Quiz 5 Polymer Properties 090213

In class we calculated the relationship between the radius of gyration, R_g, and the root-mean square (RMS) end-to-end vector R for a Gaussian polymer coil.

a) Show how the Gaussian model can be used to simplify the expression:

$$R_g^2 = \frac{1}{2N^2}\sum_{n=1}^{N}\sum_{m=1}^{N}\left(R_n - R_m\right)^2 .$$

b) Construct a 2D matrix of values from this simplified expression to show how you can obtain $R_g^2 = \frac{b^2}{N^2}\sum_{p=1}^{Z}\left(Z+1-p\right)p$

c) How would the simplified expression for R_g^2 appear if a SAW model were used?

d) Can an expression similar to that shown in b) be obtained for your answer to part c? Explain your answer.

e) What two assumptions are required for $R_g^2 = \frac{R^2}{6}$ to be true? (R is the RMS end to end distance)

2) We considered the Flory-Krigbaum equation in class.

a) What three methods were described in class for the determination of the mean end to end distance for a polymer coil.

b) Write an expression for the differential probability of a Gaussian chain having an end to end distance R, $W_0(R)dR$.

c) Calculate the most probable end to end distance using this expression of question 2b.

d) How does this compare with other methods for the determination of the mean end to end distance for a Gaussian coil? Explain the differences and similarities i.e. why is it larger or smaller.

3) For a self avoiding walk the probability of question 2a must be modified.

a) Explain the probability of exclusion expression, $p_{exclusion}\left(R\right) = \left(1-\frac{V_0}{R^3}\right)^{\frac{N^2}{2}}$.

b) Show how this expression is equal to $p_{exclusion}\left(R\right) = \exp\left(\frac{N^2V_0}{2R^3}\right)$

c) Write an expression similar to that of question 2b for a SAW chain using the expression in 3b.

d) Calculate the scaling of the most probable end to end distance with molecular weight using the expression of 3c.

e) If the athermal excluded volume, V_0, is replaced by the expression for chains with thermal interactions, $V_{thermal} = V_0\left(1-2\chi\right)$, what dependence do you expect R_g to have with temperature?

f) Write an expression for the energy of an isolated SAW chain with thermal interactions.

ANSWERS: Quiz 5 Polymer Properties 090213

Quiz 5 090213 Polymer Properties ①

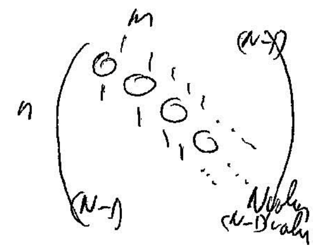
1) a)

use $R^2 = n\,l^2$

$$R_g^2 = \frac{1}{2N^2}\sum_{n=1}^{N}\sum_{m=1}^{N}(R_n - R_m)^2 = \frac{1}{N^2}\sum_{n=1}^{N}\sum_{m=n}^{N}(R_n - R_m)^2$$

$$= \frac{l^2}{N^2}\sum_{n=1}^{N}\sum_{m=n}^{N}(m-n)$$

b)



So there are $(N-1)$ value 1
& $(N-2)$ " 2
$\vdots$
1 value $(N-1)$

$z = N-1$ $\quad (z+1-p)\cdot p$

So

$$R_g^2 = \frac{b^2}{N^2}\sum_{p=1}^{z}(z+1-p)\,p$$

c) for a SAW $\quad R^2 = n^{6/5} l^2$

$$R_g^2 = \frac{l^2}{N^2}\sum_{n=1}^{N}\sum_{m=n}^{N}(m-n)^{6/5}$$

d) The matrix values are raised to the power 6/5

$N-1$ value 1
$N-2$ " $(2)^{6/5}$ So symmetry is lost
$\vdots$
1 $(N-1)^{6/5}$

②

$$R_g^{\,2} = \frac{b^2}{N^2}\sum_{p=1}^{z}(z+1-p)\,p^{6/5}$$

This cannot be solved with the power series rule.

e) ① Gaussian Chain for all separation distances $|n-m|$ (even when $(n-m)=1$).

② $N \Rightarrow \infty$

2) a) ① Summation Method $\langle R^2\rangle = \sum_{n=1}^{N}\sum_{m=1}^{N}(r_n\cdot r_m)$

② integration Method $\langle R^2\rangle = \int R^2\,p(R)\,dR$

③ Differential Method

$$\frac{d\,W_0(R^*)}{dR} = 0 \text{ at } R^* \text{ most probable value}$$

b)

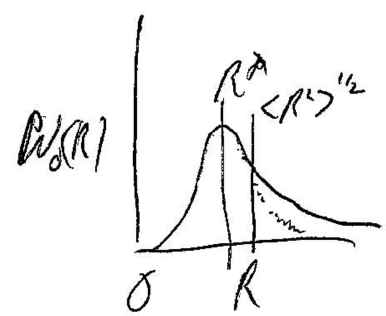
$$W_0(R)\,dR = \underset{\substack{\uparrow\\ \text{random \#}}}{Z^N}\, 4\pi R^2 \left(\frac{2\pi n\ell^2}{3}\right)^{-3/2} \exp\left(-\frac{3R^2}{2n\ell^2}\right) dR$$

c) $\frac{dW_0}{dR} = 0 = 2R\exp() - 3\frac{R^2 R}{n\ell^2}\exp()$ so $\boxed{R^2 = \frac{2}{3}n\ell^2}$

d) - Scaling between n & R is the same

$$R \sim n^{1/2}$$

- Prefactor of $2/3$ means R most probably is smaller than $\langle R^2 \rangle^{1/2}$. This means that the distribution is not symmetric about $\langle R^2 \rangle^{1/2}$ but is skewed



3) a) Prob of excluding one is $\left(1 - \frac{V_0}{R^3}\right)$

Prob of excluding N by $(N-1)$ is $\left(1 - \frac{V_0}{R^3}\right)^{N^2/2}$

b) $\exp(-x) = 1 - x + \frac{x^2}{2} \cdots$ for small x

So $\ln(1-x) = -x$ for small x

$$\left(1 - \frac{V}{R^3}\right)^{N^2/2} = \exp\left(\ln\left(1 - \frac{V_0}{R^3}\right)^{N^2/2}\right) = \exp\left(\frac{N^2}{2} \ln\left(1 - \frac{V_0}{R^3}\right)\right) = \exp\left(\frac{-N^2}{2} \frac{V_0}{R^3}\right)$$

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c)

$$W_{SAW}(R)dR = z^N 4\pi R^2 dR \left(\frac{2\pi n l^2}{3}\right)^{-3/2} \exp\left(\frac{-3R^2}{2nl^2} - \frac{N^2 V_0}{2R^3}\right)$$

d)

$$\frac{dW_{SAW}}{dR} = 0 = 2R\exp(\,) - R^2\left(\frac{3R}{nl^2} - \frac{3N^2V_0}{2R^4}\right)\exp(\,)$$

$$0 = 2 - \frac{3R^2}{nl^2} + \frac{3N^2V_0}{2R^3}$$

$$0 = 2R^3 - \frac{3R^5}{nl^2} + \frac{3N^2V_0}{2}$$

For $R \gg 1$

$$R^5 = \frac{3nl^2 N^2}{2}V_0 = \frac{3n^3l^2V_0}{2}$$

$$R \sim n^{3/5} V_0^{1/5} \left(\frac{3l^2}{2}\right)^{1/5}$$

e)

$$R_g \sim V_0^{1/5}(1-2\chi)^{1/5} \sim V_0^{1/5}\left(1 - \frac{2z\Delta\varepsilon}{kT}\right)^{1/5}$$

$$\chi = \frac{z\Delta\varepsilon}{kT}$$

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3) f)

$$E = kT\left(\frac{3R^2}{2Nl^2} - \frac{N^2}{2R^3}V_0(1-2\chi)\right)$$