ChemE 240, Homework 6
Assigned: March 3, 2007
Due: March 8, 2007

Topics: Regular solution theory, fugacity and phase equilibrium calculations, Stat Mech math (factorization), applying the canonical partition function, periodic boundary conditions.

1) We have spent a fair amount of time in class discussing regular solution theory. One of the main results (for a two component mixture) is that

\[ \frac{\Delta A}{Nk_B T} = x_1 \ln x_1 + x_2 \ln x_2 + x_1 x_2 \chi \]

where \( \Delta A = A_{\text{mix}} - A_{\text{pure}} \) and \( \chi = \frac{z}{k_B T} \left[ \frac{-\epsilon_{11} - \epsilon_{22}}{2} - (-\epsilon_{12}) \right] \).

Show mathematically that there will be no phase separation unless \( \chi > 2 \). For \( \chi \) slightly greater than 2, about what composition will the phase separation occur?

2) Tell me what fugacity is in one paragraph. Focus on how it is related to and used in equilibrium calculations.

3) Derive the following relationship for the fugacity coefficient of a pure species \( i \).

\[ \ln \phi_i = \int_0^P \left( \frac{Z_i - 1}{P} \right) dP \]

4) There have been some questions on the math in section 3.4. On page 68 in Chandler, show that the exponential factors into an uncoupled product, as shown below. This problem will not be graded, but make sure you understand the math.

\[ Q(\beta, N) = \sum_{n_1, n_2, \ldots, n_N=0,1} \exp \left[ -\beta \sum_{j=1}^N \epsilon_{n_j} \right] = \prod_{j=1}^N \sum_{n_j=0,1} \exp \left[ -\beta \epsilon_{n_j} \right] = (1 + \exp[-\beta \epsilon])^N \]

5) Consider a closed vessel filled a suspension of B droplets in A stabilized by an interfacial agent I. The total volumes of the droplet and continuous phases are \( V_A \) and \( V_B \), respectively, and the volume of the interfacial zone is \( V_I \). A very small quantity (\( N \) particles) of component C is added to the system. The energy of C is 0 in the B phase, \( \epsilon \) in the A phase, and \( \epsilon \) at the interface. Derive a formula for the fraction of C present at the interface. Explain any assumptions and define any additional variables necessary.
6) In this programming assignment, you’ll learn how to use periodic boundary conditions.

a) Generate a lattice with LxL spins
b) Initialize the spins on the left to point up (+1) and those on the right to point down (-1)
c) Pick a random site and one of its four nearest neighbors
d) Exchange the two spins
e) What happens when you pick a spin on the corner or an edge?
f) How does the mean magnetization at the interface change with the number of Monte Carlo steps taken? Plot this.
g) Turn in your code, any plots you have, and comments to these last two questions.