* Those continuous functions

Often in books you will see authors talk about the number of states in an energy *range* δU with some continuous function $\mathcal{D}(U)$ giving the density of states *per unit energy*.

Then $g(U) = \mathcal{D}(U)\,\delta U$

and so $$\log g(U) = \underset{\substack{\uparrow \\ \text{very big}}}{\log \mathcal{D}(U)} + \underset{\substack{\uparrow \\ \text{small}}}{\log \delta U}$$

so the uncertainty δU is essentially irrelevant for computing entropies at large-N

RESERVOIRS

Essentially, reservoirs are big honking chunks of stuff that a system gets in contact with.
Big enough that their temperature stays constant, for all intents and purposes.

This little (big) abstraction is very useful in doing thermal physics at constant temperature (compared, e.g., to doing it at constant energy!)

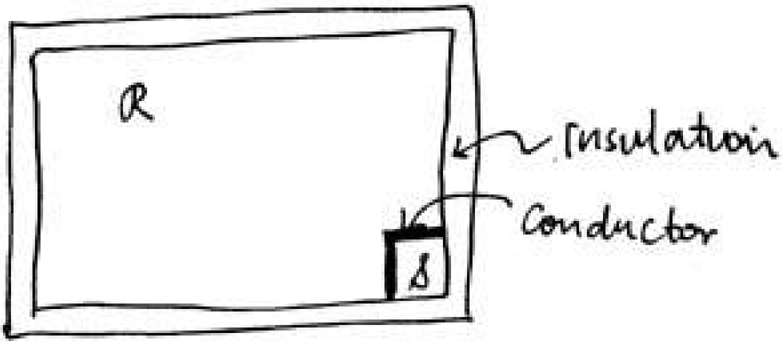
Suppose we are interested in a system $\mathcal{S}$, much smaller than the reservoir $\mathcal{R}$ but still with a macroscopic # of particles.

* Let's ask a *different* question than the ones we've asked so far:

If we want to know how likely we are to find $\mathcal{S}$ in state 1 with energy ε_1
as compared to state 2 " " ε_2,
what's the relative probability?

- The difference I emphasize here is that we're specifying precisely *which* quantum state the system $\mathcal{S}$ is in!

OK. Picture:



$$\left.\begin{array}{ll}\mathcal{R} \text{ has energy} & U_0-\varepsilon_1\\ \mathcal{S} & \varepsilon_1\end{array}\right\}\text{ if } \mathcal{S} \text{ is in state 1.}$$

Similarly if $\mathcal{S}$ is in state 2 ($\varepsilon_1 \to \varepsilon_2$).

Probabilities for the whole-banana system $R+S$ are normalized to unity

$\Rightarrow$ we can just use the ratio of degeneracies (we don't need to keep an overall factor $\frac{g_{tot}}{g_{tot}}=1$)

using $g_{tot} = g_R g_S$

$$\Rightarrow \frac{P(1)}{P(2)} = \frac{[g_R(U_0-\varepsilon_1)\cdot 1]}{[g_R(U_0-\varepsilon_2)\cdot 1]}$$

state of S is specified precisely in either state 1 or 2.

Now, let's phrase this as an entropy ratio : (KK p 61 footnote explains the math reason why)

$$\frac{P(1)}{P(2)} = \frac{\exp(\sigma_R(U_0-\varepsilon_1))}{\exp(\sigma_R(U_0-\varepsilon_2))} = \exp\left[\sigma_R(U_0-\varepsilon_1)-\sigma_R(U_0-\varepsilon_2)\right]$$

where we used $\sigma = \log g$ to get $g = \exp(\sigma)$.

- Physics: Since R is huge, $\exp(\sigma_R(U_0-\varepsilon_1))$ is not much different than $\exp(\sigma_R(U_0))$, because $\left|\frac{\varepsilon_1}{U_0}\right| \lll 1$.

Math: Let's expand σ in a Taylor series about $\varepsilon_{1,2}=0$.

For any nicely behaved function,

$$f(x+a) = f(x) + \left(\frac{\partial f}{\partial x}\right)_{a=0} a + \frac{1}{2!}\left(\frac{\partial^2 f}{\partial x^2}\right)_{a=0} a^2 + \ldots$$

Here, we will only need the first derivative tem

(and since σ_R depends on more variables usually than just U we need partial derv.)

$$\Rightarrow \sigma_R(U-\varepsilon_1) = \sigma_R(U) + \left(\frac{\partial \sigma_R}{\partial U}\right)_{N,V}(-\varepsilon_1) + \mathcal{O}(\varepsilon_1^2)$$

Then by the definition of fundamental temperature τ

$$\Rightarrow \left[\sigma_R(U_0-\varepsilon_1) - \sigma_R(U_0-\varepsilon_2)\right] = 0 - \varepsilon_1\left(\frac{1}{\tau}\right) + \varepsilon_2\left(\frac{1}{\tau}\right)$$

(the $\mathcal{O}(\varepsilon_i^2)$ terms go to zero as $N\to\infty$ by comparison)

$$\Rightarrow \frac{P(1)}{P(2)} = \exp\left(-\frac{\varepsilon_1}{\tau} + \frac{\varepsilon_2}{\tau}\right)$$

or

$$\boxed{\frac{P(1)}{P(2)} = \frac{\exp(-\varepsilon_1/\tau)}{\exp(-\varepsilon_2/\tau)}}$$

The factor $\exp(-\varepsilon/\tau)$ is called the **Boltzmann factor**.

This ↑ story will be VERY useful later on we derived for a system $\mathcal{S}$ in thermal contact with a reservoir $\mathcal{R}$ at fundamental temperature τ the relative probabilities of $\mathcal{S}$ being in a particular state 1 vs state 2

$$\frac{P(1)}{P(2)} = \frac{\exp(-\varepsilon_1/\tau)}{\exp(-\varepsilon_2/\tau)}$$

i.e. probability $P \propto \exp(-\varepsilon/\tau)$

PARTITION FUNCTION

This is a very useful object that we can use to compute thermodynamically interesting quantities

$$\circledast \quad \boxed{Z(\tau) = \sum_s e^{-\varepsilon_s/\tau}}$$

This is the sum over all states s of the system of the Boltzmann factor

unnormalized probability of being in a state s

Probability of being in state s in particular is

$$P(\varepsilon_s) = \frac{\exp(-\varepsilon_s/\tau)}{Z} \quad \Rightarrow \quad \sum_s P(\varepsilon_s) = 1 \ \checkmark$$

Notation: ε_s = energy of state s

$U = \langle \varepsilon \rangle \equiv$ average energy of system

average computed in the thermal (canonical) ensemble.

$$U = \sum_s \underbrace{P(\varepsilon_s)}_{\text{probability of being in state } s} \underbrace{\varepsilon_s}_{\text{energy of state } s}$$

* Now, a game we will often play is to use Z to compute interesting things.

Let's consider

$$\frac{\partial Z}{\partial \tau} = \frac{\partial}{\partial \tau} \sum_s e^{-\varepsilon_s/\tau}$$

$$= \sum_s e^{-\varepsilon_s/\tau} \left(\frac{+\varepsilon_s}{\tau^2} \right)$$

$$= \frac{1}{\tau^2} \sum_s \varepsilon_s e^{-\varepsilon_s/\tau} = \frac{1}{\tau^2} \underbrace{\sum_s \varepsilon_s \left(\frac{e^{-\varepsilon_s/\tau}}{Z} \right)}_{U} \cdot Z$$

So $$U = \tau^2 \frac{\partial Z}{\partial \tau} \frac{1}{Z} = \tau^2 \frac{\partial \log Z}{\partial \tau}$$

A quantity often useful is the heat capacity @ constant volume $\boxed{C_V = \left(\frac{\partial U}{\partial \tau} \right)_V}$

Application to 2-state system

* Partition function?

Let one state have zero energy, &
" second " " energy ε.

Then

$$Z = \exp(-0/\tau) + \exp(-\varepsilon/\tau)$$
$$= 1 + e^{-\varepsilon/\tau}$$

Probability of having zero energy is $P(0) = \dfrac{1}{1+e^{-\varepsilon/\tau}}$

energy ε is $P(\varepsilon) = \dfrac{e^{-\varepsilon/\tau}}{1+e^{-\varepsilon/\tau}}$

$< P(0)$ at all ε.

* Average energy?

$$U = \tau^2 \left(\frac{\partial \ln Z}{\partial \tau}\right) = \frac{\tau^2}{Z}\frac{\partial Z}{\partial \tau}$$

Now $\dfrac{\partial}{\partial \tau} Z = 0 + +\dfrac{\varepsilon}{\tau^2} e^{-\varepsilon/\tau}$

so $U = \varepsilon \dfrac{e^{-\varepsilon/\tau}}{(1+e^{-\varepsilon/\tau})}$

* Specific heat? (Constant Volume)

$$C_V = \left(\frac{\partial U}{\partial \tau}\right)_V = \text{(algebra, check this!)}$$
$$= \left(\frac{\varepsilon}{\tau}\right)^2 \frac{e^{-\varepsilon/\tau}}{[e^{-\varepsilon/\tau}+1]^2}$$