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Size of a polymer chain

Random flight, freely jointed ~~jo~~ chain

$$r_x = \sum_i b\cos\theta_i = b\sum \cos\theta_i$$

now - average over all possible configurations

$$\langle r_x \rangle = \langle b\cos\theta_i \rangle = b\sum_{i=1}^{N} \langle \cos\theta_i \rangle = 0$$
$$= \langle r_y \rangle = \langle r_z \rangle$$

Better measure

mean square end-end distance

$$\langle r^2 \rangle = \vec{r}\cdot\vec{r} = \left(\sum_{i=1}^{N} l_i\right)^2 = l_1 l_1 + l_1 l_2 + \cdots l_1 l_N$$
$$+ l_2 l_1 + l_2 l_2$$

self terms $\langle l_i \cdot l_i \rangle = b^2$ ← N of term

cross terms $\langle l_i \cdot l_j \rangle = b \langle \cos\theta_i \rangle = 0$

$$\langle r^2 \rangle = Nb^2$$

$$\boxed{\langle r^2 \rangle^{1/2}_{\text{ideal}} = N^{1/2} b}$$

root mean square end-end distance

Radius of Gyration

2nd measure – chain is an assembly of mass elements

s_i = distance to mass element i from center of mass

$$s^2 = \frac{\sum_i m s_i^2}{\sum m} = \sum_{i=1}^{N} \frac{s_i^2}{N} \equiv R_g \quad \text{radius of gyration}$$

Won't derive, but can show

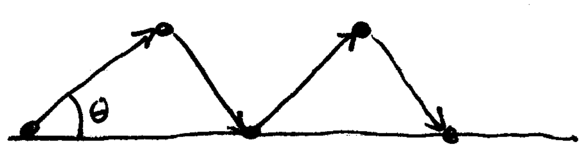
$$\boxed{R_g = \frac{\langle r^2 \rangle^{1/2}}{\sqrt{6}} = \frac{N^{1/2} b}{\sqrt{6}} \equiv \text{Radius of Gyration}}$$

$\Rightarrow$ can be measured experimentally

REAL CHAINS

- Hindrance to bond rotation
- Correlations between bond angles

Consider a chain w/ fixed bond angles but no hindrance to rotation " freely rotating



Can show: $\langle r^2 \rangle \simeq \frac{1-\cos\theta}{1+\cos\theta} N b^2$

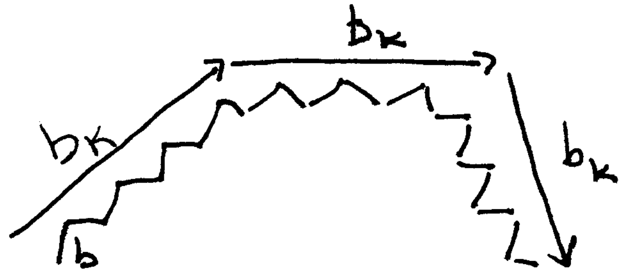
eg. $\theta = 110$, $\langle r^2 \rangle_{110} = 2 N b^2$

Polymer size still scales as Nb^2

Define $C_N \equiv$ Characteristic ratio

$$\langle r^2 \rangle_{nonideal} = N C_N b^2$$

Another model – rescale chain to account for bond correlation – Kuhn segment length



$$\langle r^2 \rangle_{nonideal} = N_K b_K^2 = N C_N b^2$$

Says real chains behave like ideal chains on some scale, defined by Kuhn segment size

	b_K (nm)
Actin	16,700
DNA	100
polyethylene	1.2
polyethylene glycol	0.34

Probability States for ideal Chain (Required for Entropy!)

Start with 1-dimension (say, x)

Chain is built by a sequence of steps in $+x$ or $-x$ direction

N = total steps

m = steps in $\oplus$ x

$N-m$ = steps in $\ominus$ x

m^* = most probable # of steps in $\oplus x = \frac{N}{2}$

Do the expt for N steps — Like coin flips ⇒ Gaussian

normalizing factor

$$P(m,N) = P\, e^{-2(m-m^*)^2/N}$$

net # steps in $\oplus$ x $= m - (N-m) = 2m - N$

Ave step length $\oplus x = \langle l_x^2 \rangle^{1/2} = \langle b^2 \cos^2\theta \rangle^{1/2} = b\langle \cos^2\theta \rangle^{1/2} = \frac{b}{\sqrt{3}}$

see Eq^n 1.45

Total distance travelled in N steps $(2m-N)$ $\sqrt{3}$ $= x = (2m-N)\, b/\sqrt{3})$

since $m^* = N/2$

$$x = 2(m-m^*)\, b/\sqrt{3}$$

$$x^2 = 2(2)(m-m^*)^2\, b^2/3$$

$$\Rightarrow \quad 2(m-m^*)^2 = 3x^2/2b^2$$

Plug in to Probability dis:

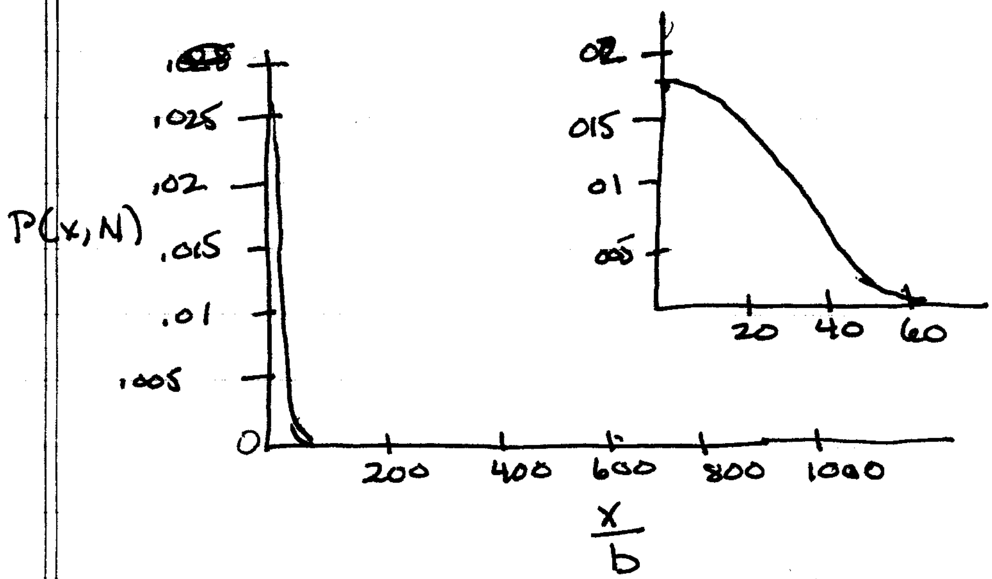
$$P(m,N) = P(x,N) = P^* e^{-3x^2/2Nb^2}$$

integral over all x must sum to 1.

$$\int_{-\infty}^{\infty} P\, e^{-3x^2/2Nb^2}\, dx = 1 \implies P^* = \left(\frac{3}{2\pi N b^2}\right)^{1/2}$$

FINALLY $$P(x,N) = \left(\frac{3}{2\pi N b^2}\right)^{1/2} e^{-3x^2/2Nb^2}$$

For chain of $N = 1000$ bonds



$P(x,N)$ = Probability that in $\underline{N}$ steps a freely jointed chain will be $\underline{x}$ distance from origin

IN 3D : radial distribution function

ideal chain $$P(r,N) = 4\pi r^2 \left(\frac{3}{2\pi N b^2}\right)^{3/2} e^{-3r^2/2Nb^2}$$