1. **The Helmholtz free energy and the canonical partition function.** In lecture I showed that in a macroscopic system $(N \gg 1)$, the Helmholtz free energy A can be equated with the logarithm of the canonical partition function Q:

$$\beta A(N, V, T) = -\ln Q(N, V, T).$$

This problem develops a different (friendlier?) way to show that connection between macroscopic thermodynamics and statistical mechanics.

(i) Start with the microscopic picture. Each microstate ν has energy $E(\nu)$, so the canonical partition function is

$$Q(N, V, T) = \sum_{\nu \text{ consistent with } N, V} e^{-E(\nu)/k_{\mathrm{B}}T}.$$

Show that

$$\left(\frac{\partial \ln Q}{\partial \beta} \right)_{V,N} = -\langle E \rangle.$$

(ii) Now let's think about the thermodynamic picture. Apply the chain rule to demonstrate that

$$\left(\frac{\partial (-\beta A)}{\partial \beta} \right)_{V,N} = -E.$$

(iii) In the thermodynamic limit $(N \to \infty)$, we replace $\langle E \rangle$ by E, which we now take to be a deterministic quantity. Hence in that limit, the derivative of $\ln Q$ with respect to β is exactly the same as the derivative of $-\beta A$ with respect to β. Conclude that it must be the case that in the large system size limit $-\beta A = \ln Q + C$, where C is some constant that does not depend on β. Why do you think we suppressed the constant in lecture?

2. **Practice with Legendre transforms and Maxwell relations.** In class we discussed how the Helmholtz free energy could be constructed as $A = E - TS$ to yield a "thermodynamic potential" which is a natural function of T, V, and N. This is to be contrasted with the first thermodynamic potential we introduced: S, a function of E, V, and N. Notice that the transformation passing from S to A is a lot like the transition from the microcanonical (constant E) to canonical (constant T) ensemble, a similarity which is very much not an accident. In that transformation from microcanonical to canonical we were motivated to study an open system which had a fluctuating energy since energy was exchanged with a very large bath. Suppose we have a system which, through interactions with the outside environment, has a fluctuating energy *and a fluctuating volume*.

(i) Show that the Gibbs free energy, $G = E - TS + pV$, is a thermodynamic potential which is naturally a function of T, p, and N by writing out an expression for dG in terms of dT, dp, and dN.

(ii) You have no doubt come across the Gibbs free energy in a chemistry class when discussing whether or not a chemical reaction would occur spontaneously. Why did you focus on the Gibbs free energy and not the Helmholtz free energy?

(iii) From multivariable calculus you should have seen that the "mixed partial derivatives" of a multi-variable function are equal. For example, let $f(x, y)$ be a function of x and y such that

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy.$$

The order of differentiation with respect to both x and y does not matter:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = \frac{\partial^2 f}{\partial x \partial y}.$$

Use this fact and your expression for dG in (i) to relate $(\partial S/\partial p)_{T,N}$ to a partial derivative involving volume and temperature. Such an equality is called a Maxwell relation. There are lots of problems in thermodynamics which require you to pull out the right Maxwell relation at the right time. I'm going to try to avoid asking you to guess when you should try to use them. Rather, I want you to focus on two main points: (1) they can always be derived from mixed partial derivatives of a thermodynamics potential and (2) they relate two different types of experiments. It is often the case that one experiment is easier to measure than the other. For example, $(\partial S/\partial p)_{T,N}$ requires a measurement of how entropy grows with pressure at fixed T and N, but you may only have a way of measuring how volume changes with temperature. In that case, the Maxwell relation saves the day.

3. **Ideal gas chemical potential.** We began our study by discussing the response to changes in three extensive macroscopic constraints, N, V, and E. We then swapped out two of those rigid constraints, V and E, for conjugate variables, p and T to allow volume and energy to fluctuate. I think you probably have a sense of how one could tune all of these five parameters: N, V, E, p and T in an experiment. The missing link is the chemical potential μ, the intensive quantity conjugate to N. I find it to be much more mysterious how one can make a giant bath with a tunable value of a chemical potential. In other words, suppose you have your system and want that system to exchange particles with a large particle reservoir with chemical potential μ. I know how to make a bath of a particular temperature with an ice bucket or a water bath. Similarly, I know how to make a bath with a particular pressure. In this problem, we show that you can make a bath with a particular μ out of a ideal gas by appropriately adjusting p and T. We assume that our bath consists of a dilute vapor, for which the ideal gas law, $pV = Nk_BT$, is a good approximation.

(i) Ideality implies that internal energy E depends only on T and N, and not on p. Show that this is true by evaluating the derivative $(\partial E/\partial p)_{T,N}$. Use as a starting point the fundamental relation

$$dE = TdS - pdV + \mu dN$$

and differentiate with respect to p at fixed T and N to get:

$$\left(\frac{\partial E}{\partial p}\right)_{T,N} = T\left(\frac{\partial S}{\partial p}\right)_{T,N} - p\left(\frac{\partial V}{\partial p}\right)_{T,N}.$$

From here, use your Maxwell relation from problem 2 and differentiate the ideal gas law.

(ii) Argue based on your result from part (i) and the property of extensivity that the energy of an ideal gas can be written in the form

$$E = N\epsilon(T).$$

(iii) The entropy of an ideal gas can be divided into two parts: that associated with intramolecular fluctuations $S_{\text{intra}} = Ns(T)$, and that associated with distributing molecules in space (i.e., center-of-mass translation), S_{trans}. In problem 1 of the last problem set, you calculated S_{trans} for a dilute system to be

$$S_{\text{trans}} = -k_{\text{B}} V [\rho \ln(\rho v) - \rho],$$

where $\rho = N/V$ and v is the volume of a microscopic lattice cell introduced for the purpose of counting. Using that result, write the total entropy $S = S_{\text{intra}} + S_{\text{trans}}$ of our ideal gas as a function of p, N, and T. (Your answer may involve the unspecified function $s(T)$.)

(iv) Combining these results, compute the Gibbs free energy, $G = E - TS + pV$, of an ideal gas. Differentiate appropriately to determine the chemical potential $\mu(T, p)$.

(v) Show that $\mu(T, p)$ can be written

$$\mu(T, p) = \mu^{(0)}(T) + k_{\text{B}} T \ln \left(\frac{p}{p_0} \right),$$

where p_0 is a reference value of pressure (e.g., 1 atm). Identify the quantity $\mu^{(0)}(T)$ in terms of T, v, and p_0. (Your answer may involve the unspecified functions $\epsilon(T)$ and $s(T)$.) Just as the temperature T regulated how much our system wanted to donate or extract energy from a temperature bath, the chemical potential regulates how much the system wants to donate or extract particles from the surrounding environment. We have just derived how that propensity for adding/removing particles can be changed by tuning the temperature and pressure.