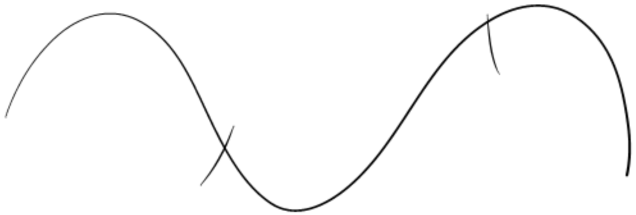


chain $\longrightarrow$ M subchains

$$\underline{\vec{R}_E} = \vec{l}_1 + \vec{l}_2 + \dots + \vec{l}_M$$

Delta function

$$\delta(x - x') = \begin{cases} \infty & x = x' \\ 0 & \text{else} \end{cases}$$

$$\int_{-\infty}^{\infty} dx\, \delta(x - x') = \int_{-\infty}^{\infty} dx'\, \delta(x - x') = 1$$

$$\boxed{\int_{-\infty}^{\infty} dx'\, \delta(x - x') f(x') = f(x)}$$

analogy:

$$f_i = \sum_j \delta_{ij} f_j$$

without proof:

$$\delta(x-x') = \frac{1}{2\pi}\int_{-\infty}^{\infty} dq \; \exp[iq(x-x')]$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} dq \; \exp[-iq(x-x')]$$

Fourier transform $f(x) \longrightarrow \tilde{f}(q)$

$$\tilde{f}(q) = \int_{-\infty}^{\infty} dx \; f(x) \; \exp[iqx]$$

Back transform:

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} dq \; \exp(-iqx)\, \tilde{f}(q) =$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} dq \; \exp(-iqx) \int_{-\infty}^{\infty} dx' \exp(+iqx')\, f(x') =$$

$$= \int_{-\infty}^{\infty} dx'\, f(x') \underbrace{\frac{1}{2\pi}\int_{-\infty}^{\infty} dq \; \exp(iq(x'-x))}_{=\delta(x'-x)} =$$

$$= \int_{-\infty}^{\infty} dx' \, f(x') \, \delta(x' - x) = f(x)$$

d-dimensional δ-function

$$\delta(\vec{r} - \vec{r}_0) = \delta(x - x_0)\, \delta(y - y_0) \ldots$$

$$= \frac{1}{(2\pi)^d} \int d^d \vec{q} \, \exp(i \vec{q} \cdot (\vec{r} - \vec{r}_0))$$

$L \to$ long $\longrightarrow P_L(\vec{R}_E)$ distrib. of $\vec{R}_E$

$S \to$ short $\longrightarrow P_S(\vec{\ell})$ " " $\vec{\ell}$

$$P_L(\vec{R}_E) = \int d^3\vec{l}_1 \int d^3\vec{l}_2 \dots \int d^3\vec{l}_m$$

$$P_S(\vec{l}_1)\, P_S(\vec{l}_2) \dots P_S(\vec{l}_m)$$

$$\delta\left(\vec{R}_E - \sum_k \vec{l}_k\right)$$

$$\int d^3\vec{R}_E\, P_L(\vec{R}_E) = \int d^3 l_1 \dots \int d^3 \vec{l}_m\, P_S(\vec{l}_1) \dots P_S(\vec{l}_m)$$

$$\underbrace{\int d^3\vec{R}_E\, \delta\left(\vec{R}_E - \sum_k \vec{l}_k\right)}_{=1} =$$

$$= \underbrace{\int d^3\vec{l}_1\, P_s(\vec{l}_1)}_{=1} \underbrace{\int d^3\vec{l}_2\, P_s(\vec{l}_2)}_{=1} \ldots \underbrace{\int d^3\vec{l}_m\, P_s(\vec{l}_m)}_{=1} = 1$$

$$\int d^3 R_E\, P_L(\vec{R}_E) \exp[i\vec{q}\cdot\vec{R}_E] = \langle \exp(i\vec{q}\cdot\vec{R}_E)\rangle =$$

$$= \int d^3\vec{l}_1\, P_s(\vec{l}_1) \ldots \int d^3 l_m\, P_s(\vec{l}_m) \int d^3\vec{R}_E \exp(i\vec{q}\cdot\underline{\underline{\vec{R}_E}})$$

$$\delta(\vec{R}_E - \underline{\underline{\textstyle\sum_k \vec{l}_k}}) =$$

$$= \int d^3\vec{l}_1\, P_s(\vec{l}_1) \cdots \int d^3\vec{l}_M\, P_s(\vec{l}_M)\, \underbrace{\exp\left(i\vec{q}\cdot \textstyle\sum_k \vec{l}_k\right)}_{=\ \exp(i\vec{q}\cdot\vec{l}_1)\cdots\exp(i\vec{q}\cdot\vec{l}_M)}$$

$$= \int d^3 l_1\, P_s(\vec{l}_1) \exp(i\vec{q}\cdot\vec{l}_1) \cdots \int d^3\vec{l}_M\, P_s(\vec{l}_M) \exp(i\vec{q}\cdot\vec{l}_M)$$

$$= \left[\int d^3 l\, P_s(\vec{l}) \exp(i\vec{q}\cdot\vec{l})\right]^M = \langle \exp(i\vec{q}\cdot\vec{l})\rangle^M$$

$$\boxed{\langle \exp(i\vec{q}\cdot\vec{R}_E)\rangle = \langle \exp(i\vec{q}\cdot\vec{l})\rangle^M}$$

Self-Similarity

P_L and P_S are essentially the same functions, except that they are governed by different length scales:

$$\left.\begin{array}{l} L: \sqrt{\langle R_E^2 \rangle} \\ \\ S: \sqrt{\langle \ell^2 \rangle} \end{array}\right\} \quad \langle R_E^2 \rangle = M \langle \ell^2 \rangle$$

$$\langle \exp(i\vec{q}\cdot\vec{R}_E) \rangle = f\left(q^2 \langle R_E^2 \rangle\right) = f\left(M q^2 \langle \ell^2 \rangle\right)$$

$$\langle \exp(i\vec{q}\cdot\vec{\ell}) \rangle = f\left(q^2 \langle \ell^2 \rangle\right)$$

$$\boxed{f(M\, q^2(\ell^2)) = f(q^2(\ell^2))^M}$$ Scaling relation

write $M \equiv x \quad q^2(\ell^2) \equiv y$

$$f(xy) = f(y)^x \qquad \Big|\ \ln$$

$$\ln f(xy) = x \ln f(y) \qquad \Big|\ y = 1$$

$$\ln f(x) = x \ln f(1) \qquad \Big|\ \ln f(1) =: A$$

$$\ln f(x) = xA$$

$$\boxed{f(x) = \exp(Ax)}$$

$$\boxed{\langle \exp(i\vec{q}\cdot\vec{l})\rangle = \exp(A\; q^2 \langle l^2\rangle)}$$

$A = ??$ $\quad q \to 0$

$$\exp(i\vec{q}\cdot\vec{l}) = 1 + i\vec{q}\cdot\vec{l} - \frac{1}{2}(\vec{q}\cdot\vec{l})^2 + \dots =$$

$$= 1 + i\vec{q}\cdot\vec{l} - \frac{1}{2}(q_x l_x + q_y l_y + q_z l_z)^2 + \dots$$

$$= 1 + i\vec{q}\cdot\vec{l} - \frac{1}{2}(q_x^2 l_x^2 + q_y^2 l_y^2 + q_z^2 l_z^2)$$

$$- [q_x q_y l_x l_y + q_x q_z l_x l_z + q_y q_z l_y l_z] + \dots$$

$$\langle \exp(i\vec{q}\cdot\vec{l}) \rangle = 1 - \frac{1}{2}\Big(q_x^2 \underbrace{\langle l_x^2 \rangle}_{\frac{1}{3}\langle l^2 \rangle} + q_y^2 \underbrace{\langle l_y^2 \rangle}_{=\frac{1}{3}\langle l^2 \rangle} + q_z^2 \underbrace{\langle l_z^2 \rangle}_{=\frac{1}{3}\langle l^2 \rangle} \Big) + \dots$$

$$= 1 - \frac{1}{6}\langle l^2 \rangle q^2 + \dots$$

$$\exp\left(A q^2 \langle l^2 \rangle\right) = 1 + A q^2 \langle l^2 \rangle + \dots$$

$$\boxed{A = -\frac{1}{6}}$$

$$\boxed{\langle \exp(i\vec{q}\cdot\vec{l}) \rangle = \exp\left(-\frac{1}{6} q^2 \langle l^2 \rangle\right)}$$

Fourier transform back:

$$P_s(\vec{\ell}) = \frac{1}{(2\pi)^3} \int d^3\vec{q}\ \exp\left(-\frac{1}{6} q^2 \langle \ell^2 \rangle\right) \exp(-i\vec{q}\cdot\vec{\ell})$$

dimensionless variables:

$$\vec{\lambda} := \frac{\vec{\ell}}{\sqrt{\langle \ell^2 \rangle}} \qquad \vec{\ell} = \sqrt{\langle \ell^2 \rangle}\ \vec{\lambda}$$

$$\vec{p} := \frac{1}{\sqrt{3}} \sqrt{\langle \ell^2 \rangle}\ \vec{q} \qquad \vec{q} = \sqrt{\frac{3}{\langle \ell^2 \rangle}}\ \vec{p}$$

$$\vec{\ell}\cdot\vec{q} = \sqrt{3}\ \vec{p}\cdot\vec{\lambda}$$

$$\frac{1}{6} q^2 \langle l^2 \rangle = \frac{1}{6} \cdot 3 p^2 = \frac{1}{2} p^2$$

$$d^3 \bar{q} = \left(\frac{3}{\langle l^2 \rangle} \right)^{3/2} d^3 \bar{p}$$

$$P_S = \frac{1}{(2\pi)^3} \left(\frac{3}{\langle l^2 \rangle} \right)^{3/2} \int d^3 \bar{p} \; \exp\left(-\frac{1}{2} p^2\right) \exp\left(-i\sqrt{3}\, \bar{p} \cdot \bar{\lambda}\right)$$

$$-\frac{1}{2} p^2 - i\sqrt{3}\, \bar{p} \cdot \bar{\lambda} = -\frac{1}{2} \Big(p^2 + 2 \left(i\sqrt{3}\, \bar{\lambda} \right) \cdot \bar{p} + \left(i\sqrt{3}\, \bar{\lambda} \right)^2$$

$$+ 3 \bar{\lambda}^2 \Big) =$$

$$= \underbrace{-\frac{1}{2} \left(\bar{p} + i\sqrt{3}\, \bar{\lambda} \right)^2} \; \underbrace{-\frac{3}{2} \bar{\lambda}^2}$$

$$P_s = \left(\frac{3}{2\pi\langle l^2\rangle}\right)^{3/2} \left(\frac{1}{2\pi}\right)^{3/2} \exp\left(-\frac{3}{2}\lambda^2\right)$$

$$\underbrace{\int d^3\vec{p}\, \exp\left[-\frac{1}{2}\left(\vec{p} + i\sqrt{3}\,\vec{\lambda}\right)^2\right]}$$

$$= \int d^3\vec{p}\, \exp\left(-\frac{1}{2}p^2\right) = (2\pi)^{3/2}$$

$$= \boxed{\left(\frac{3}{2\pi\langle l^2\rangle}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{\vec{l}^{\,2}}{\langle l^2\rangle}\right) = P_s(\vec{l})}$$

3D Gaussian

abbreviation $b \equiv$ root mean square bond length

$$P(\vec{r}_{ij}) = \left(\frac{3}{2\pi b^2 |i-j|}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{r_{ij}^2}{b^2|i-j|}\right)$$

Structure factor of the Gaussian chain

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

$$= \frac{1}{N} \sum_{ij} \exp\left(-\frac{1}{6} q^2 \langle \vec{r}_{ij}^{\,2} \rangle\right) =$$

$$= \frac{1}{N} \sum_{ij} \exp\left(-\frac{1}{6} q^2 b^2 |i-j|\right) =$$

$$= 2 \cdot \frac{1}{N} \sum_{k=0}^{N-1} (N-k) \quad \exp\left(-\frac{1}{6} q^2 b^2 k\right) - 1 =$$

$$= 2 \sum_{k=0}^{N-1} \left(1 - \frac{k}{N}\right) \exp\left(-\frac{1}{6} q^2 b^2 N \frac{k}{N}\right) - 1$$

$$x := \frac{k}{N} \qquad z := \frac{1}{6} q^2 b^2 N$$

$$x : 0 \to 1$$

$$\Delta k = 1 = N d_x$$

$$S(q) = 2N \int_0^1 dx \, (1-x) \exp(-zx) \underbrace{- 1}_{\text{neglect}} \simeq$$

$$\simeq 2N \int_0^1 dx \, (1-x) \, e^{-zx} =$$

$$= 2N \int_0^1 dx \left(1 + \frac{d}{dz}\right) e^{-zx} =$$

$$= 2N \left(1 + \frac{d}{dz}\right) \int_0^1 dx \, e^{-zx} =$$

$$= 2N \left(1 + \frac{d}{dz}\right) \left. \frac{e^{-zx}}{-z} \right|_{x=0}^{x=1} =$$

$$= 2N \left(1 + \frac{d}{dz}\right) \left(\frac{1}{z} - \frac{e^{-z}}{z} \right) =$$

$$S(q) = N \, f_D(z)$$

$$\boxed{f_D(z) = \frac{2}{z^2}\left(e^{-z} - 1 + z\right)}$$ Debye function

where $\boxed{z = \frac{1}{6} q^2 b^2 N}$

$$q \to 0 \Rightarrow z \to 0$$

$$e^{-z} = 1 - z + \frac{1}{2} z^2 - \frac{1}{6} z^3 + \dots$$

$$e^{-z} - 1 + z = \frac{1}{2} z^2 - \frac{1}{6} z^3 + \dots = \frac{z^2}{2}\left(1 - \frac{1}{3} z + \dots\right)$$

$$f_D(z) \simeq 1 - \frac{1}{3} z + O(z^2)$$

$$S(q) \simeq N\left(1 - \frac{1}{3} q^2 b^2 N \frac{1}{6} + O(q^4)\right)$$

$$S(q) \simeq N\left(1 - \frac{1}{3} q^2 \langle R_G^2 \rangle + O(q^4)\right)$$

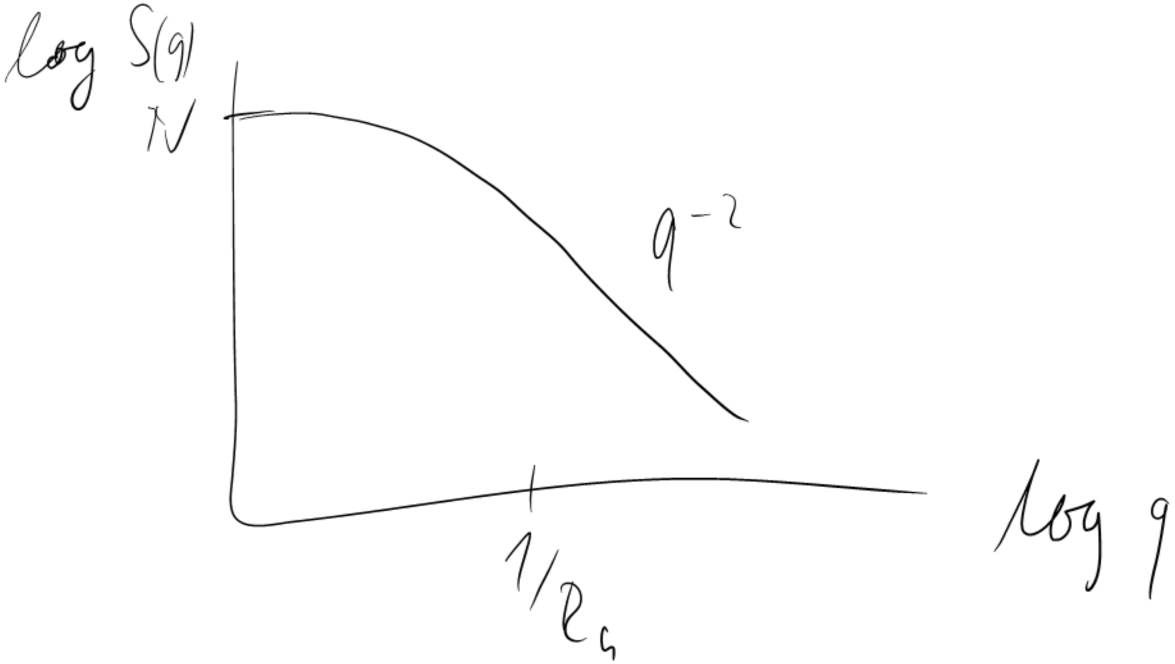
$$\langle R_G^2 \rangle = \frac{1}{6} b^2 N = \frac{1}{6} \langle R_E^2 \rangle$$

$$z = q^2 \langle R_G^2 \rangle$$

$$z \to \infty \Rightarrow f_D(z) \simeq \frac{2}{z} \qquad (\Leftrightarrow q \to \infty)$$

$$S(q) \simeq \frac{2N}{q^2 \langle R_g^2 \rangle} = \frac{2N}{q^2 \frac{1}{6} b^2 N} = \frac{12}{q^2 b^2} \propto q^{-2}$$

independent of N !



$$\frac{1}{R_H} \simeq \frac{2}{\pi} \int_0^\infty dq \, \frac{S(q)}{N}$$

$$z = \frac{1}{6} q^2 b^2 N \qquad q = \sqrt{\frac{6z}{b^2 N}} = \sqrt{\frac{6}{b^2 N}} \, z^{1/2}$$

$$dq = \sqrt{\frac{6}{b^2 N}} \, \frac{1}{2} z^{-1/2} \, dz$$

$$\frac{1}{R_H} = \frac{2}{\pi} \sqrt{\frac{6}{b^2 N}} \int_0^\infty dz \, \frac{1}{z^{5/2}} \left(e^{-z} - 1 + z \right)$$

$$\frac{R_g}{R_H} = \frac{2}{\pi} \int_0^\infty dz \, \frac{1}{z^{5/2}} \left(e^{-z} - 1 + z \right) =$$

$$= \frac{2}{\pi}\,\frac{4}{3}\sqrt{\pi} = \underbrace{\frac{8}{3\sqrt{\pi}} = \frac{R_h}{R_H}}_{=\,1.5045}$$

---

map Gaussian chain onto a bead-spring model

$$\mathcal{H} = \frac{k}{2}\sum_i \left(\vec{r}_{i+1} - \vec{r}_i\right)^2$$

spring constant k

Boltzmann factor for such a chain is

$$\exp\left(-\frac{1}{k_B T}\mathcal{H}\right) = \exp\left(-\frac{k}{2}\frac{1}{k_B T}\left(\vec{r}_2-\vec{r}_1\right)^2\right)$$

$$\exp\left(-\frac{k}{2}\frac{1}{k_B T}\left(\vec{r}_3-\vec{r}_2\right)^2\right) \dots$$

$$\exp\left(-\frac{k}{2}\frac{1}{k_B T}\left(\vec{r}_N-\vec{r}_{N-1}\right)^2\right)$$

$$\left.\begin{aligned} P(\vec{r}_{12}) &\propto \exp\left(-\frac{3}{2}\frac{\vec{r}_{12}^{\,2}}{b^2}\right) \\ P(\vec{r}_{23}) &\propto \exp\left(-\frac{3}{2}\frac{\vec{r}_{23}^{\,2}}{b^2}\right) \dots \end{aligned}\right\} \quad \begin{aligned} \frac{k}{2}\frac{1}{k_B T} &\overset{!}{=} \frac{3}{2}\frac{1}{b^2} \\ k &= 3 k_B T \frac{1}{b^2} \end{aligned}$$

$$\boxed{\mathcal{H} = \frac{3k_BT}{2b^2} \sum_i \left(\vec{r}_{i+1} - \vec{r}_i\right)^2}$$

<u>entropic</u>

elasticity

Continuum description

$$\boxed{\mathcal{H} = \frac{3k_BT}{2b^2} \int_0^N ds \left(\frac{\partial \vec{r}}{\partial s}\right)^2}$$

$$\vec{r}_{i+1} - \vec{r}_i \longrightarrow \vec{r}(s+1) - \vec{r}(s) = \frac{1}{\Delta s}\left(\vec{r}(s+\Delta s) - \vec{r}(s)\right)$$

$$\Delta s = 1 \qquad \simeq \frac{\partial \vec{r}}{\partial s}$$

1.4. The Wormlike Chain

Look at a chain which is very stiff

and not very long (i.e. contour length

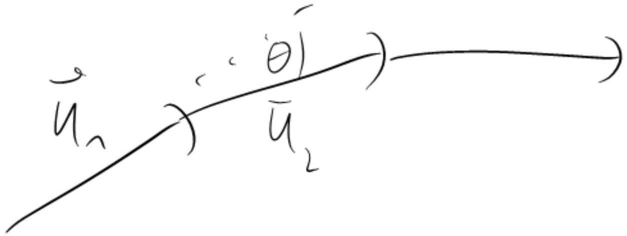
is comparable to the persistence length)

decay length

of the bond angle correlation function

$\rightarrow$ Gaussian description does not work

Aim: Try to find simple continuum description $\vec{r}(s)$



$\theta \ll 1$

$\vec{u}_1$: unit vector along bond 1

$\vec{u}_2$: " " " " "

$$\mathcal{H}_{12} \simeq \alpha \frac{\theta^2}{2} \simeq \alpha \left(1 - \cos\theta\right)$$
$$= \alpha \left(1 - \vec{u}_1 \cdot \vec{u}_2\right)$$

cont.

$\vec{r}(s) \qquad s \in [0, N]$

$\vec{u}(s)$: tangent unit vector along the curve

$$\vec{u} = \frac{\frac{\partial \vec{r}}{\partial s}}{\left| \frac{\partial \vec{r}}{\partial s} \right|}$$

$$\vec{u}^2(s) = 1 \quad \Big| \frac{\partial}{\partial s}$$

$$2 \vec{u} \cdot \frac{\partial \vec{u}}{\partial s} = 0 \qquad \vec{u} \perp \frac{\partial \vec{u}}{\partial s}$$

$$\vec{u}_2 = \vec{u}_1 + \frac{\partial \vec{u}_1}{\partial s} \underbrace{\Delta s}_{=1} + \frac{1}{2} \frac{\partial^2 \vec{u}_1}{\partial s^2} \underbrace{\Delta s^2}_{=1} + \dots \quad \Big| \cdot \vec{u}_1$$

$$\vec{u}_1 \cdot \vec{u}_2 = 1 + \frac{1}{2} \vec{u}_1 \cdot \frac{\partial^2 \vec{u}_1}{\partial s^2}$$

$$\mathcal{H}_{12} = - \frac{\alpha}{2} \vec{u}_1 \cdot \frac{\partial^2 \vec{u}_1}{\partial s^2}$$

$$\mathcal{H}_{tot} = - \frac{\alpha}{2} \int_0^N ds \, \vec{u} \cdot \frac{\partial^2 \vec{u}}{\partial s^2} =$$

$$= -\frac{\alpha}{2}\left\{ \underbrace{\frac{\partial \vec{u}}{\partial s}\cdot\vec{u}\,\Big|_0^N}_{=0} - \int_0^N ds\left(\frac{\partial \vec{u}}{\partial s}\right)^2 \right\} =$$

$$\underbrace{= \frac{\alpha}{2}\int_0^N ds\left(\frac{\partial \vec{u}}{\partial s}\right)^2 = \mathcal{H}_{tot}}$$

$u^2 = 1$ diffusion on the unit sphere