040507 Quiz 6 Polymer Properties

The concept of "screening" of interactions was developed by Debye for electrostatics where two charges are immersed in an ionic medium. The Debye screening length scales with the ion concentration, $\lambda_D \sim c^{-1/2}$. We discussed two consequences of "screening" in the semi-dilute regime of polymer solutions. First we calculated the size-scale observed in neutron scattering from a polymer solution in the semi-dilute regime, the screening length, and second we calculated the dependence of osmotic pressure on concentration in the semi-dilute regime.

a) Give the dependence of screening length on concentration for a polymer solution. Show how the overall coil size, R_F, scales with concentration if the number of concentration blobs in a coil follows, $N_B \sim (c/c^*)^{5/4}$.

b) Screening results in a "mean-field" at large size-scales. Explain what a mean field is by giving an analogy to a simple system. Is there a difference between a mean field and no field?

c) Explain how osmotic pressure is used to determine the molecular weight of a polymer by giving an expression that relates osmotic pressure to molecular weight and by describing the osmotic pressure experiment. (Indicate what is measured and how it is converted to molecular weight.)

d) Can an osmotic pressure measurement be used to determine the molecular weight of a branched polymer in solution? Explain why or why not.

e) For semi-dilute solutions the osmotic pressure scales with composition to the 9/4 power. Give the dependence predicted from the Flory-Huggins equation and explain in simple terms what causes this difference. (You might use the words: blob, structural changes, interaction, concentration, binary interaction, higher-order interactions in your answer.)

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a) $R_B \sim c^{-3/4}$ for a semi-dilute polymer solution.

$$R_F \sim R_B N_B^{1/2} \sim \left(\frac{c}{c^*}\right)^{-3/4} \left[\left(\frac{c}{c^*}\right)^{5/4}\right]^{1/2} = \left(\frac{c}{c^*}\right)^{5/8-3/4} = \left(\frac{c}{c^*}\right)^{-1/8}$$

b) The mean field is an average interaction energy and is expressed by the interaction parameter χ. In a screened system such as a dense forest at sunset, the applied field, sunlight, is screened so that only an average and directionless field can be seen, such as the isotropic glow of light in the forest during sunset. This isotropic glow is a kind of mean field. The mean field has effects on the system, i.e. it is possible to tell the difference between day and night but not the direction west beyond the screening length. Screening serves to localize interactions to shorter distances and to stabilize a system to phase separation. The local effects of interactions are unchanged. There is a difference between a mean-field and no field. For example, the Flory-Huggins equation is a mean-field equation with χ representing the mean-field. The chains are random, Gaussian. The equation predicts phase separation due to poor solvent conditions according to the value of the mean field. A system with no field can not phase separate since such an athermal system always contains an entropy term associated with miscibility.

c) In the dilute regime, $\varphi << \varphi^*$, the osmotic pressure, π, follows ideal behavior,

$$\pi = kT\frac{\varphi}{N}$$

This expression does not depend on chain scaling since only the mass to molecular weight ratio is important. In the measurement, a dilute solution is in contact with a pure solvent through a semi-permeable membrane through which solvent, but not polymer, can pass. The solvent seeks to equalize the chemical potential on both sides of the membrane by exerting a pressure, i.e. diluting, the solution. This excess pressure causes the fluid level in the solution to rise in opposition to atmospheric pressure. By measuring the height difference between the two cells, the osmotic pressure can be determined by mgh/A where A is the area of the solution column. If the solution is dilute, the mass dissolved per volume is used to calculate φ, and N can be determined from the equation given above.

d) If the solution is dilute, then the ideal gas equation, part "c", can be used to determine the molecular weight of any colloid. This is because the equation in part "c" does not depend on structural scaling of the colloid.

e) The Flory-Huggins equation predicts that in the semi dilute regime the osmotic pressure will scale with φ^2. The observed scaling is the 9/4 power so a stronger dependence on concentration. As concentration increases the polymer coils accommodate thermodynamic changes by a structural change. Screening leads to concentration blobs at large scales whereby the coils are reduced in overall size. The Flory-Huggins approach assumes binary interactions between persistence units while the des Cloiseaux approach allows for some higher-order interactions

since the screening effect is essentially a higher-order interaction, i.e. involving more than 2 persistence units. There isn't a very good answer, that I know of, to the second part of this question but it is a good exercise to attempt to answer it.