BE 25 Winter 2024
Homework #6
Due at 9 AM PST, February 22, 2024

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 $\beta = 1/k_B T$ 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 $F = -k_B T \ln Z$, 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 (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 $\kappa_T > 0$, that thermodynamic stability requires that

$$\frac{\kappa_T C_p}{VT} - \alpha^2 < 0, \tag{6.4}$$

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,

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p, \tag{6.5}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T, \tag{6.6}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p. \tag{6.7}$$

Problem 6.3 (Helix-coil transitions, 50 pts)**.**
Biopolymers are often found in helix configurations, like double helices in DNA or alpha helices in proteins. They may also be in **coil** configurations, which are disordered, typically bendy states. These are more often found at higher temperatures, as we often refer to the process of going from helix to coil as melting or denaturation. Conversely, when a denatured biopolymer adopts its helical shape, this is often called folding.

As a simple model for helix-coil character of a biopolymer, consider a biopolymer made up of N segments that are either in a helical state or a coil state. For example, a polymer with $N = 6$ segments might be `HHHHCC`, where the first four segments are helical and the last two are coiled.

We will assume that a helical segment has energy ε and a coiled segment has energy 0. (We have set the energy of the coiled state to zero since we can define an arbitrary energy scale.)

a) We define a microstate in this model to be a list of `H` or `C` values for each segment. E.g., a microstate for $N = 6$ might be `HHHHCC` as we saw above, or `HCCHCH`. Let n be the number of segments that are helical. How many microstates are consistent with a given n?

b) What is the energy of a given microstate?

c) Write down the probability mass function $P(n)$. This will involve computing the partition function. You should be able to write the partition function in a concise format if you make use of the binomial theorem.

d) Show that the average number of helical segments is

$$\langle n \rangle = x\,\frac{\partial \ln Z}{\partial x}, \tag{6.8}$$

where $x = \mathrm{e}^{-\beta\varepsilon}$. From this, compute the average fraction of helical segments, $f = \langle n \rangle / N$.

e) Sketch the average number of coiled segments versus temperature.

f) In the model we have used so far, there is a gradual transition from helical states to coiled states as the temperature rises. As a biopolymer transitions from being mostly helical to mostly coiled, it goes through states with heterogenous helix-coil regions. As an alternative model, we can consider an all-or-none model, in which all segments are helical, or all segments are coiled. There are then two microstates, `HHHHH...` and `CCCCC...`. Compute the probability that a given biopolymer is coiled as a function of temperature and make a sketch of this probability. How does this differ from your results in parts (d) and (e)?