Homework 7
Polymer Physics 2024
Due Tuesday February 27 at noon
(**pdf** file should be called: **HW 4 Group x Last Name_Name_Name_Name.pdf**)

The polymer collapse transition has been proposed as a technology for separation membranes since the time of T. Tanaka's first publications in the 1970s. Kolbeck PJ, Benaoudia D, Chazot-Franguiadakis L, Delecourt G, Mathé J, Li S, Bonnet R, Martin P, Lipfert J, Salvetti A, Boukhet M, Bennevault V, Lacroix JC, Guégan P, Montel F, *Thermally Seitchable Nanogate Based on Polymer Phase Transition* Nano Letters **23** 4862-4869 (2023) have developed separation membranes based on ion track films with electropolymerized poly(2-alkyl-2-oxazolines) lining the ion track pores. The methyl (PMeOx) and propyl (PPrOx) substituted polymers show different phase behavior in water with the PPrOx displaying an LCST near room temperature. The graphical abstract shows how this arrangement allows for thermal control of permability of pores on the order of 200nm, close to the size of biomolecules of interest such as DNA and viruses. A weak pressure difference is used to drive biomolecules through the pores.

a) Figure 3 shows the variation in frequency of DNA "translocating" through the membrane as predicted by a thermodynamic model based on the third virial coefficient (*w* in the insets). **Explain** where this transition is first order and where it is second order in these plots. **What does** "first" and "second order" transition mean? **Give** an example of each from general experience. **Which order** is necessary for a thermally induced switch? **Are there** other experimental conditions that could control this transition from your knowledge of the Flory-Krigbaum model?

b) In section S5 of the supporting information, Kolbeck derives an expression for the coil expansion factor, α. **Compare** Kolbeck's presentation with the presentation of Goldberg form the class ppt slides 51-54. **How** do the expressions differ. **Can** you explain why Kolbeck has modified the equations of Goldberg? (The Halperin and de Gennes papers are linked on the webpage.)

c) **How** does the expression for the second virial coefficient given by Kolbeck, which she terms v, differ from that of van der Waals? Is Kolbeck's equation correct? Kolbeck mentions that the distance between polymer chains on the surface is larger than the polymers end-to-end distance. **Why** is this important to the derivation?

d) Kolbeck gives a fairly obtuse description of the frequency function on the bottom of page 4864. **Compare** this equation with Poiseuille equation assuming that $\Delta P \sim P$ and **estimate** a function for $P_c{}^0$. Can you **explain** the origin or the behavior of the exponential term?

e) In Figure 2C, the θ-temperature differs between the tethered and free chains, with a lower value at small molecular weight and a larger value at higher molecular weight. For an LCST a lower θ-temperature means less miscible. **Explain** this behavior.