

These notes arose from my attempt to be more rigorous and straightforward about entropy than, say, Baierlein. I also wanted to figure out why we defined $S = k_B \log \Omega$.

First, we need to make the second law of thermodynamics hold:

$$\Delta S \geq 0, \tag{1}$$

for an isolated system. So, we need S to be an increasing function of the multiplicity, Ω . Furthermore, let us assume that S is extensive; this clearly makes sense, since the multiplicity grows as N does. This turns out to have a nice consequence: assuming S is extensive gives us a definition of temperature (in thermal equilibrium).

If we have a system placed inside some other system, such that the composite system is isolated (so (1) applies) then we have

$$S_{tot} = S_{in} + S_{out},$$

so that at thermal equilibrium,

$$\frac{\partial S_{tot}}{\partial E_{in}} = \frac{\partial S_{in}(E_{in})}{\partial E_{in}} + \frac{\partial S_{out}(E_{tot} - E_{in})}{\partial E_{in}} = \frac{\partial S_{in}(E_{in})}{\partial E_{in}} - \frac{\partial S_{out}(E_{out})}{\partial E_{out}} = 0,$$

or

$$f(T_{in}) = \frac{\partial S_{in}}{\partial E_{in}} = \frac{\partial S_{out}}{\partial E_{out}} = f(T_{out}). \tag{2}$$

This follows from the fact that $T_{in} = T_{out}$ expresses the condition for thermal equilibrium, but so does $\frac{\partial S_{in}}{\partial E_{in}} = \frac{\partial S_{out}}{\partial E_{out}}$, since this maximizes the entropy of the system. (The left side depends only on state variables for the inside, while the right depends only on state variables for the outside, so these must be functions of temperature).

We can arrive at this equation from another method, and in so doing gain information about $f(T)$. Say we have two systems in thermal contact with each other, but isolated from the rest of the universe. If $(\partial S_1/\partial E_1) > (\partial S_2/\partial E_2)$, then the total entropy will be increased if system 2 gives energy to system 1. But, this is just the statement that system 2 is hotter than system 1. So, $f(T)$ must be a decreasing function of only temperature (since this derivative alone determines hotness). We can now justify the “no work done” constraint on the derivative because if work is done, then we have $dE = dE_{work} + dE_{\Delta S}$, and this division can be chosen arbitrarily. The only way to learn about how to maximize total entropy through this derivative is by specifying that all energy changes go toward changing entropy; this is equivalent to no work being done.

This line of reasoning also shows that negative temperatures are hotter than positive ones.

Interestingly, in deriving this we never used the explicit form of S . We only used the fact that S is extensive and the second law of thermodynamics. However, these conditions are

equivalent to $S = k_B \log \Omega$. To see this, note that the second law of thermodynamics demands that S be an increasing function of only Ω : $S = g(\Omega)$. Then, since for a composite system we have $\Omega = \Omega_1 \Omega_2$, the extensivity of entropy demands that

$$g(\Omega_1 \Omega_2) = g(\Omega_1) + g(\Omega_2).$$

Since g increases monotonically with its argument, it has an inverse:

$$\Omega_1 \Omega_2 = g^{-1}(g(\Omega_1) + g(\Omega_2)) = g^{-1}(g(\Omega_1))g^{-1}(g(\Omega_2)).$$

So, we need to find a function $h = g^{-1}$ such that for any $a, b \in \mathbb{R}$, we get

$$h(a)h(b) = h(a + b).$$

(Technical note: this doesn't actually have to hold for all $a, b \in \mathbb{R}$, but rather only for those a, b that are in the range of g , that is, $a, b \in g(\mathbb{R}^+ \setminus \{0\})$. Below, we only assume that 0 is in this range, as well as a tiny interval containing 0 so we can take limits. However, this isn't really an assumption, since if $\Omega_1 = 1$ then we have $g(\Omega_2) = g(1) + g(\Omega_2)$, which proves that $g(1) = 0$, so 0 is in the range of g . Furthermore, since g is continuous, an interval containing 0 is in the range of g).

Note first that if $b = 0$ then

$$h(a)h(0) = h(a),$$

so that $h(0) = 1$. Next,

$$\begin{aligned} h'(x) &= \lim_{\delta \rightarrow 0} \frac{h(x + \delta) - h(x)}{\delta} \\ &= \lim_{\delta \rightarrow 0} \frac{h(x)h(\delta) - h(x)h(0)}{\delta} \\ &= \lim_{\delta \rightarrow 0} \frac{h(\delta) - h(0)}{\delta} h(x) \\ &= h'(0)h(x). \end{aligned}$$

Solving this differential equation gives

$$h(x) = e^{x/k_B},$$

where $k_B = 1/h'(0)$, so that

$$g(\Omega) = h^{-1}(\Omega) = k_B \log \Omega.$$

(This is the most general solution).

We now need to choose $f(T)$ to be consistent with historical convention for what defines temperature. For the best example from history, we go to the ideal gas:

$$E/N = \frac{3}{2}k_B T = \frac{\langle p_x^2 + p_y^2 + p_z^2 \rangle}{2m} = \frac{3\langle p_x^2 \rangle}{2m}, \quad PV = Nk_B T. \quad (3)$$

Fluctuations are negligible for a large system, so $\langle p_x^2 \rangle \approx \langle p_x \rangle^2$. Therefore, for most particles,

$$-c\sqrt{mk_B T} \leq p_x \leq c\sqrt{mk_B T},$$

for some constant $c > 0$. Similarly, we have

$$-L/2 \leq x \leq L/2.$$

So, the multiplicity for position $\Omega_{x,y,z} = V^N$, while the multiplicity for momentum is, for some constant $a > 0$,

$$\Omega_p = a(mk_B T)^{3N/2}.$$

Therefore,

$$\Omega = aV^N(mk_B T)^{3N/2},$$

and

$$S = k_B \log(aV^N(mk_B T)^{3N/2}) = k_B \log a + Nk_B \log V + \frac{3}{2}Nk_B \log(mk_B T).$$

Using the relation

$$T = \frac{2E}{3Nk_B},$$

we obtain

$$S = \text{stuff independent of } E + \frac{3}{2}Nk_B \log \frac{2Em}{3N},$$

or

$$S = \text{stuff independent of } E + \frac{3}{2}Nk_B \log E.$$

Therefore,

$$f(T) = \left(\frac{\partial S}{\partial E} \right)_{V, \text{ other external parameters}} = \frac{3Nk_B}{2E} = 1/T.$$

Since f is the same for every system (this follows from (2) and $T_1 = T_2$), this gives

$$\left(\frac{\partial S}{\partial E} \right)_{V, \text{ other external parameters}} = 1/T.$$

This equation holds whenever we have thermal equilibrium. Since reversible changes are slow and maintain thermal equilibrium, we have for reversible changes where no work is done:

$$dS = \bar{d}Q/T. \tag{4}$$

This is because $dE = \bar{d}Q + \bar{d}W$, and with fixed external parameters, $\bar{d}W = 0$, so that $dE = \bar{d}Q$.

The goal is now to prove that this relation holds for any reversible change. However, this follows from the fact that work is reversible, so that by definition $dS = 0$ for an adiabatic (only work-doing) change. Since S is a state variable (since multiplicity is), it does not matter if we first do an adiabatic change and then do work, or if we do it all at the same time, or anything else like that: the change in entropy is the same. So, for a reversible change we can separate the work-doing ($dS = 0$) and adiabatic ($dS = \bar{d}Q/T$) stages, proving (4) for

any reversible change. Note that (4) holds for our system under consideration; obviously, since the change is reversible ($dS_{tot} = 0$) we must have $dS_{restofuniverse} = -\bar{d}Q/T$.

Lastly, we wish to obtain

$$dS \geq \bar{d}Q/T$$

in general, where equality holds only for reversible processes. Suppose we have 2 systems in thermal contact; the composite system is isolated. Then, if a change occurs, we have

$$dS = dS_1 + dS_2 \geq 0,$$

with equality only for reversible processes. Now, suppose that system 2 is really big compared to system 1 (i.e. a reservoir), so that a little thermal change does not appreciably change the temperature of system 2, and neither does it displace it from equilibrium. Then, we may approximate this change in system 2 as reversible, so that

$$dS_2 = -\bar{d}Q/T,$$

where $\bar{d}Q$ is the amount of heat transferred *from* system 2 *to* system 1. Then, we have $dS_1 - \bar{d}Q/T \geq 0$, or

$$dS_1 \geq \frac{\bar{d}Q}{T}.$$

Since we can imagine such a composite system & reservoir setup for any system and for any process, we have proved that $dS \geq \bar{d}Q/T$ holds in general.

So, now we have, in general:

$$dE = \bar{d}Q + \bar{d}W \leq TdS + \bar{d}W,$$

where equality holds only for reversible processes. (Note: this only holds for positive temperature. If $T < 0$, then $TdS \leq \bar{d}Q$).

Now, assume that $\bar{d}W$ can be expressed in terms of exact differentials of state functions. For concreteness, assume $\bar{d}W = -PdV$. Then, we have

$$dE \leq TdS - PdV.$$

However, we can take an identical system reversibly from the initial to the final state. (Recall that the condition for reversibility is $dS = \bar{d}Q/T$, not $dS = 0$, so that we can in fact get from any initial state to any final state reversibly by adding heat/doing stuff really slowly). Since equality in the above equation holds in this case, and since all variables involved are state variables, equality must hold in general, even for irreversible processes:

$$dE = TdS - PdV.$$

We end with the reason why slow/reversible work doesn't change S : in this case, $\Delta S = q/T = 0$. Energy contributed is in the form of ordered work, such as moving a piston, and therefore doesn't change the multiplicity, as each possible microstate before the change would evolve in a deterministic way, under the influence of the work, into a given final microstate, so there is a 1-1 correspondence.