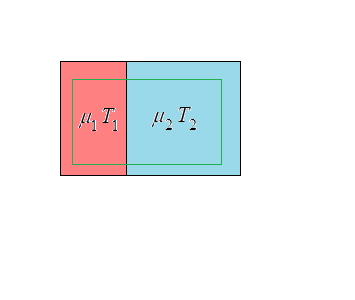
**Non-Equilibrium Thermodynamics**

Now want to examine some combined processes…as well as more miscellaneous ones.

**Heat Conduction and Diffusion**

Now suppose we have two containers at initial temperatures, chemical potentials: T1, μ1 and T2, μ2. And we suppose conduction to occur and diffusion as well. How will these occur? As before we’ll presume **P** = 0, as it is only the chemical potential and thermal gradients that evolve a **P**, and so the equilibrium distributions that characterize the separate compartments shouldn’t have it.



The balances…

where (see Laws of Thermodynamics file) IU = (U1 + p1V1)I1 + 1 – (U2 + p2V2)I2 – 2 perhaps, and I = I1 – I2. Again, the 1 and 2 terms are heat as defined via zero I1 and zero I2 respectively. But in conjunction, heat, , is defined as energy transfer at zero *net* current. So as in the previous file, need to write (well don’t *need* to, but):



where H is enthalpy of course. And then filling into the balance equations…



In order to separate out the effects, though, we will write: T2 = T1 + ΔT, and μ2 = μ1 + Δμ and do a Taylor series expansion:



Might note that Have – μ1 ≈ H1 – μ1 = TS1 (see Thermodynamic Potentials). And the ≈ kind of follows because the two systems have to be close to each other, from our linear non-equilibrium Thermodynamics formalism to apply. Well if so, then we can write H1 – μ1 + = TS1I + , which is the entropy transport out of region 1 I guess. This form is what we’ll find in the continuum transport file, where it is on surer footing. Mentioning it now, just for comparison’s sake. Anyway, so to make entropy production positive, we could say,



But there is a more general choice. So our entropy production rate takes the general form,



where,



Now instead of saying J1 = -L1F1 and J2 = -L2F2, we could instead allow cross terms whereby F2 might have a role in causing J1 and likewise F1 a role in causing J2. So we might say,



But we still must have that the entropy production rate is positive, so this puts restrictions on what the matrix L can be. The rate of entropy production is:



So in order to guarantee positive entropy production, the matrix **L** must be positive definite. This means it must have positive eigenvalues. So it’s generally taken that **L** is at least symmetric, i.e., L21 = L12, but this doesn’t alone necessitate positive eigenvalues, so…? Anyway, so we might say,



Note we can replace μ1 with μ2 or the average of the two (just as we can with the temperature) because the error made would be overall second order (since I is first order in intensive parameter difference already), and the equation is only meaningfull up to first order. It is reasonable that not just the heat, but the particle current too can depend on the temperature gradient, since a higher temperature in one compartment would certainly result in a net flow of particles in the direction of the smaller temperature since the higher T particles would be moving faster. And by same token it is reasonable that the heat current can now depend on Δμ as well as ΔT.

By the way, one defines the thermal conductivity proper as the proportionality between and ΔT when the particle current is zero. The latter condition is achieved by setting,



So filling that into the top equation,



And we can extract the cross section area of our sample to say,



where k is the so-called *thermal conductivity*. In the example with just heat conduction, our result was basically just L11/A. So we might imagine L122/L22 to be a small correction? Maybe it’s not small if we have mobile charge carriers. In any event, to work out the dynamics of the two systems, we would plug these equations into the balances,



and,



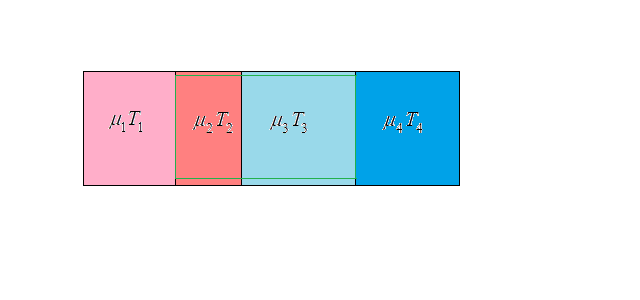
and for the second compartment,



And these equations suffice, since we have 4 unknowns: T1,2, N1,2, and four equations.

**Heat Conduction and Diffusion with open border on sides**

Consider the following setup. Let’s suppose the different compartments can be at different initial temperatures and chemical potentials. The particle current will conduct energy, and so that’ll be included in dU/dt. I’ll take my system to be just the middle two, which will leave out the entropy production terms between 1-2 and 3-4, but I want to see if we still get the same result for 2-3 that we did for the closed system above.



The balance equations would be:



And we’ll recall that we could write:



where the 12 on Have is to remind us that we’re averaging the enthalpies of particle sets 1 and 2. And then the entropy balance would look like…



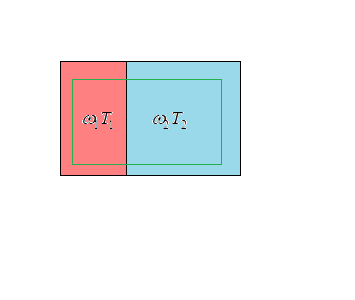
At this point, I think we have to say that the intensive properties of boxes 1 & 2, as well as 3 & 4, are similar enough to be identical, so that we can effectively form an expression for the entropy current, ‘cause again, we cannot have two different entropy currents when it’s the same species with similar properties (and properties must be similar because we’re near equilibrium). Might say then why not equate 2 and 3 as well. But…so gonna replace Have12 → H2 + p2V2 and Have34 → H3. And then also write IS12 = S2I12 (could say S1I12 but again, presuming no appreciable difference), and IS34 = S3I34.



which is equivalent to what I had before. But ostensibly it would seem that we must be missing terms ultimately 2nd order in the differences, and so not getting the entire Sint. Nonetheless this is the correct expression as can see from entropy balance on closed system. I think that the moral of the story is we really should be applying this formalism to strictly continuous systems, for which we can take the properties on either side of the boundary to be identical up to an infinitesimal error.

**Heat Conduction and Angular Momentum ‘Conduction’**

Now suppose we have two containers at initial temperatures, and mean angular velocities: T1, ω1 and T2, ω2. And we suppose conduction to occur, but no particle diffusion, while we suppose that angular momentum can diffuse from one compartment to the other. This can happen if the two do have some interaction at the border. How will these occur?



Our balance equations would be:

I think. So we know that angular momentum transfer is equal and opposite, and so the effective ‘torque’ is as well. And so is overall energy transfer. But this would mean that the rate of mechanical energy transfer and heat energy transfer are not themselves separately equal and opposite. Filling into the entropy balance,



Writing T2 = T1 + ΔT, and ω2 = ω1 + Δω, this comes to, to first order in the differences,



Then Onsager’s theorem is that the current is proportional to the force, but the currents can be proportional to cross forces too. So we may have (replacing usual Lαβ coefficients with kαβ):



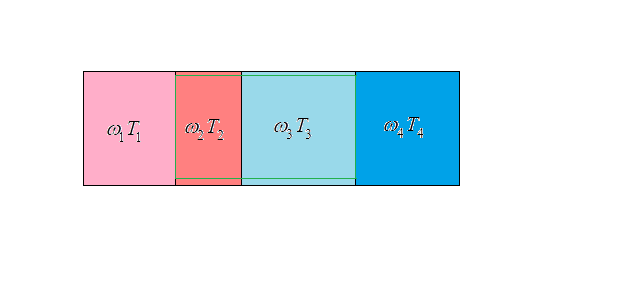
I would have a hard time imagining the off-diagonal terms are non-zero though. If we fill these, diagonal terms, say, back into the balances, we’d have:



Don’t really want to solve these. But suffice to say that when U and L are no longer changing, we must have ΔT = Δω = 0, which is reassuring, as that is what we expect on the basis of normal thermodynamics. A similar analysis should apply to translational momentum ‘collisions’.

**Heat Conduction and Angular Momentum Conduction with open border**

Now I want to do an open border calculation – meaning we can have angular momentum conduction through the ends of the border. Still not presuming particle flow though. So,



The balance equations would be:



And then the entropy balance would look like…note, again there is no convective particle current entropy so those terms are zero – but we do have diffusive entropy current.



This is same as we got before in the closed system.