100115 Quiz 2 Polymer Properties

1) In class we defined the mean square end-to-end vector for a polymer chain as,

$$\left\langle R^2 \right\rangle = \sum_{i=1}^{z}\sum_{j=1}^{z}\left\langle r_i \bullet r_j \right\rangle$$

a) For a Cartesian coordinate system what values can $r_i \bullet r_j$ have? What is a necessary condition for $r_i \bullet r_j$ to have a value?

b) In order to understand the result of double summations of this type a 2-d matrix (i vs. j) of values of the argument, $r_i \bullet r_j$, for the various i and j combinations are often constructed. For a straight line of z units show that $\langle R^2 \rangle = z^2 l^2$ using this summation and the values of $r_i \bullet r_j$ by constructing a matrix of $r_i \bullet r_j$ values for z = 4.

c) For alternating direction steps construct a matrix of $r_i \bullet r_j$ values and calculate $\langle R^2 \rangle$.

d) The square end-to-end vector $\mathbf{R}^2$ can be calculated by summing the vector steps taken in each of the 3 directions, x, y and z, and calculating the sum of the squares of the Cartesian sums, $\left\langle R^2 \right\rangle = \left(\sum_{i=1}^{z} r_{xi} \right)^2 + \left(\sum_{i=1}^{z} r_{yi} \right)^2 + \left(\sum_{i=1}^{z} r_{zi} \right)^2$. Using your answer to a) show that the dot product is equivalent to this expression, that is, show that

$$\sum_{i=1}^{z}\sum_{j=1}^{z}\left\langle r_i \bullet r_j \right\rangle = \left(\sum_{i=1}^{z} r_{xi} \right)^2 + \left(\sum_{i=1}^{z} r_{yi} \right)^2 + \left(\sum_{i=1}^{z} r_{zi} \right)^2 .$$

e) Show that this summation is equal to zl^2 for a random walk.

2) The Gaussian function describes the distribution of chain end-to-end distances for random walks.

a) Sketch a plot of the 1d Gaussian function.

b) Give the Gaussian function.

c) Indicate what part of the Gaussian function indicates that it is symmetric and what part indicates that it is a monotonically decaying function.

d) The scaled exponential function is often used to describe non-random systems, $P(R) = K \exp\left(-\beta R^{\alpha}\right)$, where β is a constant and α is usually a non-integer larger than 2. Is this a symmetric function?

e) An average projection of 3-d random walks in 1d results in the same value for σ^2 as the full 3d analysis, that is $\sigma^2 = zl^2$. In a 3-d random walk on a Cartesian lattice only 1/3 of the random walk steps occur in any one direction. Use the proposition that random placement of the no-step option does not alter a random walk to explain this.

3) a) Describe the difference between short range interactions and long range interactions.

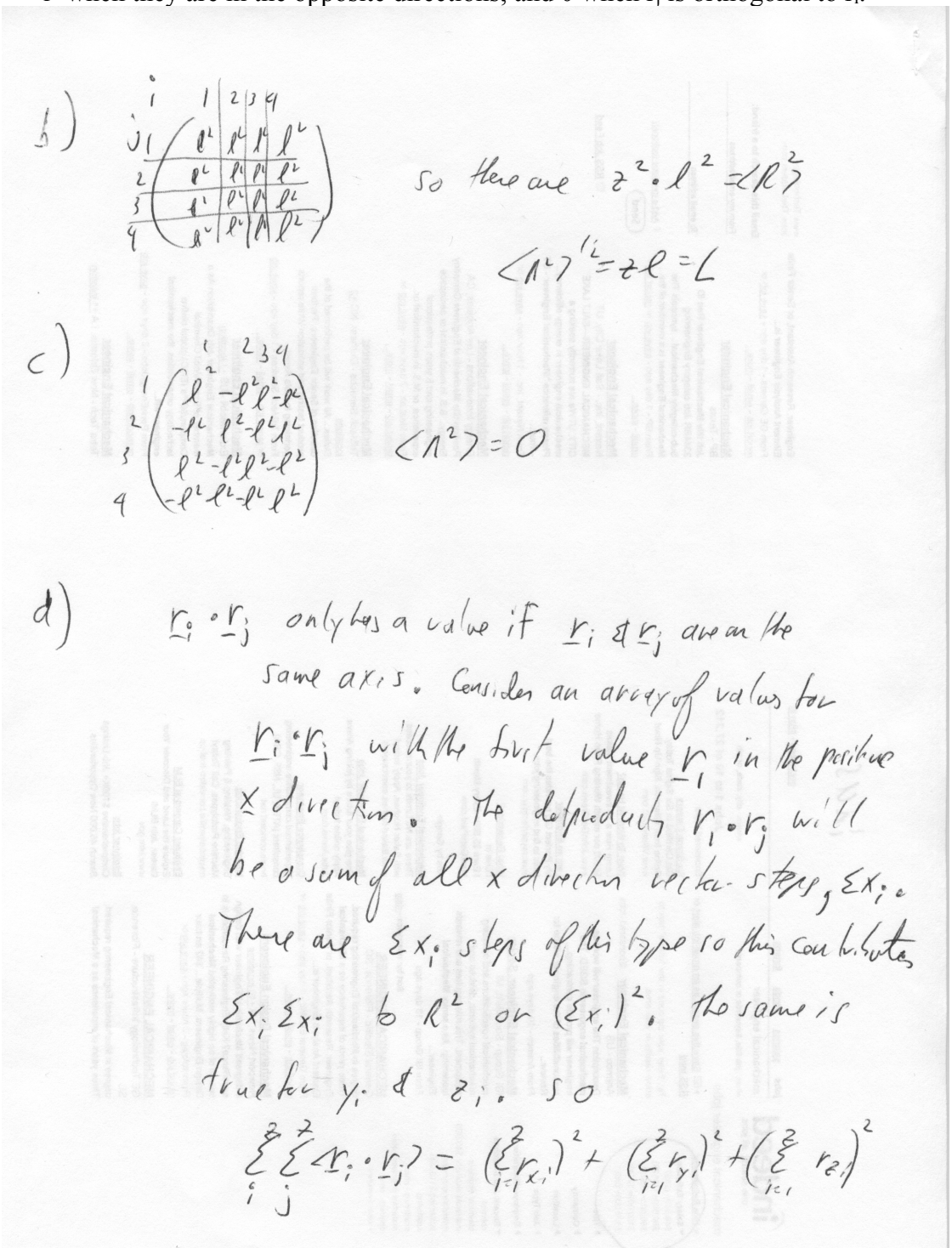
b) What is the effect of short range interactions on chain scaling?

c) Demonstrate your answer to b) by calculating the end to end distance for a walk with no back steps as done in class.

Answers **100115 Quiz 2 Polymer Properties**

1)

a) For a Cartesian coordinate system $r_i \bullet r_j$ can be + l^2 when r_i is in the same direction as r_j; - l^2 when they are in the opposite directions; and 0 when r_i is orthogonal to r_i.



2)

(2)

c) For a random walk

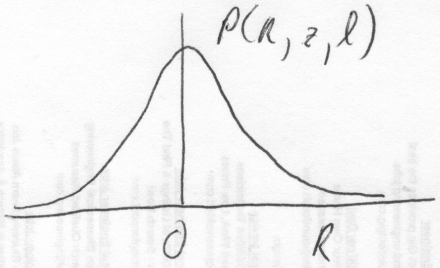
$$\sum_i \sum_j \underline{r}_i \cdot \underline{r}_j = \sum_{i=1}^{z} \sum_{j \neq i} \underline{r}_i \cdot \underline{r}_i + \sum_{i=1}^{z} \underline{r}_i \cdot \underline{r}_i$$

(the first term $\rightarrow 0$)

$$= z\ell^2$$

The first term is 0 because the walk is random

2) a)



b)

$$P(R, z, \ell) = \frac{1}{\sqrt{z\ell^2 2\pi}} \exp\left(\frac{-R^2}{2z\ell^2}\right)$$

c) $R^2 \Rightarrow$ symmetric $\quad \ominus \frac{R^2}{2z\ell^2}$ means decaying

d) No, a scaled exponential is not symmetric since R^α is not defined, $\forall \alpha > 2$ &

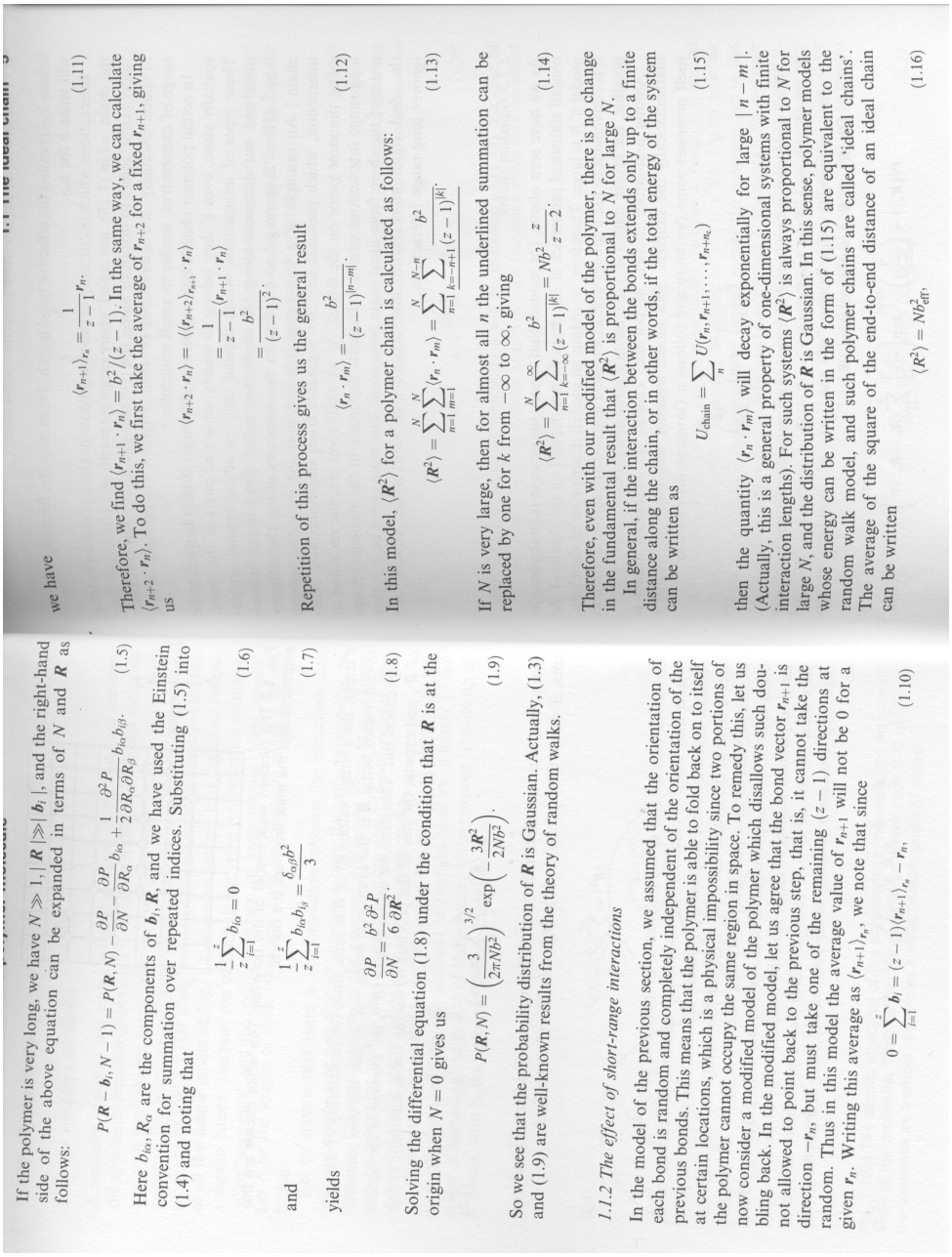
e) The orthogonal steps, that is, y & z steps for a walk in the x direction, act like non-steps and do not perturb the walk length in the x direction, that is, it has the same R^2 value.

3)

a) Short range interactions are interactions between chain units that are separated by small differences in chain index such as bond rotation restrictions, charge effects in polyelectrolytes and local steric interactions. Long range interactions are interactions between chain units that are separated by large differences in chain index, primarily the excluded volume interaction.

b) Short range interactions do not effect chain scaling. They increase the Kuhn step length and the persistence length.

c)



If the polymer is very long, we have $N \gg 1$, $|\boldsymbol{R}| \gg |\boldsymbol{b}_i|$, and the right-hand side of the above equation can be expanded in terms of N and $\boldsymbol{R}$ as follows:

$$P(\boldsymbol{R} - \boldsymbol{b}_i, N-1) = P(\boldsymbol{R}, N) - \frac{\partial P}{\partial N} - \frac{\partial P}{\partial R_\alpha} b_{i\alpha} + \frac{1}{2}\frac{\partial^2 P}{\partial R_\alpha \partial R_\beta} b_{i\alpha} b_{i\beta}. \quad (1.5)$$

Here $b_{i\alpha}, R_\alpha$ are the components of $\boldsymbol{b}_i, \boldsymbol{R}$, and we have used the Einstein convention for summation over repeated indices. Subsituting (1.5) into (1.4) and noting that

$$\frac{1}{z}\sum_{i=1}^{z} b_{i\alpha} = 0 \quad (1.6)$$

and

$$\frac{1}{z}\sum_{i=1}^{z} b_{i\alpha} b_{i\beta} = \frac{\delta_{\alpha\beta} b^2}{3} \quad (1.7)$$

yields

$$\frac{\partial P}{\partial N} = \frac{b^2}{6}\frac{\partial^2 P}{\partial \boldsymbol{R}^2}. \quad (1.8)$$

Solving the differential equation (1.8) under the condition that $\boldsymbol{R}$ is at the origin when $N = 0$ gives us

$$P(\boldsymbol{R}, N) = \left(\frac{3}{2\pi N b^2}\right)^{3/2} \exp\left(-\frac{3\boldsymbol{R}^2}{2Nb^2}\right). \quad (1.9)$$

So we see that the probability distribution of $\boldsymbol{R}$ is Gaussian. Actually, (1.3) and (1.9) are well-known results from the theory of random walks.

1.1.2 The effect of short-range interactions

In the model of the previous section, we assumed that the orientation of each bond is random and completely independent of the orientation of the previous bonds. This means that the polymer is able to fold back on to itself at certain locations, which is a physical impossibility since two portions of the polymer cannot occupy the same region in space. To remedy this, let us now consider a modified model of the polymer which disallows such doubling back. In the modified model, let us agree that the bond vector $\boldsymbol{r}_{n+1}$ is not allowed to point back to the previous step, that is, it cannot take the direction $-\boldsymbol{r}_n$, but must take one of the remaining $(z-1)$ directions at random. Thus in this model the average value of $\boldsymbol{r}_{n+1}$ will not be 0 for a given $\boldsymbol{r}_n$. Writing this average as $\langle \boldsymbol{r}_{n+1} \rangle_{\boldsymbol{r}_n}$, we note that since

$$0 = \sum_{i=1}^{z} \boldsymbol{b}_i = (z-1)\langle \boldsymbol{r}_{n+1} \rangle_{\boldsymbol{r}_n} - \boldsymbol{r}_n, \quad (1.10)$$

we have

$$\langle \boldsymbol{r}_{n+1} \rangle_{\boldsymbol{r}_n} = \frac{1}{z-1}\boldsymbol{r}_n. \quad (1.11)$$

Therefore, we find $\langle \boldsymbol{r}_{n+1} \cdot \boldsymbol{r}_n \rangle = b^2/(z-1)$. In the same way, we can calculate $\langle \boldsymbol{r}_{n+2} \cdot \boldsymbol{r}_n \rangle$. To do this, we first take the average of $\boldsymbol{r}_{n+2}$ for a fixed $\boldsymbol{r}_{n+1}$, giving us

$$\begin{aligned} \langle \boldsymbol{r}_{n+2} \cdot \boldsymbol{r}_n \rangle &= \langle \langle \boldsymbol{r}_{n+2} \rangle_{\boldsymbol{r}_{n+1}} \cdot \boldsymbol{r}_n \rangle \\ &= \frac{1}{z-1}\langle \boldsymbol{r}_{n+1} \cdot \boldsymbol{r}_n \rangle \\ &= \frac{b^2}{(z-1)^2}. \end{aligned}$$

Repetition of this process gives us the general result

$$\langle \boldsymbol{r}_n \cdot \boldsymbol{r}_m \rangle = \frac{b^2}{(z-1)^{|n-m|}}. \quad (1.12)$$

In this model, $\langle \boldsymbol{R}^2 \rangle$ for a polymer chain is calculated as follows:

$$\langle \boldsymbol{R}^2 \rangle = \sum_{n=1}^{N}\sum_{m=1}^{N} \langle \boldsymbol{r}_n \cdot \boldsymbol{r}_m \rangle = \sum_{n=1}^{N} \sum_{k=-n+1}^{N-n} \frac{b^2}{(z-1)^{|k|}}. \quad (1.13)$$

If N is very large, then for almost all n the underlined summation can be replaced by one for k from $-\infty$ to ∞, giving

$$\langle \boldsymbol{R}^2 \rangle = \sum_{n=1}^{N} \sum_{k=-\infty}^{\infty} \frac{b^2}{(z-1)^{|k|}} = Nb^2 \frac{z}{z-2}. \quad (1.14)$$

Therefore, even with our modified model of the polymer, there is no change in the fundamental result that $\langle \boldsymbol{R}^2 \rangle$ is proportional to N for large N.

In general, if the interaction between the bonds extends only up to a finite distance along the chain, or in other words, if the total energy of the system can be written as

$$U_{\text{chain}} = \sum_n U(\boldsymbol{r}_n, \boldsymbol{r}_{n+1}, \ldots, \boldsymbol{r}_{n+n_c}) \quad (1.15)$$

then the quantity $\langle \boldsymbol{r}_n \cdot \boldsymbol{r}_m \rangle$ will decay exponentially for large $|n-m|$. (Actually, this is a general property of one-dimensional systems with finite interaction lengths). For such systems $\langle \boldsymbol{R}^2 \rangle$ is always proportional to N for large N, and the distribution of $\boldsymbol{R}$ is Gaussian. In this sense, polymer models whose energy can be written in the form of (1.15) are equivalent to the random walk model, and such polymer chains are called 'ideal chains'. The average of the square of the end-to-end distance of an ideal chain can be written

$$\langle \boldsymbol{R}^2 \rangle = Nb_{\text{eff}}^2, \quad (1.16)$$

From Masao Doi "Introduction to Polymer Physics"