**Non-Equilibrium Thermodynamics**

Now let’s consider non-equilibrium thermodynamics. This formalism basically closes the entropy balance equation by postulating a phenomenological expression for int. This makes all of our balance equations closed, and so will finally give us a way to determine the time dependence of the various parameters of a system as it approaches equilibrium. Up till now, the only way we were able to ascertain some information about the behavior of the system near equilibrium was to assume that the system’s internal processes were reversible, i.e., = 0. The basic idea was to form an expression for the entropy of the composite (supplemented by expressions for entropy of individual components if necessary): S(U,V,N;**η**) where **η** are all the extra parameters that could characterize the internal state of the system, and whose balance equations we knew. Then we filled this into the entropy balance equation. From this set, some we recognized some as pertaining to the Q/T term, some to the SI term. After crossing these out on both sides, we were left with the Sint term by itself.



So this takes the form of FαJα, where Fα is the difference in some intensive parameter (like temperature or pressure), and Jα some generalized current (i.e. heat, energy, momentum, etc.). Before, when looking for the equilibrium state, we would set both **F** and **J** equal to zero (or at least that was one way to do it). If we were looking for the approximately reversible fluctuations about the equilibrium state, we’d just set **F** = 0. But of course the fluctuations about equilibrium are not reversible, because the system does eventually settle into the equilibrium state. So at this point we use Onsager’s theorem.



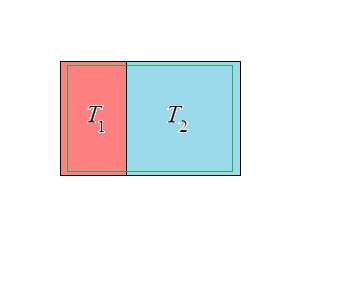
Onsager’s theorem states that close to equilibrium Jα will be proportional to Fβ so that we can write (Einstein summation notation) Jα = LαβFβ where Lαβ is symmetric matrix (this is the simplest way to guarantee positive entropy production). And then this phenomenological relationship(s) will provide us with the extra necessary info to solve for the time dependence of the system’s relaxation to equilibrium. This also explains why in our previous analysis, before NETD, to find the equilibrium state we set both J and F to zero, because if they’re proportional, then when one goes to zero so will the other. Note that there sometimes seems little motivation for a non-diagonal L, but it turns out that nature does frequently take advantage of these minimum requirements, and there frequently *are* cross terms in real experiments.

Final note: we must construct our system to include the non-equilibrium processes. If we have two interacting objects, but put our system boundary around just one of them, then we won’t be including the non-equilibrium heat transfer processes perhaps. On the other hand, doing just a global entropy balance sometimes won’t be restrictive enough (‘cause it could allow local irreversible entropy decreases – which is a no no – even while requiring increase in total irreversible entropy) and so it should sometimes be supplemented by a local balance as well.

Final final note: this procedure can be considered one intermediate to dealing with system purely in equilibrium, and ones purely out of equilibrium. I think this non-equilibrium thermodynamics we’re going to use only works when we’re still pretty close to global equilibrium. There are other formalisms which apply when we’re even further from equilibrium. In the extreme non-equilibrium case, we’d just have to resort back to classical/quantum mechanics proper.

**Heat Conduction**

Suppose we have two blocks at nearly identical initial temperatures T1 and T2­, separated by a barrier which nonetheless allows heat conduction. What would be the equilibrium temperature and when would they reach it?



We’d start with the relevant balance equations for the two compartments themselves,

Then we fill these into the entropy balance for the two compartments. Note the non-equilibrium entropy process occurs at the interface of the two blocks. So we would *have* to do an entropy balance on a control volume that includes the interface. So we would have:



Note that if we made the boundary skinnier, we still wouldn’t have heat flow across the outer boundaries because there would be no temperature difference between the inside and outside of the boundary. So then system 1 and 2 would just be the part of those guys within the boundary. Anyway, so then Onsager’s theorem is that the heat current is proportional to the ‘entropic’ force so:



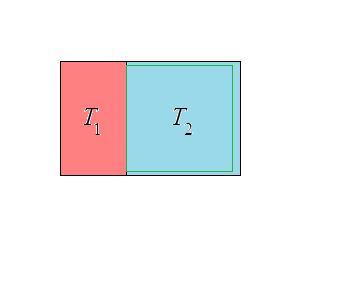
where ΔT = T2 – T1. And note we need the minus sign to ensure that int is positive (well presuming L is positive then). And this is just Fourier’s law. Note that our only requirement here is that int is positive and so we could’ve alternatively proposed = -LΔT/T1T2 or -L(ΔT)2/T1T22, etc., with suitable redefinitions of L. Our positive entropy production criterion provides no way of discriminating between these choices, really, but typically we just choose the simplest version, which is often, but not always, the choice nature makes too. Note that L is typically written in terms of more parameters, namely, L = kA/Δx, where k, A, Δx are the thermal conductivity, surface area and width of the conductor between the two substances (supposing there is one). Anyway, now we could go back and work out the behavior of the substances. And then with this equation we can solve for the temperature of the blocks as a function of time. Going back to the energy balance we have:

And we can solve for T1,2 as a function of time. Finally note that the time-independent state the system will finally settle into is indeed the equilibrium state, as setting the time-derivatives to zero → T1 = T2. Now I’m going to just experiment with different boundaries.

**Heat Conduction with control volume on just one compartment**

Let’s say we drew our boundary like this:



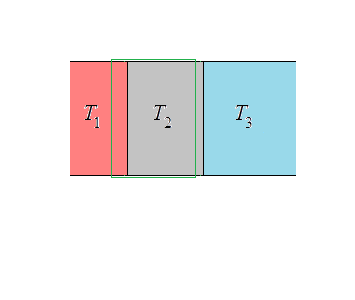
Now let’s see what we get:



So this works too, as we postulated each compartment is separately in equilibrium and so an entropy balance on either alone should give us Sint = 0. Problem is, we have no information about how the two compartments are equilibrating, and that’s why we need to enclose both.

**Heat Conduction with open borders on outside**

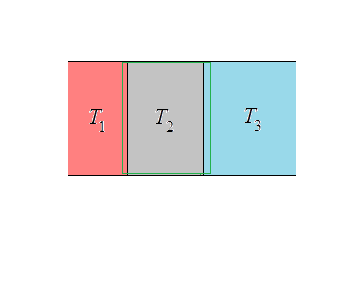
So suppose now we have three blocks connected to each other. We’d like to determine how their temperatures change. Note that we would have to make our control volume include the interface/s since otherwise there would be no non-equilibrium entropy production going on, given our assumption that the blocks themselves remain in equilibrium. For now, let’s suppose that we make it look like below:



Then we’d have (well S1,2 below would comprise just the part of 1,2 enclosed – whatever – and note that there will be no heat conduction through either (green) boundary because they split a constant temperature region)



So we get the analogous result as before. Now let’s shift the boundary again to enclose a little 1 and a little 3. Then we’ll treat the U1 and U3 referenced below as the energy of that part of the system enclosed with the green boundary.



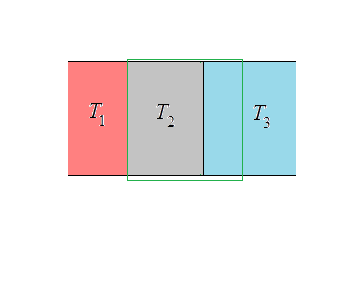
And then we’d have something like:



and so this would say that:



I believe we must have a separate relationship for each independent variable. Formally, one could say that there should be cross dependence, but I think we can rule that out on physical grounds, as interactions are only local. Further it is eminently reasonable that L1 = L2. Finally, let’s suppose that we made the boundary be right between the borders.



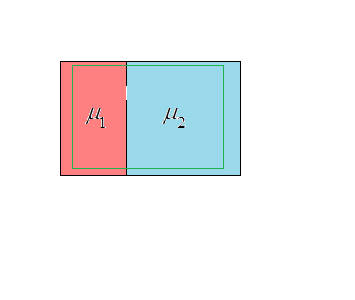
Note this time since the border straddles a temperature difference, there will be heat flux across it. Then we’d have:



as it should be again. So generally it appears we may make our system be whatever we want. But have to keep in mind that if we don’t enclose where the entropy production is happening, then we’ll just get Sint. = 0, which also is as it should be.

**Diffusion**

Now let’s look at two compartments with the same gas, say, but different initial densities, which gives rise to different initial chemical potentials, μ1 and μ2. We’ll suppose, nonetheless, that the chemical potentials are close, and we’d like to know how quickly the particles from the higher chemical potential will diffuse into the one with the lower chemical potential. I’ll presume they’re both at the same temperature however. The balance equations will obviously comprise an N and U. We might suppose that there should also be momentum balance equations for **P**. And since the center of mass of the system must shift, there must be momentum exchange between the compartments and also via the pressure of the walls of the compartments. But this momentum, should the diffusion be happening slowly, would be possessed by just a small fraction of the particles near the interface. To get into a little statistical mechanics, the momentum distribution of the particles would still be overwhelmingly Gaussian centered at zero, with just a little asymmetric bump on one end of the distribution (which end depending on which compartment). So basically the best approximation to the momentum probability distribution would be a Gaussian with average momentum centered at zero rather than one centered at its actual average momentum. So that’s what we do. And we could obviate this problem even by examining diffusion between two concentric spherical/cylindrical compartments (the inner one with radially symmetrically placed tiny holes in it of course to allow diffusion). That way the center of mass never shifts from the center and neither compartment ever acquires any momentum.



So the individual balances would look like,



where IU is total energy flux including particle current and pressure and heat if present (see Laws of Thermodynamics – either one – for information on definitions of these currents). Can say:

IU = IU1 – IU2 = (U1 + p1V1)I1 + 1 – (U2 + p2V2)I2 – 2, and I = I1 – I2, where IU1 is the energy flowing from compartment 1 to compartment 2, IU2 is the energy flowing from 2 to 1, and I1 is the current flowing from 1 to 2 and I2 is that flowing from 2 to 1. I’m supposing that the energy flow terms can comprise all possibilities: convective particle flux obviously, and concomittant pressure work (which would more likely be physically identified as diffusive energy flux if gasses are dilute), and heat possibly too. Even though there is no temperature difference between compartments, I believe there can be heat flux, at least in the technical sense of energy flow at zero net current. Now since heat flux is defined as energy flow at zero *net* current, the Q’s up above aren’t *really* heats when the two currents are considered together. Let’s separate IU into a term proportional to the net I = I1 – I2, and a remainder:



where Have is the average enthalpy (H = U + pV) per particle of the two components. The first term is just a definition and the second, is our heat term, which includes more than just the individual heat terms reckoned separately. Note we don’t have particle flow across the control volume boundaries since there is no difference in chemical potential across the boundary. But there will be across the systems’ boundary. So repeating the analysis, a global entropy balance would look like,



Then Onsager’s theorem is that the current is proportional to the entropic force so:



where L is some different coefficient. Now we could express μ(T,V,N), and since T, V are constant, we can write Δμ as proportional to Δn using Taylor series. For instance, for an ideal gas we’d have:



And assuming the temperatures are the same, then,



Filling this in, redefining L to absorb the extra factors, we’d get:



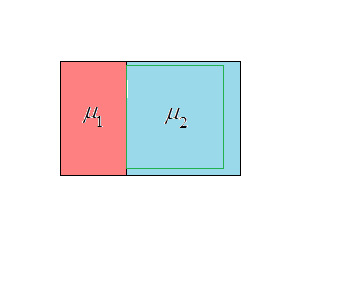
which is just Fick’s law, in the context of permeable membranes. P is the permeability (units are m/s) and A the surface area. Then we could plug this into the balance equations.

And so we could get N1,2 as a function of time. And then we could get U1,2 as well, since we’re assuming local equilibrium. And from that, we could then get IU if we wanted. So everything checks out.

**Diffusion with different control volume**

Let’s suppose we put the control volume boundary at the interface and consider a balance on 2 alone?



Now have to include the entropy transfer term SI on the RHS.



This is problematic. We have two particle/energy currents crossing the threshold (2 → 1 and 1 → 2). But we cannot have two entropy currents of the same species of particle. Can only be one current per particle species occupying same space – unless (see Thermodynamics folder/Equilibrium file discussion on entropy balance equation, or Stat Mech folder, Conservation Laws) the properties of each species are quite distinct vis a vis pressure, chemical potential, etc. But we can’t presume that either because our NETD formalism is only good for small changes in intensive parameters (so they have to be close to the same values). So we must presume these intensive parameters are almost identical. This amounts to neglecting ultimately 2nd order (in intensive parameter difference) contributions to IU (I is already 1st order in this, and the aforementioned differences in intensive parameters are additional 1st order things, so product is 2nd order). Then we’d have:



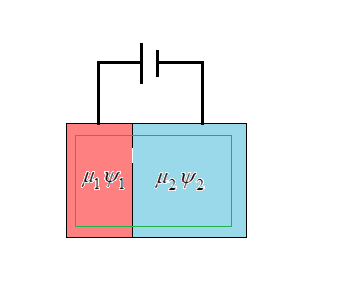
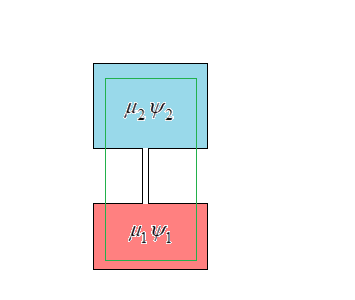
where again, H = U + pV is enthalpy, and we’re leaving off average because we’re presuming H1 and H2 are so close that we can approximate H1 or H2 by either, to our required order of accuracy, and so can just call it H. Proceeding,



where in the penultimate line we use an identity from the Equilibrium file for S, namely that S = U + pV – μ = H – μ . This is consistent with our presumption that our compartment was in quasi-equilibrium the entire time. Though actually, that doesn’t mean that there cannot be any Sint term *at all*. Really, this calculation probably doesn’t tell us too much because of the assumptions we have to make on the entropy current. Really, this calculation would only be good to first order in intensive parameter differences. And we already know that int is a second order term, as it’s the product of an intensive parameter difference and an associated current (which is presumed proportional to the intensive parameter difference as well).

**Diffusion in a force field**

Suppose go back to the pure diffusion case of two compartments prepared at initially different but close chemical potentials. And now suppose we add a force field to the mix, like with a battery (and can presume that the compartments are good conductors, say, so that the electric potential is uniform throughout perhaps) – or in the second case, a gravitational field (here we might imagine the compartments are small enough that the gravitational potential, gy, is uniform throughout. It seems kind of ambiguous whether a particle going from 1 to 2 should be carrying energy E1 or E2 into 2. But I believe that it must be carrying E1 into 2. First of all, it is certainly taking E1 out of 1, and so by overall energy conservation, this is the energy it must be carrying into 2. But secondly, consider the interface between 1 and 2 were finite, like with the gravitational field, and that the field ψ steadily ramps up from ψ1 to ψ2 in this region. Then the energy of the particle will change from (1/2)mv12 + qψ1 to (1/2)mv22 + qψ2, where v2 is the particle’s new velocity (slower if ψ2 > ψ1). But in any event, by energy conservation we’d have (1/2)mv12 + qψ1 = (1/2)v22 + qψ2 = E1. I’ll also presume **P** = 0, or close enough, at all times, just as we did in previous example. So…

The general balances would be:

again. And then carrying out the same procedure as before,



But note that the chemical potential is different than before since, presumably, for each compartment we have E(S,V,N,ψ) = U(S,V,N) + Nqψ. So we’d have:



Then Onsager’s theorem is that the current is proportional to the force so:



And from this we could work out the particle numbers in each box. But moving on, let’s observe that the entropy increase due to a current traversing a field is:



and in the context of charges flowing through an electric field we’d have:



And this makes sense b/c a wire at constant T is in a steady state, and so the entropy it generates should be equal to that which it loses (through heat loss dQ/dt, which is of course equal to IΔV).