**Specializing to Equilibrium Systems**

The balance equations developed in the previous file are quite general, even if the term δSint. is a little vague. Let’s specialize to equilibrium (or at least close to) systems now. We are interested in some sort of formula for S, i.e., the entropy of a system when it is at is maximum value.

**Formula for equilibrium entropy: functional dependence of S on E, X, N, ψ**

Using a little quantum mechanics we can make some progress. Let E be the internal energy of the system. Let Xi stand for the various parameters of the system: like volume V, area A, or momenta **P**,and **L**. Let Nk stand for the number of particles of species k appearing in the system. Note that Nk may not be a degree of freedom of the system if chemical reactions are present. In that case only the initial values of these variables would be degrees of freedom. And last, let ψ stand for the various potentials (gravity, electric, ‘magnetic’). Note that position, **r**, only enters in through the field. Aside from the fields, these are the same parameters for which we wrote down balance equation in the previous file. Specifically, these parameters would be the ones that enter into the system’s energy eigenvalues through the Hamiltonian. Moving on, from quantum mechanics we know that a system possesses an array of allowed energy levels En(Xj,Nk,ψi). Once we specify the overall energy of the system, E, then we will have delimited the range of states that the system may occupy. And we propose that in equilibrium, the entropy (really, max entropy) will only depend on the number of states it can occupy, though precisely in which fashion we will refrain from speculating, until we get to Statistical Mechanics.

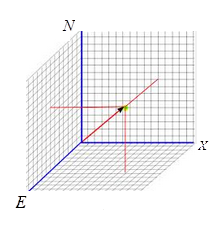


We will likely find that S is independent of some of these parameters. For instance S ought to be translationally invariant, and should also not depend on the bulk velocity of the substance – a fact we’ll take advantage of later. And I would suspect that a uniform field (or potential, rather) shouldn’t affect it either (as uniform field/potential means no field gradient → no force). What are the consequences of these symmetries I wonder? On a kind of tangential note: if a system obeys time reversal symmetry, then the entropy must be constant.

What about when the system is not in equilibrium? Well then this statement is manifestly false. For instance a gas undergoing a closed free-expansion has the same values of E, Xj, Nk, ψ­i at all times, yet its entropy changes continually (always increasing). So this statement can only hold in equilibrium. This suggests that when the system is not in equilibrium, the entropy depends on more variables than just the total energy, external parameters, and particle species numbers, and rather on additional internal variables, α, which would describe some internal structure possessed by the system: perhaps its temperature, pressure, or particle density *gradients*. So in the non-equilibrium case we might write S(E,Xj,Nk,ψi|α). For instance, if we have a system in local equilibrium, then S = ∫δs, where δs would be the entropies of the little parts. And the resultant formula could be expressed in terms of the overall E, X, N, ψi and αj = the temperature, force conjugates of the little pieces. Further, we can show, explicitly in some cases, that S is maximized when the αj all equal each other. The Landau free energy theories of magnetization are similar – they add an ‘order parameter’, usually the α = average spin or magnetization, which describes different classes of states the system may be in, for a given set of E, X, N, ψ. Going to the extreme, we could take a system constrained by E, X, N, ψ and simply rearrange and re-momentum-ize each particle at whim. Then α = microscopic state of the system = {(**r**i,**p**i)}. And we could ascertain what these positions/velocities would have to be in order to maximize entropy. But if we take this extreme approach, then we are back to N2L/quantum mechanics, which can be considered, in this context, to be extreme non-equilibrium thermodynamics.

**How to determine S(E,Xj,N­k,ψi) in principle**

Now suppose we had a substance and we wished to know what S(E,Xj,Nk,ψi) is. The way we could experimentally figure this out is through adroit use of the energy and entropy balances. We would have to start from some standard state E, Xj, Nk, ψi whose entropy we would label S0. E0 could be 0 if we wish since energy is only defined up to a constant.



I’ll imagine this on a 3D Cartesian grid, though the number of dimensions would really be greater than three if there are multiple X’s, N’s, or a ψ.

**Dependence on E**

We could determine S(E+dE,Xj,Nk,ψi) by adding some heat δQ at constant X, N. The change in energy and entropy would come from the balances:



(and so observe that in order to make δSint = 0 we have to make these changes in quasi-equilibrium manner) That would give us dS = dE/T. So as long as we keep track of T as well, we can plot out S as a function of E.

**Dependence on X**

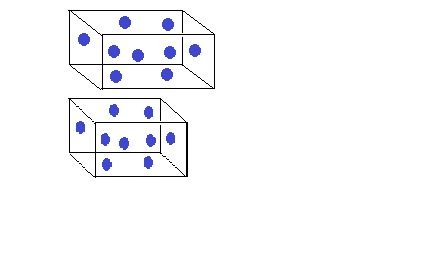
Now let’s suppose we want S(E,Xj+dXj,Nk,ψi). Then we want to change Xj by dXj without changing E by doing an amount of work δW. So we will allow the possibility of adding heat as well, since simply changing an external parameter will not alone change the entropy if it’s done quasi-statically. Then the balances would look like:



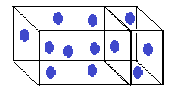
Keeping dE = 0 → δQ = -δW. And then filling this into the entropy balance we’d have dS = -δW/T. Note that this would require us to have a way of measuring how much heat we’ve delivered to a system, in order to make sure that δQ = -δW. Observe this prescription would work just as well regardless of whether X = V, A, **P**, or **L**.

**Dependence on Nk**

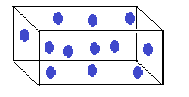
Now let’s suppose we want to know S(E,Xj,Nk+dNk,ψ­i). A way to do this is as follows. Take our box and adiabatically compress it by dV.



And then add a slice of particles dNk and volume dV, at same temperature, pressure, etc., so that no internal changes will occur when release the partition.



This will restore the volume to its original amount. Now remove the partition.



Removing the partition does not change the entropy because this is a reversible process – the situation before and after removing the partition looks the same. Note that if we have multiple species in our system we can still do this in a modified way. We would compress just the blue particles by using a semi-permeable membrane (permeable to all species except k). Then we would add a slice of just blue particles using a semi-permeable membrane as well. And then we would remove the membrane. Now we have to do all this without changing the energy. Allowing for the possibility of adding heat to the system as well, and putting this process into our balances, we have:



Now we’re supposed to do this with dE = 0 so this requires:



and plugging this into the entropy balance we’ll have our result for dS:



**Dependence on ψ**

Suppose we want to know how it changes upon adjustment of some field parameter, i.e. to ascertain what S(E,Xj,Nk,ψi+dψi) is. Have to carefully consider this one. So ψ stands for the field external to the system. If we’re looking at a dielectric/dimagnetic, then this would be the E/B field produced by free charges outside of the system, commonly denoted Ef/Bf (or, in uniform field case, could equate to D and H sans proportionality factors). If we’re looking at just a single atom within the dielectric/dimagnetic, then this would be the bulk interstitial field within the dielectric/dimagnetic, commonly denoted E/B). I’m going to presume the former case for the discussion to follow, but the latter case is exactly analogous. Changing ψ would ostensibly result in some sort of Energy change. But it doesn’t really make any sense to speak of the change of a system’s energy when we change the field, because only a constant, i.e., time-independent, field makes sense as a potential energy possessed solely by the particles within it. Well, we could have three different fields: gravity (not practically, but in principle), electric, magnetic. I guess I’ll consider all three of them. And we can write the Hamiltonian of a substance – say an insulator – in these fields, as (see e.g. QM/Many Particles/Identical Particles/Zeeman-Stark):



and Hint is something like,



where FWIW the density and polarization operators are (see Quantum Mechanics/Identical Particles/Stark-Zeeman file):



Note the Hamiltonian does not equate to energy. The actual internal energy of our substance would be modelled by Hint, whereas the last two terms in H are just how the substance ‘couples’ to the external fields, i.e., describes the forces the fields exert on our substance. Note that the external/free **B** does not couple to our H in the sense that the other two do, because it cannot do work on our system per se´ (as magnetic fields don’t do work); instead **B** shows up in the system’s internal energy via coupling to momentum and spin (it is essentially a kinetic energy term). Now **E**f(**r**) is the field produced by the ‘free charges’. It’s the external field. There would also ostensibly be an induced bound charge density which will give rise to a ‘bound charge’ field **E**b(**r**). But that would be implicitly present in Hint. The vector potential **A**(**r**) = **A**f(**r**) + **A**b(**r**) is the *total* vector potential comprising contributions from both the free external current, which produces **B**f(**r**), and the internal bound current which gives rise to **B**b(**r**). φg(**r**) is the gravitational potential. And it should also technically be the potential produced by ‘free’ masses – guess you could say, Earth, for example. Hint is the Hamiltonian associated with the internal energy of the insulator. It comprises the kinetic energy plus all the internal potential energies associated with the interactions between internal masses and charges, say. Might seem strange that **A**(**r**) and **B**(**r**), enter into the *internal* energy, since it is a field, and we would not normally think of internal energies as being coupled to external fields. Nonetheless it is so, since we should recall that (**p** – e**A)**/m is simply the physical velocity operator, **v**. And so we are just measuring kinetic energy, which is internal. Might demur that spin couples to magnetic field via -gγ**S**·**B** and so seems to an external ‘potential energy’ term. But I don’t think it is. For instance when we derive the Hamiltonian for a particle in a magnetic field, we naturally get the term -γ**L**·**B**, where γ = e/2m, from the kinetic energy, and so it seems to me that the -gγ**S**·**B** term should be thought of in similar fashion to -γ**L**·**B**, as measuring a sort of internal kinetic energy, that apparently only manifests itself in a magnetic field. Further, when we studied the Relativistic wave equation for the *free* particle, we saw that gγ**S**·**B** came out naturally upon making the substitution **p** → **p** – e**A**. So that, combined with the fact that it fucks everything up otherwise, I’m taking it to be part of the internal energy. One more comment: so increasing B will do work on the particles basically by tightening the radius of their orbits (constant B fields don’t do work, but changing ones do – via induced E from Faraday’s law). It basically squeezes them together, kind of like decreasing Volume does. That said, noting the formulas for the work these fields do (see first file in folder – or well, see Class Mech folder/Random file at end + EM folder/Insulating energy)



we could write the first law on our substance, focusing just on work accomplished by changing fields, as:



where Eint = Hint above, basically. Now we can fill this into the differential for our originally defined Hamiltonian H = Hint + [-∫**P**·**E**f + ∫ρφg]. And we’ll call the corresponding energy E´ = H. So,



and,



So we get:



If we include other forms of work, like mechanical, and also include particle transfer, then we may write:



So now we have a first law which tells us how our ‘energy’, so-defined, changes with field, and other processes. Remember though that this E´ is not a true energy; it’s the substance’s Hamiltonian, which is the sum of the substance’s true internal energy + terms which couple it to the external fields, which, since they change with time, cannot *truly* be considered as being part of the substance’s energy. And accordingly, the δW´ terms are not ‘real’ work, except for the magnetization guy.

In any event, going back to the measurement process, once we’ve augmented the field ψ → ψ + dψ, slowly, and allowed some heat transfer, we’d have:



So we’d measure δW´, and then make δQ = -δW´ so that dE´ = 0. And then we’d have from the entropy balance dS = δQ/T = -δW´/T. And so that would give us dS(E´,Xi,Nj,ψk+dψk). One drawback of this setup is that we would need to know not only how we varied the fields (not a problem I presume), but also how the mass density, polarization, and magnetization changed as well. But that’s probably not insurmountable. In a uniform free field, which is probably all we really care about, we’d have uniform polarization, magnetization, and these can probably be measured by hooking a circuit up to the thing and measuring RC, LR constants of current decay or whatever. Or we could just measure the total electric/magnetic fields within the sample, which would be related to polarization and magnetization via (presuming homogeneous fields, substances etc., where we can make identification of bound fields **E**b = -**P**/ε0 and **B**b = μ0**M** – see EM folder/Insulators for a discussion of this point) **B** = **B**f + μ0**M** and **E** = **E**f – **P**/ε0, where **E**f and **B**f are otherwise called, in this context, **D**/ε0 and μ0**H**.

Briefly, an alternative approach to all of this is to include the free fields within the system. Then there are technically no ‘external’ or ‘free’ fields to worry about, and so we don’t have any ambiguous energy-defining issues. The total Hamiltonian *would* be the energy of the system since there is no external changing field coupling and would be given by (see perhaps QM/Many Particles/Identical Particles/Zeeman again (leaving Gravity out this time, but see CM/Least Action Gravity file if want).



where Hint is something like,



(well technically, we must include the *kinetic* energies of the free particles too, but this is generally negligible, even if they form a current to supply the free magnetic field) And the 1st law would take the form (where Energy below corresponds to that measured by the H directly above).



where, if we have the requisite geometry and a homogeneous dielectric, we can equate **D** = **E**f/ε­0 and **H** = μ0**B**f. And these δWfield terms would be genuine work terms (see EM folder/Insulating Energy, etc.). Furthermore, we could calculate them fairly easily as they would just be the work required to charge the capacitor, or set up the free current in the solenoid. But we would, again, be including the energy of the fields themselves. So we’d basically be including radiation in our Hamiltonian. If we wanted to extract just the part say that corresponds to our substance, we’d still need to know **P**(r) and **M**(r), as can see in H. The next section would go here, but I can’t stand it when there is just a heading at the top of the page. I’m sure you agree. Yes of course I do; I’m me, and you. And so I’m going to add this extraneous pointless line, just to push it down a line. Ahhhh. Better.

**Introducing the conjugate variables: T, pj, μk,Mi**

Let’s consider equilibrium transformations of the entropy of the system. These are changes in E, Xj, Nk, ψi that leave the system in equilibrium, quasi-equilibrium changes in other words (well they apply to non-quasi equilibrium changes as well technically - since this is technically just a mathematical transformation – as long as the beginning and ending state are equilibrium states). In that case we will have:



where we’ve used a partial derivative identity in the second line. Now we’ll define the derivatives to be the temperature T, force conjugate pj (note pj would be the pressure, **v**, or **ω**, for X = V, **P**, or **L**), chemical potential μk, and moment Mi (which will be the -local mass density, local polarization density, or local magnetization density, in the respective context of gravitational, electric, and magnetic fields) respectively:



which makes our general equation for S look like:



The subscripts on the derivatives are there to remind us that we’re considering E as a function of S,Xj,Nk,ψi when taking the derivative, because later we might put E in terms of other variables so just writing ∂E/∂S alone for instance could be ambiguous. We should think of the collection of variables T, pj, μk, and Mi as just as good as the variables E, Xj, Nk, ψi in specifying the entropy (to some degree). And in fact it is usually easier to measure the conjugates.

**Interpretation of T**

It is profitable to look for a little less abstract interpretation of these parameters. The temperature T can be identified with the parameter T used in the last file in the entropy balance equation. How so? The definition above says T = ∂E/∂S)X,N,ψ. Keeping X, N, and ψ fixed in our formula above, we have that dS = dE/T. On the other hand, let’s consider the energy and entropy balances in the previous file. Keeping X, N, and ψ fixed in our balances, we’d have: dE = dQ (b/c no work or particle change so this is only term left), and dS = dQ/T. The last two together imply dS = dE/T. And so the two T’s must be the same.

**Interpretation of p**

Let’s consider the parameters p = ∂E/∂X)S,N,ψ. According to our formula for the entropy above, keeping S, N, and ψ, constant, we’d have dE = – pdX. Now looking at our energy and entropy balances we’d have: dE = dQ – pdX (where p is the force conjugate to X), and dS = dQ/T. But if dS = 0, then dQ = 0, which implies that dE = -pdX. So we see that the two p’s are the same. So while in equilibrium, the force conjugate p is simply the derivative above. But note that this only holds while in equilibrium. Out of equilibrium for instance, the pressure of a gas can be *much* different than what the expression p = ∂E/∂V)S,N,ψ would predict. Same goes for the other derivatives: **v** = ∂E/∂**P**)S,N,ψ, and **ω** = ∂E/∂**L**)S,N,ψ. A related observation is that if there is no heat transfer, then dW = dU. And if the entropy is kept constant, then dU = -pdV. So then dW = -pdV, if the entropy is constant. This is why pdV is often called the reversible work. But if work is done in such a way as doesn’t keep the entropy constant, i.e., irreversibly, then it could be quite different than pdV. Simple example being, if we were to almost instantaneously raise the lid of a gas to increase the volume from V → V + dV, the work done (on the gas) would be zero, because the lid would be going so fast, by presumption, as to not make contact with /exert force on any of the gas particles while moving. And yet pdV would be something for sure.

**Interpretation of μ**

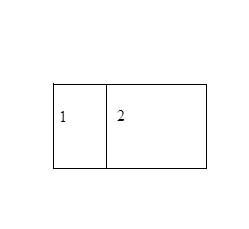
Let’s consider the chemical potential μ. According to the definition, it is μ = ∂E/∂N)S,X,ψ. Plugging this into our entropy formula above we’d have dE = μdN. Now according to our energy and entropy balances we’d have: dE = dW + dQ + EdN, and dS = dQ/T + SdN­ (note the dQ doesn’t come from the additional particles themselves, but from whatever heat we may have to add/subtract from the system to keep the entropy constant). Speaking of … since dS = 0 we have dQ = -SdN. Putting this into the energy balance we get: dE = (W + E – TS)dN. Comparing our result from our formula to our result from the balances, we can say μ = E + W – TS, which is basically the energy added to the system but subtracting off the heat necessary to extract to keep the system at constant entropy.

**Interpretation of M**

Finally we can consider M = -∂E/∂ψ)S,X,N. In the electric and magnetic field case, looking back on our expression for the (pseudo) work done on the system comprising the bound charges, we see that M would be P and, well, M respectively. If we have an inhomogeneous field, like ψ(x), then our relationship would read m(x) = -δE/δψ(x)|S,X,N, where δ/δ is a functional derivative. And m(x) would be the local moment. If we include the fields within the energy, then, m would be E/ε0 and μ0H, respectively. Might see the Quantum Mechanics/Identical Particles/Stark-Zeeman file for how this is consistent with not-including the external fields within the energy vis a vis calculating the polarization or magnetization density. This file is conspiring against me. Now I’ve got a heading at the bottom of *this* page. Take that!

**Measuring the conjugates**

We would like to consider how to measure the conjugates T, pj, μk, and Mi. Additionally we will establish some important results about interacting systems. First let’s consider temperature. Suppose we have two substances in thermal contact with each other so that they can exchange heat, but are otherwise isolated.



Then from our discussion in the previous file, we know that the combined system will attain equilibrium at maximum entropy. Technically, applying our entropy balance equation…



and from before we said that dSint./dt will increase internal entropy until it reaches maximum, if left alone. Let’s consider this process. So let’s consider S(E,X,N,ψ). We would like to determine the highest entropy equilibrium state available to the system. Note that we do not have to assume that the system explores these states in a quasi-equilibrium manner, but could fluctuate with non-zero dSint. between them. Proceeding…



where E is the total fixed amount of energy. Since the other variables are fixed, but E1 is free to vary, we must have:



And so we see that the T’s of systems in thermal contact with each other will eventually equate as they come to equilibrium. \*Note\* we implicitly assumed that we can separate the energy of the particles into E = E1 + E2, but if the particles are heavily interacting, this would be impossible. And so then we’d have E = E1 + E2 + E12, where E12 is some interaction potential energy. In that case, our formalism would yield:



Now generically speaking we would want to minimize E12 to maximize S2, since S grows with energy. This result makes sense because when we have two interacting objects, they will settle in the configuration which minimizes their interaction potential energy (think ball settling at bottom of a hill). And then once that’s been fixed, minimizing w/r to E1 would result in equation of temperatures.

Now suppose that the system could also exchange Xj with each other. For instance if they were two gasses they could exchange volume as if one expands then the other would contract, preserving total volume. Or the two systems could exchange translational or angular momentum (like with the viscosity example in the classical mechanics file, though for the moment, we’re not considering particle exchange (could still happen if just have two objects sliding past each other)). Then we could write…



So then, maximization requires the two partials equal zero. And so we’d have:



And so we see that the force conjugates p would also equal if their corresponding X’s are capable of exchange. The force conjugate of **P** is **v**, and force conjugate of **L** is **ω**; so this means that particle exchange would result in the velocities of the center of mass of the two systems leveling out, as well as their angular velocities – interesting! This provides us with another window into elastic/inelastic collisions. Suppose particles were exchangeable too, due to a permeable membrane perhaps. In that case we would straightforwardly conclude:



**Measuring T**

These findings suggest ways to measure a system’s T, p, and μ by comparing to a standard substance. For instance consider the temperature. And let’s suppose we have a gas in a piston or metal rod for instance, kept at constant pressure, which we’ll call the thermometer. If we place the thermometer in thermal contact with some body, it will absorb or give off heat to come to equilibrium with that body. And so the thermometer will expand or contract. And so we could correlate T with its length. We could say T\*= T0 + αΔL for instance. So this at least would give us *some* temperature scale. If we were interested in the *absolute* temperature scale, or at least the one we presently use, then we could use our thermometer on an ideal gas. We would find that V = Nkf(T\*)/p. And then we could simply *define* the absolute temperature T as f(T\*). In any event, with our thermometer in hand we could determine the temperature of any system. We would just have to make the thermometer small so it wouldn’t draw a lot of heat when placed in thermal contact with the system so that it wouldn’t change the temperature of the system as it’s measuring it.

**Measuring p**

Measuring the parameter p is usually straightforward, especially if it is just the pressure. But if necessary we could use a vial of gas with a piston top. Suppose we keep it insulated, and apply pressure to it. We could mark off the volumes corresponding to particular pressures. Then when we place it in contact with the system, it will directly measure the pressure. For the other X’s this would require measurement of **v** or **ω**, which is simple enough in principle.

**Measuring μ**

But now let’s consider μ. Perhaps easiest at this point would be to take the formula for μ that we will get later for the ideal gas. So we can presume that we know μ(T,p,N) for an ideal gas. Then we could just make part of the system we’re measuring semi-permeable to that particle species, stick the small empty vial on that membrane, and see how many particles fill it up. And we can measure the vial’s T, p, N therefore, and therefore its chemical potential will be known. And so then this must be the substance’s chemical potential as well.