# Physics 406: Homework 11

1. **Maximum entropy:** Some people believe that the correct way to derive statistical mechanics is to start with the Shannon expression for the entropy:

$$\sigma = -\sum_s p(s) \log p(s),$$

and assume that the equilibrium state is the state that maximizes this.

   (a) Maximize $\sigma$ with respect to $p(s)$, subject to the necessary constraint that

$$\sum_s p(s) = 1, \tag{1}$$

   using the method of Lagrange multipliers (or any other method that you are familiar with) and show that the maximum corresponds to the microcanonical ensemble

$$p(s) = \frac{1}{g},$$

   where $g$ is the number of states accessible to the system.

   (b) Maximize subject to both Eq. (1) and the constraint that the mean energy is fixed:

$$\sum_s \varepsilon_s p(s) = U, \tag{2}$$

   and show that the maximum corresponds to the canonical ensemble

$$p(s) = \frac{e^{-\varepsilon_s/\tau}}{Z},$$

   where $\tau$ and $Z$ enter through Lagrange multipliers. (They are of course the temperature and the partition function in more familiar language.)

   (c) Finally, maximize $\sigma$ subject to (1), (2), and the constraint that the mean number of particles in the system is fixed:

$$\sum_s N_s p(s) = N, \tag{3}$$

   and show that the maximum corresponds to the grand canonical ensemble

$$p(s) = \frac{e^{-(\varepsilon_s - \mu N_s)/\tau}}{\mathcal{Z}},$$

   where again $\tau$, $\mu$, and $\mathcal{Z}$ enter through Lagrange multipliers.

2. **The heat-bath algorithm:** An alternative algorithm to the Metropolis Monte Carlo algorithm is the **heat bath** algorithm. The acceptance probability for a move in this algorithm is

$$P(\mu \to \nu) = \frac{e^{-\frac{1}{2}\Delta\varepsilon/\tau}}{e^{-\frac{1}{2}\Delta\varepsilon/\tau} + e^{\frac{1}{2}\Delta\varepsilon/\tau}},$$

where $\Delta\varepsilon = \varepsilon_\nu - \varepsilon_\mu$.

(a) Show that this acceptance probability satisfies detailed balance for the Boltzmann probability distribution.

(b) The heat-bath algorithm is not usually used because it is less efficient than the Metropolis algorithm—for an efficient algorithm we want $P(\mu \to \nu)$ to be as large as possible. Draw a sketch of the acceptance probabilities of the heat-bath and Metropolis algorithms for a range of values of $\Delta\varepsilon$ around zero. For what values of $\Delta\varepsilon$ is the acceptance probability greater for the Metropolis algorithm than for the heat-bath algorithm?

(c) What is the maximum ratio by which $P(\mu \to \nu)$ for the Metropolis algorithm exceeds $P(\mu \to \nu)$ for the heat-bath algorithm, and at what energy difference $\Delta\varepsilon$ does this happen?

3. **Calculating the free energy and entropy:** The free energy is quite hard to calculate in a numerical simulation. Perhaps the simplest way to do it is the following.

   (a) Write down an expression for the internal energy in terms of the partition function. Rearrange and integrate to get an expression for the partition function. Hence derive an expression for $F$ in terms of an integral over $U$. Assuming that the ground state energy is zero, make sure your expression gives the correct value for $\tau = 0$. Calculation of the free energy thus involves measuring $U$ at a variety of different temperatures and integrating numerically to get $F$.

   (b) We could use this result to calculate the entropy from $\sigma = (U - F)/\tau$, but there is another alternative. Write down an expression for the heat capacity of a system in terms of a derivative of the entropy. Hence find $\sigma$ as an integral over temperature. Suggest a way to measure the heat capacity using measurements of the energy of the system *without* using a derivative. (Hint: we've already seen the answer to this in a previous homework problem.)