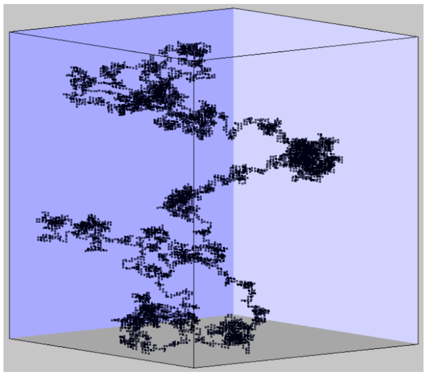
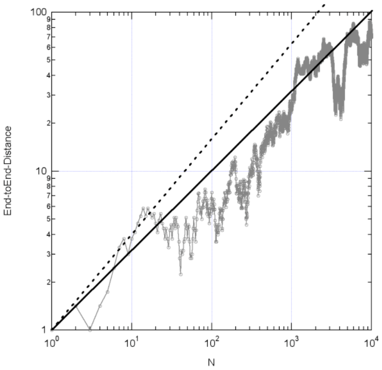
070604 Final Polymer Properties

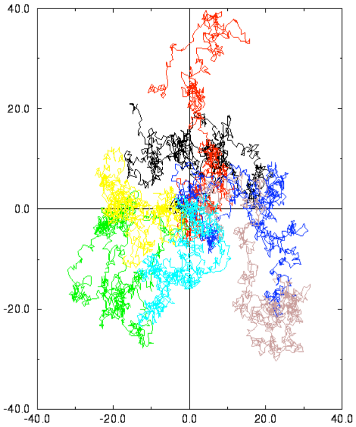
The polymer chain is modeled as a random structure as if the atoms of an ideal gas were tied together in a string. The following picture (a) shows an attempt at simulating a random walk on a cubic lattice. (b) shows the distance from the start of the chain as a function of chain index. (c) shows 7 such walks.



(a)



(b)



(c)

Q1:1) Do you agree or disagree with the following statements (explain your position):

a) The walk in (a) is not random because there are several locations where clustering can be seen and clustering is not random.

b) The walk in (a) is not random because it crosses itself in several locations.

c) Figure 1 (b) shows the end to end distance as a function of chain index but because the walk does not follow the lower line it is not random. (Explain the lower line.)

d) The walks in (c) are not random because they vary in length and direction.

Q1:2) A series of simulations of the type shown above could be used to generate a probability distribution for the end-to-end distance of random walks of length N steps. (Figure 1 (c) above shows 7 2D-simulations for example.)

a) What function, P(R) would describe the probability of finding a walk of length R as a function of N and the step length l_K?

b) Give this function.

c) Is this a symmetric function about 0? Explain.

Q1:3) Using the function you wrote in question 2 it is possible to calculate moments of the distribution, for example the mean, <R>, is given by $\langle R\rangle = \int R\, P(R)\, dR$.

a) Give the value of <R>. In words explain this value.

b) Give the value of $\langle R^2\rangle$. In words explain this value.

c) Give the value of $\langle R^3\rangle$. In words explain this value.

Q1:5) Random walks are often constructed using a cubic lattice. How do you think this lattice effects the walk, that is how would a walk on a square lattice differ from a walk on a cubic lattice or a random walk in 3D space that is freely jointed?

Q2:1) The total number of random walks on a cubic lattice for n-steps is $N_{Gaussian} = 6^n$. Of these the number of SAW's is given by de Gennes as, $N_{SAW} = 4.68^n n^{1/6}$ so that the probability of a SAW is given by $(0.78)^n\ n^{1/6}$. What is a SAW? Why would such a walk be so much less probable than a random walk?

Second Quiz (5 Questions)

Q3:2) The Mark-Houwink Equation relates the intrinsic viscosity $[\eta]$ to the molecular weight of a polymer, $[\eta] = kM^a$. We find that "*a*" has a theoretical value of 0.5 and 0.8 but that many polymers such as cellulose display values much higher than 0.8.

a) What is the intrinsic viscosity? (give an equation)
b) Describe how a value of 0.5 could be obtained
c) Describe how a value of 0.8 could be obtained
d) The intrinsic viscosity of a synthetic protein (polylysine) was measured for several molecular weights and it was found that $[\eta]$ didn't depend on molecular weight and that k had a value of 2.9 when the volume fraction was used for the concentration in the equation of part (a). Were these experiments in error? (Explain your reasoning.)

Q3:3) Stokes Law explains the relationship between the friction factor, f, and the size of a particle, R_H.

a) What is the friction factor?
b) Give Stokes Law.
c) Explain the functionality in R_H by an analysis of units.
d) For an ellipsoidal (hotdog) balloon would Stokes law be appropriate to describe the drag force as the balloon traveled through air?

Q3:4) Drag is considered a macroscopic phenomena while diffusion is considered a microscopic phenomena in that it involves atomic or molecular motion. The Fluctuation Dissipation Theorem, D = kT/f, relates the microscopic to the macroscopic by considering that fluctuations of concentration associated with diffusion (and driven by kT) are dissipated through macroscopic mechanisms, i.e. drag and the friction factor. Show that the units are correct for the above expression for the diffusion coefficient by

a) Calculating the units of D using Fick's First Law. (J is mass/(length^2 time)
b) Comparing these units with the units of kT/f (kT has units of energy or force * distance).
c) If you considered R_H to be the end-to-end distance for a polymer chain which would have a larger diffusion coefficient, a Gaussian coil or a SAW coil?
d) Could you compare the diffusion coefficient of the two of part c with a rod following the same approach? Explain.

Q5:3) The following scattering function (the Ornstein-Zernike Function) has been proposed as a simplified Debye equation,

$$I(q) = \frac{\xi^2 / K^2}{1 + q^2 \xi^2}$$

where ξ is the correlation length. Show that this function has similar limits to the Debye equation at high and low-q. (Is there a relationship between ξ, K and R_g?)

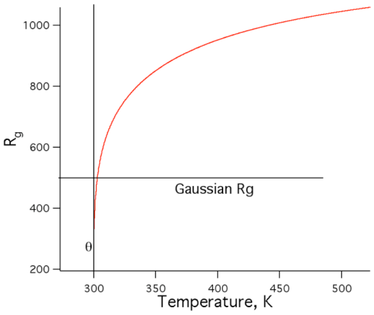
$$I(q) = \frac{2}{Q^2}\left(Q - 1 + \exp(-Q)\right) \text{ where } Q = q^2 R_g^2 \qquad \text{Debye Equation.}$$

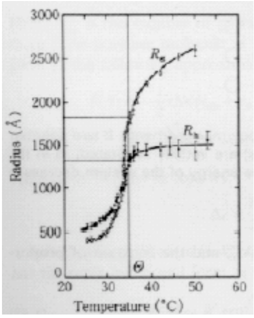
At low x (x<<1), $\exp(+x) = 1 + x/1! + x^2/2! + x^3/3! + \ldots$ and
$\exp(-x) = 1 - x/1! + x^2/2! - x^3/3! + \ldots$

Q5:4) The Flory-Krigbaum analysis results in an expression for the coil size with temperature,

$$R_F = N^{3/5} l_K^{2/5} \left(V_0 \left(1-2\chi\right)\right)^{1/5} = N^{3/5} l_K \left(1-\frac{2z\Delta\varepsilon}{kT}\right)^{1/5}$$

which is plotted to the right, next to experimental data.





a) Why is a blob model needed to describe this behavior? (What is the structural model associated with the Flory-Krigbaum coil, that is what does it look like? What is the nature of the expanded to collapsed coil transition, what structural pathway does the chain take to the collapsed state?)

b) Sketch the scattering pattern log I(q) vs log q showing the structural model for the thermal blob theory for this transition.

c) Sketch a molecular model for this transition.

d) Calculate the temperature (χ) dependence of the thermal blob size.

Third Quiz (5 Questions)

Q5:5) In class we discussed the screening of interactions with increase in concentration.

a) At what concentration should you begin to consider screening?

b) How would this concentration vary for coils of the same mass that were collapsed, R ~ $n^{1/3}$, Gaussian, SAW coils or extended rods, R ~ n?

c) What is the screening length?

d) For electrostatics the energy of interaction between two charges in dilute conditions is given by $U_{Dilute}(r) = \frac{kq_1q_2}{\varepsilon r}$. In concentrated conditions this energy is $U_{Concentrated}(r) = \frac{kq_1q_2}{\varepsilon r}\exp\left(-\frac{r}{\lambda_D}\right)$. Show that the two expressions are identical for small r.

Q6:2) Explain how a polymer in an osmometer is similar to an ideal gas by:

a) Sketch an osmometer and describe the source of the excess pressure on the polymer side.

b) Write a virial expansion (Taylor Power Series expansion) in concentration from the ideal gas law.

c) Compare this expression with the expression obtained from the Flory-Huggins Equation,
$\pi = kT\, c\, [1/N + (1/2 - \chi)\, c]$. Be sure to explain the term 1/N.

d) Previously we obtained $(1 - 2\chi)$ as an expression for the excluded volume. Why does the virial expansion contain 1/2 of this term?

Q6:3) At high concentration the osmotic pressure follows $c^{9/4}$.

a) Is this consistent with the Flory-Huggins expression of question 2?

b) What is the overlap concentration? Why is this important to semi-dilute solutions?

c) Above the overlap concentration can the osmotic pressure depend on molecular weight?

d) Obtain the $c^{9/4}$ dependence of osmotic pressure on concentration above the overlap concentration by considering the concentration blob and it's scaling dependencies.

Q6:4) a) For a mixture of two macromolecular components of molecular weight n_A and n_B give expressions for the critical volume fraction and the critical interaction parameter.

b) Show that the critical interaction parameter for a polymer solution of extremely high molecular weight is ½.

c) Show that the critical interaction parameter for a symmetric polymer blend is 2/n.

d) Temperature can be converted to χ directly making a χ versus composition phase diagram possible. Why would one plot χn versus composition rather than temperature or χ versus composition for a phase diagram?

Q6:5) a) Sketch the Gibbs Free energy obtained using the Flory Huggins equation for a symmetric polymer blend below the critical temperature, at the critical temperature and above the critical temperature.

b) Show from the plot where the critical point, binodal and spinodal curves arise.

c) Sketch the phase diagram (χn versus composition or temperature versus composition) indicating how it was obtained from the free energy curves and show the regions where spinodal decomposition and nucleation and growth would be observed.

d) Why is it rare to observe spinodal decomposition despite the wide area it occupies in the phase diagram?

e) What is special about the critical temperature? Explain the behavior of a system near a critical point.