean square projection of a on x given by

$$\bar{a}_x^2 = \frac{a^2}{3}$$

For 3D (given without proof)

$$P_x = \frac{\beta}{\Pi^{1/2}} e^{-\beta^2 x^2} dx$$

where $\beta^2 = \dfrac{3}{2ra^2}$

Probability of finding end with coordinate (x,y, z) in element dxdydz.

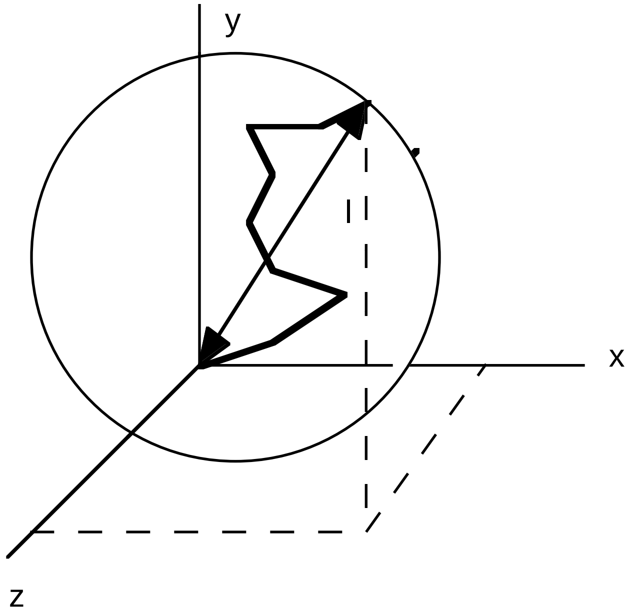
$P_{xyz}, = P_x P_y P_z dxdydz$

$$= \frac{\beta^3}{\Pi^{3/2}} e^{-\beta^2\left(x^2 + y^2 + z^2\right)} dxdydz \quad \ldots (1)$$

where $\beta^2 = \dfrac{3}{2ra^2}$

Eliminate direction

What is probability of finding chain with an end-to-end distance between l and l + dl.



end could be anywhere on shell dist l form origin

$$\mathbf{P_{xyz}} = \frac{\beta^3}{\Pi^{3/2}} \, \mathbf{e}^{-\beta^2(x^2 + y^2 + z^2)} \mathbf{dxdydz}$$

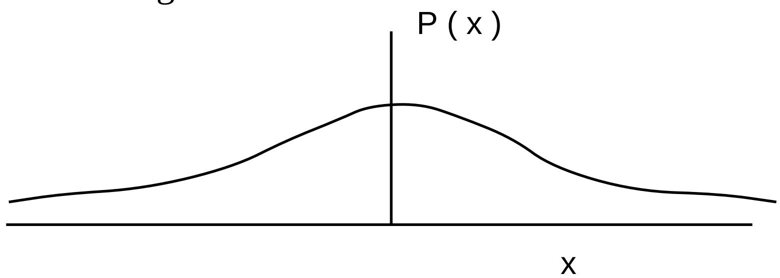
Prob end in a shell of inner radius l and outer radius l + dl.

$$\mathbf{P_1} = \frac{\beta^3}{\Pi^{3/2}} \, \mathbf{e}^{-\beta^2 l^2} \, \mathbf{4\Pi \, l^2 dl}$$

$$\mathbf{P_l} = \frac{4\beta^3}{\Pi^{1/2}} \, \mathbf{l^2 e^{-\beta^2 l^2} dl}$$

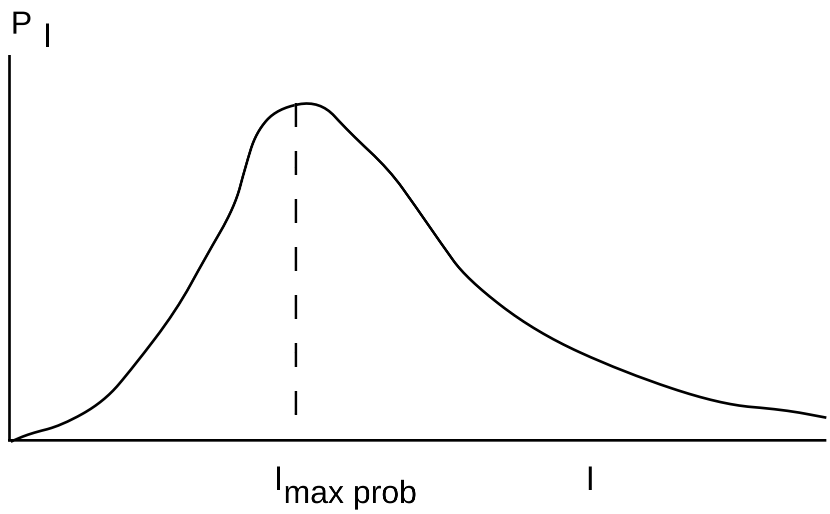
P_x plot

Max at origin



P_l plot

Max at finite value of l



We have a prob distribution and need "average" or representative length scales of that distribution. We could take moments (as with the MW distribution) ,however it is traditional to take one of the following.

5.3 Average Properties

a) **Radius of maximum probability** $l_{max,\ prob.}$

$$\frac{dP_l}{dl} = \frac{8\beta^3}{\Pi^{1/2}} e^{-\beta^2 l^2}\left(1 - \beta^2 l\right) = 0$$

Yields $$l_{max\ prob} = \frac{1}{\beta} = \left(\frac{2}{3}\right)^{1/2} ar^{1/2}$$

b) **Average radius** $\bar{l}$ (which is in fact the first moment)

$$\bar{l} = \frac{\int_o^\infty P_l l dl}{\int_o^\infty P_1 dl} = \frac{2}{\Pi^{1/2}} \frac{1}{\beta}$$

Yields $$\bar{l} = 2\left(\frac{2}{3\Pi}\right)^{1/2} ar^{1/2}$$

c) **Root mean square end-to-end distance** l_o

$$\mathbf{l_o} = \left(\overline{l^2}\right)^{1/2} = \left[\frac{\int P\, l^2 dl}{\int P_l dl}\right]^{1/2} = \left(\frac{3}{2}\right)^{1/2} \frac{1}{\beta}$$

this is not the 2nd movement

Yields $\mathbf{l_o = ar^{1/2}}$

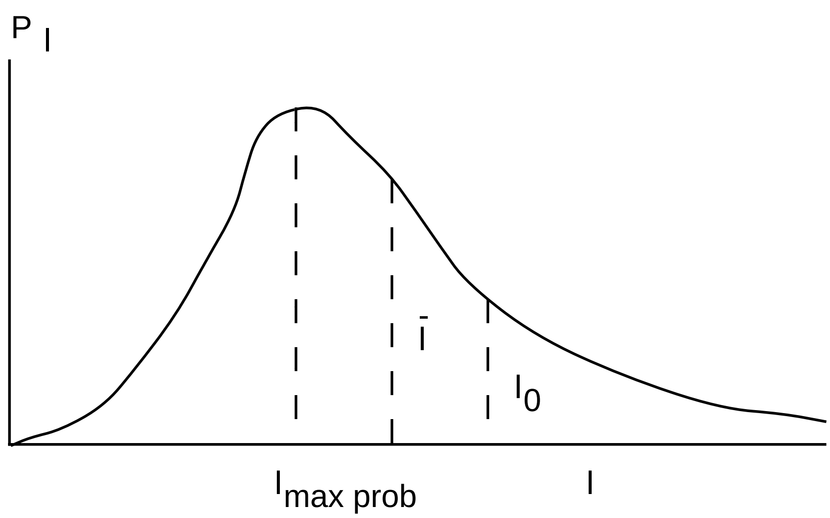
Ex. let r =5000, a = 0.2 Nm $(2.0\,\dot{A})$

$l_{max\ prob}$ = 11.55 nm $(115.5\,\dot{A})$

$\bar{l}$ = 13.05 nm $(130.5\,\dot{A})$

l_o = 14.9 nm $(149.0\,\dot{A})$

$l_{max\ prob} < \bar{l} < l_o$



Note extended length of chain L = r a

$$= 5 \times 10^3 \times 2 = 10^4\,\dot{A} = 1\,\mu m$$

(Justification for integration limits of P_x distribution)

Extension ratio necessary to stretch chain from random coil to extended chain λ_o

$$\lambda_o = \frac{L}{l_o} = \frac{ra}{r^{1/2}a} = r^{1/2}$$

say

For r = 5 x 10^3, λ_o = 70 (a big number)

If chain exists in random configuration, the overall dimensions of chain is very much less than its extended length

l_o typically 10 - 100 nm

Random coils

The story so far

r = nos repeat units

a = chain length

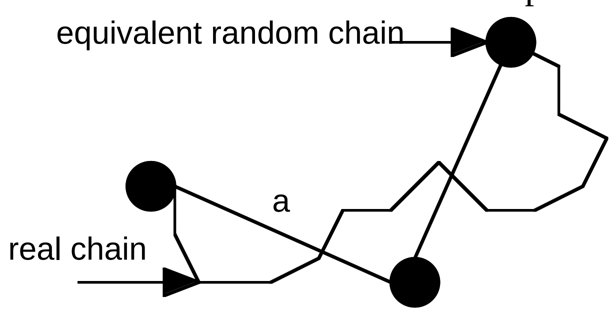
l = end-to-end distance

RMS end-to-end distance $\underline{l_o = ar^{1/2}}$

5.4 The equivalent random chain

Real polymer chains

Real chains may have finite bond angles between repeat units. This and other effects leads to the concept of the <u>equivalent random chain</u>.



We can (in principle) measure l_o of real chain (light scattering) l_o^R

We can (with difficulty) measure extended length of real chain L = L^R

Match l_o and L for real and equiv random chain.

$\mathbf{l_o = ar^{1/2} = l_o^R}$

$\mathbf{L = ar = L^R}$

So

$$\mathbf{a} = \frac{[l_o R]^2}{L^R}, \quad \mathbf{r} = \left[\frac{L^R}{l_o{}^R}\right]^2$$

Ex PE $\quad \underset{\substack{\leftrightarrow \\ 2.54\dot{A}}}{[CH_2 - CH_2]}$

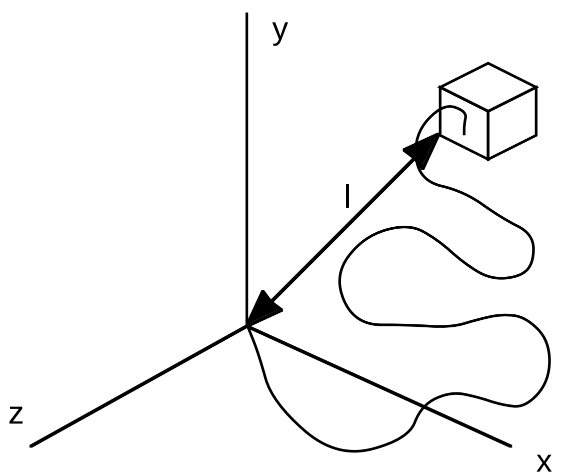
Link length of equiv. random chain = $16.7\dot{A}$

So simply replace equiv. random chain a and r and treat these as random coils.

5.5 Application of random coil concept - Entropy springs

5.5.1 Individual polymer chains and entropy springs

One chain end at origin, other in vol $d\tau$ dist l from origin



$$\mathbf{P_l} = \frac{\beta^3}{\pi^{3/2}} e^{-\beta^2 l^2} d\tau$$

where P_1 is prob of finding end is vol $d\tau$

$$\beta^2 = \frac{3}{2ra^2}$$

r = equiv nos links

a = length of equiv repeat unit

Number of chain configerations available W for chain

$$\mathbf{W} = \mathbf{C\,P(l)}d\tau$$
$$= \mathbf{C^1 \exp\left(-\beta^2 l^2\right)}d\tau$$

From Statistical Mechanics

S = **k lnW** k = Bolts Const.

k = 1.3806 x $10^{-23} JK^{-1}$

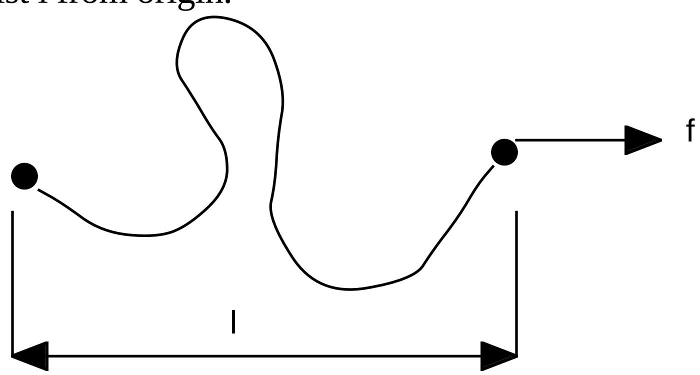
$$\mathbf{S = k\ ln\left(c^1 exp\left(-\beta^2 l^2\right) d\tau\right)}$$

$$\mathbf{S} = C'' - k\beta^2 l^2$$

Entropy of chain is a max when l = 0
" " ' " " min " 1 = ra
Chain stretches → entropy decreases.

5.5.2 The tension, f, in a single chain

Fix one end at origin. Determine force f on other end when held at dist l from origin.



Assume reversible process

$$\mathbf{dW = dU - TdS}$$

$$\mathbf{dW = fdl}$$

$$\mathbf{f = \frac{dW}{dl} = \left[\frac{\partial U}{\partial l}\right]_T - T\left[\frac{\partial S}{\partial l}\right]_T}$$

Assume $\left[\frac{\partial U}{\partial l}\right]_T = 0$ (Justification comes from temp dependance of

Elasticity for rubbers. See Treloar if worried about this).

but $S = C'' - k\beta^2 l^2$

so $\quad \dfrac{\partial S}{\partial 1} = -2k\beta^2 l$

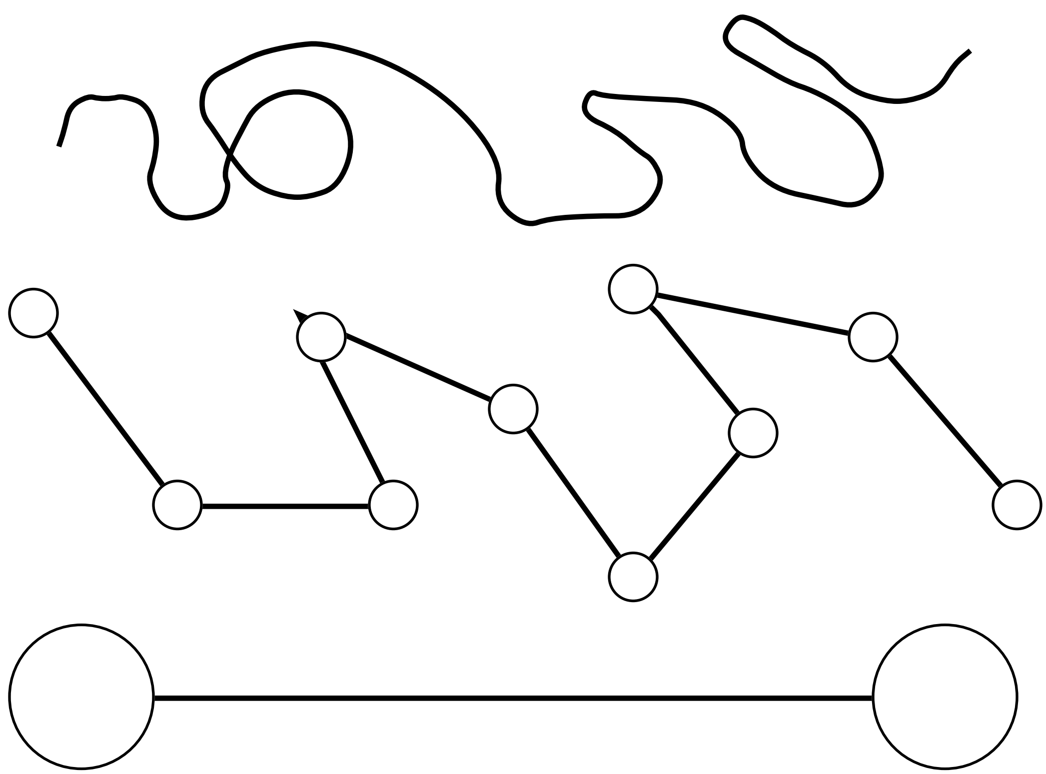
so $\quad f = 2kT\beta^2 l$

$$\mathbf{f = \frac{3kT}{ra^2}\, l}$$

- Single chain behaves as Hookian spring with zero unstrained length.
- Elastic response is entropic. Origin of elasticity in rubbers, polymers solns and melts (not polymer solids where elasticity can be entropic and or internal energy change).
- Note, F increases with inc T (surprise)?
  " " " " l
  " decreases with inc nos repeat units (MM).

5.5.3 Modelling the behaviour of individual polymer chains

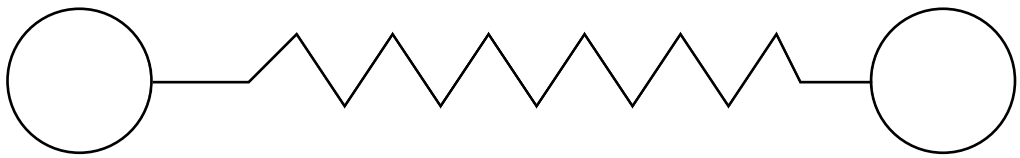
Points of hydrodynamic interaction



5.5.4 **The Dumbell polymer chain and its associated "Rouse relaxation time"**

The dumbell chain is a viscoelastic chain. It possesses Elasticity, from entropy and viscosity from hydrodynamic interaction.

Elasticity $\Rightarrow$ Entropy $\quad \mathbf{f_E = -Kl}$



Entropic force is always trying to bring ends together

$$K = \frac{3kT}{ra^2}$$

prop to end-to-end separation

Viscosity $\Rightarrow$ assume hydrodynamic interaction concentrated at ends

Stokes flow $\quad \mathbf{f_v = 6\pi D\, \eta_o\, U}$

___________Dia of sphere
Solvent viscosity Velocity of end

Rouse relaxation time λ_R

Stretch chain to end-to-end separation l_o. Follow relaxation behaviour.
Fine balance on end (ignore inertia).

$$\sum \mathbf{F_i} = \mathbf{m}\ddot{\mathbf{x}} = \mathbf{0}$$

$$\sum \mathbf{F_i} = \mathbf{0}$$

$$(-f_E) + f_v = 0$$

$$\Pi D\eta_o \frac{dl}{dt} = -\frac{3kT}{ra^2} \times l$$

$$\frac{dl}{l} = -\lambda_R dt$$

$$l = l_o e^{-t/\lambda_R}$$

where $\lambda_R = \frac{\Pi D\eta_o}{3kT} ra^2$

What is D? (Guess!) $D \approx \frac{ar}{20}$ say

So $\lambda_R = \frac{\Pi\eta_o a^3 r^2}{10\ kT}$

Note $M = M_o r$

$$\lambda_R = \frac{\Pi}{10} \frac{\eta_o a^3}{kT} \frac{(M)^2}{M_o^3}$$

So $\lambda_R \propto M^2$

Relaxation time increases with $(MM)^2$

Ex. $\eta_o \sim 10^{-3}$ Pas

a ~ 1 nm (say)

r ~ 10^{-3} (say)

$\underline{\lambda_R \sim 10^{-3}\ 10^{-4}\ s}$

Polymers in dilute solution Relaxation times

$\lambda \sim 10^{-1}$ ________ $\rightarrow$ $10^{-5}\ s^{-1}$

high MM low MM

Polymers, conc soln and melt (extra hydrodynamic interaction)

$\lambda \sim 10^{3}$ _________ $\rightarrow$ $10^{-3}\ s^{-1}$

high MM low MM

Most polymers samples are polydisperse hence most polymer samples will possess a range/spectrum of relaxation times.______