20.110/2.772/5.601 & 20.114
Homework #8
Due Friday, Nov 18, 3 pm

1. **The Subtle Effects of Phase Partitioning**.

   a. In class we expressed the partition coefficient $K_A^B = \frac{x_{sB}}{x_{sA}}$. Values of partition coefficients are usually reported as $K_A^B = \frac{c_{sB}}{c_{sA}}$. Show what the relationship is between the two expressions, using appropriate physicochemical properties of the components A & B.

   b. Most mammalian cells, when placed in culture, adhere to the proteins adsorbed on the surface of the culture substrate via specific cell surface receptors called integrins. If the cells are plated at low density, they can migrate around the surface through a process of extending a lamellopod, forming new adhesions to the substrate, loosening adhesions at the rear, and then contracting (via the actin-myosin cytoskeleton), which detaches the rear of the cell and lets it move forward. The process of cell migration is extremely important in development, wound healing, cancer progression, and response to infection. The migration process can be studied by time lapse video microscopy.

   In a common experimental set-up, a Petri dish is placed on a warmed microscope stage and the cells are photographed every 5 min for 12-24 hr. To prevent evaporation of the culture medium during this time, a ~1 mm thick layer of mineral oil is layered on top of the culture medium. Water has a very low solubility in mineral oil.

   Several students in a particular laboratory successfully measured migration of fibroblasts using this method, and found it to be robust. However, a when a new student started to measure migration behavior of liver cells, the cells died rapidly. The liver cell culture medium contains a steroid hormone that is essential for normal cell behavior. The steroid has a partition coefficient $K_{water}^{oil} = \frac{c_{s,oil}}{c_{s,water}} = 34$ and is present in the culture medium at an initial concentration of 10 nM.

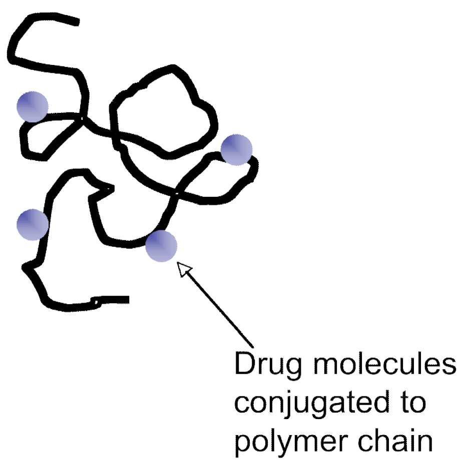
   If the depth of the culture medium is 3 mm and the thickness of the mineral oil layer is 1 mm, what is the concentration of steroid in the culture medium after equilibrium between the oil and the medium is established?

2. **Free Energy of Mixing Polymers**. Free radical polymerization processes are often easy to carry out, but the product is typically polydisperse in molecular weight. In other words, the product contains molecules with molecular weight 2n, 3n, 4n, 5n…..100n (or greater) where n is the molecular weight of the monomer. It is thus often desirable to purify the product to remove the low molecular weight components. Explain why cooling the polymer solution can precipitate the higher molecular weight

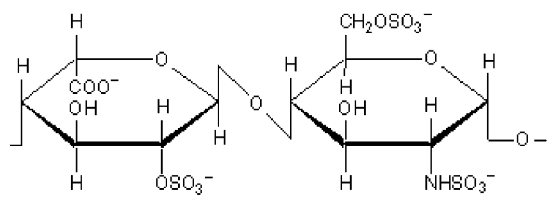
molecules preferentially compared to the lower molecular weight molecules (and you may assume that the cooling is done by a series of quasi-equilibrium steps).

3. **Polymer sizes.** You are interested in using a biological polymer, heparan sulfate, as a polymeric prodrug- a polymer used as a carrier with drug molecules conjugated to the chain- for treatment of cancer (illustrated by the schematic below). The size of the polymer coil in solution will determine whether or not the conjugate will stay in the bloodstream for extended periods or be rapidly filtered out by the kidneys, and thus is a key parameter to optimize. The chemical structure of heparan sulfate is also given below. The anionic sulfate groups are sensitive to the pH of the chain's surroundings- at lower pH, the sulfate groups become protonated (uncharged). Using your expressions for polymer coil dimensions and the following data, answer the questions below:

bond length in chain = b = 0.15 nm
characteristic ratio at pH 7.4 = 6.4



Example repeat units of heparan sulfate:



a. The root-mean-square end-to-end distance of the heparan sulfate you are using is found to be 32 nm in pH 7.4 aqueous solution. Given this result, calculate the number of bonds N in the chain for the 'stiff' freely jointed chain model (this is not an ideal chain).
b. Based on the data from part (a), what is the Kuhn length and number of Kuhn segments N_K for the chain at pH 7.4?
c. When the chain is dissolved in pH 9.0 aqueous solution, more of the sulfate groups of the chain become ionized. The measured end-to-end distance under these conditions is 55 nm. How many real bonds make up one Kuhn segment length under these conditions?

4. Dill and Bromberg # 32-4
5. Dill and Bromberg # 32-7

4. ***An 'ideal' solvent expands a polymer chain.*** (Dill and Bromberg 32-4)
If a polymer chain is composed of the same monomer units as the solvent around it, the system will be ideal in the sense that the polymer–polymer interactions will be identical to polymer–solvent interactions, so = 0.
(a) Write an expression for the most probable radius R for a chain in an ideal solvent.
(b) Show that such a chain is expanded relative to a random-flight chain.
(c) Describe the difference between an ideal solvent and a -solvent.

5. ***Using elasticity to compute chain concentrations.*** (Dill and Bromberg 32-7)
Figure 32.12 shows the stress–strain properties of a rubber band. Use the figure and chain elasticity theory to:
(a) Estimate the number of polymer chains in a cubic volume 100Å on each side.
(b) If each monomer occupies 100Å^3, what is the length of each chain between junction points?

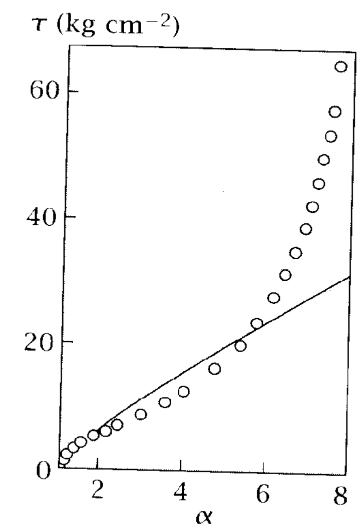


Figure 32.12 Stretching a rubber string gives stress τ versus elongation α, (○) experimental data; (——) curve predicted by Equation (32.34). Source: P Munk, *Introduction to Macromolecular Science*, Wiley, New York, 1989. Data are from LRG Treloar, *Trans Faraday Soc* **40**, 59 (1944).