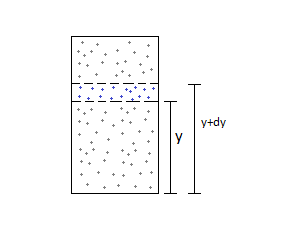
**Ideal Gas (mostly) in a Field**

Now I’d like to consider the characteristics of something equilibrating under the influence of an external field. The procedure we’ll use this time is a little bit different than last time. Last time we considered the system to be comprised of local equilibrium slices, and we will here too. But then we calculated the total entropy and maximized it subject to overall energy and particle number constraints. Here we’ll do it a little differently. We’ll write down the local balance equations and liberally set them to zero, as befits a time-dependent, equilibrium condition. But we can also calculate the int term and set *it* to zero, which should also be true in equilibrium. These conditions should all be equivalent to the entropy maximization procedure used before.

**Example. Substance in a field**

Wanna consider a general substance (though illustrated as ideal gas) in a vertical box, in a field, say gravitational ψ = gy, so that potential energy is φ = mψ. And want to see that we get the pressure equation to come out like we know it should, basically like Archimedes principle. To that end, I’m going to isolate the section between [y,y+dy] with imaginary partitions. And I’ll color it differently.



Like will do in the NETD continuum transport file, we can write the balance on the differential element:



(could’ve also used the momentum balance equation, but I’m not for some reason, just presuming it is zero the whole time instead) Plugging the balances into the s balance, and using Ts = (ε + p – μn):



Now let’s write this as:



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



We could stop here and collect our independent terms together:



As we’ll see when get to NETD, equilibrium requires all products of terms be zero. So,



So means T is constant throughout, and the pressure gradient is equal to the external force density. FWIW, the Gibbs-Duhem equation dp = sdT + ndμ = ndμ means that we can write the last one as:



With this information, we could say the local free energy density is, if we’ve a gas, f(x) = u(x) – Ts(x) = (f/2)n(x)kT - n(x)kln(Tf/2/n(x)Φ), and work out n(x) by using that ∇p = nF equation, or the chemical potential equation – whichever – and integrating to get F = ∫dx f(x).

**Example. Ideal Gas in a potential field reprised**

Now I’m going to do the same example, but going to whip out that momentum balance equation.



In equilibrium most of these terms are zero. We get:



So,



We found this same equation above. For a gas which is locally ideal, we could say,



Filling this in, we have:



Note that here T could still be position dependent. Only general entropy considerations (well, or local, as in the previous example) would tell us that it must be constant throughout.

So this is what we got above/previous file way back when. We used all the same pieces of information as there, just implicitly. We presumed eventually that the temperature T is constant throughout (this is the equivalent to maximization of entropy, or zero entropy production, vis a vis energy fluctuations), and we presumed a momentum balance/i.e., balance of forces (this is basically equivalent to maximization of entropy, or zero entropy production, vis a vis particle fluctuations, i.e., the chemical potential equation), and we presumed the ideal gas law p = nkT (this is same as presuming the ideal gas formula for chemical potential). Might stop to emphasize that the pressure is increasing, physically, as we go down the column, because the density of the gas is increasing. And it’s increasing at just the right rate as to make the pressure sufficient to ‘support’ the column of gas above it.

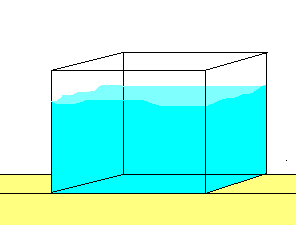
Well now that we have the pressure, p(y,T), we can say the internal energy density is:



and with this, we can get the entire internal energy by integrating U = ∫u(T,y)dy. And with the internal energy we can also get the entropy, Free Energy, etc.

**Example. Liquid under influence of gravity**

Consider a liquid under influence of gravity,



We can use the momentum balance equation (from Laws of Thermodynamics – continuum) to get the pressure variation with depth, even if we can’t get the more general thermodynamic potentials.



In equilibrium most of these terms are zero. We get:



π is the pressure tensor, which we can take to be diagonal, and in equilibrium. So,



(y is going in the vertical direction) A liquid is mostly incompressible. So we can therefore treat n(y) as constant.



In the constant gravitational field case, ψ(y) = gy of course, and we can write this as p = p0 – ρgy, which accords with the well known result (y is going down into fluid and would be negative; if we write y = -h, then it looks like the way this result is usually presented). Might stop to emphasize that the pressure is increasing, physically, as we go down the column, because the density of the liquid is increasing (ever so slightly). And it’s increasing at just the right rate as to make the pressure sufficient to ‘support’ the column of liquid above it. But a liquid’s density hardly has to increase at all to for the pressure to go up substantially.