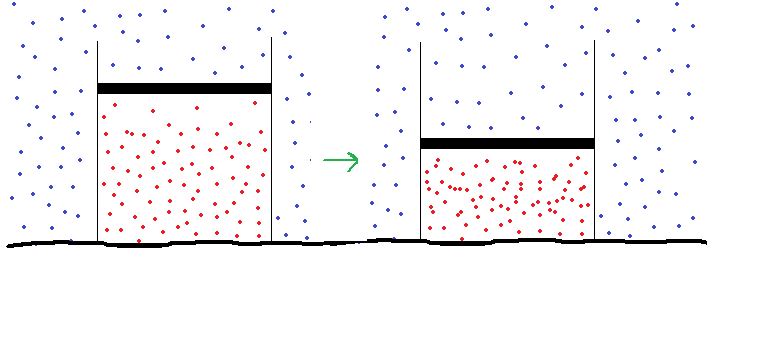
**Non-Equilibrium Thermodynamics**

Going to reprise some examples I did earlier, in the context of equilibrium thermodynamics.

**1. Gas and weight, open to environment**

Suppose we have a gas cylinder and we’re supporting a lid on top with mass mℓ. Let’s say it is initially at equilibrium at pgas0, Tgas0, and air also at pair0 , Tair0. And then we let the lid drop on the gas with initial energy/momentum Eℓ0, Pℓ0 (energy includes speed and height) and let it go. If the gas can exchange heat with the outside, what will be the final values of all these things after equilibrium is reestablished? And how would these things change while equilibrium is approached?



We did this example before, but assumed reversible fluctuations. Now we’ll not. So we have, for the various components (gas, lid, air):



where Q is the heat exchanged between the gas and the ambient air. And now we fill into the composite entropy balance:



Like before we presume the gas and air have already expanded to their max volumes. So we say: Vgas = Vℓ, Vair = V - Vℓ. And then…



But this equation is a little less restrictive than the situation actually is. As we’ll recall from our work on this problem before, we need to supplement this entropy balance with the ones for the individual compartments.

So to make all of these entropy terms positive, we could say:



And so we see that the p-π, and π-p guys must indeed separately be proportional to ℓ. Filling this into the momentum balance of the lid, we have:



Can see that this does predict the equilibrium value of the pressure pgas = pair + mℓg/A. To find oscillations can set Pℓ = mℓ/A, and,



Tair and pair are two extra unknowns, though related. To eliminate them, we can use the energy conservation equation, like we did in the equilibrium analysis in pervious file.



So we could solve for Tair in terms of Vℓ. Next, pair = NairkTair/(V-Vℓ). And so we can get pair in terms of Vℓ and now we’re all done. Practically speaking, though, Tair and pair would basically be constant, and we can solve the equation treating them so. The equilibrium volume is given by , which implies:



If look for the ODE that governs small oscillations about the equilibrium point, then we’d get:



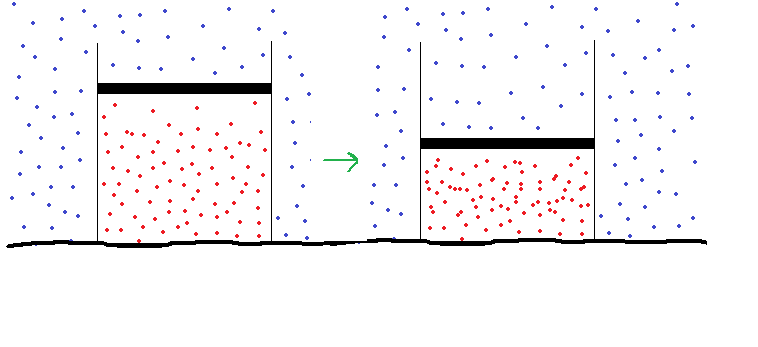
the solution to which is roughly:



So now we get the exponential decay to the equilibrium state that we knew we must have.

**2. Gas and weight, thermally isolated from environment**

Suppose we have a gas cylinder with a lid on top with mass mℓ. Let’s say it is initially at equilibrium where p0 = pair, T0 = Tair, and V0. And then we drop the lid on the gas and let it go. If it *can’t* exchange heat with the outside, what will be its new T1, p1, V1, after equilibrium is reestablished? And how would these things change while it approaches equilibrium? Let’s take the gas to be massless for the sake of discussion – doesn’t change anything essential.



We’ll start with balances on the three interacting objects again. These are mostly the same as before.



And now we fill into the composite entropy balance



where we will again presume that the gas and air have expanded to fill their respective volumes, and treat Vℓ, Uair, Ugas as independent variables. So,



Now at this point we would acknowledge that Vgas = Vℓ = V – Vair. And so,



Again we can supplement this equation with entropy balances on the individual compartments, like we did above, and demonstrate that each of the two terms in the last line must separately be positive. So we say:



We can then plug this into the lid balance equation as before:



Guess I won’t pursue this further though, except to say that this does clearly show the volume will exponentially decay to rest, such that we have:



as predicted by the equilibrium conditions before.

**Irreversible mechanical energy loss**

Suppose that we drop a block on the ground so that it comes to rest, or maybe slide it along the floor so that friction slows it down, and we’ll suppose there is no heat current either – remember friction doesn’t actually do any work because the ridges in the floor just ‘catch’ the ridges in the block, but the point of contact between the two doesn’t move. The easiest way to do this is to decouple the mechanical and internal energy, and so write the balances. So we would just write the energy balance as some sort of energy drain.



and then working out the entropy balance equation:



and so we’d have:



which makes sense of course. The other way could be like this. We’ll put Emech. and U back together,



And then we’d have S(E,V,P,N). And filling this into the entropy balance equation we’d have:



I guess at this point I could say that, well, **F**∙**v** = ∂Emech./∂t (which is certainly true from mechanical standpoint). And so we’re back to the original statement. Finally, note that Onsager’s criterion would give us a friction force postulate that **F** = -L**v**, which is true in the laminar air resistance case, though not in the surface friction case. But really, any formula whereby Sint is guaranteed to be positive would work, so we could just say: **F** = -L, which would match the surface friction situation.