A Story of

Thermodynamics and Statistical Mechanics series codename: effortBluePrint

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Abstract

This has been written at a time when physics majors had become too magical a place. Lets start shall we?

1 Unordered List

• In Clausious inequality, with half the process reversible, half irreversible, you're able to show that

$$\int \frac{dq}{T} \le \Delta S$$

then for a thermally isolated system, you say the lhs is zero and conclude that for such a system the entropy always increases. Now why wouldn't

$$\Delta S = \int \frac{dq_r}{T}$$

also =0 if the system is thermally isolated? [in case you've forgotten, you had resolved this with Diksha]

Comment: You had also using this, shown the equivalence (partly atleast) of the Careothedeory's statement of the first law.

- Kardar's page 101, why does the first order change in entropy, δS have to be zero for a given first order reversible change of coordinates by δx .
- Is entropy really a state function even when $\int dq/T$ is done on an irreversible path? What happens stat mechanically?
- How to map the $\oint dq/T < 0$ to the $\Delta S > 0$ in stat mechanics?

For now, I have to just ensure I don't use classical thermodynamics results and proceed.

I got some answers today. Here are the questions that got answered.

- Equivalence of Careotheodeory's statement and Kelvin's statement (partly) is essential. Then from Careotheodeory's statement, one can show extensivity of entropy. This way you know the entropy caused by bringing two systems separately at equilibrium into thermal contact. So what you learnt is that in thermodynamics, its easier to show Kelvin's statement and getting to careotheodeory's to show extensivity of entropy takes work. In statmech, the extensivity of entropy naturally pops and increase in entropy of two systems brought in contact is easier to calculate. However, to show that there's an increase in entropy when irreversible work is done on a system is not straight forward (atleast not obvious) in statmech, which was super simple in thermodynamics. So you need to complete the square.:)
- If we do work on a system with constant force (talking about thermodynamics), then $dW \leq J.\delta x$, where dW is the work done on the system. This is said to happen because there's dissapation. The work done is irreversible when the equality doesn't hold. But if I don't consider any dissepative forces, then were does the energy go? The answer is simply that in that case, δx will be a function time. It will keep oscilating and your thermodynamic coordinates won't be well defined.
- The previous problem was motivated by trying to construct the gibbs canonical ensamble.
 - The first part of this is that figuring how T and J are physically different and yet their mathematical formulation almost identical. The difference lies in the understanding that $\delta Q_1 = -\delta Q_2$ while the corresponding term for J being $\delta W_1 \neq -\delta W_2$ in general. So if we use the (and stupidly enough) first law of thermodynamics, then to make the analysis identical to that of the micro canonical ensamble, i'll have to come up with a system in which $\delta W = 0$.
 - But since we're doing statmech, when we make the system as shown (look at your notes, its just a box, with a diathermal wall, with a spring on the right side), we just need to write the hamiltonian. This is $H_1 + H_2 + U_{\rm spring}$. So this does it in principle! Your analysis is the same as that of the canonical ensamble, with $H_2^{\rm Old} = H_2 + U_{\rm spring}$. The paradox comes if you think of the first law and expect $E = {\rm const}$ while $dE \neq 0$ if you write $dE = dQ + dW = dW \neq 0$. The problem is that in thermodynamics, for the internal energy, we never considered 'potential energy' thus its change is not included. So yes. That's that. [this seems like non-sense now. We have dW so it must include work done by both the spring and (work done on) the system. Just that the work doesn't cancel because there's friction.]
 - Also, the system corresponding to the energy H is simply the same as gibbs, except that the diathermal wall is now adiabatic.
- I'm gettting a new class of doubts

— How are we modelling friction in our Hamiltonian? It seems to not matter at all!