Quiz 10
Polymer Physics
March 29, 2017

Osmotic pressure is used to measure the number average molecular weight of a polymer.

a) Explain how this measurement is conducted by drawing a sketch of a semi-permeable membrane device. Explain how an ideal gas analogy is used to obtain the osmotic pressure.
b) Flory obtained the following expression for osmotic pressure,

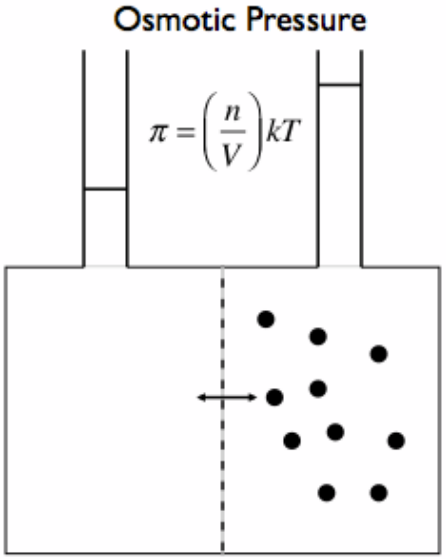
$$\Pi = \frac{kT}{V_c}\left(\frac{\phi}{N} + \left(\frac{1}{2} - \chi\right)\phi^2 + \ldots\right)$$

How is this expression related to your ideal gas expression in part a?
c) des Cloizeaux proposed a scaling relationship that described the power-law dependence in the semi-dilute regime for good solvents. Derive this scaling relationship.
d) What would des Cloizeaux's result be in a theta solvent? What about for extended, rod-like chains with $d_f = 1$? Comment on these results.
e) Why might it be important to obtain the number average molecular weight compared to higher order moments such as the viscosity average molecular weight?

Answers: Quiz 10
Polymer Physics
March 29, 2017

a) Why might it be important to obtain the number average molecular weight compared to higher order moments such as the viscosity average molecular weight?

a) If the colloid molecules are imagined to be gas atoms they would exert a pressure π. For ideal gas molecules, $\pi V=nkT$, and n/V is the concentration ϕ. This yields the ideal osmotic pressure equation, $\pi = \phi\, kT$. Replacing the mass concentration for the number concentration yields, $\pi = ckT/N$, where N is the number average molar mass and c is the mass concentration.



b) The Flory expression's first term is the ideal law. The second term is a term in a Taylor series expansion of the ideal law. The term $(1/2 - \chi)$ is the second virial coefficient.

c) If a concentration blob model is used, above the overlap concentration the osmotic pressure doesnot depend on molar mass N. The concentration is renormalized by c/c*, $\pi = (c/c^*)^P\, ckT/N$, where $c^* \sim N^{-4/5}$. Since $\pi \sim N^0$, $-1 + 4P/5 = 0$; $P = 5/4$, so $\pi \sim c^{9/4}$.

d) For a theta solvent $c^* \sim N^{-1/2}$, so $-1 + P/2 = 0$; $P = ½$, so $\pi \sim c^3$. This does not agree with the Flory result and disagrees with experiment. For a rod particle $c^* \sim N^{-2}$, so $-1 + 2P = 0$, so $\pi \sim c^{3/2}$. This seems to indicate that the des Cloiseaux result is coincidental to the good solvent mass fractal dimension.

e) For a polydisperse polymer the number average reflects the mean of the distribution so it is a better measure of the properties compared to high order molecular weight moments that reflect more on the high-molecular weight tail of the distribution. Most techniques yield a higher order moment than the first order moment.