**The Potentials & Maxwell’s Relations**

Now let’s go over some foundational mathematical work on equilibrium thermodynamic systems. To start, we’re going to introduce more functions to consider, besides the entropy. The entropy, S, is a function of E, X, N, ψ. Therefore the energy (or more properly, if we have fields present, the *Hamiltonian* – see last file) E, is a function of S, X, N, ψ whose differential is given by dE = TdS – pdX + μdN + Mdψ. T, p, μ, and M are the conjugates of S, X, N, and ψ of course. What if we wanted a function (for practical reason to be evinced shortly) which switched the roles of T and S, and/or p and X, μ and N, and/or M and ψ. We can easily create such a function. For instance consider F = E – TS. Its differential is dF = dE – d(TS) = TdS – pdX + μdN – TdS – SdT – Mdψ = -SdT – pdX + μdN – Mdψ . So we see that it’s a function similar to E but where the roles of T and S are switched, since ∂E/∂S = T, but ∂F/∂T = (-)S. In general, subtracting the product of a term and its conjugate from a function will switch the roles of the term and conjugate. Probably the main reason these potentials are useful is that, as we’ll see at some point, they are the functions which will be extremized (usually minimized), with their arguments held constant, as the substance approaches thermal equilibrium (I guess see the chemical reactions file). We already know entropy to be maximized when E, V, N, ψ are held fixed. And F we’ll find to be maximized when T, V, N, ψ are held fixed. And similarly for the other potentials.

**Common thermodynamic potentials w/r to the internal energy**

To that end, consider the common functions. I will, for the sake of discussion assume that only V is a given X variable. Later we’ll consider what changes if we add **X** = **P**, **L** back in as possibilities. Also, I’ll assume that the field is zero, as is commonly done in the introductory case. So for now then, E = U, the internal energy in the absence of fields. I’ll also assume only one species of particle.



Might note that it appears these functions are continuous everywhere – even across phase boundaries. For instance, S(U,V,N) is continuous everywhere because as increase E from liquid to gas, say, S is always increasing. And apropos, F = U – TS, we have thes same, as increase T infinitesimally between liquid and gas boundary, we’ll have ΔU = L, and ΔS = L/T. And so these cancel, and F is continuous. Let’s consider the differentials of these potentials. Let’s consider H:



and so we see that it is a ‘natural’ function of S, p, N. Let’s consider F:



and as we saw this means it is a natural function of T, V, N. Now let’s consider G:



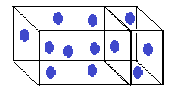
So it is a natural function of T, p, N. And last we’ll consider L:



and so it is a natural function of T, V, μ. These potentials are worth memorizing because they show up a lot. I wouldn’t bother memorizing their differentials, since it follows from their definitions. And of course the differentials and equality of cross partials follow. These are called *Maxwell’s relations*.

**Scaling relations for the potentials**

For a given system, when you increase its size (volume and number of particles) by some factor b, a so-called *extensive* quantity will also increase by this factor, while a so-called *intensive* quantity would not change at all. For instance consider the entropy of a homogeneous system (note even multi-phase substances can be considered homogeneous for these purposes I believe). Recall in the previous lecture when we put together two boxes of particles with the same entropy (per particle) and same energy (per particle). The total entropy in this case was S1 + S2.



And then we removed the partition. And still the entropy was S1 + S2 b/c the system was indistinguishable from before. So in this way we see that starting with a box of particles with entropy S1, if we add to it the same box, the entropy would be S1 + S1 = 2S1. And if we add three such boxes, the total entropy would be 3S1. So generally, if we increase the size of a homogenous system by b, its entropy will increase by the same factor. So generally, the entropy of a homogeneous system is an extensive quantity.

What about energy? For example consider a non-interacting system of particles. If all particles have only KE, then if you increase the system size by a factor b, and thereby increasing the volume and number of particles by a factor b, you will thereby increase the energy by a factor of b. So such a system would be extensive. Suppose there is an external field, **g**, resulting in a potential energy Mgycm. If you increase widthwise the size of the system by a factor b, then you will increase its mass by this factor w/o changing ycm and so the total potential energy will increase by b. If you increase height-wise the size of the system, then you would increase M by factor b, but also change ycm by a factor of b. And so the energy would actually increase by a factor of b2 in this case. So such a system wouldn’t be considered extensive. Now consider inter-particle interactions. For example, consider a system in which the particles interact via predominantly short range forces, described by some potential Φ(**r**) = 1/rn. The potential energy between two particles in the system would be:



Summing over all pairs, we get,



where the integral proceeds over the volume of the particles are contained in. Then let's assume uniform density, as usually prevails, and change variables to center of mass coordinates:



So now see that if we're dealing with the electric force, where n = 1, we will end up with a factor of R2 from the integral. In this case the potential energy is not extensive since increasing the system size (N → bN, V → bV, R → b1/3R) will change the energy by a factor of b5/3. But usually in thermodynamics we are not dealing with a ball of charge. Rather we are dealing with neutral substances whose interactions fall off faster. For instance, the Van der Waals potential energy goes as 1/r6, and also has a short range repulsion so that there is an effective cut-off to the force at small distances, d. Let's see what U would be in that case. We would have:



and so we see that such an interaction does give rise to an extensive internal energy. So the upshot is, as long as the force falls off quickly enough, the potential energy will be extensive. These are the systems we are dealing with in thermodynamics. So we see that the internal energy is in this case an extensive parameter. And likewise, so are all the potentials defined above. And the fact that extensive parameters increase in proportion to the size of the system leads to simple but important constraints on their form.

What about temperature? Well temperature T = dU/dS, and as the ratio of two extensive quantities, it wouldn’t change with size. So temperature would be an intensive quantity. Pressure also wouldn’t change by similar arguments. So that would be an intensive quantity. Now since energy is an extensive (presumably) variable, it will obey the following equation:



Let’s take the derivative of this equation w/r to λ, and evaluate at λ = 1.



If we plug this into the definitions of the potentials then we get a set of interesting identities for homogeneous systems:



An important consequence of homogeneity is the Gibbs-Duhem equation. Consider the differential of U, and let’s compare it with the differential of the expression above:



So there we have for homogeneous substances:



Notice all the differentials are of intensive quantities. Consider now a different consequence of homogeneity. Let’s go back to:



and set λ = 1/N, where N is the total particle number. Then we have:



U is the average energy per particle and so this equation says that the average energy per particle is a function of just the entropy per particle, and volume per particle, but not the overall number of particles. Proceeding similarly, and using the expressions for the potentials in the previous highlighted box, we can say:



Of course this also follows from simply dividing our previous results by N. Finally, we can work out useful differential relationships from the left half of these equalities. For instance, we said that

U = U(S,V,1). And so it follows that dU = TdS – pdV. Secondly, H(λS,p,λN) = λH. And setting λ = 1/N we have: H = H(S,p,1) → dH = TdS + Vdp (we get V instead of V when evaluating the p derivative because note that N is evaluated at 1, and so this is the volume of 1 particle). In like manner, F(T,λV,λN) = λF → F = F(T,V,1) → dF = -SdT + pdV. And G(T,p,λN) = λG → dG = -SdT + Vdp. And finally L(T,λV,μ) = λL →

dL = -SdT – pdV + Ndμ. Of course, N = 1, but I’ll keep it, for symmetry purposes.



Finally, if we equate the differentials above with the differentials of the corresponding potentials’ right hand side equality in the green box, we’ll note that we recover the Gibbs-Duhem equation, divided by N. Now let’s suppose we set λ = 1/V, instead of 1/N. Then for U, the scaling relation would imply:



So u is a function only of s and n. Doing this similarly for the others we’d find:



Note that u(s,n), h(T,p,n), f(T,n), g(T,p,n), and ℓ(T,μ). So what are their differentials? Well u = U(s,1,n) → du = Tds + μdn. h = H(s,p,n) → dh = Tds + dp + μdn. f = F(T,1,n) → df = -sdT + μdn. g = G(T,p,n) → dg = -sdT + dp + μdn. And finally, ℓ = L(T,1,μ) → dℓ = -sdT – ndμ. So altogether we have:



Finally, if we equate the differentials above with the differentials of the corresponding potentials’ right hand side equality in the green box, we’ll note that we recover the Gibbs-Duhem equation, divided by V.

**Adding more species of particles**

If we add more species of particles, then we’d have:



Let’s consider the differentials of these potentials. Let’s consider H:



and so we see that it is a ‘natural’ function of S, p, Nk. Let’s consider F:



and as we saw this means it is a natural function of T, V, Nk. Now let’s consider G:



So it is a natural function of T, p, Nk. And last we’ll consider L:



and so it is a natural function of T, V, μk. Now since energy is an extensive (presumably) variable, it will obey the following equation:



Let’s take the derivative of this equation w/r to λ, and evaluate at λ = 1.



If we plug this into the definitions of the potentials then we get a set of interesting identities for homogeneous systems:



An important consequence of homogeneity is the Gibbs-Duhem equation. Consider the differential of U, and let’s compare it with the differential of the expression above:



So there we have for homogeneous substances:



Notice all the differentials are of intensive quantities. Consider now a different consequence of homogeneity. Let’s go back to:



Now let’s suppose we set λ = 1/V. Then for U, the scaling relation would imply:



So u is a function only of s and n. Doing this similarly for the others we’d find:



and,



Finally, if we equate the differentials above with the differentials of the corresponding potentials’ right hand side equality in the green box, we’ll note that we recover the Gibbs-Duhem equation, divided by V.