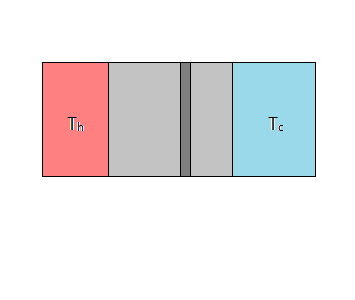
**Non-Equilibrium Thermodynamics on continuum**

Now I’m going to look at a few continuum cases. The NETD formalism probably works better here than in the finite case.

**Heat conduction**

Suppose that we just have a thermal conductor held between two different reservoirs. The conductor will come to some eventual steady state temperature profile, and we’d like to know what it is. As well how quickly it gets there, assuming some initial temperature.



Then we’d like to consider heat transport through the conductor, a piece of which I’ve isolated, between positions x and x + dx. Let’s consider the energy balance of this piece. We’ll presume we only have heat conduction, which means that we demand v = 0 throughout. And that n doesn’t change. So,



And plugging this into the entropy balance equation for this piece,



and so we have the entropy production term, and according to Onsager’s theorem, jq ~ L∇(1/T), which is equivalent to, redefining L,



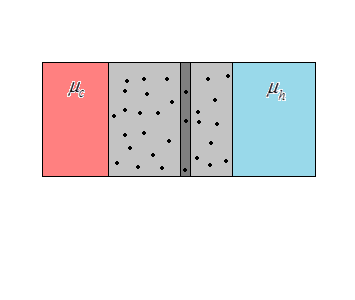
And we’d recognize L as the thermal conductivity, or well actually, L = kA where k is the thermal conductivity, and A is the area. Plugging this back into the energy balance we’d have:



Can also see from the equation that temperature will stop changing when L∇2T = 0, with boundary conditions that temperature must equal those reservoirs. Say we just wanted the steady-state situation. Then we could say du/dt is zero. But it doesn’t look like we could get very far starting from here. All we could say then is that the internal entropy production matches the external entropy flux. But it wouldn’t say jq ~ -∇T I don’t think. So I think we can only get the steady state stuff by going through the time-dependent stuff.

**Diffusion**

Now let’s say we have two reservoirs held at same temperature but different chemical potentials. We’ll have to presume that the conductor is now some sort of gas (could be electron gas in solid, or whatever) that can move in response to the chemical potential. So we’d like to work out what the final particle density profile will be. And would be nice to know the particle current as well.



Now we have diffusion thanks to the impurities present (that’s what those dots are), and these will seek to maintain/reimpose equilibrium. The local equilibrium function would be at temperature T, and chemical potential μ(r). Note that even though the gas will diffuse in a preferred direction thanks to the chemical potential gradient, and thereby acquire some current with average velocity v, this will not form part of the local equilibrium distribution feq, as the collisions seek rather to destroy this velocity. So we’ll just have: . Still, I’m going to throw the momentum balance in there just to see what it looks like. And the balances for this piece between x and x + dx would be:



Expanding the s(ε,n) entropy term and plugging in the balances, and using Ts = (ε + p – μn):



Solving for sint, and simplifying,



Now for sint we need only keep terms to 2nd order in smallness (the generalized currents should be 1st order, and the generalized forces, being proportional to those by Onsager’s theorem, will also be 1st order – and so the product 2nd order), as that is the limit of our calculation’s accuracy. In general, equilibrium quantities are zeroth order, non-equilibrium quantities/responses (like gradients of intensive parameters for instance) are 1st order, and *their* gradients smaller still at second order. So if we write this as:



it is clear that the first term is 2nd order, but the last two are 3rd order at least. So we can discard them. So now we have:



We could stop here and do Onsager, but I want to put this in terms of the chemical potential. So let’s use the Gibbs-Duhem equation: dp = sdT + ndμ (or can at least justify dπ can be replaced by dp because dp = ndμ, which is first order, and so -vdp is second order for sure). But since T is constant, we have:



And according to Onsager, we must have:



(and of course j = nv) and plugging them into the balance equations we get, recalling we can replace π with p to our requisite level of accuracy:

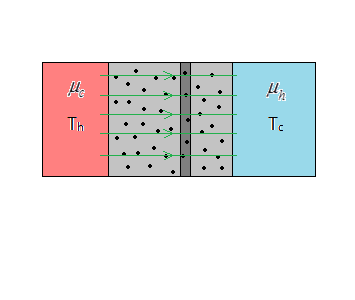


where n, T, μ, will all be functions of position of course. For instance, for an ideal gas, the solutions will take the form:



**Electrical, Thermal Conduction, etc.**

Suppose we add a constant (in time) force field, and some internal impurity things, held between two reservoirs at constant, but different, temperatures and chemical potentials. This would be like a battery, except we’d make the temperatures the same.



And let’s say that our particles are drifting rightwards in this force field, making (elastic) collisions with a stationary set of impurities, which I’ll assume for the sake of simplicity is truly rigid so that it doesn’t absorb any energy from the particles – all collisions are elastic, kind of like with the friction force. This is same implicit assumption I made above. And like above, the net velocity these particles acquire is caused by the temperature and chemical potential gradients (well, and Force, i.e., potential energy gradient sort of). So it is not an equilibrium property of the particles. Rather, the impurities, which scatter the particles, will attempt to return the partcles to equilibrium with a zero net/average speed. So like above, we’ll have s(ε,n) – not considering the force F to be some conservative field, but a perturbation disrupting equilibrium. Still going to display the momentum balance though. The balances would be:



Plugging the balances into the s balance, and using Ts = (ε + p – μn):



Now as in the previous example, I’ll write:



and neglect the 3rd order (at least) in smallness terms. Then we have:



We could stop here and collect our independent terms together:



and do the usual with Onsager’s theorem, setting jq proportional to the temperature and pressure/potential gradients, and v proportional to these as well (in different way of course). But instead of leaving it in terms of pressure, to make connection with the statistical mechanics analysis (see Stat Mech folder/Conduction), I’m going to put the pressure gradient in terms of the chemical potential gradient. We can do this with the Gibbs-Duhem equation, dp = sdT + ndμ. So then we have:



So then we must have, according to Onsager, the proportionality between currents and gradients is a symmetric matrix, L.



where s = ε + p – μn (but I’m leaving it as s to make better connection with stat mech). It is worthwhile to compare this result to the results we find in the Stat Mech/RTA conductivity or Boltzman conductivity files. They are quite analogous. Again (I) should not balk at there being more than just jq in that energy current on the LHS. Even just a temperature gradient should give us a net velocity, and so current, and this will produce more than just a heat current, but also an energy flux current, etc. We can identify a lot of these coefficients. The proportionality between current and force is basically the conductivity, σ: if we were dealing with electrons in an electric field, then we’d have: L22 = -σT/e2, or in other words,



Let’s turn to the thermal conductivity. It’s the proportionality between heat current and temperature gradient at zero current. So we could say,



and plug into the first equation,



We can identify thermal conductivity k as:



All this matches up well with NESM, which will provide means to calculate these phenomenological transport coefficients. Now let’s consider the thermal power. It’s the coefficient between the electric field (presuming it’s the one responsible for the force, F), and the temperature gradient, at zero current: E = S∇T. Setting the current to zero, we already have found that,



So dividing by, e,



So we have:



These generic results congrue very well with the results for, and relationships between, these coefficients in the Statistical Mechanics folder.