BE 25 Winter 2025
Homework #6
Due at 9 AM PST, February 25, 2025

Problem 6.1 (Connections between free energy and entropy, 25 pts).
Consider a system whose microstates are described by the Boltzmann distribution, that is the probability of realizing microstate i is

$$P_i = \frac{\mathrm{e}^{-\beta E_i}}{Z}, \tag{6.1}$$

where $\beta = 1/k_BT$ and

$$Z = \sum_i \mathrm{e}^{-\beta E_i} \tag{6.2}$$

is the partition function. Given the probability mass function above, that the free energy, often called the Helmholtz free energy, is $F = -k_BT\,\ln Z$, and the result we derived in lecture, $S = k_B\beta\,\langle E\rangle + k_B\ln Z$, show the following results.

a) Show that the expectation value of the energy, $\langle E\rangle$, is

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial\beta} = \frac{\partial \beta F}{\partial \beta}. \tag{6.3}$$

b) Show that $F = \langle E\rangle - TS$.

c) Show that $S = -\partial F/\partial T$.

As we discussed in lecture, taken together these results show that the free energy is a Legendre transform of the energy. *Hint*: It is up to you, but I found in all cases that it is easier to start with the right hand sides of the above equations and verify that they equal the left.

Problem 6.2 (Grouping microstates, 10 pts).
As a motivating example for this problem, consider a biomolecule that can be in a helical or coiled state. However, there are several microstates corresponding to the helical state. For example, there are many configurations of the molecule due to bond vibrations that are still classified as helical. Similarly, there are several other microstates corresponding to the coiled state.

Now let us generalize. Imagine we have a set of microstates for a system and we can put each microstate into a specific group. We will refer to these groups as macrostates. In the motivating example, we have two macrostates, helical and coiled. We will index the macrostates with i and the microstates within each macrostate with

j such that the energy of microstate j in macrostate i is E_{ij} and the partition function for the system is

$$Z = \sum_i \sum_j \mathrm{e}^{-\beta E_{ij}}. \tag{6.4}$$

Show that the probability of the system being in macrostate i is

$$p_i = \frac{\mathrm{e}^{-\beta F_i}}{Z}, \tag{6.5}$$

where F_i is the free energy of macrostate i. That is, F_i is the free energy of a system that consists only of microstates in macrostate i.

Problem 6.3 (From discrete to continuous, Boltzmann to Gaussian, 15 pts)**.**
This problem was inspired by problem 10.14 of Dill and Bromberg.

In this problem we will explore how a Gaussian distribution arises from a Boltzmann distribution when the energy is a quadratic function of an observed variable. We will do this through a simple example problem.

Imagine a protein that binds a ligand. When the ligand is a distance x_0 from the center of the protein, the energy of the ligand-protein interaction is minimal. We can write down the energy as a function of the position x of the ligand relative to the center of the protein, $E = E(x)$. We do not know what $E(x)$ is, so we can write it as a Taylor expansion about x_0,

$$E(x) = E_0 + \left.\frac{\mathrm{d}E}{\mathrm{d}x}\right|_{x=x_0} (x - x_0) + \frac{1}{2}\left.\frac{\mathrm{d}^2E}{\mathrm{d}x^2}\right|_{x=x_0} (x - x_0)^2 + \cdots . \tag{6.6}$$

The first derivative vanishes at x_0 because that position has minimal energy. Truncating the Taylor series to second order, we have

$$E(x) = E_0 + \frac{k}{2}(x - x_0)^2, \tag{6.7}$$

where we have defined the spring constant

$$k \equiv \left.\frac{\mathrm{d}^2E}{\mathrm{d}x^2}\right|_{x=x_0}. \tag{6.8}$$

a) Let $P(x)$ be the probability that the ligand is at position x. Write down the x-dependence of $P(x)$, ignoring any normalization constants.
b) From your expression in part (b), you can derive a normalization constant. In class, we have been considering discrete states, but here, x is continuous.

While there are subtleties to moving from a discrete distribution to a continuous, in many applications you can in practice simply replace

$$\sum_{\text{all values of } x} \longrightarrow \int \mathrm{d}x. \tag{6.9}$$

Perform the necessary integral (or otherwise reason the result) to get the normalization constant and write a complete expression for $P(x)$.

c) What is the average position, $\langle x \rangle$?

d) What is the mean square deviation from this position, $\langle (x - \langle x \rangle)^2 \rangle$, also called the variance? Importantly, comment on how the variance depends on the thermal energy $k_B T$. (It will help you to notice that the distribution you derived is Gaussian, also called normal.) Finally, sketch $P(x)$.

Problem 6.4 (Bounds on susceptibilities, 25 pts).

a) Prove that the isothermal compressibility κ_T is positive for a thermodynamically stable system with a constant number of particles.

b) We showed in lecture that thermodynamic stability requires that $C_p > 0$. Show that in addition to $C_p > 0$ and $\kappa_T > 0$, thermodynamic stability requires that

$$\frac{\kappa_T C_p}{VT} - \alpha^2 < 0, \tag{6.10}$$

for a system with a constant number of particles, where α is the thermal expansivity. This means that while α can be positive or negative (or zero), it is nonetheless constrained in the values it may take.

As a reminder,

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p, \tag{6.11}$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T, \tag{6.12}$$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p. \tag{6.13}$$

Problem 6.5 (van der Waals fluids, 25 pts).
An equation of state for a van der Waals fluid is

$$p = \frac{Nk_BT}{V - Nb} - \frac{N^2a}{V^2}, \tag{6.14}$$

where a and b are positive constants.

a) Consider a plot of p vs v, where $v = V/N$ is the molar volume (the inverse of the number density), for a given temperature. What must be true about this curve for the fluid to be thermodynamically stable for all densities?

b) The **critical point** is established at the temperature below which the fluid can exhibit a thermodynamic instability. Provide reasoning as to why the critical point occurs when

$$\left(\frac{\partial p}{\partial v}\right)_T = \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0. \tag{6.15}$$

c) Find the critical point (k_BT_c, v_c, p_c) in terms of the constants a and b.

d) Define **reduced variables** $\tilde{p} = p/p_c$, $\tilde{T} = T/T_c$, and $\tilde{v} = v/v_c$. Write the above equation of state in terms of the reduced variables. In doing so, does any a- or b- dependence remain?

e) Use a computer to make a plot $\tilde{p}$ versus $\tilde{v}$ for $\tilde{T} = 0.9, 1$, and 1.1. Comment on what you see in the plots.

f) What do you think would happen if we controlled the temperature and pressure such that $\tilde{T} = 0.9$ and $\tilde{p} = 0.5$?