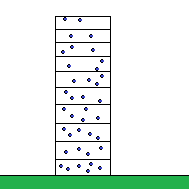
**Ideal Gas in Field**

Now I’d like to consider the characteristics of an ideal gas equilibrating under the influence of an external field. Procedure is as usual: we write down the known initial conditions, as well as known final conditions. Our procedure will be to propose that the system components are locally in equilibrium at some energy density u(x) and particle density n(x). From this we can get the local entropy density s(x). Then we’d get the total entropy S(x) = ∫dx s(x). Presuming overall energy conservation U = ∫dx u(x), and particle number conservation N = ∫dx n(x), this will give us an expression S(U,N,A,h|u(x),n(x)) for the total entropy in terms of U, N, A (area of box), h (height of box) and the unknown functions u(x), n(x) which describe the equilibrium state and non-equilibrium states. The equilibrium state will be distinguished from the non-equilibrium states by finding the u(x) and n(x) which maximize S. We’ll do this via functional minimization (or, maximization in this case).

**Example. Potentials for ideal gas in a gravity field**

Let’s try to predict what the potentials would be for an ideal gas in a possibly non-uniform gravitational field, such that potential energy is PEg = ∫ψ(y)λ(y)dy, where λ = dm(y)/dy = mdn(y)/dy is the linear mass density of the gas. In a uniform field, for instance, ψ(y) = gy. And let’s also try to get the density profile as well.



To facilitate the calculation, let’s imaginarily partition the gas into infinitesimal sections of height dy. And let’s say that the density of particles in each section is n(y), and has internal energy density u(y).

And we can write the entropy density, assuming local equilibrium, as:



where ε = u + mψ(y), and ε is the total energy density of the slice of gas at y, whereas u is the internal energy density at that point. The local entropy of the ideal gas should just be a function of kinetic energy of ideal gas. And so we can write the total entropy as:



where |n(y), u(y) means that our (as yet non-equilibrium) entropy expression depends on these additional variables. Now the equilibrium entropy is just the non-equilibrium entropy maximized w/r to its free internal variables at fixed volume and energy, i.e. maximized according to these constraints these constraints:



So we must find the n(y) and u(y) which maximizes S subject to the constraint of constant energy and particle number. So differentiating w/r to n we get:



Differentiating w/r to u we have:



I’m going to define -1/λ = T. Of course we can show that this T is just the actual temperature of the gas. Filling this into the n equation we have:



Applying the normalization condition we have:



We can define the integral:



So n(y) is given by:



and the internal energy density is:



What is the equilibrium entropy then? Filling in n(y) and u(y) we get:



Note that it is of course a function*al* of ψ(y). Now let’s put this in terms of the canonical variable E. So we would have:



And from here we can form the free energy.



Filling in υ(T,a,h,ψ(y)), we have:



So this is a neat result, which gives us an explicit example of the free energy being a function*al* of a field. We could get this result much more easily using Statistical Mechanics, but the fact we can get it at all, using just regular Thermodynamics, is pretty cool I think. Gonna take a moment to calculate the moment m(x) = δF/δψ.



Our use of letter m for moment is propitious since in this context it is the mass density as a function of height (x). Note m is really a function*al* of ψ as well. Calculating υ(T,A,h,ψ(y)) analytically would probably be next to impossible for most ψ(y)’s but still it can be done in principle. Well let’s specialize to a uniform field so that ψ(y) = gy. Then,



And so,



And,



And then F = E – TS.



which also is pretty neat. Could also write this as:



where Φ´ is a different constant. Let’s consider this (the highlighted) expression in the limit that h → 0. Then we have:



which is as we expect. It is the ideal gas free energy with a tiny correction due to the gravitational potential energy of the gas. What is the pressure of this gas at top? Well,



We’ve divided by A because ∂F/∂h would just give the force at the top. Must divide by A to get pressure then. Could also write this as:



And note that n(h)/A is just particles/unit volume at top. Written in this form it coincides with the ideal gas equation. Note that if g → 0 we get:



as required. Also, if h → 0 then we get the same thing basically. Let’s consider a different scenario: h → ∞. Then,



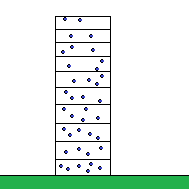
And in fact we can write S as a function of E, etc.,



Cool!

**Example. Ideal Gas in a gravity field reprised (little more general)**

Let’s do the same problem again, from a little more general perspective,



And consider our entropy equation again,



where s is the entropy density of an ideal gas. And recall again, that we must maximize entropy w/r to



So must do following, in general,



recalling differential relationship ds = du/T – (μ/T)dn (see Equilibrium Systems). Differentiating w/r to u we have,



So bottom guy says temperatures of all slices are the same, as we know is true in thermal equilibrium. So we’ll say λ = -1/T. And filling this into the top equation we have:



So far this has been completely general, and would apply to solids, or liquids, or gasses. But now we’ll fill in the ideal gas chemical potential.



Then supposing we know the pressure at x = 0, we can say:



which we’ll observe coheres with what we might expect from statistical mechanics. With the pressure, we can now get the potentials. Well, really the particle density would be better:



n(0) would be determined from the requirement that N = ∫0hn(y)dy. And then the entropy density is:



And then the total entropy would be:



Energy is:



and then of course we could get the free energy F = E – TS.

**Example. Obtaining Thermodynamic Potentials w/o Considerg g to be a Conservative Field**

I think it’s worthwhile to consider how we’d get the free energy, if we didn’t consider **g** as a potential field, but rather just as a force, which happens to be conservative. And we’d try to maximize S subject to first law constraint on energy change and then constant particle number too. So we’d have:



And then work is (see Equilibrium Systems file):



And must have W + Q = ΔU. Of course I’m presuming Q = 0 here, and so δU = δW. And also assuming δN = 0 overall. So we must find the u(y) and n(y) which maximize S subject to the energy balance and particle balance.



And so these equations define u in terms of ‘T’, and then n in terms of y, etc., just like before. And so then we could get s(u,n), integrate to get S, U, etc. Well proceeding, equating the coefficients of the differentials to zero, we see we have u,



I’m going to define -1/λ = T. And then the other equation yields:



Applying the normalization condition we have:



We can define the integral:



So n(y) is given by:



and the internal energy density is:



What is the equilibrium entropy then? We should find as before:



And for E we should likewise find::



And from here we can form the free energy.



as before.

**Example. Adiabatic Changes in g**

Consider a system with a uniform field, and h = ∞. Say we slowly change the field strength from g1 to g2, while keeping the system insulated. What would be the change in temperature of the system?

We have:



Well, for incremental changes, we can say, from the Equilibrium Systems file:



where E is the energy including the potential energy. Incrementing, we have:



So integrating our separable equation, we find:



We can write this as:



where C is some constant. A simpler route is to simply look at the entropy.



Then we see that keeping S constant while changing g, does indeed require T1+f/2/g = C. Say we doubled the field from gto 2g. How would T change?



Okay. If it’s oxygen, then this works out to 21/(1+5/2) = 21/(7/2) = 22/7.

**Example. Sudden Changes in g**

Say we *suddenly, and adiabatically,* change the field strength from g1 to g2, while keeping the system insulated. What would be the change in temperature of the system? What would be its change in entropy?

We’ll recall,



For sudden changes, we can say, from the Equilibrium Systems file:



where E is the energy including the potential energy. Working this out, we have:



So our equation reads:



And we can get the entropy change from the entropy formula.



Let’s say we doubled the field. What then?



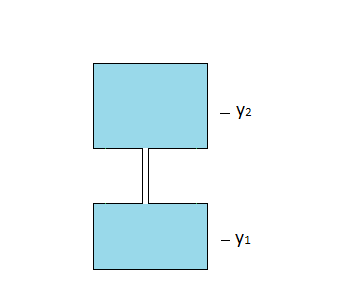
The argument of ln( ) is always greater than 1, so ΔS is always positive, reassuringly. What if we halve the field?



The argument of ln( ) is again greater than 1, so ΔS is always positive in this case too, as it should be.

**Example. Two compartment ideal gas in a potential field**

Say we had an ideal gas in a two-level container. We’ll say the containers are small enough that we can consider each to be at solely their indicated positions.



So say we have N particles of gas confined to some part of the container, given energy E. Then let’s work out how much would settle in the bottom part vs. top part, etc. So say in the bottom container we have gas given by E1 = U1 + N1gy1, N1 and in the top by E2 = N2gy2, N2. Then the state of the gas would be such as to maximize entropy. So we’d say:



where S1 and S2 are both the ideal gas entropy functions. And then we’d maximize this subject to energy and particle number constraints:



And so putting S in terms of the free independent variables, U1, N1, we have:



Now maximizing w/r to U1 we have:



So temperatures are equal of course. And more specifically, given s = knln[(1/ΦΦn)(2u/kfn)f/2] → T = 2U/fNk, we have:



Maximizing w/r to N1, we have:



where we use T1 = T2. Or, more specifically, using the formula for μ found in a previous file, we have:



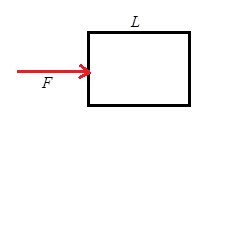
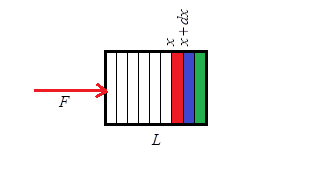
Using the energy equation, this simplifies a little to:



Well, we can at least solve these two equations for U1, N1 numerically if nothing else. I imagine that if we did this problem, but at constant T, rather than E, we’d find the relationship between the gas numbers would be according to canonical ensemble in stat mech.

**Example. Gas in an accelerated reference frame**

Consider the following contrived example. Suppose we have a gas box, initially at equilibrium, with volume V0, temperature T0 (room temperature), pressure p0 (atmospheric pressure presumably). But then suppose we push the box with a force F. What will be its length in the steady state case?

First, we could straight away appropriate our result apropos the gravitational field, and just replace g with ‘a’ = F/Nm, and h with L. In that case we’d have:



To determine L we would set the pressure A-1∂F/∂L = p0 at L = L,



This does reduce to the proper equation as F → 0. In that case:



Another way to do it would be to use the constitutive relations directly. How would things change if the gas were in an insulated box? Clearly it would come to equilibrium w/in itself and so we would just replace T as room temperature with T as internal temperature. But what would that T be?