Physics 406: Homework 3

1. **Maxwell relations:** We have seen that a small change in the internal energy of a pressure/volume systems is related to the change $\mathrm{d}S$ in entropy and $\mathrm{d}V$ in volume by $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$. We also saw that a change in the enthalpy H is given by $\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p$.

   (a) In week 3 we saw that the free energy F of a system is $F = U - TS$. What is the equivalent expression to the equations above for a small change $\mathrm{d}F$ in the free energy?

   (b) By using the fact that the order of partial derivatives doesn't matter, we know that

   $$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}.$$

   Use this to prove the **Maxwell relation**

   $$\left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial p}{\partial S}\right|_V.$$

   (c) Use the fact that $\partial^2 F/\partial V \partial T = \partial^2 F/\partial T \partial V$ to prove another similar Maxwell relation.

   (d) And derive yet a third from the enthalpy. Look at this last relation. Describe briefly what the two sides represent. Remember that a small amount of heat flowing in or out of a system is $\mathrm{d}Q = T\,\mathrm{d}S$, and that a process at constant entropy is thus one in which no heat enters or leaves a system.

2. **Combinatorics:** A famous carnival toy is a machine that drops a large number of marbles at the top of a pyramid of nails tacked to a board like this:

marbles dropped here
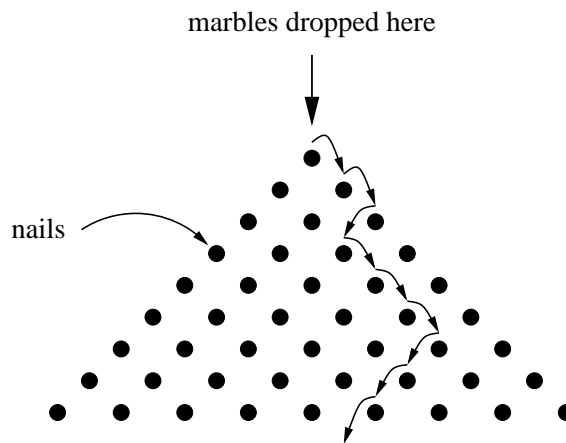
nails

The marbles fall down and at each step have a 50% chance of going right or left.

   (a) If there are N rows of nails total, write down an expression for the number of paths $g(N,l,r)$ that a marble can take that make l steps to the left and r steps to the right. Eliminate l and r in favor of the distance $x = r - l$ traveled to the right to get the same number in terms of N and x only.

   (b) If $N = 10$, how many ways are there of traveling distance $x = 10$ to the right? How many ways are there of traveling distance zero?

(c) If $N = 10$, about how many marbles will have to be dropped before even a single one of them goes all the way to the right-most slot? And how many if $N = 20$?

(d) When many marbles are dropped, what is the expected mean distance $\langle x \rangle$ traveled, averaged over all of them? And what is the standard deviation of the distance?

(e) So if you had to say where a single marble dropped would land, between about which values of x would you feel reasonably confident saying it would end up, if $N = 100$? (If you want to be really precise, you could say which values would you have 90% confidence it would land between, but any sensible answer will do for this question. Saying that x lies between -100 and 100 is not a good answer!)

3. **Temperature:** We have seen that for a system of fixed volume and number of particles, the temperature τ and entropy σ are related by

$$\frac{1}{\tau} = \frac{\partial \sigma}{\partial U},$$

where U is the internal energy. Thus we can calculate a rough value for the temperature of a system by comparing a small change ΔU in the internal energy with the corresponding change $\Delta \sigma$ in the entropy thus:

$$\tau = \frac{\Delta U}{\Delta \sigma}. \tag{1}$$

(a) For the system of magnetic "spins" (i.e., dipoles) that appears in Chapter 1 of Kittel and Kroemer's book:
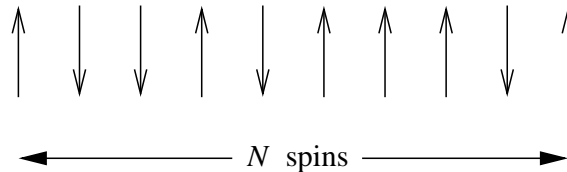
write down the internal energy U of the system in a magnetic field B in terms of the magnetic moment m of one of the dipoles, and the spin excess s defined by

$$2s = N_\uparrow - N_\downarrow,$$

where $N_\uparrow$ and $N_\downarrow$ are the numbers of spins pointing up and down respectively. Also write down the multiplicity $g(N, N_\uparrow)$ in terms of s. What is the entropy in terms of s?

(b) What is the change in energy when the spin excess goes from s to $s + 1$? Show that the corresponding change in entropy is

$$\Delta \sigma = \ln \frac{\frac{1}{2}N - s}{\frac{1}{2}N + s + 1}.$$

(c) Calculate a rough expression for the temperature τ of the system from Eq. (1) above. What is the value of τ if $N = 20$, $s = 2$, and $m = 1$, $B = 1$?