080114 Quiz 1 Polymer Properties

The polymer coil in a melt state is described as a Gaussian chain, a Brownian chain and a random (drunken) walk. These three names reflect different characteristics of the chain.

1) Give the meaning of each of these names and explain how they apply to a polymer chain:

a) Gaussian Chain (discuss how the Gaussian probability relates to the chain),b) Brownian Chain (discuss how Brown's observation of diffusion relates to the chain) and

c) Random walk (discuss how computer simulations using Monte Carlo (random choice) approaches relate to the chain).

2) The following figure shows five random walks produced in a computer algorithm. The authors indicate, in the paper, that this figure supports the idea that the walks become denser at higher particle concentration (shown as insets by the walks).



Fig. 10 Snapshots of aggregate structures at different silica volume fractions as calculated by R MC (pH5, B40-series).

From: *Structure of interacting aggregates of silica nanoparticles in a polymer matrix: small-angle scattering and reverse Monte Carlo simulations* Oberdisse J, Hine P, Pyckhout-Hintzen W *Soft Matter* **3** 476-485 (2007).

a) Do you agree that the figures support the idea that the walks become denser at higher particle concentration? (Discuss the relevance of a single random walk to determining the statistics of random walks.)

b) The 6% structure contains about 99 beads and is about 20 beads in diameter. Could you calculate the mass fractal dimension, d_{fr} from these numbers? (If yes show how, if no explain why not.)

c) If you were shown the walk for the 15% silica sample could you determine if the simulation produced random walks from this single result?

3) In class we discussed the Gaussian distribution function.

a) Write the normalized 1-d Gaussian probability function, $P_{1d}(R,n,l)$ and show how $\langle R \rangle$, $\langle R^2 \rangle$, and $\langle R^3 \rangle$ are calculated using this function.

b) Sketch the distribution curves corresponding to $P_{1d}(R,n,l)$ and the three moments given above and give the value for these three moments and the integral of $P_{1d}(R,n,l)$.

c) Show how the value for $\langle R^2 \rangle$ as a function of n and l can be obtained. Show how a similar scaling relationship can be obtained from the plot of the second moment distribution curve.

ANSWERS: 080114 Quiz 1 Polymer Properties

1) a) The Gaussian probability, P(R,n,l), gives the probability of a walk of length R for n steps of length l if the steps are in random directions. The most probable walk is of length 0. The RMS walk length is $n^{1/2}l$.

b) Brown observed particle diffusion paths that followed a random walk. He observed that the RMS distance traveled scaled with $t^{1/2}$ and that the mean distance traveled was 0. If the Brownian walk is connected with mer units we create a random walk whose length follows Gaussian statistics.

c) Monte Carlo methods can generate a random walk by considering each step of a walk is in a random direction either on a lattice or in free space. The resulting walk follows Brownian statistics in that the average length is 0 and the RMS length is $n^{1/2}l$ where the walk takes n steps of length l.

2) a) First the walks shown do not significantly differ from each other in terms of density. Secondly, a single image of a series of random walks is of little significance as was shown in class. The figure is misleading and doesn't really show what the authors intended.

b) You can calculate the mass fractal dimension since $n \sim (R/l)^{df}$, and assuming the proportionality constant is 1 we have, $99 = 20^{df}$, so $d_f = \ln(99)/\ln(20) = 1.53$. This is less dense than a random walk.

c) No, a single random walk is of little use in determining the scaling nature of the algorithm. We saw in class that a random walk Monte Carlo simulation can produced a wide variety of walks.

3) a)
$$P_{1d}(R,n,l) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{R^2}{2nl^2}\right); \qquad \langle R \rangle = \int_{-\infty}^{\infty} RP_{1d}(R,n,l)dR = 0;$$
$$\langle R^2 \rangle = \int_{-\infty}^{\infty} R^2 P_{1d}(R,n,l)dR = nl^2; \quad \langle R^3 \rangle = \int_{-\infty}^{\infty} R^3 P_{1d}(R,n,l)dR = 0$$
$$\int_{0}^{0} \int_{0}^{0} \int_{0}^{1} \int_{0}^{0} \int_{0}^{$$

c) $\langle R^2 \rangle = \langle r_i \bullet r_j \rangle = \sum_{1} r_i^2 + \sum_{i=0} \sum_{j=0 \neq i} r_i \bullet r_j = nl^2$ where the second summation is 0 because there is no correlation between i and j vectors.

A similar result can be obtained by setting the derivative at the maximum of the R^2 curve above to 0 resulting in $R^{*2} = 2nl^2$.