Entropy and Probability: The Boltzmann Factor

- In equilibrium each microstate is equally likely. So the probability to be in any single microstate is

$$\boxed{\mathbb{P}_m \equiv \frac{1}{\Omega_0(E)}}$$

For a six-sided die, there are six outcomes $\Omega_0 = 6$. The prob. of one is $\frac{1}{6}$

The "0" in $\Omega_0(E)$ and $S_0(E)$ notates the number of states when the energy *is not* partitioned.

- Now what is the probality of partitioning the energy into E_1 and E_2? There are many configurations with this partition of energy: $\Omega_1(E_1)\Omega_2(E_2)$ of them to be precise. Then since each outcome is equally likely, the probability of this partition is (see slides)

$$\boxed{P(E_1, E_2) = \Omega_1(E_1)\Omega_2(E_2)/\Omega_0(E)}$$

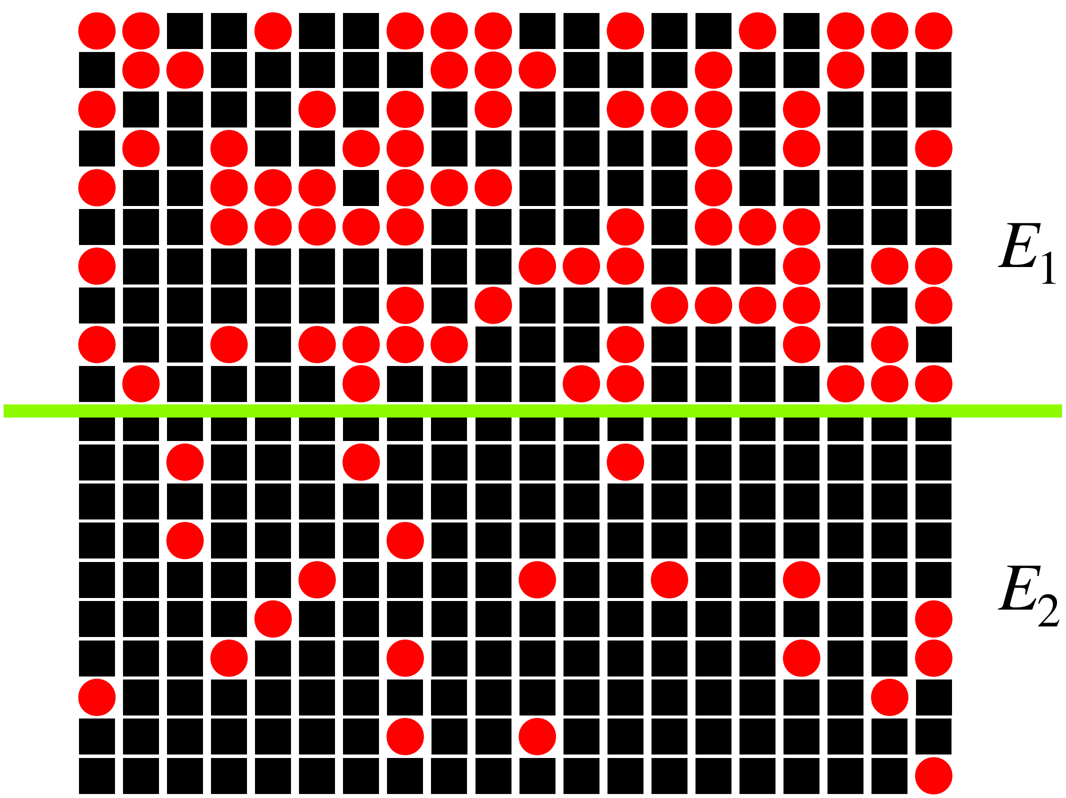
$$= \frac{\#\text{ of states with partitition } E_1 \text{ and } E_2}{\text{Total }\#\text{ of states with } E}$$

In terms of logs $S = k\ln\Omega$, $\Omega = e^{S/k}$ we have

$$\boxed{P(E_1, E_2) = \frac{e^{(S_1 + S_2)/k}}{e^{S_0/k}} = e^{(S_1 + S_2 - S_0)/k}}$$

The total energy is fixed so $S_0(E)$ is constant

Two thermalized states, separated by a partition



$E_1 = 80\,\Delta$

$E_2 = 20\,\Delta$

The macro state is

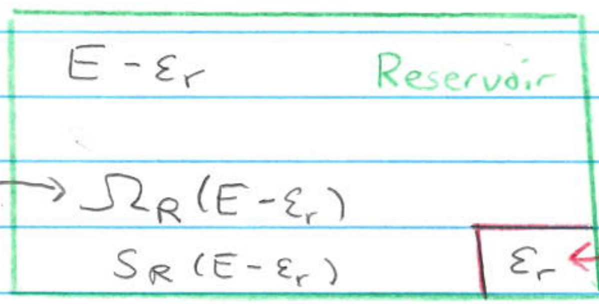
$$(E_1, E_2) = (80{,}20)$$

When the partition is removed the system hops exploring configurations with different partitions of energy.

- In Homework you will calculate the probability of partitioning 100 units of energy amongst the 400 of atoms.

- Now suppose we have a single small independent subsystem and require it be in a single state r with energy ε_r. The remaining subsystems form a large "reservoir". Since energy is conserved the energy of the reservoir is $E - \varepsilon_r$

Entropy of reservoir



Subsystem in one state

The probability of this partition is

$$P_r = P(E - \varepsilon_r, \varepsilon_r) = \frac{\Omega_R(E - \varepsilon_r) \cdot 1}{\Omega_0(E)}$$

this is a constant indep of ε_r

We are partitioning: $\Omega_1 = \Omega_R$, and $\Omega_2 = 1$ since system 2 is in a single state r

So the ratio of two probabilities for state #1 and #2 is:

$$\frac{P_1}{P_2} = \frac{\Omega_R(E - \varepsilon_1)}{\Omega_R(E - \varepsilon_2)} = e^{(S_R(E - \varepsilon_1) - S_R(E - \varepsilon_2))/k}$$

Now expand since $\partial S / \partial E = 1/T$ we have

$$\frac{S_R}{k}(E - \varepsilon_1) = \frac{S_R}{k}(E) - \frac{1}{k} \frac{\partial S_R}{\partial E} \varepsilon_1$$

$$= \frac{S_R}{k}(E) - \frac{\varepsilon_1}{kT}$$

So with an analogous result of ε_2 we find

$$\boxed{\frac{P_1}{P_2} = e^{-(\varepsilon_1 - \varepsilon_2)/kT}}$$

So up to a constant the probability to be in a state r with energy ε_r is:

$$P_r = \frac{1}{Z} e^{-\varepsilon_r / kT}$$

normalizing constant