Physics 406: Homework 6

1. **Entropy of the two-state system:** In class we looked at a system with two states of energies 0 and ε, in equilibrium with a thermal reservoir at temperature τ.

   (a) For this system, calculate the internal energy U and the free energy F.

   (b) Thus calculate the entropy of the system σ.

   (c) What is the value of the entropy at large temperatures? What is the simple physical reason for this value?

2. **Integral approximations:** Using integral approximations, find approximate values for the sums:

$$\text{(a)} \quad \sum_{n=1}^{\infty} \frac{1}{1+e^{\alpha n}}, \qquad \text{(b)} \quad \sum_{n=1}^{N} \ln n, \qquad \text{(c)} \quad \sum_{n=0}^{\infty} \frac{1}{(\beta+n)^3},$$

   where α and β are positive constants. Hint: notice the limits on the sums. (You can work out the integrals quite easily, but you can also look them up in tables if you prefer or get your calculator to do them if you have one of those fancy calculators that does that stuff.)

3. **Fluctuations in the energy:** A system has many states denoted by $i = 1, 2, 3\ldots$ with energies ε_i. It is in equilibrium with a thermal reservoir at temperature τ, which means that it hops from one state to another over time. Thus there will be fluctuations in the energy of the system—small amounts of energy will enter and leave the system from the reservoir. Just as we calculated the width of distributions previously by calculating their standard deviation, we can calculate the width of the energy distribution, i.e., the size of the energy fluctuations, by calculating the standard deviation of energy.

   (a) Write down the partition function for the system, and differentiate it to show that the internal energy of the system is

$$U = \langle \varepsilon \rangle = \tau^2 \frac{\partial \ln Z}{\partial \tau}.$$

   (b) Now show that the mean *squared* energy of the system is

$$\langle \varepsilon^2 \rangle = \frac{\tau^2}{Z} \frac{\partial}{\partial \tau} \left(\tau^2 \frac{\partial Z}{\partial \tau} \right).$$

   (c) Hence show that the standard deviation $\sigma_U = \sqrt{\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2}$ of the energy is given by

$$\sigma_U = \tau \sqrt{\frac{\partial U}{\partial \tau}}.$$

   (d) Rewrite this in terms of the heat capacity of the system. Note thus that the fluctuations in the energy—a microscopic quantity—are directly related to the heat capacity—a macroscopic quantity. By measuring one, we can measure the other. This result is often used in computer simulations of thermal systems. You measure the fluctuations of the energy and so calculate what the heat capacity must be.

4. **Interstellar hydrogen:** There is a low density of hydrogen between the stars, typically about one H_2 molecule per cm^3. Some of this exists as molecules and some of it is in the atomic state—i.e., it is pairs of hydrogen atoms. It takes about $\varepsilon_b = 4.5$ eV to break a hydrogen molecule in two.

   Consider a cubic box of volume $V = 1\ \text{cm}^3$ with a single hydrogen molecule in it, which you can treat as a point particle of mass $2m_p$, where m_p is the proton mass.

   (a) Calculate or write down the partition function Z_m for such a point particle at temperature τ.

   (b) Now supppose we split the molecule into two H atoms. What is the partition function Z_a for the whole system (both atoms in the same box), assuming that the atoms do not interact? An important point to remember is that the two atoms are quantum mechanically identical and therefore subject to Gibbs's $1/N!$ argument. Also you should allow for the energy of binding. That is, the energy of each state of the system is 4.5eV higher than it would otherwise be because we had to do some work to split the molecule apart.

   (c) Now consider all possible states of the system, both molecular and atomic. What is the complete partition function Z for the whole system?

   (d) The temperature of the gas in our local region of space is believed to be about a million Kelvin (due to heating from the stars). Calculate the probability that our hydrogen is in the atomic state at this temperature. Also calculate the temperature at which the transition from molecular to atomic hydrogen takes place, which we define as the temperature at which the probability of being in the atomic state reaches 50%. (The simplest way to solve this last part is probably just to plug numbers into the equations until you get something that works.)

   You should find that at 10^6 K the hydrogen is almost certain to be in the atomic state, not the molecular one, even though the molecular state has lower energy. And this is true—most interstellar hydrogen is atomic.