090126 Polymer Properties Quiz 3

1) In class we considered that short range interactions could be modeled by considering a walk where the chain can not backtrack to a previous step.
   a) Calculate the mean step $\langle \mathbf{r}_{i+1} \rangle_{SRI}$ for the case where the previous step, $\mathbf{r}_i$, is forbidden. Explain your function.
   b) Show how this expression can be used to calculate $\langle \mathbf{r}_i \bullet \mathbf{r}_j \rangle_{SRI}$.
   c) Show how your answer to b can be used to calculate $\langle R^2 \rangle_{SRI}$ using the relationship $\sum_0^\infty x^n = 1/(1-x)$ for x << 1.
   d) In last week's quiz we determined that there were 5.2 ethylene units in a Kuhn step of polyethylene. Use this to calculate the coordination number, z, for polyethylene.
   e) From your answer to "d)" does the path of a polyethylene chain have a higher or lower coordination number compared to a 3-d Cartesian coordinate lattice? Explain why this is the case.

2) The hydrodynamic radius can be determined by a dilute solution viscosity measurement.
   a) Describe conceptually what a dilute solution is?
   b) Does the intrinsic viscosity, $[\eta]$, depend on concentration for a dilute solution? Explain why or why not.
   c) Give the Einstein linear equation for viscosity as a function of concentration.
   d) How is the intrinsic viscosity related to the hydrodynamic size (radius)?
   e) How does the intrinsic viscosity depend on molecular weight for a Gaussian chain and an expanded coil, $d_f = 5/3$.

3) There are three main size parameters to describe the coil size.
   a) List these three parameter and briefly describe what they are.
   b) Two of these parameters can be directly related through an analytic expression while the third does not have a direct functional relationship. Give the direct relationship.
   c) Explain why the third parameter does not have a direct relationship.
   d) Dynamic light scattering can be used to determine the hydrodynamic radius, R_H. Explain what is measured in a dynamic light scattering experiment.
   e) What is a time autocorrelation function?

ANSWERS: 090126 Polymer Properties Quiz 3

1) a) $\langle \mathbf{r}_{i+1} \rangle = 0 = (z\text{-}1)\langle \mathbf{r}_{i+1} \rangle_{SRI} + (-\mathbf{r}_i)$

The step i+1 would average to 0 if there were no short-range interaction. With prohibition of the preceeding step direction ($-\mathbf{r}_i$) the sum of the SRI average which occurs z-1 times and the forbidden step yields the 0 average. So,

$\langle \mathbf{r}_{i+1} \rangle_{SRI} = \mathbf{r}_i/(z-1)$

b) The factor (z-1) propogates like a probability so that for n steps separating $\mathbf{r}_i$ and $\mathbf{r}_j$ we have, $\langle \mathbf{r}_i \bullet \mathbf{r}_{i+n} \rangle_{SRI} = b^2/(z\text{-}1)^n$.

c) This can be used to calculate $\langle R^2 \rangle_{SRI}$,

$$\left\langle R^2 \right\rangle_{SRI} = \sum_{i=1}^{n}\sum_{j=1}^{n}\left\langle r_i \bullet r_j \right\rangle = b^2 \sum_{i=1}^{n}\sum_{j=1}^{n} 1/(z-1)^{|i-j|}$$

$$= b^2 \sum_{i=1}^{n}\sum_{k=0}^{\infty} 1/(z-1)^{k} = b^2(z-1)/(z-2)$$

d) z = 2.12

from

$$(z-1)/(z-2) = 5.2^2$$

e) 3-d Cartesian system has z = 6 so this is much lower than the Cartesian coordination number. This is because the polyethylene chain is highly constricted due to bond angle constraints.

2) a) A dilute solution is a polymer solution below the overlap concentration. The overlap concentration, c*, is the concentration within the coil, mass of coil/volume of a coil. In a dilute solution each polymer molecule can be considered an individual coil that does not interact with other coils.

b) The intrinsic viscosity does not depend on concentration for dilute solutions because there is not interaction between coils.

c) $\eta = \eta_0(1 + c[\eta])$

d) The intrinsic viscosity is the volume of a coil, $4\pi R_H^3/3$, by the mass of a coil.

e) For fractals the size scales with $\text{mass}^{(1/df)}$ so the intrinsic viscosity scales with $\text{mass}^{(3/df-1)}$. For a Gaussian coil $d_f = 2$ so the intrinsic viscosity scales with $\text{mass}^{0.5}$. For an expaned coil $d_f = 5/3$ so the intrinsic viscosity scales with $\text{mass}^{0.8}$.

3) a) The end to end distance R^2 which is calculated from theory or simulations.
The radius of gyration, R_g^2, which is measured by scattering and can be directly related to R^2.
The hydrodynamic radius R_H which is a measure of the dynamic size in terms of Stokes law for the drag coefficient of the coil, $\xi = 6\pi\eta R_H$.

b) For a Gaussian coil $6\ R_g^2 = R^2$.

c) The drag coefficient depends on the extent that the solvent drains from the coil and on the inherent average asymmetry of the coil so it is not directly related to the other sizes.

d) The fluctuation of light from a scattering volume associated with the motion of polymer or other colloids in a laser beam is measured. You observe the fluctuation in terms of the correlation function as a function of time.

e) The correlation function is the double sum of the intensity at time t_i times the intensity at time t_j where i and j are varied in the double sum. It is a measure of how correlated the intensity is with itself over a time span $\Delta t = |t_i - t_j|$. This decays in Δt following an exponential decay, $\exp(-Dtq^2)$.