Entropy From Partition Fcns

- For simplicity consider the two state system again, though the results easily generalize.

We counted the number of configurations for N independent systems, with N_0 systems in the ground state and N_1 systems in the excited state, we found (slide)

$$\ln \Omega = \ln \frac{N!}{N_0! N_1!} \simeq -\sum_{i=0}^{1} N_i \ln \frac{N_i}{N}$$

The probability is $P_i = N_i / N$ to be in the i-th state. The number of configurations is then

grows linearly with N

$$\boxed{\ln \Omega = -N \sum_i P_i \ln P_i}$$

- Each independent subsystem that is added increases $\ln \Omega$ by a constant ammount on average

$$S = k \ln \Omega = N S_1$$

S_1 is defined as the entropy per cite. Also called S_{sys}.

Where

$$\frac{S_1}{k} \equiv -\langle \ln P_i \rangle = -\sum_i P_i \ln P_i$$

Now the prob to be in state - i is

$$P_i = \frac{e^{-\beta \varepsilon_i}}{Z}$$

$$-\ln P_i = \beta \varepsilon_i + \ln Z$$

So

$$\frac{S_1}{k} = -\langle \ln P_i \rangle = \langle \underbrace{\beta \varepsilon_i}_{\text{Const}} + \underbrace{\ln Z}_{\text{constant}} \rangle$$

☆ $\boxed{\frac{S_1}{k_B} = \beta U_1 + \ln Z}$, where $U_1 = \langle \varepsilon \rangle$ is the average energy of the syste

This gives a way to determine the entropy of a independent system: Find $\ln Z$ and find the mean energy $U_1 = -\partial \ln Z / \partial \beta$.

- The fundamental result is written in a couple of other ways -- take your pick:

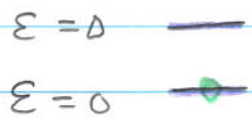
$$\boxed{\begin{aligned} &(1) \quad \ln Z = -\beta F \\ &(2) \quad F = -kT \ln Z \\ &(3) \quad Z = e^{-\beta F} \end{aligned}}$$

$F \equiv U - TS$

Free Energy

Ex 1 : Two State Again

- Pick a site (see slide), the remaining sites form a bath at temperature T. The sites partition function and energy are:



$$Z = 1 + e^{-\beta\Delta}$$

$$\ln Z = \ln(1 + e^{-\beta\Delta})$$

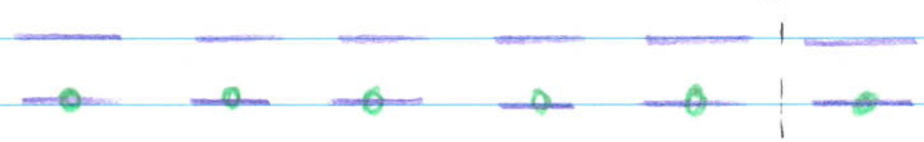
$$U_1 = \langle \varepsilon \rangle = \frac{\Delta e^{-\beta\Delta}}{1 + e^{-\beta\Delta}}$$

- Then the entropy from a single site is

$$\frac{S_1}{k} = \frac{\beta\Delta e^{-\beta\Delta}}{1 + e^{-\beta\Delta}} + \ln(1 + e^{-\beta\Delta})$$

This is graphed below

(1) This is shown in the following graph. In the low T limit all atoms are in the ground state

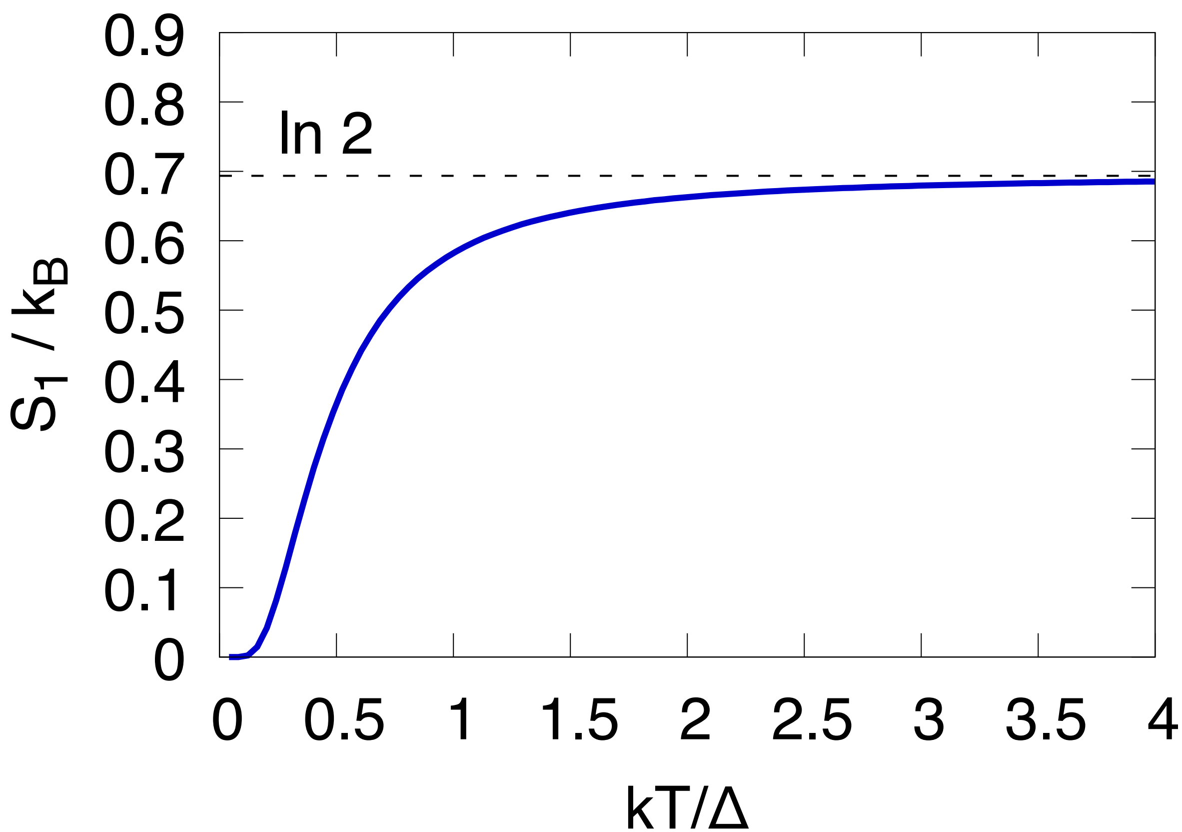


additional system in grnd state

The additional system does not increase $\Omega = 1$. And so $S_1 = 0$

(2) In the opposite limit each atom can be in either state, since $k_B T \gg \Delta$, without penalty

Entropy of Two State System



The number of states $2^N = \Omega$. Each additional atom gives on average a factor of 2 more states. So in this limit

$$\frac{S}{k} = \ln \Omega = N \ln 2 = N S_1$$

and we expect S_1 to approach $\ln 2$. This is what is seen in the graph.

- Mathematically at high Temperature $\beta \Delta \to 0$ and $e^{-\beta \Delta} \to 1$ so

$$S_1 \to 0 + \ln(1+1) = \ln 2$$