Stat Mech Study Session

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1 Entropy Maximum/Energy Minimum

After dancing around the issue for a while, we managed to figure out why it is that the maximum entropy hypothesis (i.e., the second law of thermodynamics) implies a minimum energy hypothesis (and vice versa). Most of this comes either from the notes from 6 September 2005 or from IMSM pp. 11-13.

First, one thing which will clarify IMSM a little bit: the E on page 12 is *not* the same as the E on page 13. Think of the page 12 E as E_{tot}.

Now, our goal is to prove that the unconstrained energy is a minimum. The first thing you have to do is to convince yourself of (or just accept) the second law as it is presented in IMSM, p.8.

We start out by splitting some system into two subsystems. When relaxed, these subsystems have energies $E^{(1)}$ and $E^{(2)}$. The energy for the total system is kept constant at $E_{\text{tot}} = E^{(1)} + E^{(2)}$. Then, by way of some constraint, we change the energies of the subsystems by a quantity ΔE. Since the total energy is constant, if one subsystem increases in energy by ΔE, the other must decrease by the same. Therefore, the second law (maximum entropy) gives us:

$$\begin{aligned} S_{\text{constrained}} &< S_{\text{unconstrained}} && (1) \\ S(E^{(1)} - \Delta E, X^{(1)}) + S(E^{(2)} + \Delta E, X^{(2)}) &< S(E^{(1)} + E^{(2)}, X^{(1)} + X^{(2)}) && (2) \end{aligned}$$

Since $S(E)$ is continuous (*i.e.* there exists a value of $S(E)$ for every value of E), we know that there is some E such that

$$S(E^{(1)} - \Delta E, X^{(1)}) + S(E^{(2)} + \Delta E, X^{(2)}) = S(E, X^{(1)} + X^{(2)}) \tag{3}$$

What is important to note here is that the right-hand side of this equation represents an unconstrained system with some total energy E, whereas the left-hand side is the constrained system with total energy $E^{(1)} + E^{(2)}$. All other quantities in equation (3), including S, are equal, so now we just want to find a way to compare E and $E^{(1)} + E^{(2)}$.

As it happens, $S(E)$ is a monotonically increasing function (that is, $S(E) < S(E') \Leftrightarrow E < E'$). There we know from equation (2) that the E in equation (3) satisfies the inequality

$$\begin{aligned} E &< E^{(1)} + E^{(2)} && (4) \\ E_{\text{unconstrained}} &< E_{\text{constrained}} && (5) \end{aligned}$$

which, in comparison to equation (1) (entropy maximization), we can easily recognize as *energy minimization.*

We also came up with an alternative argument. I'm a little unsure as to whether or not I was making the connection between the physics and the math correctly, so although the math described below is definitely correct, it's possible that the physical interpretation is totally wrong. With that caveat, here's the thought:

$$0 < T \equiv \underbrace{\left(\frac{\partial E}{\partial S}\right)_{\mathbf{X}}}_{+} = \underbrace{-}_{-} \underbrace{\left(\frac{\partial E}{\partial \mathbf{X}}\right)_{S}}_{?} \underbrace{\left(\frac{\partial \mathbf{X}}{\partial S}\right)_{E}}_{-} \tag{6}$$

where the sign of $(\partial \mathbf{X}/\partial S)_E$ is equal to the sign of its reciprocal, which we have from the second law. The proof for the differential identity used is the subject of exercise 1.9. Obviously, the question mark has to be filled by plus sign for the equality to be satisfied, which gives us the energy maximization principle.

2 Thermal Equilibrium from Variational Theorems

This just involves stepping through the proof on IMSM p. 14, or doing exercise 1.3. Exercises will be typed up later (probably much later).

3 Legendre Transforms

We didn't go into too much detail on Legendre transforms, but I think we hit the main points. I'll try to address three issues: why we do Legendre transforms, how they work, and how to find the one you want.

3.1 Why?

To explain why we use Legendre transforms, we have to start talking about ensembles and conjugate variable pairs. Thermodynamic variables come in pairs of extensive variables and associated intensive variables. Pressure is an intensive variable associated with the extensive variable volume. Temperature is (essentially, by definition) the intensive variable associated with entropy.

A state function can be completely described by any set of variables which contains one variable from each pair. These are called the "natural variables" of the system, and are the variables which are differentials in the differential form of the state function. To illustrate with an example, the differential for the energy of a one-component system is given by:

$$dE = T\ dS - p\ dV + \mu\ dN$$

Energy is therefore a state function of the set of natural variables (S, V, N). In practice, we can often determine the number of particles N and the volume of the system V, but we can't directly measure the entropy. So the ensemble associated with the variables (S, V, N) (the microcanonical ensemble) isn't particularly useful experimentally. However, we can measure the conjugate variable of entropy, which is temperature. Since the set (T, V, N) still has one variable from each conjugate pair, it can still be used to describe the system. This ensemble is the canonical ensemble. Associated with each ensemble is a Legendre transform of the state function, called an auxiliary function. For the canonical ensemble, it is called the Helmholtz energy, A.

3.2 How? (in the abstract)

There's really only one trick to doing Legendre transforms, although sometimes you'll have to do it more than once. In the rest of this subsection, S represents some state function (not necessarily entropy), and the conjugate variable pairs are (p, q) and (x, y). In order to perform a Legendre transform for a given state function, follow these steps:

1. Isolate the differential of the state function on one side of the equation. For example, you might want to write
   $$dS = f(p, q, x, y)$$
   for some function f.
2. Identify the natural variables of the state function as you have written it. They will be the ones that show up as a differential in the function f. For example you might have
   $$dS = p\ dq + x\ dy,$$
   in which case dS is a function of the differentials dq and dy, so the natural variables are (q, y).
3. Identify which natural variables need to be switched for their conjugate partners. Suppose you had the state function above, but were asked to give the Legendre transform of S in the ensemble described by (p, y). You will therefore need to switch the roles of p and q to make it so that p is a natural variable and q is not. You can switch them, because they are conjugate pairs.
4. (The trick!) The new auxiliary function will be given by taking the differential of the difference of the state function and the product of the conjugate pair identified in the previous step. For this example, that is $d(S - pq)$, and the math works out as follows:
   $$\begin{aligned} d(S - pq) &= dS - d(pq) \\ &= dS - p\ dq - q\ dp \\ &= p\ dq + x\ dy - p\ dq - q\ dp \\ &= x\ dy - q\ dp \end{aligned}$$
   The second line comes about because of the product rule in differentiation, and the third line is simply the replacement of our original definition of dS from above. Note that this process had no effect on the $x\ dy$ term, which will always be the case when the conjugate pairs are uncoupled (as they should be in thermodynamics).
5. Repeat steps 2 through 4 until no more variables need to be switched. For the state function with the natural variables (p, y), we would be done. If we needed to describe our ensemble with (p, x), we could repeat the previous step for the conjugate pair x and y.

3.3 How? (in practice)

The subsection above explained the mathematical details of how to do a Legendre transform. But in practice, you will always be able to write thermodynamic functions as a sum of variables multiplied by its conjugate differential. That makes the suggestive results above easy to use with the following steps:

1. Isolate the differential of the state function for which you want to construct a Legendre transform, written as a function of the natural variable differentials and their conjugate variables.
2. For each pair you need to switch, switch the differentials and change the sign in front.
3. There is no third step.

One thing worth mentioning is the importance of the first step: if you're asked to construct a Legendre transform of entropy for a single component system, instead of one of energy, you need to first isolate the entropy. (See IMSM exercise 1.6) From the differential of energy as given in subsection 3.1, the differential for entropy would be:

$$dS = \frac{1}{T} dE - \frac{p}{T} dV + \frac{\mu}{T} dN$$

In this case, the natural variables would be (E, V, N) and their respective conjugate variables would be $(1/T, p/T, \mu/T)$. Don't let it confuse you when after the transform you end up with things like $E\ d\frac{1}{T}$. That's correct, and now you have the natural variable $1/T$.