**Balance Equations**

Now we’ll look at the entropy balance equation, which is called the H-theorem in this context

**2nd Law of Thermodynamics**

In this context, it’s called Boltzman’s H-theorem. Not everything should follow conservation laws. We know that entropy should always be increasing, at least in closed system. So Boltzman was able to prove a version of the 2nd law of thermodynamics starting from the two-particle interaction Boltzman equation. Entropy is typically defined as:



(see for example the Classical MFT file, where this was ultimately the definition) But shouldn’t it be?



This way it matches up with the formula for an ideal gas. For instance for a classical ideal gas we could write (now setting kB → 1):



which is correct. Might note that our result is translationally invariant too, since if replace k → (k-mu) we get same result. Anyway, I guess I’ll stick with the original expression for S though. I guess the difference is just that in their expression up top, all the gas particles are distinguishable in some sense, whereas when we subtract the kBlnN! term, we’re presuproposing the gas particles are indistinguishable. This term comes from the d3Nrd3Np 🡪 d3Nrd3Np/N! thing we do when treating particles as indistinguishable. So,



Actually, let’s consider just the entropy density:



So let’s take the derivative w/r to time,



Now we fill in the two-particle interaction + impurity interaction Boltzman equation (note this is the classical interaction term, not the *semi-classical* one, so if you want a quantum/low T equation, you’ll have to put *that* one in),



and do integrations by parts:



And then,



Where we use the continuity equation. And now,



Now consider the two particle collision term, which I’ll call int(2).



Note all variables are integrated over, so they’re all dummy variables. Going to call k to be k2. And k´ to be k´2.



Now switch k1 and k2. Since they’re dummy variables, we get the same thing:



Adding two together, and dividing by two, we get:



Then switch primed and unprimed variables:



where we note that the two W’s are the same, thanks to time-reversal symmetry. Now add our two expressions together, and divide by two:



Next we note that for any x and y, it is the case that [x-y][ln(x)-ln(y)] is non-negative. And so this term is always positive. Pretty cool. So this an internal entropy production term. Now consider the single particle collision term,



Can make same manipulations on the single particle collision term:



And so by the same token, this is always positive. So it’s also an entropy generation term. So we can combine the two into one total sint term, and write:



If we were to say, integrate both sides over r, we’d clearly get (since ∂/∂r would go away) dS/dt ≥ 0, in accordance with the 2nd law of Thermodynamics. But anyway, we can recognize that ∂/∂r term as an entropy transport term. I would expect the heat current jq to come out of this though. Hmmmmmm. Let’s introduce the average velocity **u**(r,t) that we used above/before. Then we can say:



So now we have:



So comparing to our expression from Thermodynamics (Laws of Thermodynamics / Continuum), the middle guy has to be jq/T. Well, I guess **j**q *could* be something else; we could add and subtract a term, Δ**j**, from **j**q, and as long as ∇·Δ**j** ≥ 0 at all times, then the extra term could be shoveled into int, and we say **j**q – Δ**j** would be our new heat current. But I guess we’ll go with it for now.



So we’d be saying that **j**q is basically the entropy transport, **j**s (× T) in the frame of reference where the average particle velocity, and therefore current, is zero. It does go to zero when we use f(**r**,**k**) = feq(**r**,**k**) = exp(-β(k2/2m + φ(r) – μ). Since then **u** = 0, and then the integrand is odd in **k**. So that checks out. And then we’d have:



**Comment**

Say we have a distribution f = f1 + f2, where 1 and 2 don’t overlap much at all. Almost all the properties, like energy density, energy current, etc., are linear, and so for any property A, we’d have <A> = ∫fA = ∫f1A + ∫f2A = <A>1 + <A>2. But for entropy is:



and so this doesn’t hold exactly. But if f1 and f2 are very non-overlapping then we have:



because in the third line, for whatever value of k we have f1 to be non-zero, f2 will be zero, and vice versa. So this means that entropy is approximately additive for even identical particles as long as their properties, i.e., distribution functions, are quite distinct?