050408 Quiz 2 Polymer Properties

a) Show that the geometric progression rule is correct. $\sum_{k=0}^{\infty} \alpha^k = \frac{1}{1-\alpha}$

Then use this rule to show that a chain that does not backtrack (short range interaction) is Gaussian.

b) What is the difference between the persistence length, the Kuhn step length, the bond length and the statistical segment length (effective bond length)? How do these lengths relate to the characteristic ratio, C_∞, of Flory?

c) What is the partition function, Z? How does it relate to the probability of a system having a particular configuration of sites or elements? (Define a configuration, a system, a site or element and a state of a site.)

d) Sketch a Neumann projection for butane and show the trans, gauche+ and gauche- configurations. Plot the molecular energy versus bond rotational angle for butane based on the Neumann projection. Show that pentane contains two butane configurations.

e) For polyethylene each pair of mer units provides a pentane like structure. Sketch the Ising model for a magnetic material with 9 elements in 2D space with up and down spins and indicate the relationship between the polyethylene chain and the Ising model. Show how, in both cases, binary interaction of neighboring sites can be used to calculate the partition function.

ANSWERS: 050408 Quiz 2 Polymer Properties

a) $\left(\sum_{k=0}^{\infty} \alpha^{k}\right)(1-\alpha)$

$$= \sum_{k=0}^{\infty}\alpha^{k} - \sum_{k=1}^{\infty}\alpha^{k} = 1 + \left(\sum_{k=1}^{\infty}\alpha^{k} - \sum_{k=1}^{\infty}\alpha^{k}\right) \rightarrow 0$$

$$= 1$$

$$\langle r_{i+1}\rangle_{SRL} = \frac{r_i}{(z-1)} \quad \text{since } \langle r_{i+1}\rangle_{Gauss} = 0 = (z-1)\langle r_{i+1}\rangle_{SRL} - r_i$$

$$\langle R^2\rangle = \sum_{i=1}^{N}\sum_{j=1}^{N}\langle \underline{r}_i \cdot \underline{r}_j\rangle = \sum_{i=1}^{N}\sum_{k=-\infty}^{\infty}\frac{b^2}{(z-1)^{|k|}}$$

$$= N b^2 \sum_{k=0}^{\infty}\frac{2}{(z-1)^{k}} = N b^2\left(\frac{2(z-1)}{(z-2)}\right)$$

so $\alpha = z-1$ & $\sum_{k=0}^{\infty}\frac{1}{(z-1)^{k}} = \frac{1}{1-\frac{1}{(z-1)}} = \frac{(z-1)}{z-2}$

or
$\langle R^2\rangle \sim N$ so chain is Gaussian

b) $C_\infty = \frac{\langle R_0^2 \rangle}{n b^2}$

b = bond length
1.54 Å for PE

n = # bonds $\left(\frac{2\,MW}{M_0}\right)$

Statistical Segment length use n and solve for b'_{ss}

$$b'_{ss} = \left(\frac{\langle R_0^2 \rangle}{n}\right)^{1/2} = \sqrt{C_\infty b^2}$$

Kuhn length assume a real step length

Contour Length $= n_K l_K$

$R_{eted} = n_K^{1/2} l_K$

$$C_\infty = \frac{n_K^2 l_K}{n b^2}$$

Persistence length

$l_K = 2 l_p$ (Long Chains)

c)

$$Z = \sum_{\psi_i} \exp\left(\frac{-\Delta E_i}{k_B T}\right)$$

ψ_i ↑ configuration of sites

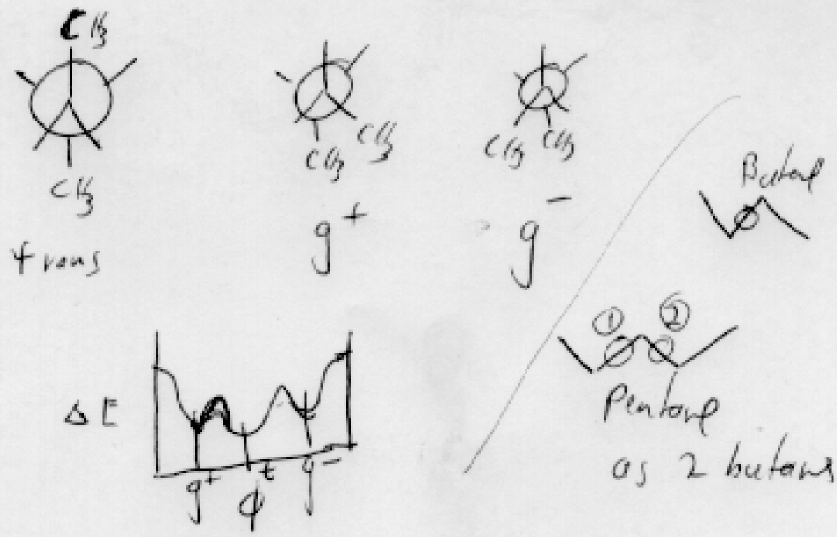
System = collection of sites

configuration = arrangement of sites of different states

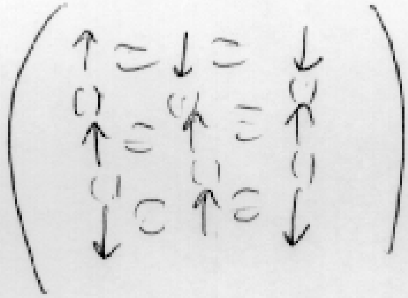
site = an element of the system that can display states

The probability of a given configuration ψ_i $= \dfrac{\exp^{-\frac{\Delta E_i}{k_B T}}}{Z}$

d)



(e)



Ψ_i

up & down states

12 pairs of spins "( )"

each pair is similar to a pentane unit of polyethylene

except that PE has 3 choices $t\ g^+\ g^-$

The Energy for the configuration is calculated from

$$\Delta E_i = w_0 \sum_{12\,\text{pairs}} S_i S_{i+1}$$

S is $+1$ or -1 for magnets

w_0 is energy for transition from $\uparrow\uparrow$ to $\uparrow\downarrow$

$$\boxed{Z = \sum_{\Psi_i} \exp\left(\frac{-\Delta E_i}{kT}\right)}$$

ΔE_i can be calculated for all possible configurations