Practice Test

1. **Gibbs-Duhem Equation.**
   a. Using Gibbs-Duhem equation, show that
   \[
   \left( \frac{d\mu_A}{dX_A} \right) / \left( d\mu_B/dX_B \right) = X_B / X_A
   \]
   b. Now show that you get the same relationship from equations of ideal solutions, namely for components A and B (at const. T and P):
   \[
   \mu_A = \mu_A^0 + RT \ln X_A \\
   \mu_B = \mu_B^0 + RT \ln X_B
   \]
2. **Swelling of rubber networks: entropy springs in 3D.** Suppose a hydrophilic rubber network that is initially a solid, cubic block of polymer is isotropically swollen in water. In an isotropic deformation, the x, y, and z dimensions of the sample change identically; the fractional deformation in each direction is $\lambda$.

a. Derive an expression for the elastic force resisting swelling of the network in terms of the number of network chains $m$, temperature, the chain parameters $N$ and $b$, and the fractional deformation of the network, $\lambda$.

b. Show that this restoring force is proportional to the volume of the swollen network to the 1/3 power.
3. Measurement of partition coefficients: You add 1 mg of a bile acid with a molecular weight of 400 to a small vial containing 1 mL of a model oil that represents cell membranes and 1 mL of 0.1M NaCl in water. You observe that all of the bile acid dissolves and determine that the concentration of the bile acid in the salt water phase is 0.005 mg/mL at equilibrium. What is the partition coefficient for bile acid, K, into the oil from water? You add 10 mg and observe that the bile acid does not all dissolve. In this case, the concentration in the salt water phase is 0.08 mg/mL at equilibrium. What is the concentration of bile in the oil phase for this case?
If you have time, or want to do it instead of 1, do 4:

4. **Proteins are polymers, too.** We derived in class the end-to-end distance of the freely-jointed chain model of polymers, which makes use of an extremely simple set of assumptions to determine the polymer chain conformation. The model turns out to be very useful for real random coil polymers because we can re-scale the polymer chain, viewing a stiff polymer chain with \( N \) segments of length \( b \) as an ideal chain that has a smaller number of segments \( N_k \) that have a longer length \( b_k \), to account for the tendency of stiff chains to have runs of bonds that largely point in the same direction in space.

Recently, the persistence length (which is equivalent to twice the Kuhn’s statistical segment length \( b_k \)) of a major glycosaminoglycan polymer component of cartilage was characterized by a research team in Materials Science and Biological Engineering here at MIT, by adsorbing the polymers to a substrate and directly imaging the individual (very large, by polymer standards) macromolecules using atomic force microscopy (L. Ng et al., *J. Struct. Biol.* 143, 242-257 (2003)). Two AFM images of the molecules, aggrecans, are shown below. Aggrecans have a ‘bottle-brush’ molecular structure, with a linear polymer backbone and side chains that extend away from the backbone. The two images above are from fetal and adult cartilage. The following data were collected for these molecules:

<table>
<thead>
<tr>
<th>Macromolecule</th>
<th>Contour length, ( L ) (nm)</th>
<th>Kuhn’s length ( b_k ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fetal aggrecan</td>
<td>398</td>
<td>55</td>
</tr>
<tr>
<td>Adult aggrecan</td>
<td>352</td>
<td>41</td>
</tr>
</tbody>
</table>

The bond length of these molecules \( b \) is 1.2 nm.

a. Calculate the characteristic ratio for adult aggrecan molecules.
b. Calculate the number of effective bonds in the fetal aggrecan molecule, \( N_k \).
c. How many *real* bonds along the aggrecan backbone are included within one Kuhn segment of the aggrecan polymer?
d. Calculate the ratio of end-to-end distances of fetal to adult aggrecan molecules.