10/16/02

Chem 664
Handout #8

Some properties of $\mathbb{P}_{3D}(N, \underline{R})$, the probability density of ETE vector for 3D random walk:

$$\mathbb{P}_{3D}(N,\underline{R}) = \left(\frac{3}{2\pi N b^2}\right)^{3/2} e^{-3R^2/2Nb^2}$$

for short, $\mathbb{P}(\underline{R}) = \left(\frac{3}{2\pi \langle R^2\rangle}\right)^{3/2} e^{-3R^2/2\langle R^2\rangle}$

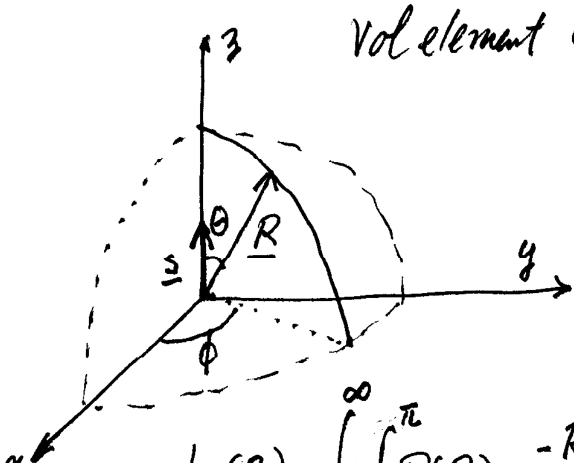
The moments generating function of $\mathbb{P}(\underline{R})$

$$L(\underline{s}) \equiv \int_{-\infty}^{\infty} \mathbb{P}(\underline{R})\, e^{-\underline{R}\cdot\underline{s}}\, d\underline{R}\,,$$

a Laplace transform analog of $\mathbb{P}(\underline{R})$, note that $-\infty \le \underline{R} \le \infty$ hence it is different from the usual L-tranform, $0 \to \infty$ for the indept variable

Since $\underline{s}$ is an arbitrary vector, we can let it be pointed in the z-direction such that $\underline{R}\cdot\underline{s} = R\,s\cos\theta$

Vol element $d\underline{R} = R^2 \sin\theta\, d\theta\, d\phi\, dR$



$$\int_0^{\pi} e^{-Rs\cos\theta}\sin\theta\, d\theta = \int_{-1}^{1} e^{-Rsx}\, dx$$

$$\left[\begin{array}{l} x \equiv \cos\theta \\ \theta = 0,\ x = 1 \\ \theta = \pi,\ x = -1 \\ dx = -\sin\theta\, d\theta \end{array}\right]$$

$$= -\frac{1}{Rs}\left(e^{-Rs} - e^{+Rs}\right)$$

$$= \frac{2}{Rs}\sinh(Rs)$$

$\sinh u = \frac{1}{2}(e^{u} - e^{-u})$

$$L(\underline{s}) = \int_0^{\infty}\int_0^{\pi} \mathbb{P}(\underline{R})\, e^{-Rs\cos\theta}\sin\theta\, d\theta \left[\int_0^{2\pi} d\phi\right] dR = \int_0^{\infty} \mathbb{P}(\underline{R})\, 4\pi R^2 \frac{\sinh(Rs)}{Rs}\, dR$$

$$= \int_0^{\infty} \mathbb{P}(\underline{R})\, 4\pi R^2 \frac{\sinh(Rs)}{Rs}\, dR \quad \left[\frac{\sinh x}{x} = 1 + \frac{x^2}{3!} + \frac{x^4}{5!} + \frac{x^6}{7!} + \cdots\right]$$

$$= \int_0^{\infty} \mathbb{P}(\underline{R})\left[1 + \frac{1}{3!}R^2 s^2 + \frac{1}{5!}R^4 s^4 + \cdots\right] 4\pi R^2\, dR$$

$$= 1 + \frac{1}{3!}\langle R^2\rangle s^2 + \frac{1}{5!}\langle R^4\rangle s^4 + \cdots \text{ (only even moments)}$$

Returning to full evaluation of $L(\underline{s})$

$$L(\underline{s}) = \int_{-\infty}^{\infty} \mathbb{P}(\underline{R}) e^{-\underline{R}\cdot\underline{s}} \, d\underline{R} = \int_{-\infty}^{\infty} \left(\frac{3}{2\pi\langle R^2\rangle}\right)^{3/2} e^{-3R^2/2\langle R^2\rangle} \cdot e^{-\underline{R}\cdot\underline{s}} \, dR_x dR_y dR_z$$

$$= \left[\int_{-\infty}^{\infty} \left(\frac{3}{2\pi\langle R^2\rangle}\right)^{1/2} e^{-3R_x^2/2\langle R^2\rangle} e^{-R_x s_x} dR_x\right] [y\text{-term}][z\text{-term}]$$

$$= \left(\frac{3}{2\pi\langle R^2\rangle}\right)^{3/2} \left[\left(\frac{2\langle R^2\rangle\pi}{3}\right)^{1/2} e^{\langle R^2\rangle s_x^2/6}\right] [y\text{-term}][z\text{-term}]$$

$$\int_{-\infty}^{\infty} e^{-ax^2-bx} dx = \int_{-\infty}^{\infty} e^{b^2/4a} \cdot e^{-\left(\sqrt{a}\,x + \frac{b}{2\sqrt{a}}\right)^2} dx$$

$$= e^{b^2/4a} \int_{-\infty}^{\infty} e^{-u^2} \frac{du}{\sqrt{a}} = e^{b^2/4a} \left(\frac{\pi}{a}\right)^{1/2}$$

$$\because \int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1} a^n}\sqrt{\frac{\pi}{a}}$$

$$\int_{-\infty}^{\infty} e^{-u^2} du = 2\cdot\frac{\sqrt{\pi}}{2}$$

$$= e^{\langle R^2\rangle s_x^2/6} [y\text{-term}][z\text{-term}] = e^{\langle R^2\rangle s^2/6}$$

$$s^2 = s_x^2 + s_y^2 + s_z^2$$

$$\boxed{L(\underline{s}) = e^{\langle R^2\rangle s^2/6}}$$

a function only of $\langle R^2\rangle$, meaning that higher moments are all function of $\langle R^2\rangle$

Returning to the series expansion

$$L(\underline{s}) = 1 + \frac{1}{3!}\langle R^2\rangle s^2 + \frac{1}{5!}\langle R^4\rangle s^4 + \frac{1}{7!}\langle R^6\rangle s^6 + \cdots$$

$$\frac{dL(\underline{s})}{ds} = \frac{2}{3!}\langle R^2\rangle s + \frac{4}{5!}\langle R^4\rangle s^3 + \frac{6}{7!}\langle R^6\rangle s^5 + \cdots$$

$$\frac{d^2L(\underline{s})}{ds^2} = \frac{2}{3!}\langle R^2\rangle + \frac{4\cdot 3}{5!}\langle R^4\rangle s^2 + \frac{6\cdot 5}{7}\langle R^6\rangle s^4 + \cdots$$

$$\langle R^2\rangle = \frac{3!}{2}\left[\frac{d^2L(s)}{ds^2}\right]_{s=0}, \quad \langle R^4\rangle = \frac{5!}{4\cdot 3\cdot 2}\left[\frac{d^4L(\underline{s})}{ds^4}\right]_{s=0}$$

Also $$L(\underline{s}) = 1 + \frac{\langle R^2\rangle s^2}{6} + \frac{1}{2!}\left(\frac{\langle R^2\rangle}{6}\right)^2 s^4 + \frac{1}{3!}\left(\frac{\langle R^2\rangle}{6}\right)^3 s^6 + \cdots$$

$$\langle R^{2p}\rangle = \frac{(2p+1)!}{p!}\left(\frac{\langle R^2\rangle}{6}\right)^p$$

Free Energy of an ideal chain

Entropy of an ideal chain $S = +k \ln \Omega$ (Boltzmann Postulate)

Ω = Total number of conformational states

$$S(N, \underline{R}) = k \ln \Omega(N, \underline{R})$$

Probability density for $\underline{R}$ with N steps,

$$\mathbb{P}(N, \underline{R}) = \frac{\Omega(N, \underline{R})}{\int_{-\infty}^{\infty} \Omega(N, \underline{R})\, d\underline{R}} = \left(\frac{3}{2\pi \langle R^2 \rangle}\right)^{3/2} e^{-3R^2/2\langle R^2 \rangle}$$

Hence, $\Omega(N, \underline{R}) = \mathbb{P}(N, \underline{R}) \cdot \int_{-\infty}^{\infty} \Omega(N, \underline{R})\, d\underline{R}$

$$S(N, \underline{R}) = -\frac{3}{2} k \left(\frac{R^2}{\langle R^2 \rangle}\right) + \underbrace{\frac{3}{2} k \ln\left(\frac{3}{2\pi \langle R^2 \rangle}\right) + k \ln \int_{-\infty}^{\infty} \Omega(N, \underline{R})\, d\underline{R}}_{\text{fcn only of } N \;\equiv\; S(N, 0)}$$

Helmholtz free energy of an ideal chain,

$$A(N, \underline{R}) = U(N, \underline{R}) - TS(N, \underline{R}) \approx \frac{3}{2} kT \left(\frac{R^2}{\langle R^2 \rangle}\right) + A(N, 0)$$

Note that we use A instead F, commonly used in physics literature

$U(N, \underline{R}) \approx 0$, ideal chain assumption

U is indep't on $\underline{R}$

$$\left(\frac{\partial A(N, \underline{R})}{\partial \underline{R}}\right)_{T,V} = f \text{ (force for maintaining ETE vector at } \underline{R})$$

$$\left(\frac{\partial G(N, \underline{R})}{\partial \underline{R}}\right)_{T,P} = f \text{ ('')}$$

$$f_x = \left(\frac{\partial A}{\partial R_x}\right)_{T,V} = \frac{3}{2} kT \frac{1}{\langle R^2 \rangle} \left[\frac{\partial}{\partial R_x}(R_x^2 + R_y^2 + R_z^2)\right]_{T,V}$$

$$= \frac{3}{2} kT \frac{1}{Nb^2} \cdot 2R_x = \left(\frac{3kT}{Nb^2}\right) R_x$$

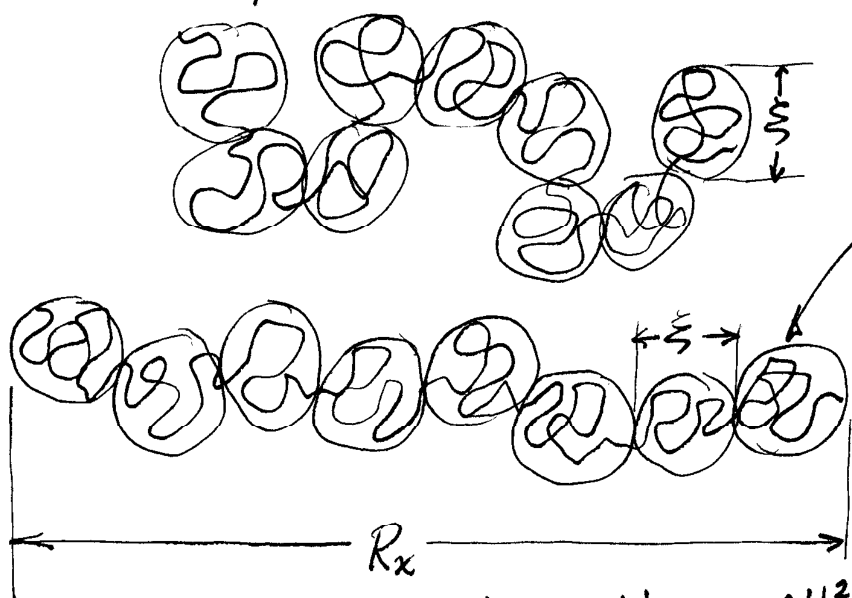
$$f_x = \left(\frac{3kT}{Nb^2}\right)R_x, \quad f_y = \left(\frac{3kT}{Nb^2}\right)R_y, \quad f_z = \left(\frac{3kT}{Nb^2}\right)R_z$$

all represent Hook's law, $f = K(\Delta X)$, force $\propto$ displacement with spring const K.

$\underline{f} = \left(\frac{3kT}{Nb^2}\right)\underline{R}$, the force necessary to hold an ideal chain at $\underline{R}$ with a spring const that increases with T and decreases with the [number] of Kuhn segment N and with the segment size b. This holds true only if $|\underline{R}| << R_{max} = Nb$

Scaling of $A(N, \underline{R})$

- Linear displacement of an ideal chain:



tension blob, suffering no perturbation in conformational state upon stretching

$\xi^2 = b^2 g$, g = # of Kuhn segment within a blob

$$R_x \approx \xi\left(\frac{N}{g}\right) \approx \xi\frac{N}{(\xi^2/b^2)} = \frac{Nb^2}{\xi}$$

$\frac{N}{g}$: # of blobs aligned along x-axis

Therefore, $\xi = \frac{Nb^2}{R_x}$

$$g = \frac{N^2b^2}{R_x^2} = \frac{R_{max}^2}{R_x^2}$$

$$g = \frac{\xi^2}{b^2} = \frac{N^2b^4/R_x^2}{b^2}$$

Tension affects chain conformation, but not in length scales less than ξ. it aligns the tension blobs along the $\hat{x}$-axis, hence one degree of freedom is restricted for a blobs. $A = (\text{Thermal energy})\cdot(\#\text{ of blobs}) \approx kT\frac{N}{g} \approx kT\frac{R_x^2}{Nb^2}$

For scaling argument

$$A \approx kT\left(\frac{N}{g}\right) \qquad \text{to be compared to}$$
$$\approx kT\left(\frac{R_x^2}{Nb^2}\right) \qquad A(N,\underline{R}) = \frac{3}{2}kT\frac{R^2}{\langle R^2\rangle} + A(N,0)$$

$$f_x = \left(\frac{\partial A}{\partial R_x}\right)_{T,V} \approx kT\frac{R_x}{Nb^2} \approx \frac{kT}{\xi},$$ force along the tension axis is thermal energy divided by blob size

Hookian force $\propto R_x$ with const kT/Nb^2

What is the limit of applicability? $f_x = \frac{kT}{b} = \frac{1.34\cdot 10^{-23}\cdot 300}{10^{-9}}$

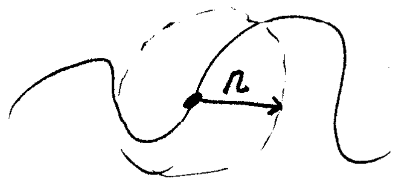
$\cong 4\cdot 10^{-12}\,N$

For DNA case, the limit is $f_x = \frac{1.34\cdot 10^{-23}\cdot 300}{100\cdot 10^{-9}}$

$b = 100\,nm \qquad \cong 4\cdot 10^{-14}\,N$

$l_p = 50\,nm$

Pair correlation function of an ideal chain



"monomer"

# of Kuhn segment with r

$n = (r/b)^2, \quad \langle r^2\rangle = nb^2$

Probability of finding a monomer at a distance r from the reference

$$g(r) \approx \frac{n}{r^3} \approx \frac{r^2/b^2}{r^3} \approx 1/rb^2$$

density of monomer

Exactly, $g(r) = \frac{3}{\pi r b^2}$

$g(r)\downarrow$ as $r\uparrow$ $\qquad g(r) \approx \frac{n}{r^3} \approx \frac{1}{rb^2} \sim r^{D-3}$

if $n \sim r^D$ $\qquad D = 2$

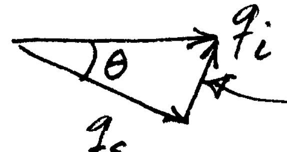
"Porosity" of an ideal chain

$\left(\frac{R}{r}\right)^3 - \left(\frac{R}{r}\right)^2$ empty sites, $n \approx (r/b)^2$ occupation # in a cell

Measurement of Chain Dimension by Scattering

Only possible if the scatterer is large enough to give rise to the angular dependence of scattered intensity

Scattering wave vector $\underline{q} \equiv \underline{q}_i - \underline{q}_s$, θ is the scattering angle



$$\underline{q}_i = \frac{2\pi n}{\lambda}\hat{\underline{u}}_i$$

$$\underline{q}_s = \frac{2\pi n}{\lambda}\hat{\underline{u}}_s$$

$$|\underline{q}| \equiv q = 2q_i \sin(\theta/2) = \frac{4\pi n}{\lambda}\sin(\theta/2)$$

In light scattering, $\dfrac{Kc}{R_\theta} = \dfrac{1}{MP(\underline{q})} + 2A_2 c + \dots$

$P(\underline{q})$ is called form factor,

$$\equiv I_s(q)/I_s(0) = \frac{1}{N^2}\sum_i\sum_j\langle\cos[\underline{q}\cdot\underline{h}_{ij}]\rangle$$

$$= \frac{1}{N^2}\sum_i\sum_j\langle e^{i\underline{q}\cdot\underline{h}_{ij}}\rangle = \frac{1}{N^2}\sum_i\sum_j\left\langle\frac{\sin q h_{ij}}{q h_{ij}}\right\rangle$$

$$= \frac{1}{N^2}\sum_i\sum_j\left\langle\left[1 - \frac{(qh_{ij})^2}{3!}+\dots\right]\right\rangle$$

$$\frac{\sin x}{x} = 1 - \frac{x^2}{3!}+\frac{x^4}{5!}-\dots$$

$$= 1 - \frac{q^2}{6N^2}\sum_i\sum_j\langle h_{ij}^2\rangle+\dots$$

$$= 1-\frac{q^2}{3}R_g^2+\dots = 1 - \frac{16\pi^2}{3(\lambda/n)^2}R_g^2\sin^2(\theta/2)+\dots$$

if $qR_g<1$

$$1/P(q) \approx 1 + \frac{16\pi^2 n^2}{3\lambda^2}R_g^2\sin^2(\theta/2)$$

$$\frac{Kc}{R_\theta} = \frac{1}{M}\left[1 + \frac{16\pi^2 n^2}{3\lambda^2} R_g^2 \sin^2(\theta/2)\right] + 2A_2 c + \cdots$$

$$\lim_{c\to 0} \frac{Kc}{R_\theta} = \frac{1}{M}\left[1 + \frac{16\pi^2 n^2}{3\lambda^2} R_g^2 \sin^2(\theta/2)\right], \quad qR_g < 1$$

$$\lim_{\theta\to 0} \frac{Kc}{R_\theta} = \frac{1}{M} + 2A_2 c + \cdots$$

$P(q)$ for ideal chain

$$P(q) = \frac{1}{N^2}\sum_i \sum_j \int_{-\infty}^{\infty} \left(\frac{\sin q h_{ij}}{q h_{ij}}\right) \mathbb{P}(\underline{h}_{ij})\, d\underline{h}_{ij}$$

$$\mathbb{P}(h_{ij}) = \left(\frac{3}{2\pi|j-i|b^2}\right)^{3/2} \exp\left[-\frac{3h_{ij}^2}{2|j-i|b^2}\right]$$

$$d\underline{h}_{ij} = 4\pi h_{ij}^2\, dh_{ij}$$

$$\int_{-\infty}^{\infty}\left(\frac{\sin q h_{ij}}{q h_{ij}}\right)\cdot \mathbb{P}(\underline{h}_{ij})\, d\underline{h}_{ij} = \int_0^{\infty} 4\pi \left(\frac{\sin q h_{ij}}{q h_{ij}}\right) e^{-h_{ij}^2/x}\, h_{ij}^2\, dh_{ij}$$

$$= \frac{4\pi}{q}\int_0^{\infty} (\sin q h_{ij})\, h_{ij} \cdot e^{-h_{ij}^2/x}\, dh_{ij} = \frac{4\pi}{q}\cdot\frac{\pi^{1/2} q x^{3/2}}{4} \cdot e^{-q^2 x/4}$$

$$x \equiv \frac{2|j-i|b^2}{3}$$

$$P(q) = \frac{1}{N^2}\sum_i\sum_j e^{-\frac{q^2 b^2 |j-i|}{6}}$$

$$= \frac{2}{Q^2}\left[e^{-Q} - 1 + Q\right], \quad Q \equiv q^2 b^2 N/6 = q^2 R_g^2$$