

ChemE 240, Homework 9

Assigned: March 22, 2007

Due: April 5, 2007

1) Consider an incompressible fluid mixture of two components, A and B, with molecular densities ρ_A and ρ_B , respectively. For this system, the Helmholtz energy per unit volume, A/V , is

$$A/V = T[\rho_A \ln(\rho_A v) + \rho_B \ln(\rho_B v)] + \alpha \rho_A \rho_B + \gamma T \rho_A$$

where α , γ , and v are constants, $\rho_A + \rho_B = \rho$ is a constant too, and T is temperature.

a) Determine the pressure of the mixture as a function of the thermodynamic variables T and ρ_A and the constants α , γ , v , and ρ .

b) Determine the chemical potential of species A as a function of T and ρ_A and the constants α , γ , v , and ρ .

c) Demonstrate that for a range of temperatures and densities, the given free energy expression violates thermodynamic stability. Temperature T is a function of density ρ_A at the boundary of that region of instability. Determine that function, expressing your result in terms of the constants α , γ , v , and ρ .

d) The mixture might avoid the violation in stability by phase separating into an inhomogeneous system. A fluid interface would then separate one phase rich in A from another rich in B. In this scenario, what is the critical temperature, and what is the critical density of species A? Express your answers in terms of the constants α , γ , v , and ρ .

e) Derive equations for the values of ρ_A for the two phases when these phases are coexisting.

f) Show that for conditions close to the critical temperature and density

$$|\Delta\rho_A| \sim (T_C - T)^\beta$$

where T_C is the critical temperature, $\Delta\rho_A$ is the difference between the densities of species A for the two coexisting phases, and β is a "critical" exponent with value $\beta=1/2$.

2) Consider a two-component gas of non-interacting classical structureless particles with mass m_A and m_B at a temperature T .

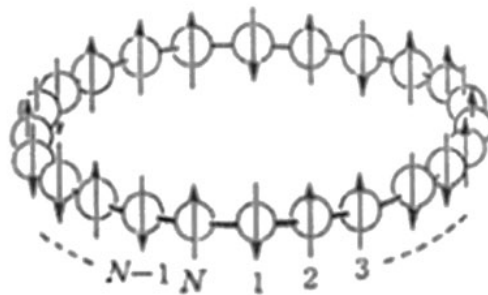
a) Calculate exactly the grand canonical partition function, Ξ for this system as a function of the volume V , temperature T , and the chemical potentials μ_A and μ_B . Your result should look like

$$\Xi = \exp(zV)$$

where z is a function of T , μ_A , μ_B , m_A , and m_B .

- b) From the result of part (a), determine the pressure, p , as a function of T and the average particle densities ρ_A , and ρ_B .
- c) For 1 cc of a 50/50 mixture of A and B at STP, compute the relative root mean square of the density fluctuations, $\left[\langle (\delta\rho)^2 \rangle / \rho^2 \right]^{1/2}$, where $\rho_A + \rho_B = \rho$.
- d) Calculate the probability of observing a spontaneous fluctuation in 1 cc of a 50/50 mixture of gas at STP for which the instantaneous density differs from the mean by one part in 10^6 .

3) Suppose that N Ising spins are arranged along a ring



and that the energy of this system is given by

$$E = -J \sum_{j=1}^N \sigma_j \sigma_{j+1} \quad , \quad (\sigma_{N+1} \equiv \sigma_1)$$

where σ_i can take on the value of +1 or -1. Show that the expression for its free energy is

$$A = -Nk_B T \ln \{ 2 \cosh(J / k_B T) \}$$

Find the relation between the specific heat and the temperature. Plot $C/(Nk_B)$ vs $k_B T/J$.

4) Determine the magnitude of the spontaneous magnetization of a 1-D Ising model at zero temperature. Start with the partition function for the 1-D case and no magnetic field. Show and explain why the spontaneous phase transition occurs at $T \rightarrow 0$.

5) Problem 5.4 on page 124 of Chandler

6) Let's follow up on Prof Balsara's lecture on March 22. The first part of the lecture shows how we can write the partition function of a 2-d Ising magnet as

$$Q = \sum_{N_+} \sum_{N_{++}} \exp(-\beta E(N_+, N_{++})) \quad (1)$$

The next part of the lecture shows how to write the partition function as

$$Q = \sum_{L=-1}^{+1} \frac{N!}{\left[\frac{N}{2}(1+L)\right]! \left[\frac{N}{2}(1-L)\right]!} \exp\left[\left(\frac{\beta J_z}{2} L^2 + \beta \mu H L\right) N\right] \quad (2)$$

In the next part of the lecture we arrive at the expression

$$\bar{L} = \tanh[\beta H \mu + \beta J_z \bar{L}] \quad (3)$$

Finally, we arrived at an expression for the critical temperature, T_c , for the case of no external magnetic field.

$$T_c = \frac{J_z}{k_B} \quad (4)$$

- a) Show how to get from equation (1) to (2).
- b) What is \bar{L} ? How do we find the value of \bar{L} given in (3) from (2)?
- c) Explain why for $\beta J_z < 1$ we have that $\bar{L} = 0$. Explain how we arrive at equation (4) and what having a critical temperature means for a 2-d Ising magnet.

7) NOTE: This code will be due on Friday, April 13. You are free to turn it in with the rest of this homework set (on April 5) but if you'd like to work on this after the exam that's fine too. If you decide to turn it in on April 13 you can email me your answers or drop them off in 301 Gilman.

Here we go, this coding assignment will involve simulating the Ising model.

The Ising model approximates the behavior of a magnet by dividing the bulk material into N smaller domains, each with its own magnetic dipole (spins $\sigma_i = \pm 1$). The mean magnetization $\langle M \rangle$ is the sum of these spins and $\langle m \rangle$ is the mean magnetization per spin $\langle M \rangle / N$. Adjacent spins interact in such a way that when the spins are identical, the system energy is lowered by J , the coupling constant. When the spins are oppositely signed, the energy is raised by J . (Hint: It may be helpful to non-dimensionalize this quantity along with the temperature, T). The Ising model operates by randomly attempting to flip spins and accepting the flip with a certain probability. This method is called the Metropolis Algorithm (and obeys detailed balance, which we will discuss later).

To simplify this, here are the steps your simulations should take:

- a. Begin with an $L \times L$ lattice of sites randomly populated with spins ± 1 . You should make L at least 100.
- b. Using periodic boundary conditions, randomly pick a site and attempt to "flip" the spin. The flipped spin should be accepted with the following probability:

$$P = \exp\left[\frac{\Delta E}{k_B T}\right] = \exp\left[\frac{\Delta J \sum_{\langle i,j \rangle} \sigma_i \sigma_j}{k_B T}\right]$$

This expression may look pretty complicated, but all it really says is that you must compute the energy difference between when the spin is flipped and when it isn't. Presumably, you would want to sum over the entire lattice to get the energy, but this is asking for too much. We only need to consider the energy difference of the nearest neighbors. This is why the sum is written over $\langle i,j \rangle$ where these indices refer to the neighboring spins. Hint: set J/k_B equal to 1.

- c. Repeat this process N times (so that each spin has on average one time to flip) for each time step.
- d. Record $\langle m \rangle$ vs. time data.

What I want you to hand in:

- a. The code you used to run these simulations.
- b. Make a plot of one trajectory showing $\langle m \rangle$ vs. time. Note on the plot what temperature you used. Make sure the run is long enough so that equilibrium is reached.
- c. Collect data at a bunch of different temperatures. Create a diagram showing $\langle m \rangle$ vs. T. Do you notice a phase transition? What is the value of T where this order-disorder transition occur (this is the critical point. Hint: see Chandler page 134)? Give a qualitative explanation for the shape of the plot. Is stability violated?