**The Potentials & Maxwell’s Relations**

Now we’ll examining adding momentum, both translational and rotational, as well as external fields, to our potentials.

**Adding translational momentum into potentials and scaling relations**

Now let’s consider how things change if we add **P** to the list of parameters X. Then the energy of a substance at equilibrium can be written E(S,V,**P**,Nk). We can express the differential relationship as:



A word is waranted regarding **v**. Since we are defining E, **P**, N, etc., as time averages (see Thermodynamics on continuum file), it brings into question exactly what this **v** is. We can ascertain what it must be by making use of the stipulation that S(E,**P**) be independent of a uniform velocity boost **s** (seems reasonable to say that an objects entropy shouldn’t be dependent on the velocity of the observer). And this would require, from the equation above, that:



and so we have:



which is not the average velocity of the center of mass, actually, but obviously, the average momentum over average mass, which must still be rather close to the center of mass velocity I’d think. One further observation, the differential form of S suggests that we may write the energy as:



And the differential dE relationship above would follow from this expression (note that the differential **v**∙d**P** follows because Nk are being held constant). Next I’ll take a brief moment to consider how/if intensive parameters change when the system has a net velocity vs. before. Going back to our analysis, we’ll note that T = ∂E/∂S)V,N,P = ∂U/∂S)V,N so the temperature is not changed by this. Similarly, neither is p. However μ is:



(remember that in second line we’re keeping **P** constant!) Also, **v** = ∂E/∂**P**)S,V,N. OK, now we will be interested in the scaling of the energy expression. So consider:



(and observe that if we increase the size of the system by a factor λ, then the total momentum will increase by this factor, since we’ll be adding more particles at the same average velocity **v**). Or another way to say it, this follows from the formula for E = U + (1/2)Mv2, since if increase size of system by λ, then total mass increases by λ, and so then momentum also increases by λ (v will remain same). I’m also implicitly assuming that the field is roughly constant over the size of the volume. Doing the usual, as in the previous file, we have:



This is somewhat surprising since **v**∙**P** ≠ KE. But if we keep in mind the definition of μ, this works out.



Yay! So everything checks out. Next we’ll investigate concommitant Gibbs-Duhem equation. So,



So there we have for homogeneous substances:



Again, it relates all the intensive variable differentials. Then we’ll observe dividing the result of the scaling equation by V gives us:



Furthermore, since:



we have the differential relationship (see previous file),



And we can be sure that ∂ε/∂s = T since ∂ε/∂s)N,P = ∂(E/V)/∂(S/V))V,N,P = ∂E/∂S)V,N,P = T, etc. We can transfer to other potentials via Legendre Transformation, for instance F(T,V,**v**,Nk) = E – TS – **P**∙**v**. Can introduce a Grand (Landau) Potential as well, L(T,V,**v** ,μk) = F – ΣkμkNk. And so we’d have:



Dividing by volume we’d get:



This also follows from the fact that:



Finally, note that we would have the differential relationship,



or



**Adding angular momentum into potentials and scaling relations**

Anyway. So what if we want to add angular momentum to this situation? There are a few scenarios. I can imagine that the whole thing is like a rigid-ish rod rotating about some point. In this case we’d have: E(S,V,**P**,**L**,Nk) = U(S,V,Nk) + P2/2M + L2/2I. But in this scenario, the function will not be homogeneous, since L2/2I = (1/2)Iω2, and I = ∫dr∙mr2. And if I have a sphere for instance, then increasing its size and particle numbers by λ would result in a change equal to ΔErot. = (1/2)(ΔI)ω2, where I = (2/5)MR2 ~ MV2/3 → ΔI = (λM)(λV)2/3 = λ5/3I. So let’s not explore this possibility. The balance equations weren’t written for this scenario anyway. Instead let’s consider a bunch of rotators distributed uniformly throughout the volume, each with angular momentum Lmolecule. Such a situation readily occurs in the case of dimagnetic materials. So then increasing the size of the system would simply increase the number of such rotators, and so Erot = NL2molecule/2Imolecule → (λN)L2molecule/2I = λErot. So this would scale homogeneously. So let’s work out this scenario. We’d have: E(S,V,**P**,**L**,Nk) = U(S,V,Nk) + P2/2M + L2/2I, where L = NLmolecule and I = NImolecule. And it seems that we would have to commit to **ω** being defined as dE/d**L**, similarly to what we did with the **v**, **P** relationship. And so then the differential relationship would be:



Again, we should define what we mean by **ω**. I think we can assert that a uniform boost of all rotors by angular velocity **s** should again leave S invariant (we could simply imagine that we’ve boosted the rate of rotation of our own coordinate system). And this would require:



and so we have:



which is not the average angular velocity, but again should be pretty close one imagines. Also this matches the definition for **ω** that we derived in the Thermodynamics/Continuum file, so there. One further observation, the differential form of S suggests that we may write the energy as:



The new chemical potential would look like this:



(remember in second line we’re keeping L constant!) Also, ω = ∂E/∂L)S,V,N. OK, now we will be interested in the scaling of the energy expression. So consider:



Doing the usual, we have:



The corresponding Gibbs-Duhem equation is:



And so we have:



Again, it’s relating the differentials of all intensive variables. Secondly, let’s observe that, dividing by V, we have:



Furthermore, since:



we have the differential relationship,



**Adding fields into potentials and scaling relations**

Last we’ll make a few comments about the external field. Suppose that I were considering a bunch of electric or magnetic dipoles in an electric or magnetic field. Then still I should have something like E(S,X,Nk,ψ) (remembering this E is not a true energy per se´, see Equilibrium Systems file, but rather the Hamiltonian). Now -∂E/∂ψ = M, which would be the electric or magnetic moment, or total mass of system if in uniform gravitational field. Now of course the dipole energy is, for a single one, E = -pψcosθ. But θ isn’t a variable that shows up in E. Why not? Well M would have to implicitly take into account all of the different θ distributions. But yeah, including θ would be like including the spring-like chemical bond deformations ‘x’ in E, and this obviously isn’t done. It only shows up through the external parameter V. And likewise ‘θ’ only shows up through M. In any event, suppose for the sake of discussion that the field (potential really) were uniform throughout the volume, and suppose that the substance’s energy is homogeneous (so that angular momentum must be of that particle form mentioned). Then we have:



And if it is homogeneous then of course we have:



Taking derivative w/r to λ we get:



The corresponding Gibbs-Duhem equation would look like,



and so we have:



Again, all the intensive variables’ differentials are connected. Setting λ = 1/V we get:



What if the field is itself position-dependent? Then E would be a functional E(S,V,**P**,**L**,Nk,ψ(x)). The differential relation would be:



where M (x) = -δE/δψ(x) by definition. This would destroy homogeneity though, and so we wouldn’t have a straight-forward Gibbs-Duhem equation. The new chemical potential would look like this:



where q is the ‘charge’ connecting the particle to the field. So there.

**Patchy equilibrium potentials and extra d.o.f.**

Often our substance isn’t in equilibrium, but we can model it as the union of two or more systems which are themselves in equilibrium, just not with each other. One such case arises when we study plasmas, and we have an electron and ion gas which are approximated as being in equilibrium separately and then maybe interacting with each other. Defining the ‘velocity’ of the species k as **v**k = <**P**k>/<mk>, and for the sake of discussion, considering a position dependent field, more or less uniform over the species, then we may write:



where ψ1 could be the same as ψ2, or not. And equivalently, we may write:



and if energy is exchanged, volume exchanged, momentum exchanged, or particles exchanged (if relevant, and as long as the systems are not coincident in this case), then we can see that these two entropy terms will combine to give rise to the usual equilibrium entropy, as a function of a single E, V, **P**, N, ψ1, ψ2.

**Ex.**

One case where different fields would be relevant is when we work with compartmentalized ionic solutions in an electric field. Then we could write:



Anyway, this is a convenient way to split up the system. But of course this expression would contain non-equilibrium contributions to the energy I suppose, since the equilibrium conditions are not yet imposed. And this is evinced by the fact that there are too many variables present. In reality, Si, Vi, Ni are not true independent variables in the description of the system. Only S = S1 + S2, X = V1 + V2, N = N1 + N2, ψ1, ψ2 would be. And of course this follows from the equilibrium conditions that T1 = T2, μ1 = μ2, etc. And N1, N2 would be determined as a consequence of E(S,X,N,ψ1,ψ2). In particular Ni = (1/q)∂E/∂ψi.

**Ex.**

Another example would be a slender vertical tube connecting two larger containers at positions y1 and y2. We could write the energy of the gas as:



And this would be a formula that describes a range of situations beyond equilibrium. But again, only S, X, N, y1, and y2 are true independent variables.

**Ex.**

Though there isn’t necessarily a field involved, chemical reactions are another example. We can often write:



But only S, V and the *original* particle species numbers are truly independent variables.

**Ex.**

A further generalization of the former examples would be when there is a fully position dependent field. In that case the energy would be kind of be a ‘functional’ of ψ(x), noted as E(S,X,N,{ψ(x)}) I suppose. And we could write, assuming just a single species for now,



where m(x) would be the moment density at x. Again, for a lot of field problems, we know m(x) would be qn(x), or some variation on that, where q is the coupling constant of the particle to the field, i.e. m or q for gravitational or electric fields. I suppose m(x) would be just as legitimate a variable as ψ(x), and could be made a proper variable with the approximate Legendre transform – but it would be illegitimate to have *both* variables at once.