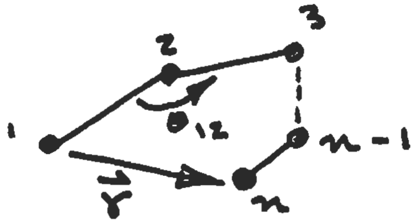
Chain Conformation

- Freely-jointed chain



$$0 \le \theta_{ij} < \pi$$

$$r^2 = \vec{r} \cdot \vec{r} = (\vec{l}_1 + \vec{l}_2 + \cdots + \vec{l}_n) \cdot (\vec{l}_1 + \vec{l}_2 + \cdots + \vec{l}_3)$$

$$= (\vec{l}_1 \cdot \vec{l}_1 + \vec{l}_2 \cdot \vec{l}_2 + \cdots + \vec{l}_n \cdot \vec{l}_n)$$

$$+ 2(\vec{l}_1 \cdot \vec{l}_2 + \vec{l}_1 + \vec{l}_3 + \cdots + \vec{l}_n \cdot \vec{l}_{n-1})$$

$$= nl^2 + 2l^2 (\cos\theta_{12} + \cos\theta_{13} + \cdots + \cos\theta_{n,n-1})$$

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

R = rms end-to-end distance $= \langle r^2 \rangle^{\frac{1}{2}} = \sqrt{n}\, l$

ratio to contour length $= \frac{R}{L} = \frac{\sqrt{n}\, l}{nl} = \frac{1}{\sqrt{n}}$

1-D Random Walk

Probability of n_R steps to right, n total

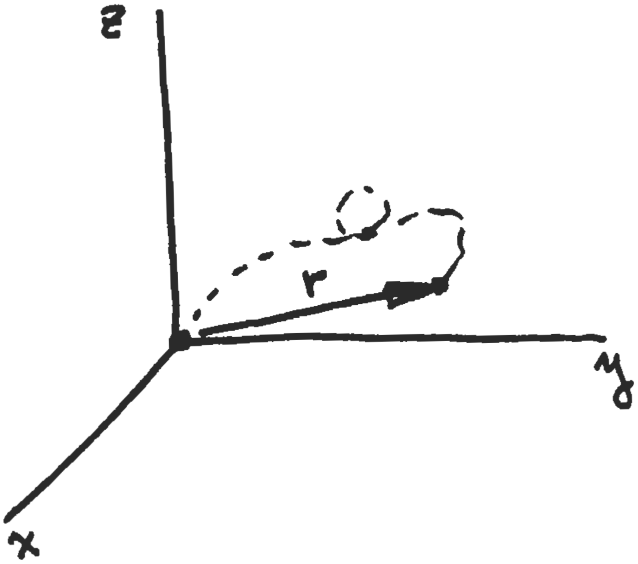
$$\Omega(n_R, n) = \frac{n!}{n_R!\, n_L!} \cdot P_R^{n_R} P_L^{n_L}$$

$$P_R = P_L = .5, \quad n = n_R + n_L, \quad x = (n_R - n_L) \cdot l$$

$$\ln y! \approx y \ln y - y \quad , \quad y \text{ large}$$

$$\Omega(x, n) = \frac{\beta}{\sqrt{\pi}} \exp\left(-\beta^2 x^2\right), \quad \beta = \frac{1}{\sqrt{2nl^2}}$$

• Gaussian chain



$$\Omega_1(r) = \frac{\beta^3}{\sqrt{\pi}} \exp\left(-\beta^2 r^2\right)$$

$$= \frac{\beta^3}{\sqrt{\pi}} \exp\left[-\beta^2 (x^2+y^2+z^2)\right]$$

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

After deformation:

$$\Omega_2 = \frac{\beta^3}{\sqrt{\pi}} \exp\left[-\beta^2 (\lambda_x^2 x^2 + \lambda_y^2 y^2 + \lambda_z^2 z^2)\right]$$

Entropy change

$$\Delta S = k \ln \frac{\Omega_2}{\Omega_1} = \frac{-k}{2} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$

Work per unit volume

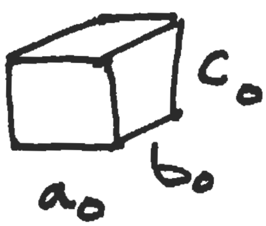
$$\Delta W_v = -T\Delta S_v = + \frac{NkT}{2} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$

$N = \#$ segments$/m^3$

Extension Ratio

$$\lambda = \frac{L}{L_o} = \frac{L_o + \delta}{L_o} = 1 + \frac{\delta}{L_o} = 1 + \epsilon$$

volume change:



$$\frac{\Delta V}{V} = \frac{abc - a_o b_o c_o}{a_o b_o c_o}$$

$$= \frac{\lambda_x a_o \cdot \lambda_y b_o \cdot \lambda_z c_o - a_o b_o c_o}{a_o b_o c_o}$$

$$= \lambda_x \lambda_y \lambda_z - 1$$

for rubber $\Delta V = 0 \rightarrow \lambda_x \lambda_y \lambda_z = 1$

- Uniaxial extension

$$\lambda_x = \lambda, \quad \lambda_y = \lambda_z = \frac{1}{\sqrt{\lambda}}$$

$$F = \frac{dW}{dL} = \frac{d\,(V \cdot \Delta W_v)}{L_0\, d\lambda} = A_0 \frac{NkT}{2}\left(2\lambda - \frac{2}{\lambda^2}\right)$$

$$\sigma_{engr} = \frac{F}{A_0} = NkT\left(\lambda - \frac{1}{\lambda^2}\right)$$

- Biaxial extension $\lambda_x = \lambda_y = \lambda$

$$\lambda_z = \frac{1}{\lambda_x \lambda_y}$$

$$\Delta W_v = V \cdot \frac{NkT}{2}\left(\lambda^2 + \lambda^2 + \frac{1}{\lambda^4} - 3\right)$$

$$F_x = \frac{\partial(\Delta W_v)}{\partial x} = \frac{1}{X_0}\frac{\partial(\Delta W_v)}{\partial \lambda} = \frac{1}{X_0} \cdot V \frac{NkT}{2}\left(4\lambda - \frac{4}{\lambda^5}\right)$$

$$= \frac{XYZ}{X/\lambda} \cdot 2NkT\left(\lambda - \frac{1}{\lambda^5}\right)$$

$$\sigma_{true} = \frac{F_x}{YZ} = 2NkT\left(\lambda^2 - \frac{1}{\lambda^4}\right)$$