Introduction to Theoretical Polymer Physics

Books:

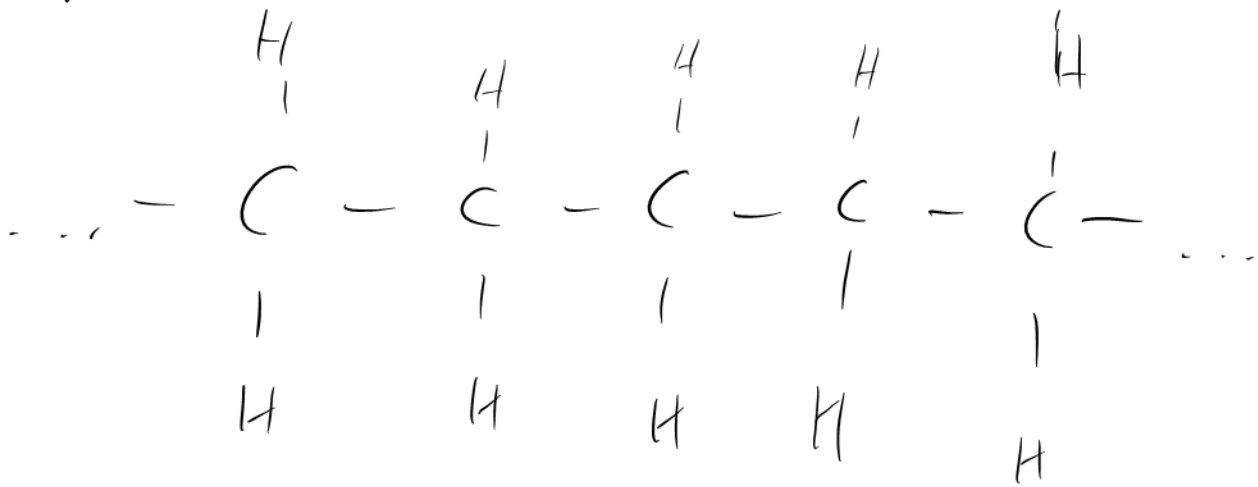
- P.G. de Gennes, Scaling concepts in polymer physics, Cornell Univ. Press 1979
- M. Doi, S.F. Edwards, The Theory of Polymer Dynamics Oxford Univ. Press, 1988

- A. Y. Grosberg, A. R. Khokhlov, Statistical physics of macromolecules, AIP, 1994
- M. Doi, Introduction to polymer physics, Oxford Univ. Press, 1996
- P. J. Flory, Principles of polymer chemistry, Cornell Univ. Press, 1953
- P. J. Flory, Statistical mechanics of chain molecules, Interscience, NY, 1969

1. Random Walk Models for Flexible Polymer chains

1.1 Flexibility

study polyethylene (PE)



conformation: arrangement of atoms in space methane

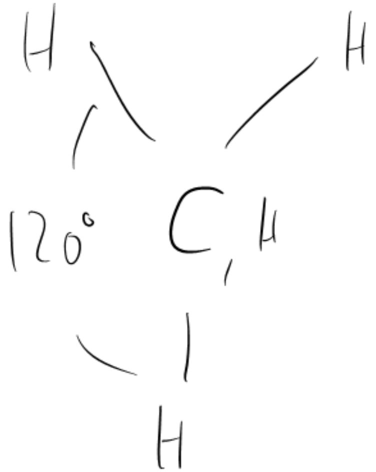
θ_t = tetrahedron angle = 109.47°

$$\cos\theta_t = -\frac{1}{3}$$

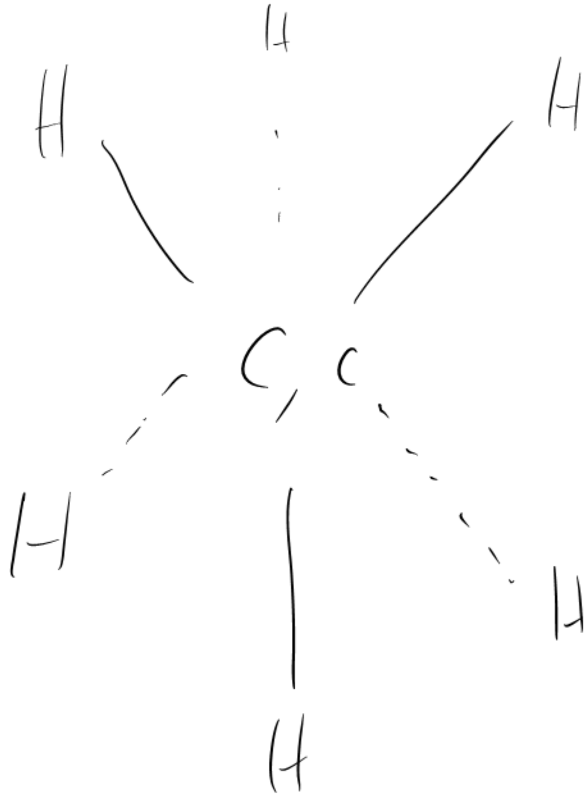
ethane

top view

methane:



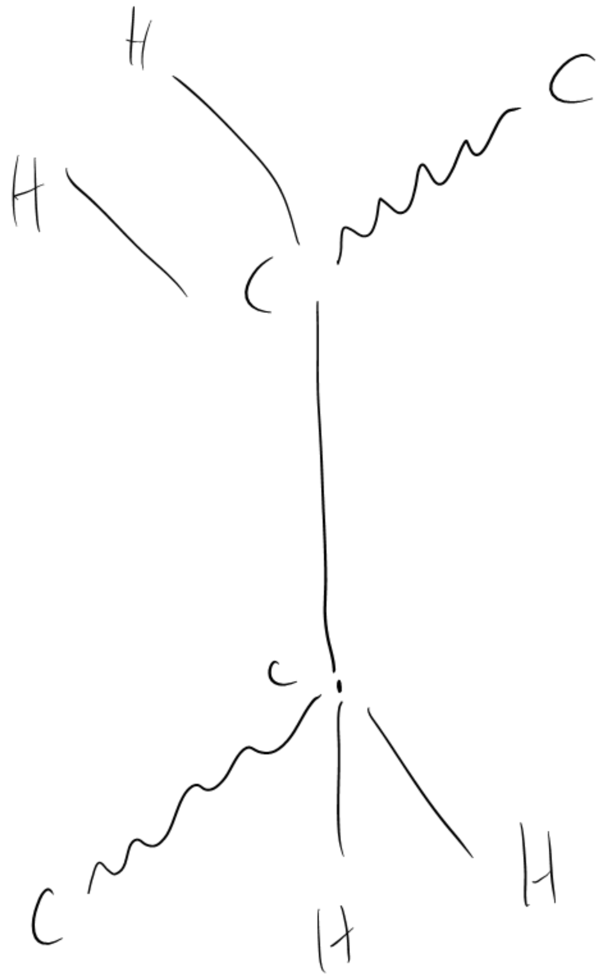
ethane



— top tetrahedron

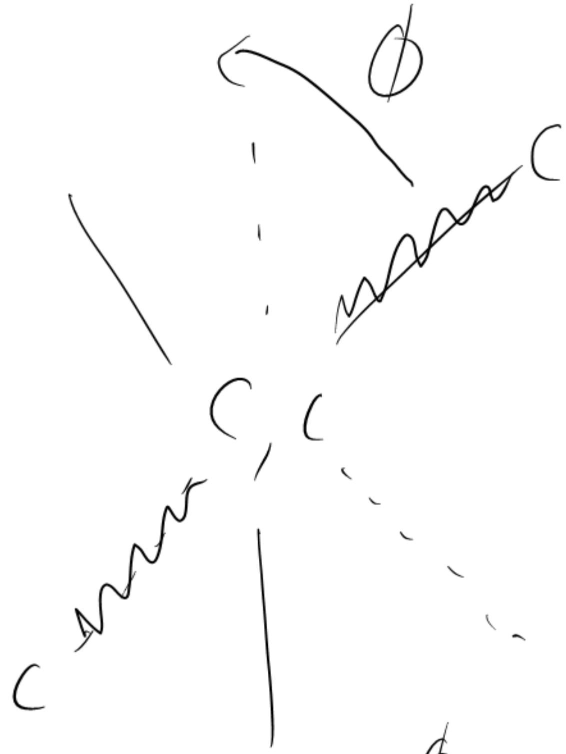
- - - - lower tetrahedron

PE:



trans

top view:

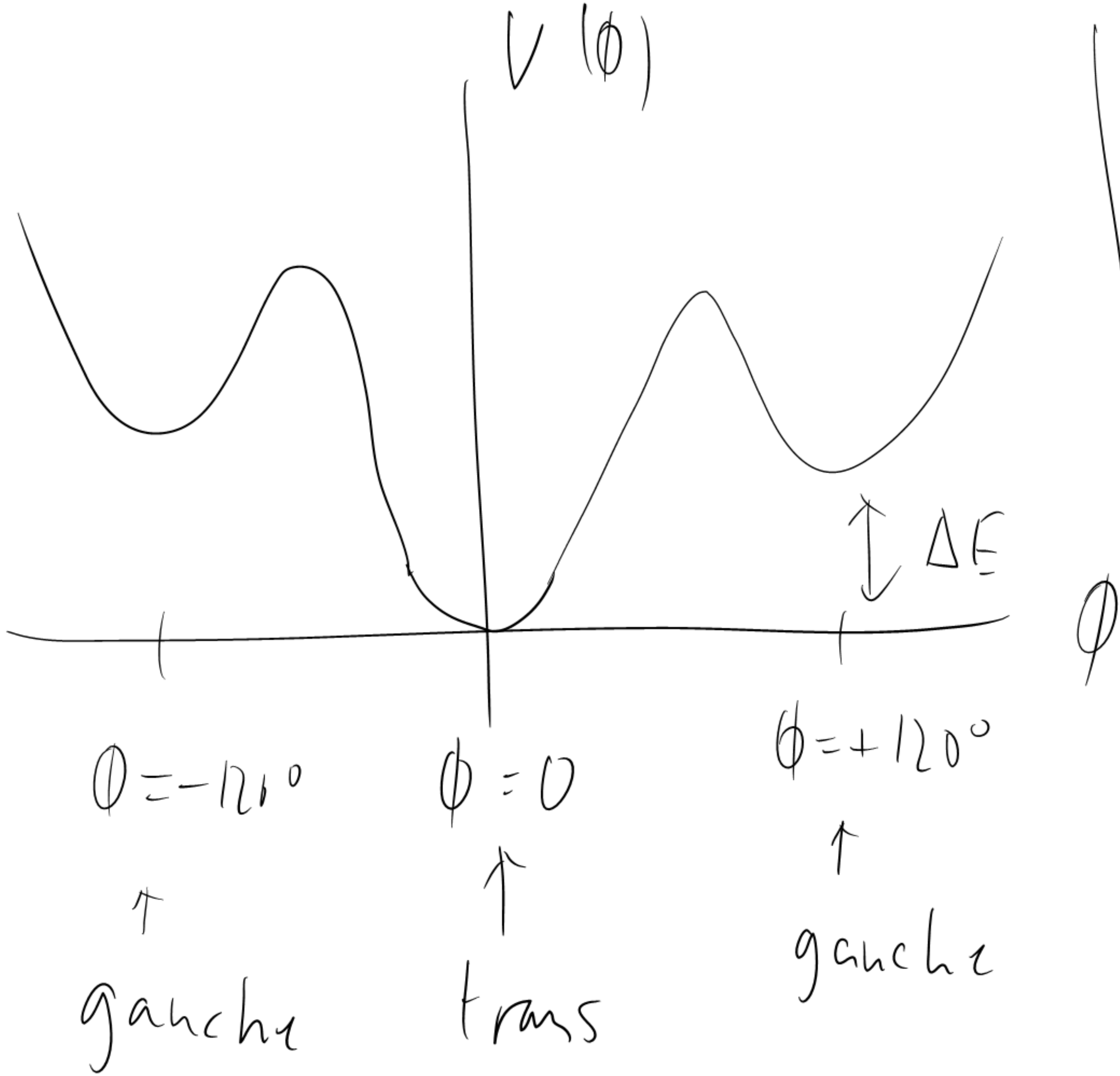


trans

$\phi = 0 \rightarrow$ trans

$\phi = \pm 120^{\circ}$

$\rightarrow$ gauche



$k_B T = 0$

$\rightarrow$ all trans

$k_B T \simeq \Delta E$

gauche defect is "thermally possible".

typically room temperature or above.

→ proliferation of gauche defects

→ MANY defects → MANY conformations

→ STATISTICAL APPROACH!

→ intra-molecular entropy!

1.2. Simple RANDOM WALK models

1.2.1. Freely Jointed Chain

N monomers, $\vec{r}_i$ coordinates, $N-1$ bonds

$$|\vec{r}_{i+1} - \vec{r}_i| = l \,, \quad \vec{r}_{i+1} - \vec{r}_i = \vec{l}_i$$

no further constraints,

orientation completely random $\Rightarrow$

thermal average

$$\langle \vec{l}_i \cdot \vec{l}_j \rangle = \begin{cases} l^2 & i = j \\ \langle \vec{l}_i \rangle \cdot \langle \vec{l}_j \rangle = 0 & \end{cases}$$

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases} \qquad \langle \vec{l}_i \cdot \vec{l}_j \rangle = l^2 \delta_{ij}$$

end-to-end vector

$$\vec{R}_E = \vec{r}_N - \vec{r}_1 \qquad \langle \vec{R}_E \rangle = 0$$

$$\langle \vec{R}_E^2 \rangle = \langle (\vec{r}_N - \vec{r}_1)^2 \rangle = \langle \left(\sum_i \vec{l}_i \right)^2 \rangle =$$

$$= \sum_{ij} \langle \vec{l}_i \cdot \vec{l}_j \rangle = l^2 \sum_{ij} \delta_{ij} = l^2 (N-1)$$

$$\simeq l^2 N$$

$$\begin{array}{cc} & j \longrightarrow \\ i \downarrow & \begin{pmatrix} \circ & & \\ & \ddots & \\ & & \ddots \end{pmatrix} \end{array}$$

$$R_E := \sqrt{\langle \vec{R}_E^2 \rangle} = \ell N^{1/2}$$

$$\boxed{R_E \propto N^{1/2}}$$

scaling law, holds for <u>all</u> random walks!

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center of mass: $\vec{R}_{cm} = \frac{1}{N} \sum_{i=1}^{N} \vec{r}_i$

$$\langle R_g^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} \left\langle (\vec{r}_i - \vec{R}_{cm})^2 \right\rangle$$

mean square gyration radius

alternative representation:

$$\langle (\vec r_i - \vec r_j)^2 \rangle = \langle [(\vec r_i - \vec R_{cm}) - (\vec r_j - \vec R_{cm})]^2 \rangle =$$

$$= \langle (\vec r_i - \vec R_{cm})^2 \rangle + \langle (\vec r_j - \vec R_{cm})^2 \rangle$$

$$- 2 \langle (\vec r_i - \vec R_{cm}) \cdot (\vec r_j - \vec R_{cm}) \rangle \qquad \Big| \sum_{ij}$$

$$\Rightarrow \sum_{ij} \langle (\vec r_i - \vec r_j)^2 \rangle = 2N \cdot N \langle R_g^2 \rangle$$

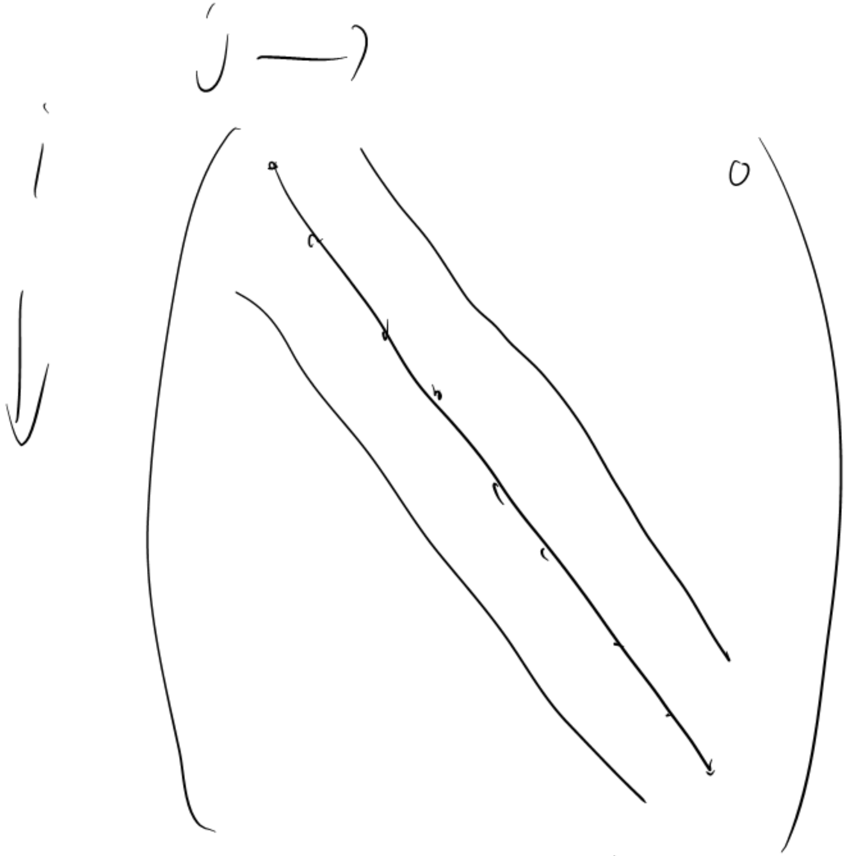
$$- 2 \langle \underbrace{\sum_i (\vec r_i - \vec R_{cm})}_{=0} \cdot \overbrace{\sum_j (\vec r_j - \vec R_{cm})}^{=0} \rangle$$

$$\boxed{\langle R_G^2 \rangle = \frac{1}{2N^2} \sum_{ij} \langle (\bar{r}_i - \bar{r}_j)^2 \rangle}$$

$\langle R_G^2 \rangle = ??$ for the freely jointed chain

$\langle (\bar{r}_i - \bar{r}_j)^2 \rangle = \ell^2 |i-j|$ subchain of length $|i-j|$

$$\Rightarrow \langle R_G^2 \rangle = \frac{\ell^2}{2N^2} \sum_{ij} |i-j|$$



$|i-j| = 1$, # elements: $N-1$

$|i-j| = 0$, # elements: N

$|i-j| = 1$

$$\langle R_i^2 \rangle = \frac{l^2}{2N^2} \Big\{ 2\cdot 1\cdot (N-1) + 2\cdot 2\cdot (N-2) + 2\cdot 3\,(N-3) + \dots + 2\cdot (N-1)\cdot 1 \Big\} \cong$$

$$\cong \frac{l^2}{N^2}\left(1\cdot(N-1) + 2\cdot(N-2) + 3\cdot(N-3) + \dots + (N-1)\cdot 1\right)$$

$$\cong \frac{l^2}{N^2}\int_0^N dx\; x\,(N-x) = \frac{l^2}{N^2}\left[N\frac{N^2}{2} - \frac{N^3}{3}\right] =$$

$$= l^2 N \cdot \frac{1}{6} = \frac{1}{6}\langle R_E^2\rangle$$

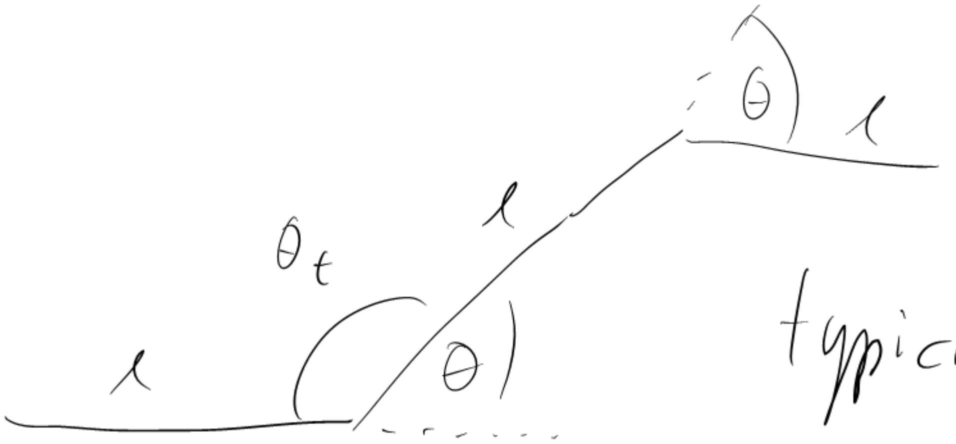
$$R_G =: \sqrt{\langle R_G^2\rangle} = \frac{1}{\sqrt{6}}\, R_E$$

$$\boxed{\frac{R_G}{R_E} = \frac{1}{\sqrt{6}}}$$

holds for all random walks

"universal amplitude ratio"

1.2.2. Freely Rotating Chain



θ fixed

typical $\theta = 180° - \theta_{tetr.}$

$\simeq 70{,}6°$ $\quad \cos\theta = \frac{1}{3}$

$$|\vec{r}_i - \vec{r}_{i+1}| = l$$

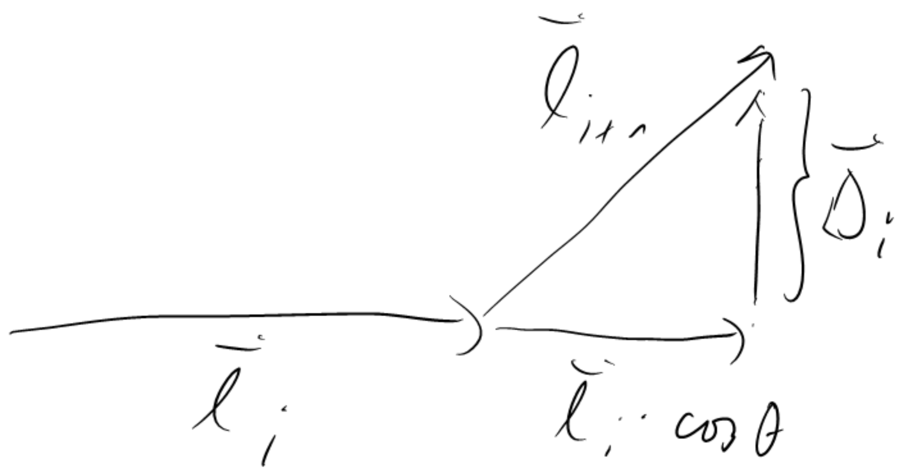
$$\langle \vec{l}_{i+1} \cdot \vec{l}_i \rangle = l^2 \langle \hat{n}_{i+1} \cdot \hat{n}_i \rangle = l^2 \cos\theta$$

$$\hat{n}_i := \frac{1}{l} \vec{l}_i$$ unit vector

$$\vec{l}_{i+1} = \vec{l}_i \cos\theta + \vec{\Delta}_i$$ ← random

$$\langle \vec{\Delta}_i \rangle = 0$$

$\vec{\Delta}_i \cdot \vec{l}_i$



$\vec{\Delta}_i$ is independent from all previous bonds

$$\vec{l}_{i+k} = \vec{l}_{i+k-1} \cos\theta + \vec{\Delta}_{i+k-1} =$$

$$\left(\vec{l}_{i+k-2} \cos\theta + \vec{\Delta}_{i+k-2}\right) \cos\theta + \vec{\Delta}_{i+k-1} =$$

$$= \vec{l}_i \cos^k\theta + \vec{D}_i \cos^{k-1}\theta + \vec{D}_{i+1}\cos^{k-2}\theta + \dots$$

$$\dots + \vec{D}_{i+k-1} = \vec{l}_{i+k} \quad \Big| \cdot \vec{l}_i , \langle\,\rangle$$

$$\langle \vec{l}_{i+k} \cdot \vec{l}_i \rangle = l_i^2 \cos^k\theta = l^2 \cos^k\theta$$

exponential decay along the chain

$$\langle R_E^2 \rangle = \left\langle \left(\sum_{i=1}^{N-1} \vec{l}_i \right)^2 \right\rangle = \sum_{ij} \langle \vec{l}_i \cdot \vec{l}_j \rangle =$$

$$= l^2 \sum_{ij} \cos^{|i-j|}\theta =$$

$$= l^2 \Big\{ (N-1)\cdot 1 + 2(N-2)\cos\theta + 2(N-3)\cos^2\theta$$

$$+ \dots \Big\}$$

series can be extended to ∞ because of exponential decay!

$$= l^2 (N-1) + 2l^2 \left(N-1 - \cos\theta \frac{d}{d\cos\theta} \right) \cos\theta$$

$$+ 2l^2 \left(N-1 - \cos\theta \frac{d}{d\cos\theta} \right) \cos^2\theta + \dots =$$

$$= l^2 (N-1) + 2 l^2 \left(N-1- \cos\theta \frac{d}{d\cos\theta} \right) \left(\cos\theta + \cos^2\theta + \dots \right)$$

$$= 2 l^2 \left(N-1- \cos\theta \frac{d}{d\cos\theta} \right) \left(1 + \cos\theta + \cos^2\theta + \dots \right)$$

$$- l^2 (N-1) = \text{(geometric series)}$$

$$= 2 l^2 \left(N-1- \cos\theta \frac{d}{d\cos\theta} \right) \frac{1}{1-\cos\theta} - l^2 (N-1)$$

$$\underset{N \to \infty}{\cong} \frac{2 l^2 N}{1-\cos\theta} - l^2 N = l^2 N \frac{1+\cos\theta}{1-\cos\theta}$$

$$\boxed{\langle R_E^2 \rangle = l^2 N \frac{1+\cos\theta}{1-\cos\theta}}$$

Def.:

$$C_\infty := \frac{\langle R_E^2 \rangle \big|_{\text{stiff}}}{\langle R_E^2 \rangle \big|_{\text{flexible}}} = \underline{\underline{\frac{1+\cos\theta}{1-\cos\theta}}} \quad (N \to \infty)$$

$$\cos\theta = +\frac{1}{3} \Rightarrow C_\infty = 2$$

PE (reality):

$$C_\infty = 6.7$$

1.2.3 Independent Rotational Potentials

l fixed, Θ fixed, but ϕ has a potential

$$\mathcal{H} = \sum_{i=3}^{N-1} V(\phi_i) \qquad \text{potential } V(\phi)$$

ϕ is not defined for $i=1$, $i=2$

observable $A(\phi_3, \phi_4 \ldots)$, $\langle A \rangle = ?$

statistical mechanics $\Longrightarrow$ $\qquad \beta = 1/(k_B T)$

$$Z = \frac{1}{2\pi} \int_0^{2\pi} d\phi_3 \, \frac{1}{2\pi} \int_0^{2\pi} d\phi_4 \ldots \frac{1}{2\pi} \int_0^{2\pi} d\phi_{N-1} \, e^{-\beta \mathcal{H}}$$

$$\langle A \rangle = \frac{1}{Z} \frac{1}{2\pi} \int_0^{2\pi} d\phi_3 \cdots \frac{1}{2\pi} \int d\phi_{N-1} \; A \; \exp(-\beta \mathcal{H})$$

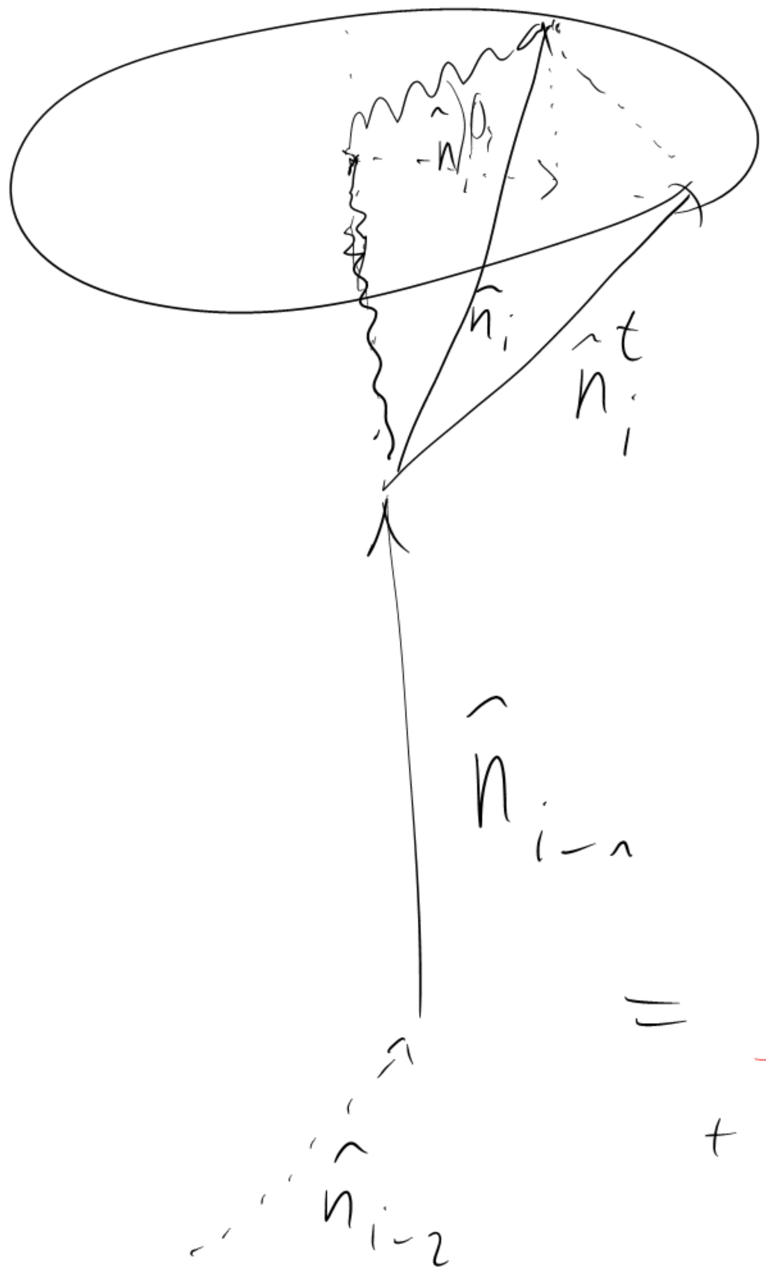
$$\exp(-\beta \mathcal{H}) = \exp\left(-\beta V(\phi_3) - \beta V(\phi_4) - \ldots - \beta V(\phi_{N-1})\right)$$

$$= \exp(-\beta V(\phi_3)) \exp(-\beta V(\phi_4)) \ldots \exp(-\beta V(\phi_{N-1}))$$

$$\hat{n}_i = \frac{\breve{\ell}_i}{\ell}$$

trans $(\phi_i = 0)$:

$$\hat{n}_i = \hat{n}_{i-2}$$



$\hat{n}_i^t$: trans

$$
\begin{aligned}
\tilde{n}_i = {} & \tilde{n}_{i-1}\left(\hat{n}_i^t \cdot \hat{n}_{i-1}\right) \\
& + \left[\hat{n}_i^t - \hat{n}_{i-1}\left(\hat{n}_i^t \cdot \hat{n}_{i-1}\right)\right] \cos\phi_i \\
& + \hat{n}_{i-1} \times \left[\hat{n}_i^t - \hat{n}_{i-1}\left(\hat{n}_i^t \cdot \hat{n}_{i-1}\right)\right] \sin\phi_i
\end{aligned}
$$

$$
\begin{aligned}
= {} & \underline{\hat{n}_{i-1} \cos\theta} + \\
& + \left[\hat{n}_{i-2} - \underline{\hat{n}_{i-1} \cos\theta}\right] \underline{\cos\phi_i} \\
& + \hat{n}_{i-1} \times \hat{n}_{i-2} \sin\phi_i
\end{aligned}
$$

$$\langle \hat{n}_i \cdot \hat{n}_1 \rangle = \langle \hat{n}_{i-1} \cdot \hat{n}_1 \rangle \cos\theta \left(1 - \langle \cos\phi \rangle\right)$$

$$+ \langle \hat{n}_{i-2} \cdot \hat{n}_1 \rangle \langle \cos\phi \rangle$$

$$+ \langle (\hat{n}_{i-1} \times \hat{n}_{i-2}) \cdot \hat{n}_1 \rangle \underbrace{\langle \sin\phi \rangle}_{= 0 \text{ symmetry}}$$

$$f_i := \langle \hat{n}_i \cdot \hat{n}_1 \rangle$$

$$f_1 = 1 \qquad f_2 = \cos\theta$$

$$\boxed{f_i = a f_{i-1} + b f_{i-2}}$$

$$a = \cos\theta \left[1 - \langle \cos\phi \rangle\right]$$

$$b = \langle \cos\phi \rangle$$