120417 Quiz 2 Polymer Properties

1) The persistence length of a polyelectrolyte involves the contribution of two terms, one associated with the persistence length in the absence of charge and one that relates to Coulombic interactions.

$$l_{\rm p} \approx l_0 + l_{\rm p}^{\rm OSF} \approx l_0 + \frac{l_{\rm B} f^2}{4 (\kappa b)^2}$$

Andrey V. Dobrynin Macromolecules 2005, 38, 9304-9314

a) Explain what factors favor one term over the other.

b) The Coulombic term includes three length scales, the bond length, b, the Bjerrum length, $l_{\rm B}$, $(l_{\rm B} = e^2/\epsilon k_{\rm B}T$ is the distance at which the Coulomb interaction between two elementary charges e in a dielectric medium with the dielectric constant is equal to the thermal energy $k_{\rm B}T$) and the Debye screening length, κ^{-1} . Explain what the Debye screening length is.

c) All three of the distances in part c are fairly short in length but the electrostatic persistence length can be rather large. Qualitatively explain how these three lengths can give rise to an electrostatic persistence length that is an order of magnitude larger than any one of these three lengths. (There is not a straight-forward answer to this.)

d) In class we defined the ratio of enthapic to entropic energy changes for a counter ion $u \equiv \frac{e^2}{e^2}$

as $\varepsilon = \varepsilon a kT$, show that this term is also equal to the ratio between two of the primary lengths for the polyelectrolyte. In this context what occurs when u =>1? e) Explain what counter ion condensation means.

2) In class we considered long range interactions by first discussing excluded volume.

a) Consider the interaction of two hard core spheres. What is the volume excluded from one sphere by the other sphere?

b) If the two spheres were confined to a space of radius R what is the probability that the two spheres do not overlap?

c) If there were N spheres in the same volume, what is the probability that no two spheres overlap considering only binary interactions?

d) Use $exp(-x) \sim (1-x)$ (and ln(1-x) = -x) for small x to write an exponential probability for exclusion of spheres from each other.

e) Explain how this calculation might be complicated by considering elliptical particles rather than spheres. For elliptical particles do you expect a larger or smaller excluded volume compared to spheres for the same particle volume?

- 3) a) Plot Temperature versus composition for a upper critical solution temperature polymer solution where the polymer has a finite molecular weight.
 - b) Use the plot of part a) to show that the theta temperature is a kind of critical point.
 - c) What is the interaction parameter, χ ?
 - d) What occurs when $\chi = \frac{1}{2}$ for a polymer solution? (Use the plot of part a.)
 - e) Explain any simiarities between an ideal gas and a polymer chain in solution with $\chi = \frac{1}{2}$.

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1) a) In the notes we discuss the factor "u" that is defined in part d). If u is greater than 1 charge leads to larger persistence and the second term dominates and if u is less than 1 charge doesn't have a big effect and the first term dominates. Other factors are the rigidity of the chain caused by restrictions to bond rotation, the presence of conjugated bonds in the back bone of the polymer and the presence of flexible bonds such as an ether linkage. These all effect the persistence in the absence of charge.

b) The Debye screening length quantifies the distance over which charge interaction decays when counter ions are present. The decay follows and exponential decay, $(1/r\kappa) \exp(-r\kappa)$. This should be compared with the decay of 1/r form when there are no counter ions present.

c) If the charge interaction lengths such as the Bjerrum length or the screening length become substantially larger than the bond length then the charge interactions can have an effect on bond rotation. This could be a large effect, essentially preventing bond rotation. Since all of the chain flexibility comes from bond rotation, restrictions to this rotation can have a cumulative effect on the chain persistence that is much larger than the length scales associated with charge interaction, as long as these charge length scales are larger than the bond length. There are probably other answers to this question.

d) u is the ratio of the Bjerrum Length to the bond length. When u goes to 1 the charge interactions just begin to exceed the bond length making hindrance of bond rotation by charge interactions possible.

e) Counter ion condensation occurs when the interaction potential between ions and counter ions is larger than the thermal energy available to a counter ion, kT. The counter ion condenses on the ion attached to the chain.

2) a) One sphere center is 2r away from another sphere when the spheres touch so the volume that is excluded is a sphere of radius 2r. $16\pi r^3/3$.

b)
$$P=1-V_{\text{excluded}}/V_{\text{available}} = 1-(r/R)^3$$

c) $(1-(r/R)^3)^{N2/2}$

d) $\exp(\ln((1-(r/R)^3)^{N2/2})) = \exp((N^2/2)\ln((1-(r/R)^3))) \sim \exp(-N^2(r/R)^3/2)$

e) Depending on the orientation interaction of ellipsoids could result in a higher or a lower excluded volume. For random orientation of ellipsoids we would have a larger excluded volume.



FIG. 1. Schematic phase diagram of a polymer solution in the space of the temperature T and the volume fraction ϕ . The coexistence curve separates a dilute solution of collapsed chains [at $\phi_{coex}^{(2)}$] from a semidilute solution of overlapping chains [at $\phi_{coex}^{(2)}$]. These two branches of the coexistence curve merge at a critical point $T_c(N)$, $\phi_c(N)$. For $N \rightarrow \infty$ the critical point merges with the Θ point of a dilute polymer solution [$T_c(N \rightarrow \infty) \rightarrow \Theta$, $\phi_c(N \rightarrow \infty) \rightarrow 0$] and the unmixing transition has a tricritical character. At $T = \Theta$, the chain conÆgurations are ideal Gaussian coils, while their structure at $T_c(N)$ is nontrivial.

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b) The critical temperature (temperature at the peak of the two phase region) follows $T_c = \theta - 2\theta/\sqrt{N}$ and the critical composition at the peak of the two phase region follows $\Phi_c = 1/\sqrt{N}$ so as N goes to infinity the theta temperature is the critical point at zero composition of the polymer.

c) $\chi = z\Delta\epsilon/kT$ it is the average enthalpy change on mixing per monomer per kT when a polymer is put in a solvent.

d) When $\chi = \frac{1}{2}$ the excluded volume vanishes and the polymer behaves like an ideal Gaussian

$$E(R) = kT\left(\frac{3R^2}{2nt^2} + \frac{n^2 V_c(\frac{1}{2} - \chi)}{R^3}\right)$$

coil since

e) When $\chi = \frac{1}{2}$ the chain becomes an ideal chain since the monomers can effectively pass through each other, there is no excluded volume (on average). This is the same condition that is needed for an ideal gas, that gas atoms pass through each other and there is no excluded volume.