$$\hat{n}_i = \vec{\ell}_i / |\vec{\ell}_i|$$

θ bond angle, fixed

ϕ dihedral angle

$$\boxed{\mathcal{H} = \sum_{k=3}^{N-1} V(\phi_k)}$$

ϕ_k mutually independent

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

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

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

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

$$\langle \cos\phi \rangle = \frac{\int_0^{2\pi} d\phi \, \cos\phi \, \exp(-\beta V(\phi))}{\int_0^{2\pi} d\phi \, \exp(-\beta V(\phi))} \qquad \beta = \frac{1}{k_B T}$$

"initial conditions": $\boxed{f_1 = 1, \quad f_2 = \cos\theta}$

<u>ansatz</u>: $\boxed{f_i = \lambda^{i-1}}$ → into recursion relation

$$\lambda^{i-1} = a\lambda^{i-2} + b\lambda^{i-3} \quad \Big| : \lambda^{i-3}$$

$$\boxed{\lambda^2 = a\lambda + b} \Rightarrow \boxed{\lambda_{1/2} = \frac{a}{2} \pm \sqrt{\frac{a^2}{4} + b}}$$

more general: $f_i = \alpha\lambda_1^{i-1} + \beta\lambda_2^{i-1}$

<u>also</u> solves recursion relation

init. cond. $\Rightarrow \quad 1 = \alpha + \beta \quad \Rightarrow \beta = 1 - \alpha$

$$\cos\theta = \alpha \lambda_1 + \beta \lambda_2 =$$

$$= \alpha (\lambda_1 - \lambda_2) + \lambda_2 \quad \Rightarrow \alpha = \frac{\cos\theta - \lambda_2}{\lambda_1 - \lambda_2}$$

$$\Rightarrow \beta = \frac{\lambda_1 - \cos\theta}{\lambda_1 - \lambda_2}$$

$$\left\langle \left(\sum_i \hat{n}_i \right)^2 \right\rangle = \sum_{ij} \langle \hat{n}_i \cdot \hat{n}_j \rangle =$$

$$= (N-1) + 2(N-2) f_2 + 2(N-3) f_3 + \dots \simeq$$

$$\simeq N + 2N (f_2 + f_3 + \dots) =$$

$$= N + 2N \sum_{k=1}^{\infty} \left(\alpha \lambda_1^k + \beta \lambda_2^k \right) =$$

$$= N + 2N \sum_{k=0}^{\infty} \left(\alpha \lambda_1^k + \beta \lambda_2^k \right) - 2N$$

$$C_\infty = -1 + 2 \left(\frac{\alpha}{1-\lambda_1} + \frac{\beta}{1-\lambda_2} \right) = \dots =$$

$$= \frac{1 + \cos\theta}{1 - \cos\theta} \; \frac{1 + \langle \cos\phi \rangle}{1 - \langle \cos\phi \rangle}$$

PE: $C_\infty = 3.4$

reality: $C_\infty = 6.7$

<u>reason</u>: neglected correlations between ϕ_i

$$V(\phi_3) + V(\phi_4) + \dots \longrightarrow$$

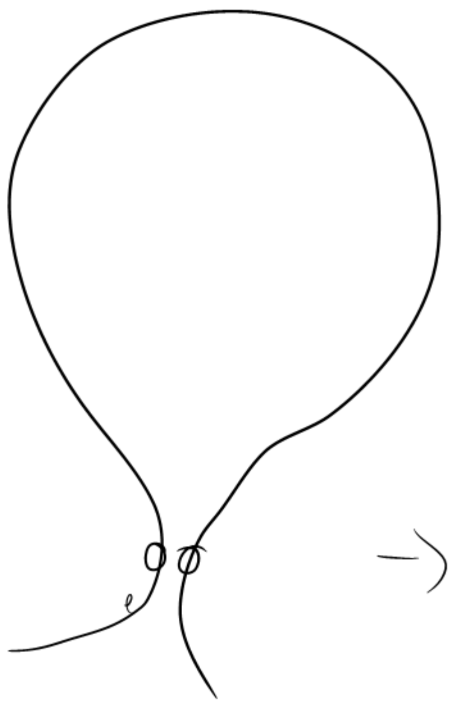
$$V(\phi_3) + V(\phi_4) + \dots + U(\phi_3, \phi_4) + U(\phi_4, \phi_5) + \dots$$

$+ \dots$ higher orders, up to some finite range

$\longrightarrow$ "rotational isomeric state" models

<u>exponential</u> decay of the bond angle correlation function $\langle \hat{n}_i \cdot \hat{n}_j \rangle$

also neglected: excluded volume effect



pairs of monomers:

- distance short in real space
- " long along the backbone

→ interaction along backbone is long-ranged

if excluded volume is relevant →

$\langle \hat{n}_i \cdot \hat{n}_n \rangle$ decays like a power law

Excluded volume is important in polymer solutions
(good solvent)

" " " UNIMPORTANT in polymer melts
(SCREENED)

↓

FLORY THEOREM

1.3. The Gaussian Chain

Assumption: Interaction of finite range along the chain, $T > 0 \rightarrow$ probability for a defect $> 0 \rightarrow$ angular correl. fct. decays exponentially

$$\langle \vec{R}_E^2 \rangle = \sum_{ij} \langle \vec{l}_i \cdot \vec{l}_j \rangle \simeq N \langle l^2 \rangle + 2N \underbrace{\sum_{i=2}^{\infty} \langle \vec{l}_i \cdot \vec{l}_1 \rangle}_{< \infty}$$

$$= \underbrace{N \langle l^2 \rangle C_\infty}$$

<u>Idea:</u> Introduce new bond length

$$l' = \sqrt{C_\infty \langle l^2 \rangle} \Rightarrow \langle \vec{R}_E^2 \rangle = l'^2 N$$

→ mapping of the orig. chain onto a freely jointed chain. Typically, $l' > l$

We have kept N constant

What about the contour length?

orig.: $L = N\langle|\vec{l}|\rangle$, $L' = N\langle|\vec{l}'|\rangle$

$$= N \sqrt{C_\infty \langle l^2 \rangle} > L$$

$\uparrow$
typically

<u>Kuhn:</u> - Keep $\langle R_E^2 \rangle$ const
- Keep L "

but allow for $N' \neq N$

$$\left.\begin{aligned} l'^2 N' &= C_\infty \langle l^2 \rangle N \\ l' N' &= \langle |\vec{l}| \rangle N \end{aligned}\right\} \boxed{l' = C_\infty \frac{\langle l^2 \rangle}{\langle |\vec{l}| \rangle}}$$

Kuhnian segment length

$$\frac{N'}{N} = \frac{\langle |\vec{l}| \rangle}{l'} = \frac{1}{C_\infty} \frac{\langle |\vec{l}| \rangle^2}{\langle l^2 \rangle}$$ typically $N' < N$

<u>Disadvantages</u> of the Kuhn model: Freely jointed chain, i.e. fixed bond length.

↳ easy to calculate R_E, R_G

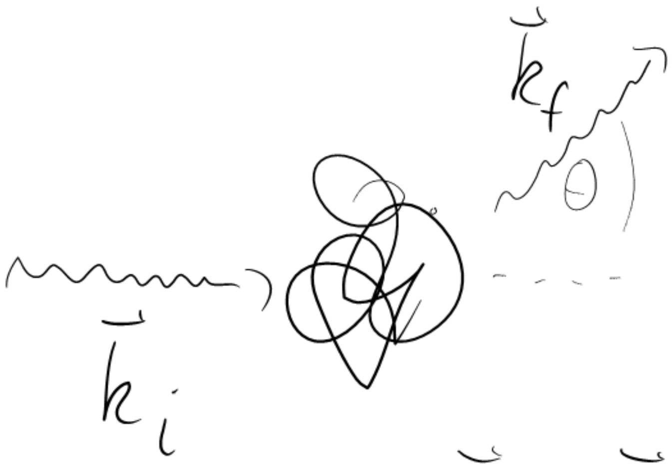
↳ hard to " : R_H hydrodynamic radius

$S(q)$ structure factor

Def. Structure factor:

$$S(q) = \left\langle \frac{1}{N} \left| \sum_{n=1}^{N} \exp\left(i\, \vec{q} \cdot \vec{r}_n\right) \right|^2 \right\rangle$$

excursion into scattering:



$$\vec{q} = \vec{k}_f - \vec{k}_i$$

wave number

$$k = \frac{2\pi}{\lambda} = |\vec{k}_i| = |\vec{k}_f|$$

wave length

elastic scattering

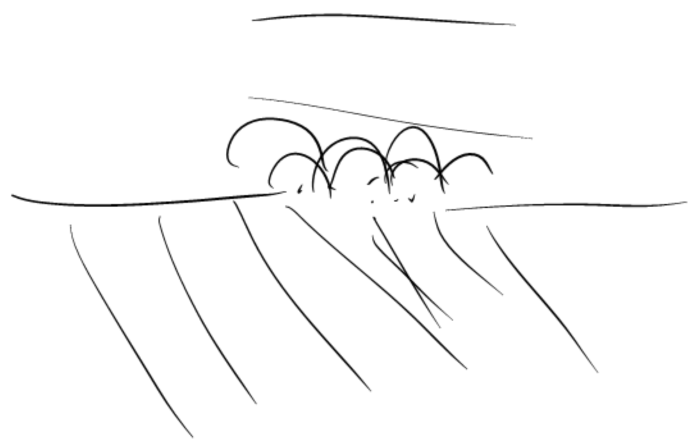
incoming : $\exp(+i\,\vec{k}_i \cdot \vec{r})$

outgoing: $\exp(+i\,\vec{k}_f \cdot \vec{r})$

transition ampl.

$$\langle \exp(i\vec{k}_i \cdot \vec{r}) \,|\, \exp(i\vec{k}_f \cdot \vec{r}) \rangle$$

$$= \exp\left(i(\vec{k}_f - \vec{k}_i) \cdot \vec{r}\right)$$



$$S(q) = \frac{1}{N} \left\langle \left| \sum_n \exp(i \vec{q} \cdot \vec{r}_n) \right|^2 \right\rangle =$$

$$\vec{r}_{nm} = \vec{r}_n - \vec{r}_m$$

$$= \frac{1}{N} \left\langle \sum_{nm} \exp\left(i\vec{q}\,(\vec{r}_n - \vec{r}_m)\right) \right\rangle =$$

$$= \frac{1}{N} \left\langle \sum_{nm} \exp\left(i\vec{q} \cdot \vec{r}_{nm}\right) \right\rangle =$$

$$= \frac{1}{N} \sum_{nm} \left\langle \frac{1}{4\pi} \int d\Omega_r \, \exp\left(i\vec{q} \cdot \vec{r}_{nm}\right) \right\rangle$$

$$\downarrow \; d\Omega = \sin\theta \, d\theta \, d\phi$$

$$= d(\cos\theta)\, d\phi = du\, d\phi$$

$$\int d\Omega_r \, \exp(i\vec{q}\cdot\vec{r}) =$$

$$= \int_0^{2\pi} d\phi \int_{-1}^{1} du \, \exp(iqru) =$$

$$= 2\pi \left. \frac{\exp(iqru)}{iqr} \right|_{u=-1}^{u=+1} = 2\pi \frac{\exp(iqr) - \exp(-iqr)}{iqr} =$$

$$= 2\pi \frac{2i\sin(qr)}{iqr} = 4\pi \frac{\sin(qr)}{qr}$$

$$\frac{1}{4\pi} \int d\Omega_r \, \exp(i\vec{q}\cdot\vec{r}) = \frac{\sin(qr)}{qr}$$

$$S(q) = \frac{1}{N} \sum_{nm} \left\langle \frac{\sin(q r_{nm})}{q r_{nm}} \right\rangle$$

$$\langle R_G^2 \rangle = \frac{1}{2N^2} \sum_{nm} \langle r_{nm}^2 \rangle$$

Hydrodynamic radius R_H:

$$\frac{1}{R_H} = \frac{1}{N^2} \sum_{\substack{m,n \\ m \neq n}} \left\langle \frac{1}{r_{nm}} \right\rangle$$

$\rightarrow$ requires probability $P(r_{nm})$

relation $S(q) \leftrightarrow R_H$?

$$S(q) = 1 + \frac{1}{N} \sum_{n \neq m} \left\langle \frac{\sin(q r_{nm})}{q r_{nm}} \right\rangle$$

$$\frac{S(q) - 1}{N} = \frac{1}{N^2} \sum_{n \neq m} \left\langle \frac{\sin(q r_{nm})}{q r_{nm}} \right\rangle \quad \Big| \int_0^\infty dq$$

$$\int_0^\infty dq \, \frac{S(q) - 1}{N} = \frac{1}{N^2} \sum_{n \neq m} \left\langle \int_0^\infty dq \, \frac{\sin(q r_{nm})}{q r_{nm}} \right\rangle$$

$$x = q r_{nm}$$

$$q = \frac{x}{r_{nm}}$$

$$dq = \frac{dx}{r_{nm}}$$

$$= \frac{1}{N^2} \sum_{n \neq m} \left\langle \frac{1}{r_{nm}} \underbrace{\int_0^\infty dx \, \frac{\sin x}{x}}_{\pi/2} \right\rangle =$$

$$= \frac{\pi}{2} \frac{1}{R_H}$$

$$R_H = \left[\frac{2}{\pi} \int_0^\infty dq \, \frac{S(q) - 1}{N} \right]^{-1}$$

relation $S(q) \leftrightarrow R_G$? $q \to 0$ behavior

$x \to 0$

$$\sin x \cong x - \frac{1}{3!} x^3 + \frac{1}{5!} x^5 \dots$$

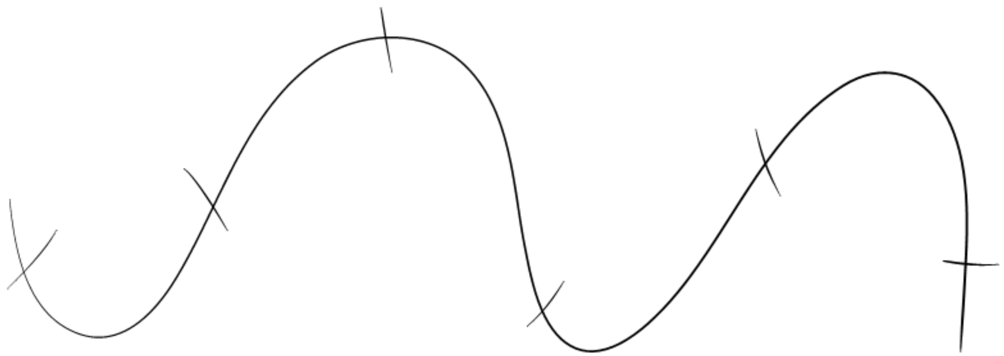
$$\frac{\sin x}{x} \cong 1 - \frac{1}{6} x^2 + \dots$$

$$S(q) \cong \frac{1}{N} \sum_{nm} \left\langle \left(1 - \frac{1}{6} q^2 r_{nm}^2 + \dots \right) \right\rangle =$$

$$= N - \frac{1}{6} q^2 \frac{1}{N} \underbrace{\sum_{nm} \langle r_{nm}^2 \rangle}_{2N^2 \langle R_G^2 \rangle} + \dots =$$

$$= N\left(1 - \frac{1}{3} q^2 \langle R_g^2 \rangle + \dots\right) = S(q)$$

<u>Idea</u> for a long chain → sub-divide into M sub-chains



chain = concatenation of M subchains of identical length

subchain is very long, i.e. <u>is</u> a random walk

$$\breve{\bar{R}}_E(\text{whole chain}) =$$

$$= \breve{\bar{R}}_E(\text{1st subchain})$$

$$+ \breve{\bar{R}}_E(\text{2nd} \quad " \quad)$$

$$+ \breve{\bar{R}}_E(\text{3rd} \quad " \quad) + \ldots$$

$$\ldots + \breve{\bar{R}}_E(\text{Mth} \quad " \quad) =$$

$$= \boxed{\breve{\bar{l}}_1 + \breve{\bar{l}}_2 + \breve{\bar{l}}_3 + \ldots + \breve{\bar{l}}_M}$$

$\breve{\bar{l}}_1, \breve{\bar{l}}_2, \breve{\bar{l}}_3 \ldots$

have all identical statistical properties

ADD UP a large number of random variables with identical distribution

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CENTRAL LIMIT THEOREM

$X_1, X_2, \ldots, X_M$ random variables

identical distribution

$\sum_n X_n$ will be Gaussian if M is large

and $\langle X^2 \rangle - \langle X \rangle^2$ is finite

Gaussian:

$\xi = \langle X \rangle$

$$P(X) = \frac{1}{\sqrt{2\pi \sigma^2}} \exp\left(- \frac{(X - \xi)^2}{2\sigma^2} \right)$$

$\sigma^2 = \langle X^2 \rangle - \langle X \rangle^2$