Physics 212 – Problem Set # 3

(due Friday, October 21)

1. The system of a liquid and gas has a first-order phase transition. Along the line of the transition, liquid and gas coexist at the same pressure with very different densities. As you follow the coexistence line to higher temperatures, the densities of the liquid and the gas become closer. The gas is compressed at higher temperature along this curve, while the liquid expands. At a certain point, the two densities become equal. Then the difference between the liquid and gas disappears. This is a critical point.

   We can model this behavior using the Ising model.

   (a) Consider first the situation of an ideal gas. Write the classical partition function for a gas of n molecules in a volume V, in 3 dimensions, taking the Hamiltonian to be

   $$\mathcal{H}_0 = \sum_j \frac{p_j^2}{2m} \tag{1}$$

   Don't forget the Gibbs factor $1/n!$ taking into account that the molecules are identical particles. [Note that n is extensive; I use lower case to distinguish n from N, which will appear later.]

   (b) Compute the pressure as

   $$p = -\frac{\partial F}{\partial V}\bigg|_{n,T} \tag{2}$$

   and verify the ideal gas law. Compute the chemical potential

   $$\mu = (\partial F/\partial n)|_{V,T} \ . \tag{3}$$

   (c) Compute the grand canonical partition function

   $$\Xi(\mu, T) = \sum_n \int d\Pi_n \frac{1}{n!} e^{\beta(\mathcal{H}_0 - \mu n)} \tag{4}$$

   The associated free energy is Φ, given by $\Xi = e^{-\beta\Phi}$. Φ is related by F by a Legendre transformation

   $$\Phi = F - \mu n \ . \tag{5}$$

   (d) Show, by the general rules for Legendre transformations, that

   $$n = -\frac{\partial \Phi}{\partial \mu}\bigg|_{V,T} \qquad p = -\frac{\partial \Phi}{\partial V}\bigg|_{\mu,T} \tag{6}$$

   Φ is extensive, but μ is intensive. Use this information to argue that

   $$\Phi = -p(T, \mu)V \ . \tag{7}$$

   Check the ideal gas law again.

(e) A more realistic liquid-gas system has a potential V between molecules. This gives a term

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V} \ , \qquad \mathcal{V} = \frac{1}{2} \sum_{i,j} \int dx_i dx_j \ V(x_i, x_j) \tag{8}$$

in the Hamiltonian, and in general it is not so easy to compute the partition function when this term is included. Show that it is still true, however, that the terms from the integral over the p_j do not contribute to the pressure. Let's drop these terms from here on.

(f) We can model the effects of the interaction $\mathcal{V}$ using the Ising model. This treatment is called a *lattice gas.* Consider a square lattice of N sites with a spin S_i at each site taking values $S_i = \pm 1$. Take the lattice spacing to be 1, so $N = V$. Let $S_i = +1$ represent a molecule and $S_i = -1$ represent no molecule. Show that

$$n = \frac{1}{2} \sum_i (S_i + 1) \tag{9}$$

Let n_i be 1 if there is a molecule on the site i and 0 if not.

(g) Starting from the Ising model Hamiltonian

$$\mathcal{H}_{Ising} = -J \sum_{i,\nu} S_i S_{i+\nu} - H \sum_i S_i \ , \tag{10}$$

convert S_i to n_i. Show that the Ising model partition function is converted to a grand canonical partition function for a gas with an interaction

$$V(i,j) = V_0 \, \delta_{i,j} - 4J \sum_\nu (\delta_{i,j+\nu} + \delta_{i,j-\nu}) \ , \tag{11}$$

with $V_0 \to +\infty$. That is, the Ising model gives a gas with molecules restricted to the lattice sites, with a hard-core repulsion and an attractive interaction with a range of one lattice site. Show that

$$\mu = 2H - 12J \ . \tag{12}$$

and that the grand partition function can be computed as

$$\Xi(\mu, T, V) = e^{-N\beta(3J-H)} Z_{Ising}(T, H, N) \ . \tag{13}$$

(h) We can now work out the physics of the lattice gas from the expression for the free energy of the Ising model. Using the approximation of mean field theory, we computed that this free energy is given by the minimum with respect to h of the function

$$F(h) = N \Big\{ -T \log 2 \cosh \beta h - 3J \tanh^2 \beta h - (H - h) \tanh \beta h \Big\} \tag{14}$$

Construct Φ, compute the derivative with respect to μ, and show that

$$n = \frac{1}{2} N (\tanh \beta h + 1) \ . \tag{15}$$

Why is this expected?

(i) To gain confidence, explore the dilute gas limit of the expression (14). This is found in the limit of large negative chemical potential, i.e., H large and negative. Show that, in this limit, $\tanh \beta h \to -1$. Show that this gives a pressure following the ideal gas law.

(j) Next, find the pressure corresponding to the Ising model critical point at the mean field theory critical temperature $T_c = 6J$.

(k) Going back to our calculations of the Ising model in mean field, show that, for $H = 0$ and T just below T_c, the value h_* that minimizes (14) is

$$h_* \approx \sqrt{3} T_c (1 - T/T_c)^{1/2} \tag{16}$$

(l) Using just this leading term for simiplicity, evaluate the pressure of the lattice gas as function of the temperature, and find the coexistence curve in the p vs. T plane. Set $6J = T_c = 1$ to draw the curve.

(m) Similarly, evaluate the density $\rho = n/V$ for the liquid and gas on the coexistence curve, and plot the two densities in the (ρ, T) plane. The density changes discontinuously across the coexistence curve in the (p, T) plane.

I hope that you see that this model does give a qualitative description of the liquid-gas critical point.