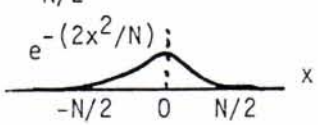
Chm 4130 Midterm #1 Problems

~~CHAPTER~~ 6 ~~28~~

Derivation of Eq. 6-43 from 6-42:

$$\langle m \rangle = \sqrt{\frac{2}{\pi N}} \left[\int_{-N/2}^{N/2} x\, e^{-(2x^2/N)}\, dx + \frac{N}{2} \int_{-N/2}^{N/2} e^{-(2x^2/N)}\, dx \right]$$

But each integral represents an area, and since the area for $|x| > (N/2)$ is negligible, we may as easily extend the integration limits to $\pm\infty$.



Next, note that $xe^{-(2x^2/N)}$ is an "odd" function (see p. 782), because $f(-x) = -f(x)$. Therefore the area of that function between -N/2 and +N/2 is automatically zero.

Therefore, $\langle m \rangle = \sqrt{\frac{2}{\pi N}} \left(\frac{N}{2}\right) \int_{-\infty}^{\infty} e^{-(2x^2/N)}\, dx$.

Next, since the function, $e^{-(2x^2/N)}$ is "even" (see p. 782), because $f(-x) = f(x)$, the preceding integral becomes,

$$\langle m \rangle = \sqrt{\frac{2}{\pi N}} \left(\frac{N}{2}\right)(2) \int_{0}^{\infty} e^{-(2x^2/N)}\, dx \quad .$$

Finally, from integral tables (Eq. E-25 on page 783),

$$\int_0^{\infty} e^{-ax^2}\, dx = (1/2)\sqrt{\frac{\pi}{a}} \quad , \text{ with } a = \frac{2}{N} \text{ in this case,}$$

$$\langle m \rangle = \sqrt{\frac{2}{\pi N}} \left(\frac{N}{2}\right)(2)\sqrt{\frac{\pi N}{2}}\,(1/2) = \frac{N}{2} \quad . \qquad \text{Q.E.D.}$$

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2. To compute the root-mean-square number of steps, begin from

$$\langle (m - \bar{m})^2 \rangle = \sqrt{\frac{2}{\pi N}} \int_{m=0}^{N} (m - \bar{m})^2\, e^{-(2(m - \bar{m})^2/N)}\, dm \quad .$$

Let $x = (m - \bar{m})$, so that $dx = dm$, to obtain

$$\langle (m - \bar{m})^2 \rangle = \sqrt{\frac{2}{\pi N}} \int_{-N/2}^{N/2} x^2 e^{-(2x^2/N)} dx = 2\sqrt{\frac{2}{\pi N}} \int_0^{N/2} x^2 e^{-(2x^2/N)} dx$$

because $x^2e^{-(2x^2/N)}$ is an "even" function (see p. 782).

2.8, cont. The closest available integral from tables (E-27, p.784) is $\int_0^\infty w^2\, e^{-w^2}\, dw = (1/4)\sqrt{\pi}$.

Therefore, again extend the integration limit to infinity (see preceding page) and change variables to

$$w = x\sqrt{\frac{2}{N}} \quad \text{so that} \quad x = w\sqrt{\frac{N}{2}} \quad ,$$

$$\frac{2x^2}{N} = w^2 \quad , \text{ and}$$

$$dx = dw\sqrt{\frac{N}{2}} \quad , \text{ to give}$$

$$\langle (m - \bar{m})^2 \rangle = 2\sqrt{\frac{2}{\pi N}}\,(N/2)\sqrt{\frac{N}{2}} \int_0^\infty w^2\, e^{-w^2}\, dw$$

$$= 2\sqrt{\frac{2}{\pi N}}\,(N/2)\sqrt{\frac{N}{2}}\,\frac{\sqrt{\pi}}{4} = \frac{N}{4} = \frac{\bar{m}}{2} \quad . \qquad \text{Q.E.D.}$$

Derivation of Eq. 6-47:

$$P_N(m)\, dm = P_t(y)\, dy \quad \text{and} \quad (m - \bar{m}) = y/2\ell \quad .$$

But $P_N(m) = \sqrt{\frac{2}{\pi N}}\, e^{-[2(m-\bar{m})^2/N]} = \sqrt{\frac{2}{\pi N}}\, e^{-(2(y/2\ell)^2/N)}$

$$= \sqrt{\frac{2}{\pi N}}\, e^{-(y^2/2\ell^2 N)} \quad , \text{ and}$$

$$dm = (1/2\ell)\, dy \quad , \text{ so,}$$

$$P_N(m)\, dm = \sqrt{\frac{2}{\pi N}}\,(1/2\ell) e^{-(y^2/2\ell^2 N)}\, dy = P_t(y)\, dy, \quad \text{where}$$

$$P_t(y)\, dy = \sqrt{\frac{1}{2\pi N\ell^2}}\; e^{-(y^2/2N\ell^2)} \quad . \qquad \text{Q.E.D.}$$

3 3.(a) $\langle y \rangle = \int_{y=-\infty}^{\infty} y\, P_t(y)\, dy = \frac{1}{\sqrt{2\pi N\ell^2}} \int_{-\infty}^{\infty} y\, e^{-(y^2/2N\ell^2)}\, dy$.

But the function, $y \exp(-y^2/2N\ell^2)$ is "odd" (p. 782), so

$\langle y \rangle = 0$.

3 3.(b) Similarly, $y^2 = \frac{1}{\sqrt{2\pi N\ell^2}} \int_{-\infty}^{\infty} y^2\, e^{-(y^2/2N\ell^2)}\, dy$, but this time the function inside the integral is "even" (p. 782), so

$\langle y^2 \rangle = \frac{2}{\sqrt{2\pi N\ell^2}} \int_0^{\infty} y^2\, e^{-(y^2/2N\ell^2)}\, dy$. From tables (E-27, page 784), we find $\int_0^{\infty} w^2\, e^{-w^2}\, dw = \frac{\sqrt{\pi}}{4}$, so change variables to $\frac{y^2}{2N\ell^2} = w^2$, or,

$y^2 = 2N\ell^2 w^2$ and $dy = \sqrt{2N\ell^2}\, dw$, and substitute:

$$\langle y^2 \rangle = \left(\frac{2}{\sqrt{2\pi N\ell^2}}\right)(2N\ell^2)\left(\sqrt{2N\ell^2}\right)\int_0^{\infty} w^2\, e^{-w^2}\, dw$$

$$= \left(\frac{2}{\sqrt{2\pi N\ell^2}}\right)(2N\ell^2)\left(\sqrt{2N\ell^2}\right)\left(\frac{\sqrt{\pi}}{4}\right) = N\ell^2 \quad , \text{ or}$$

$\boxed{\langle y^2 \rangle = \ell\sqrt{N}}$ = root-mean-square distance after N random steps, each of length, ℓ. This result is the princi-

4 3. $H_3C-(CH_2)_{(N-2)}-CH_3$ is the polymer. If there are N carbons, there will be (N-1) links, but when N is large, $(N-1) \cong N$.

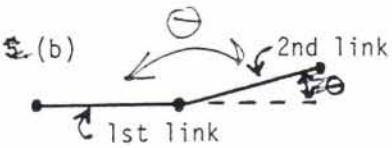
4 5. (a) $\sqrt{\langle r^2 \rangle} = \ell\sqrt{N}$

$$85\ \text{Å} = 1.54\ \text{Å}\sqrt{N} \quad ; \quad N = (85/1.54)^2 = \underline{3046\ \text{links}} \quad .$$

Molecular weight = (# links)(molec. wt per link)

$$= (3046)(14) = \underline{42{,}600} \quad .$$

4 5. (b)



For $\theta = 90°$, the walk is truly "random" (see Fig. 6-2). For $\theta > 90°$, the average end-to-end rms distance will be <u>larger</u> than for a random coil, since each step is "stretched" away from the previous one. For $\theta < 90°$, the rms end-to-end distance will be <u>smaller</u> than for a true random coil.

A detailed calculation (Tanford, pp. 154-156) shows that

$$\sqrt{\langle r^2 \rangle} = \ell\sqrt{N}\sqrt{\frac{1 + \cos\theta}{1 - \cos\theta}}\ \frac{(\pi - \theta)}{(\pi - \theta)}$$

Thus, since $\cos\theta = \cos(180 - 109.5) = 0.334$,

$$\sqrt{\langle r^2 \rangle} = \ell\sqrt{N}\sqrt{\frac{(1+0.334)}{(1-0.334)}} = (\ell\sqrt{N})\sqrt{2} \quad ,$$

and the <u>actual</u> polymethylene chain is predicted to be longer by a factor of $\sqrt{2}$ than a random coil with 90° angles between successive links.

$S/N \equiv \sqrt{\#cts}$

$\#cts \propto t$

6. 4. Signal-to-noise = S/N = constant $\cdot \sqrt{t}$.

$$S/N_{original} = \text{constant} \cdot \sqrt{t_1} \quad ;$$

$$S/N_{new} = \text{constant} \cdot \sqrt{t_2} = 1.35 \cdot (S/N)_{original}$$

↑ i.e., 35% better

Thus, $1.35 = \sqrt{\frac{t_2}{t_1}}$; $\frac{t_2}{t_1} = 1.35^2 = 1.822$, or

$t_2 = 1.82\ t_1$: we must count for 1.82 times as long.

Derivation of Eq. 8-22 from Eq. 8-21 ("dead time" determination):

Eq. 8-21: $\frac{A_1}{1 - A_1\tau} + \frac{A_2}{1 - A_2\tau} = \frac{A_{12}}{1 - A_{12}\tau}$. Clear fractions:

$$\frac{A_1(1 - A_2\tau) + A_2(1 - A_1\tau)}{(1 - A_1\tau)(1 - A_2\tau)} = \frac{A_{12}}{1 - A_{12}\tau} \quad .$$ Cross-multiply:

$$A_1(1-A_2\tau)(1-A_{12}\tau) + A_2(1-A_1\tau)(1-A_{12}\tau) = A_{12}(1-A_1\tau)(1-A_2\tau), \text{ or,}$$

FYI

$$A_1(1-A_2\tau-A_{12}\tau+A_2A_{12}\tau^2)+A_2(1-A_1\tau-A_{12}\tau+A_1A_{12}\tau^2) =$$

$$A_{12}(1-A_1\tau-A_2\tau+A_1A_2\tau^2) \quad .$$

Now if the dead time is short, $\tau \gg \tau^2$, and we may safely neglect the terms marked with "↑" as small compared to the rest:

$$A_1 - A_1A_2\tau-A_1A_{12}\tau+A_2-A_1A_2\tau-A_2A_{12}\tau = A_{12} - A_1A_{12}\tau - A_2A_{12}\tau \quad ;$$

$$A_1 + A_2 - A_{12} = 2A_1A_2\tau \quad , \text{ or,}$$

$$\boxed{\tau = \frac{A_1 + A_2 - A_{12}}{2A_1A_2}}$$ (Eq. 8-22: Q.E.D.)