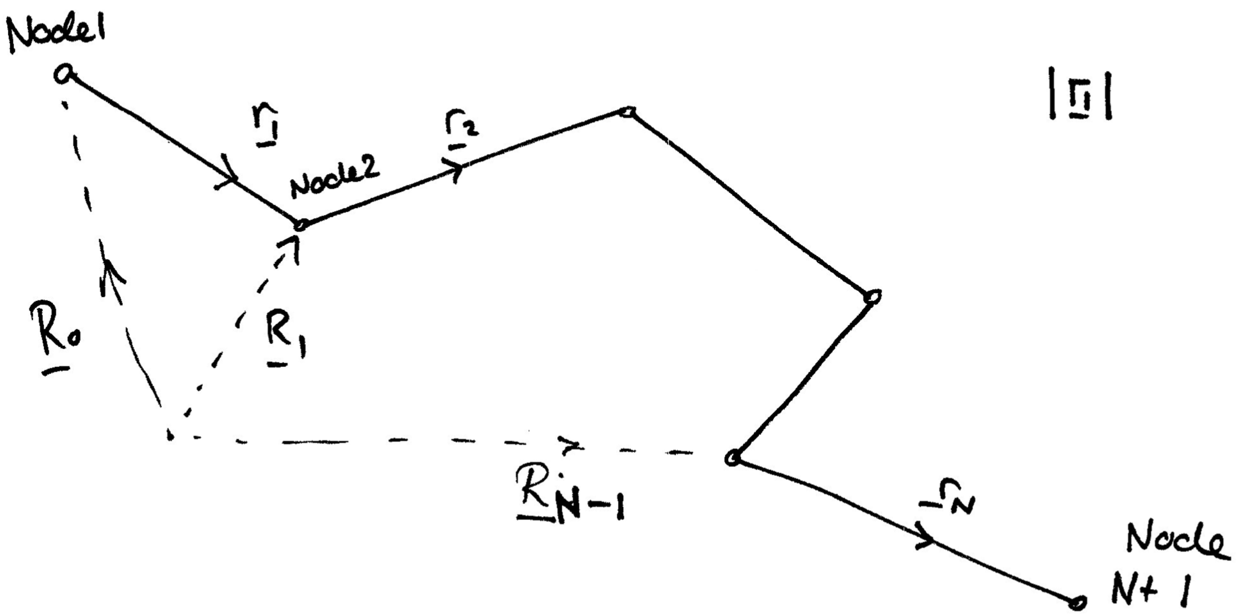
1.1 The freely jointed chain model (FJC)

1.1.1 The freely jointed chain without force



i) N links, of fixed length b

ii) The orientation of the tangent $\underline{t}_i = \frac{1}{b}\underline{r}_i$ is independent of other tangents and randomly chosen.

iii) No excluded volume effects.

<u>Def</u>

Def^n The average of a quantity $\underline{a}$ is given by

$$\langle \underline{a} \rangle := \int_{(\mathbb{R}^3)^N} dV \; \underline{a}(\underline{r}_1, \dots, \underline{r}_N)\, p(\underline{r}_1 \dots \underline{r}_N)$$

Where $p(\underline{r}_1 \dots \underline{r}_N)$ is the probability distribution function for the configuration state $\underline{r}_1 \dots \underline{r}_N$.

Here $\quad p = \prod_{i=1}^{N} \frac{1}{4\pi b^2} \delta(|\underline{r}_i| - b)$

but different distributions would be used when the angles are not independent

The chain end-to-end displacement is $\underline{R} := \underline{R}_N - \underline{R}_0$

$$= \sum_{i=1}^{N} \underline{r}_i$$

Its mean value is

$$\langle \underline{R} \rangle = \int_{(\mathbb{R}^3)^N} dV \left(\sum_{i=1}^{N} b\,\underline{t}_i \right) \frac{1}{(4\pi b^2)^N} \delta(|\underline{r}_1| - b) \ldots \delta(|\underline{r}_N| - b)$$

$$= \frac{(b^2)^N}{(4\pi b^2)^N} b \int \underbrace{d\Omega_1 \ldots d\Omega_N}_{\text{Solid angles}} \; \underline{t}_1 \; + \cdots\cdots$$

$$d\Omega_1 = d\theta_1 d\varphi_1 \sin\theta_1$$

$$= \frac{b}{(4\pi)^N} \cdot (4\pi)^{N-1} \underbrace{\int d\theta_1 d\varphi_1 \sin\theta_1 \begin{pmatrix} \sin\theta_1 \sin\varphi_1 \\ \sin\theta_1 \cos\varphi_1 \\ \cos\theta_1 \end{pmatrix}}_{\underline{0}} + \cdots\cdots$$

$$= \underline{0}$$

However, the second moment $\langle \underline{R}^2 \rangle$ is useful as its square root gives the lengthscale of variation of the end-to-end displacement.

$$\underline{R}^2 = \sum_{i=1}^{N} \underline{r}_i \cdot \sum_{j=1}^{N} \underline{r}_j = \sum_{i=1}^{N} \underline{r}_i \cdot \underline{r}_i + \sum_{i \neq j} \underline{r}_i \cdot \underline{r}_j$$

<u>For $i \neq j$</u>

$\langle \underline{r}_i \cdot \underline{r}_j \rangle = \langle \underline{r}_i \rangle \cdot \langle \underline{r}_j \rangle$ as $\underline{r}_i, \underline{r}_j$ uncorrelated

$= 0$, as $\langle \underline{r}_i \rangle = 0$ by similar calc to above.

$$\langle \underline{R}^2 \rangle = \left\langle \sum_{i=1}^{N} \underline{r}_i \cdot \underline{r}_i \right\rangle = \sum_{i=1}^{N} \langle \underline{r}_i \cdot \underline{r}_i \rangle = N \langle \underline{r}_1 \cdot \underline{r}_1 \rangle$$

by symmetry

b^2 and stop

$$= N \int_{(\mathbb{R}^3)^N} dV \, (\underline{r}_1 \cdot \underline{r}_1) \, \frac{1}{(4\pi b^2)^N} \, \delta(|\underline{r}_1| - b) \ldots$$

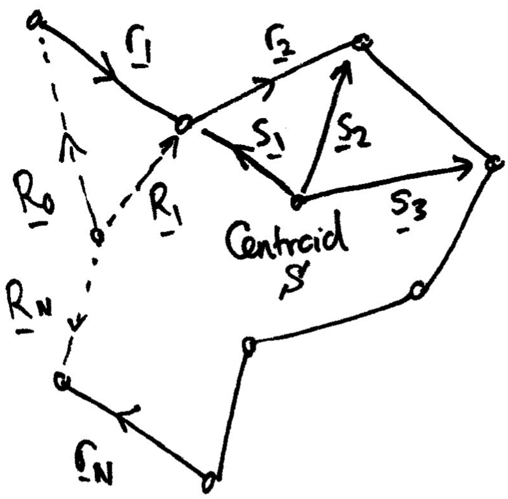
$$= N b^2 \int_{(\mathbb{R}^3)^N} dV \, p(\underline{r}_1 \ldots \underline{r}_N) = N b^2 \quad \text{as } p \text{ is a p.d.f.}$$

$$\therefore \sqrt{\langle \underline{R}^2 \rangle} = \text{Root mean square of } \underline{R} = b\sqrt{N}$$

Analogous to root mean square of displacement random walker after N steps ... ie Brownian motion.

1.1.2 Gyration Radius

Defn The gyration radius, s, is the root mean square distance of a collection of points relative to their centroid.



$$\therefore \quad s^2 = \left(\sum_{i=0}^{N} \underline{s}_i \cdot \underline{s}_i \right) \frac{1}{N+1}$$

where

$$\underline{S} = \frac{1}{N+1} \sum_{i=0}^{N} \underline{R}_i$$

$$\underline{s}_i = -\underline{S} + \underline{R}_i$$

Theorem (Lagrange)

$$s^2 = \frac{1}{(N+1)^2} \sum_{0 \le i < j \le N}' \underline{r}_{ij}^2$$

where $\underline{r}_{ij} = \underline{R}_j - \underline{R}_i$.

Proof See example sheets.

Example Find $\langle s^2 \rangle$ in terms of b, N.

Solution Given $j>i$ in Lagrange's theorem, take $j>i$ below.

$$\underline{r}_{ij} = \underline{R}_j - \underline{R}_i = \left(\underline{R}_0 + \sum_{p=1}^{j} \underline{r}_p\right) - \left(\underline{R}_0 + \sum_{q=1}^{i} \underline{r}_i\right) = \sum_{p=i+1}^{j} \underline{r}_p .$$

$$\underline{r}_{ij}^2 = \sum_{q,p=i+1}^{j} \underline{r}_p \cdot \underline{r}_q = \sum_{p=i+1}^{j} \underline{r}_p \cdot \underline{r}_p + \sum_{q \ne p \in (i+1 \dots j)} \underline{r}_p \cdot \underline{r}_q$$

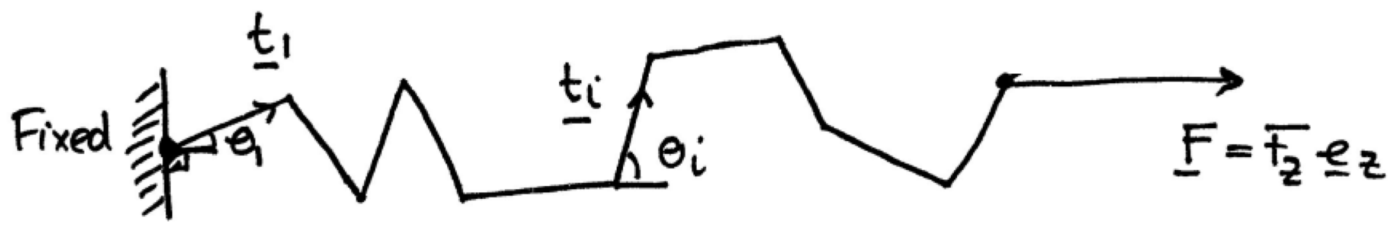
$$\therefore \langle \underline{r}_{ij}^2 \rangle = (j-i) \langle \underline{r}_i^2 \rangle = (j-i) b^2 .$$

$$\therefore \langle s^2 \rangle = \frac{1}{(N+1)^2} \sum_{0 \le i < j \le N} \langle r_{ij}^2 \rangle = \frac{b^2}{(N+1)^2} \sum_{0 \le i < j \le N}' (j-i)$$

$$= \frac{b^2}{(N+1)^2} \sum_{j=1}^{N}' \sum_{i=0}^{j-1} (j-i) \overset{k=j-i}{=} \frac{b^2}{(N+1)^2} \underbrace{\sum_{j=1}^{N} \underbrace{\sum_{k=1}^{k=j} k}_{\frac{j(j+1)}{2}}}_{\frac{1}{2}\left(\sum_{j=1}^{N} j^2 + \sum_{j=1}^{N} j\right)}$$

$$\therefore \langle s^2 \rangle = \frac{b^2}{(N+1)^2} \cdot \frac{1}{2} \Bigg[\underbrace{\frac{N(N+1)(2N+1)}{6} + \frac{N(N+1)}{2}}_{\frac{N}{3}(N+1)(N+2)} \Bigg] = \frac{b^2 N(N+2)}{6(N+1)}$$

1.1.3 Freely jointed chain model with external force



Assumptions
(i) FJC, fixed at one end
ii) Constant Force
iii) Equilibrium with thermal bath, temperature T.*

* This is different to previous assumption... $\theta_1 \dots \theta_N$ no longer uniformly distributed

Objective Find the force-displacement relation.

i.e. $\langle \underline{e}_z . \underline{R} \rangle$ as a function of $\underline{F} = F_z \underline{e}_z$

$\therefore m\dot{x}^2 + V = m\dot{x}^2 - Fx = E$
for constant F
$\therefore \Delta$ Internal energy $= -Fx$

$$m\ddot{x} = +F = -\nabla V$$
$$m\ddot{x}\,\delta x = \underbrace{F\delta x}_{\text{work}} = -\nabla V \delta x$$
$$m\ddot{x}\frac{\delta x}{\delta t}\delta t = F\dot{x}\delta t = -\nabla V \dot{x}\,\delta t$$

Work done on chain by extending it by a displacement $\delta\underline{R}$

$$\delta W = \underline{F} . \delta \underline{R} = F_z \underline{e}_z . \delta \underline{R} = F_z\, b \sum_{i=1}^{N} \cos\theta_i$$

as

$$\delta \underline{R} = b\,\delta \sum_{i=1}^{N} \underline{t}_i = b\,\delta \sum_{i=1}^{N} \begin{pmatrix} \sin\theta \cos\varphi_i \\ \sin\theta_i \sin\varphi_i \\ \cos\theta_i \end{pmatrix}$$

$\therefore$ Change in internal energy of chain is

$$-\sum \delta W \to -\int dW = -\int \underline{F} . d\underline{R} = -F_z\, b \int d \sum_{i=1}^{N} \cos\theta_i$$
$$= -F_z\, b \sum_{i=1}^{N} \cos\theta_i$$

$$\therefore \left\{ \begin{array}{c}\text{Internal energy} \\ \text{of chain}\end{array} \right\} \text{ is } -F_z b \sum_{i=1}^{N} \cos\theta_i + \underbrace{E_0}_{\text{Constant.}}$$

In fact this is zero, as we can assume we start from a zero energy state; in any case its explicit inclusion does not alter any result below.

Statistical Mechanics

By considering the maximisation of entropy for the combined system of the chain and heat bath

$$\text{Prob}\left(\begin{array}{c}\text{System in state} \\ \{\theta_1, \dots \theta_N\}\end{array} \right) \propto \exp\left[\frac{-E(\theta_1, \dots, \theta_N)}{k_b T} \right]$$

← different to previous assumption ∴ Averaging procedure different below.

where $E(\theta_1, \dots \theta_N)$ is the internal energy associated with $\{\theta_1, \dots, \theta_N\}$.

$$\therefore \text{Prob}\left(\begin{array}{c}\text{System in state} \\ \{\theta_1 \dots \theta_N\}\end{array} \right) = \frac{\exp\left[\frac{-E(\theta_1, \dots \theta_N)}{k_b T} \right]}{\int \underbrace{d\Omega_1 \dots d\Omega_N}_{\text{Solid angles}} \exp\left[\frac{-E(\theta_1, \dots \theta_N)}{k_b T} \right]} := \frac{e^{\frac{-E(\theta_1, \dots \theta_N)}{k_b T}}}{Z}$$

Sum over all possible configurations of $\{\theta_1 \dots \theta_N\}$

Canonical Partition function of Statistical Mechanics

From the above $E = \underbrace{\cancel{E_0}}_{\text{Const}} - F_z b \sum_{i=1}^{N} \cos\theta_i$

0

$$\therefore Z = \left[\int d\Omega_1 \ldots d\Omega_N \left(e^{\frac{F_z b}{k_b T} \sum_{i=1}^{N} \cos\theta_i} \right)\right]$$

$$= \left(\int d\theta_1 d\varphi_1\, e^{+\alpha\cos\theta_1} \sin\theta_1\right) \ldots \left(\int d\theta_N d\varphi_N\, e^{+\alpha\cos\theta_N} \sin\theta_N\right)$$

where $\alpha = \frac{F_z b}{k_b T}$

$$= (2\pi)^N \underbrace{\left[\int_0^{\pi} d\theta \sin\theta\, e^{+\alpha\cos\theta}\right]}_{\frac{2\sinh\alpha}{\alpha}}^N$$

$$= \left(\frac{4\pi\sinh\alpha}{\alpha}\right)^N$$

$$\therefore \boxed{\mathrm{Prob}\left(\begin{matrix}\text{System in state}\\ \{\theta_1, \ldots, \theta_N\}\end{matrix}\right) = \left(\frac{\alpha}{4\pi\sinh\alpha}\right)^N e^{+\alpha \sum_{i=1}^{N} \cos\theta_i}}$$

$$\underbrace{\langle R_z \rangle}_{b\sum_{i=1}^{N}\cos\theta_i} = \frac{1}{Z} \int d\Omega_1 \ldots d\Omega_N\, e^{\left(\alpha \sum_{i=1}^{N} \cos\theta_i\right)} \cdot b \sum_{i=1}^{N} \cos\theta_i$$

$$= \frac{1}{Z}\left(b \frac{\partial}{\partial\alpha} \int d\Omega_1 \ldots d\Omega_N\, e^{\alpha \sum_{i=1}^{N} \cos\theta_i} \right)$$

$$= \frac{b}{Z}\frac{\partial Z}{\partial\alpha} = b\frac{\partial \ln Z}{\partial\alpha}$$

$$= b \frac{\partial}{\partial\alpha}\left[\ln\left(\left(\frac{4\pi\sinh\alpha}{\alpha}\right)^N\right)\right]$$

$$= bN\left[\coth\alpha - 1/\alpha\right]$$

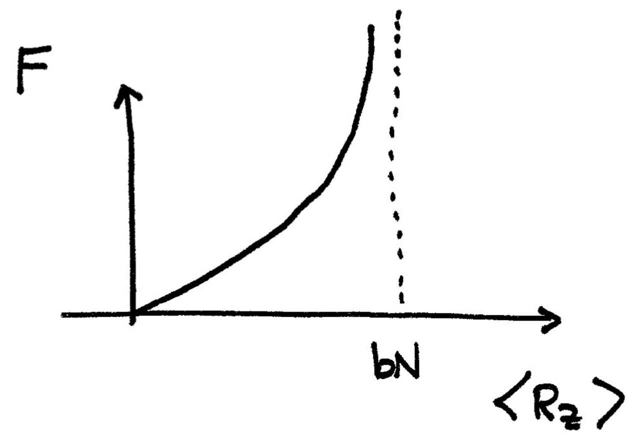
$\therefore \langle R_z \rangle = bN\mathcal{L}(\alpha)$ where $\mathcal{L}(\alpha) := \coth\alpha - 1/\alpha$ is the Langevin function.

Recall $\alpha := \frac{Fb}{k_b T}$.

$\therefore \lim_{F\to\infty} \langle R_z \rangle = bN$, maximal extension.

For F sufficiently small that $\alpha \ll 1$, $\langle R_z \rangle = \left(\alpha/3 + O(\alpha^2)\right) Nb$

$$= \frac{Nb^2}{3k_bT} F + O(F^2)$$



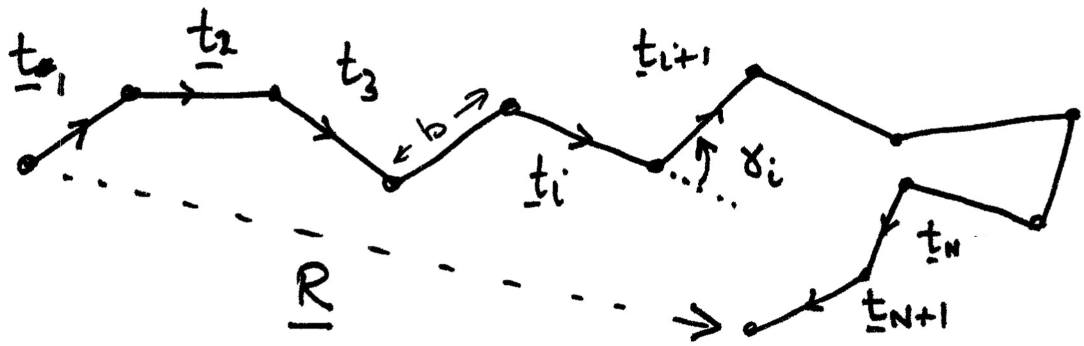
Aside We have $\langle R_z \rangle = b\frac{\partial \ln Z}{\partial \alpha} = b\frac{\partial F}{\partial \alpha}\frac{\partial \ln Z}{\partial F}$

$$= kT\frac{\partial \ln Z}{\partial F}$$

Worm Like Chain Models

Including the effects of bending stiffness

Discrete Model   Kratky-Porod (1949)



Internal Energy $E = -K \sum_{i=1}^{N} \underline{t}_i \cdot \underline{t}_{i+1} = -K \sum_{i=1}^{N} \cos\gamma_i$

Analogous to Freely Jointed Chain Model.

Partition Function

$$Z = \int d\Omega_1 \ldots d\Omega_N \; e^{\frac{K}{k_b T} \sum_{i=1}^{N} \cos\gamma_i}$$

$$\overset{\text{as before}}{=} \left(\frac{4\pi \sinh\lambda}{\lambda} \right)^N \quad \text{where } \lambda = \frac{K}{k_b T}$$

For stiff polymers $\lambda = \beta K \gg 1$

We can determine $\langle \underline{R} \cdot \underline{R} \rangle = \langle R^2 \rangle = b^2 \left\langle \left(\sum_i \underline{t}_i \right)^2 \right\rangle$