071019 Quiz 4 Morpholgoy of Complex Materials

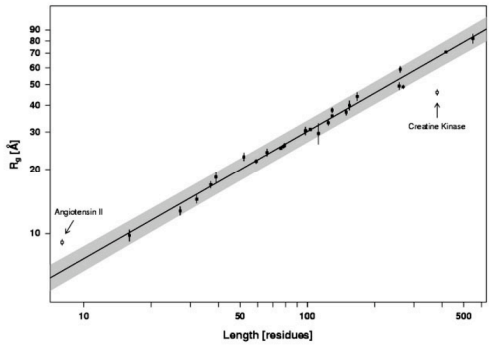
Polymers in dilute solution display a stochastic hierarchy described by statistics. This is in contrast to the deterministic hierarchy of proteins characterized by discrete structures.

1) a) From a stochastic (governed by the statistics of random disorder) view what is the primary structure for a polymer in dilute solution?
b) Give an equation that defines this primary structure and explain how this equation is related to a statistical view of a random structure.
c) This equation is of similar form to the linear absorption equation (Beer's Law). Explain the relationship.
d) Explain the error in the following equation (does it describe a linear decay?),

$$d\left(\left\langle t(s)\bullet t(0)\right\rangle\right)=\left\langle t(s)\bullet t(0)\right\rangle\left(\frac{1}{l_p}\right)ds$$

e) For a sample displaying linear absorption (following Beer's Law) we can obtain the optimum thickness for a diffraction experiment by realizing that the diffracted intensity is proportional to the sample thickness, t, and proportional to the transmitted intensity (I_{diff} = t exp(-μt)). The maximum intensity is found from the derivative to be at a thickness t = 1/μ. In view of this what does the value l_p correspond to?

2) The stochastic secondary structure for a polymer coil in dilute solution is described by the Gaussian probability function, $P(R) = k \exp(-R^2/(nl^2))$
a) The integral of $R^2P(R)$ yields $R^2 = nl^2$. Show that the derivative of this function yields the same scaling behavior (i.e. find the most probable, maximum probability).
b) What is the relationship between this analysis and the mathematical description of diffusion.
c) Write a similar probability function for a self-avoiding walk (SAW).
d) What is the resulting scaling function for end-to-end distance?
e) Kohn et al. (2004 PNAS) published the following graph for a wide range of "unfolded proteins". From this plot do proteins obey stochastic hierarchies in the "unfolded" state? What are the problems with this proposition?



Kohn graph shows a slope of ~0.6.

3) Dilute polymer coils do not display super-secondary structure but display a kind of sub-secondary structure associated with thermal equilibration of stochastic hierarchies.

a) Give an expression for the free energy of a Brownian coil based on the Gaussian Function and comparison with the Boltzman function.

b) Calculate the spring constant for an isolated coil, k_{spr}, using this expression ($dE/dR = F = k_{spr} R$).

c) If $R \sim n^{1/2}l \sim \xi_F$, where ξ_F is the tensile blob size, explain how you can obtain $\xi_F = kT/F$ and explain the behavior of the tensile blob sub-secondary structure with applied force.

d) Give an expression for the free energy of an isolated self-avoiding walk (SAW).

e) Give an expression for the thermal blob size, ξ_T, based on this free energy expression and explain the sub-secondary structural behavior in temperature.

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1) a) The primary structure is the persistence length.

b) $\left\langle t(s) \bullet t(0) \right\rangle = e^{-s/l_p}$

The coil follows a random walk similar to the walk of the red ball shown in class. In that case depending on the density of gas atoms hitting the ball the persistence length changed though the ball moved in a random manner for distances larger than a cutoff size. Below this size the motion is ballistic on average, that is it moves in a straight line or for the case of a polymer coil, it can be represented by a rod. The rods length is $2l_p$ if we consider freely jointed, Kuhn rods.

c) Beer's Law $(I/I_0) = e^{(-\mu t)}$ describes the decay in intensity with sample thickness due to linear absorption. Beer's Law depends on linear absorption $dI = -I\ \mu\ dt$. For the persistence length we consider a linear decay the correlation of the chain tangent.

d) This equation describes a linear increase. We need a "-" sign to describe a decay similar to the linear absorption function given in question c.

e) It is the length most likely to be observed as a ballistic step in a random walk.

2) a) Set the derivative of $R^2P(R)$ to 0 and solve for R* yields $2/3\ nl^2$.

b) In diffusion the moving molecule follows a path whose end-to-end distance follows a Gaussian function in time so the RMS path length is proportional to $t^{1/2}$. Time, t, is analogous to n for the polymer coil.

c) $P_{SAW}(R) = \exp\left(-\frac{3R^2}{2nl^2} - \frac{n^2V_c(1-2\chi)}{2R^3}\right)$

d) $R \sim n^{3/5}\ l_p$

e) The plot shows the dependence $R_g \sim n^{3/5}$ consistent with SAW scaling. Problems are that "unfolded proteins display residual secondary structure and are polyelectrolyes so are unlikely to display good solvent scaling.

3) a) $E_a = (3kTR^2)/(2nl^2)$

b) $k_{spr} = 3kT/(nl^2)$

c) $F = k_{spr}\ \xi_F = 3\xi_F kT/(nl^2) \sim 3\xi_F kT/(\xi_F^2) \sim kT/\xi_F$ so $\xi_F \sim kT/F$

As the force applied to the ends of the coil increase the chain extends by forming a rod at large scales composed of random walks at a small scale.

d) $E_{a,SAW} = \frac{3R^2}{2nl^2} + \frac{n^2V_c(1-2\chi)}{2R^3}$

e) $\xi_T = l_p/(1-2\chi)$ where $\chi \sim 1/T$. As the temperature drops the coil collapses from a small scale first and to larger scales as the temperature approaches the critical point for phase separation where the entire coil becomes Gaussian.