HOMEWORK 6

- Show all the work/derivation with neat writing (this counts for the score). Engineering paper should be used. Each student should finish the homework independently.

1. For a lattice model of solvent and solute molecules having the same size (as studied in class), derive the following mixing entropy equation:

$$S_{mix} = k\, ln(W) = -kN[\phi \ln(\phi) + (1-\phi)\ln(1-\phi)] \quad (1)$$

using the fact that

$$W = \frac{N!}{Np!Ns!}, \text{ and } ln(N!) = N ln\, N - N \text{ (Stirling's Formula)} \quad (2)$$

where N_p and N_s are the number of solute and solvent molecules on the lattice, respectively.

2. The size effect of polymer solutions can be discussed by the lattice model shown in Fig. 1, where a polymer is represented by N_b segments (represented by black circles) connected by bonds. The segment corresponds to a monomer before the polymerization reaction. Here, for simplicity, it is assumed that the segment and solvent molecules have the same size. For such a model the free energy density is given by

$$f_{mix}(\phi) = \frac{kT}{v_c}\left[\frac{1}{N_b}(1-\phi)\ln 1-(\phi) + \phi\ln(\phi) + \chi\phi(1-\phi)\right] \quad (3)$$

Assume that $kT/v_c = 1$.

a) If $N_b = 1$, plot the mixing free energy density for following values of $\chi = (1, 1.3, 1.5, 1.7\ 1.9, 2.1, 2.3, 2.5, 2.8)$. The x-axis should be ϕ and the y-axis should be f_{mix}. The value of ϕ varies from 0 to 1.
b) In each plot from (a) for different values of χ, find the values of ϕ corresponding to the minima of f_{mix}. Now plot χ on the x-axis and the values you found with ϕ on the y-axis.
c) Repeat the above exercise from part (a) – (b) with $N_b = 30$. Comment on the difference in your results between $N_b = 1$ and $N_b = 30$.

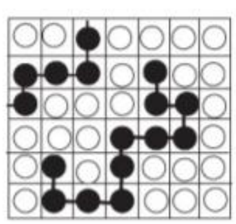

Figure 1: *Lattice model for polymer solutions. A polymer is represented by N_b dark circles connected in series. The building block of the polymer (i.e., the dark circle) is called the segment.*

3. Consider confining a hydrogel brick between two glass plates such that it cannot deform in the vertical direction ($F_{13} = F_{31} = F_{23} = F_{32} = 0, F_{33} = 1$). Now we put this structure into a solution and let the hydrogel swell. Due to the confinement, the gel can only expand horizontally with deformation gradient $F = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & \lambda & 0 \\ 0 & 0 & 1 \end{bmatrix}$, where λ is the stretch ratio along direction 1 and 2.

   a) Express the volume fraction of solvent ϕ in terms of λ.
   b) In class, we derived the Helmholtz free energy ΔU in terms of ϕ for homogeneous swelling. Using your result in (a), derive ΔU for this problem.
   c) Assuming the interaction parameter $\chi = 0.1$, find the volume fraction ϕ at the swelling equilibrium, you can solve it either analytically or numerically.
   d) Now let's remove the glasses so that the gel can also expand freely along the vertical direction. Repeat the process from (a)-(c) and find the new equilibrium state (hint: the deformation gradient becomes $F = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & \lambda & 0 \\ 0 & 0 & \lambda \end{bmatrix}$). Compared to (c), does the gel increase its volume or decrease? Explain the physical reason.