

Equilibrium and Entropy

- Consider an ensemble of N two state systems



- For definiteness take $N=400$ with 100 of them excited. $N_0=300$ (number in ground state, state 0) and $N_1=100$ (Number in excited state, state 1). $\bar{n} = N_1/N = 1/4$ is the mean number of quanta of energy per site

$$E = N_1 \Delta = N \Delta \bar{n}(E)$$

- One way to share the N_1 units of energy amongst the atoms is shown on the next slide (a). It is not a typical configuration. A more typical configuration is shown in (b).

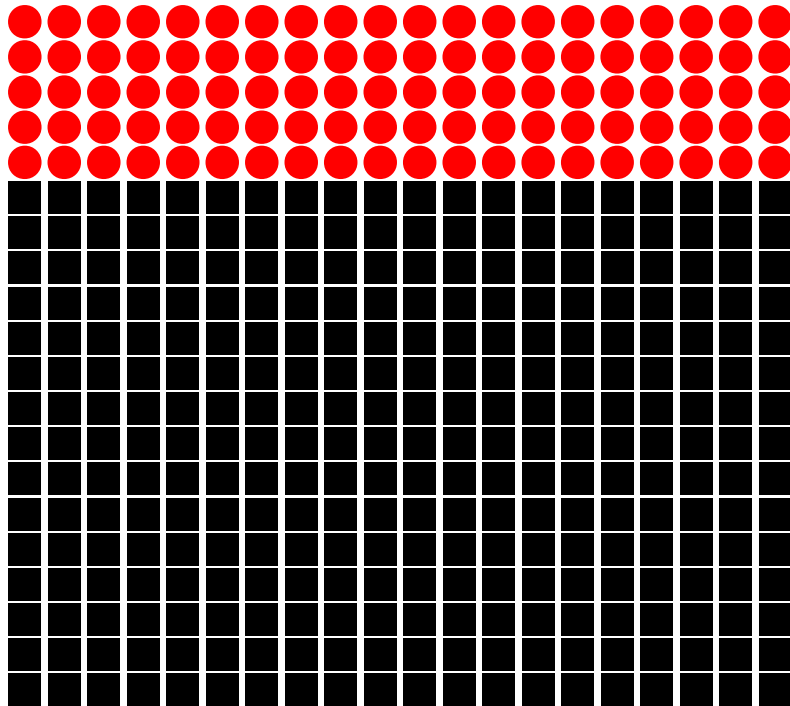
The two configurations (a) and (b) are known as "microstates", since the status of every particle is specified. If I just tell you the total energy E and number N , I have told you the "macro state"

(see slides)

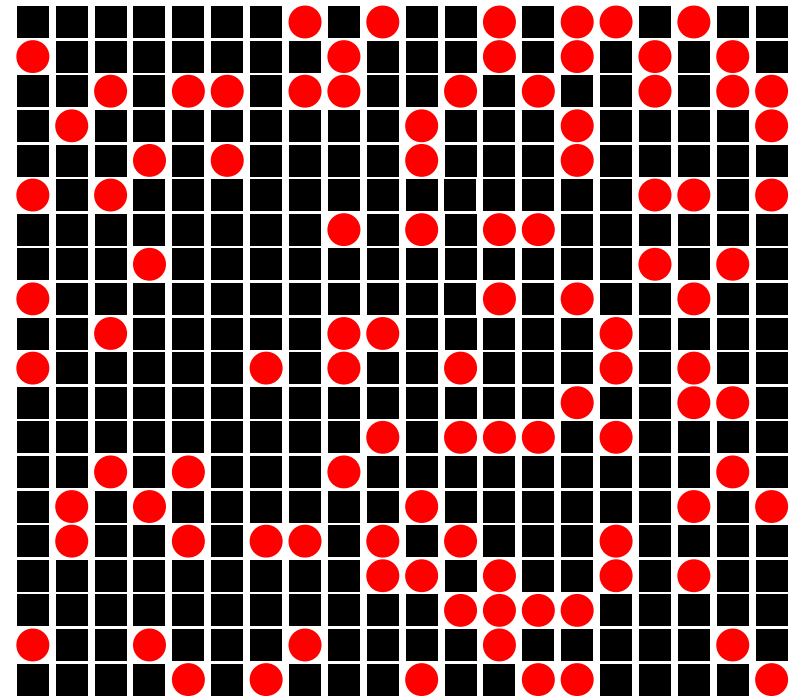
- Suppose at time $t=0$, I have an ordered macro-state as shown in (a). Then suppose I make a "hop" taking an excited state at random, and placing its energy into an atom in the ground state, chosen at random. This hop can happen: it conserves energy. The system can now be in one of 30,000 states

(see slide)

Ordered versus typical state: e^{225} states in total



Ordered state: 400 atoms, 1/4
are excited, $E = 100 \Delta$



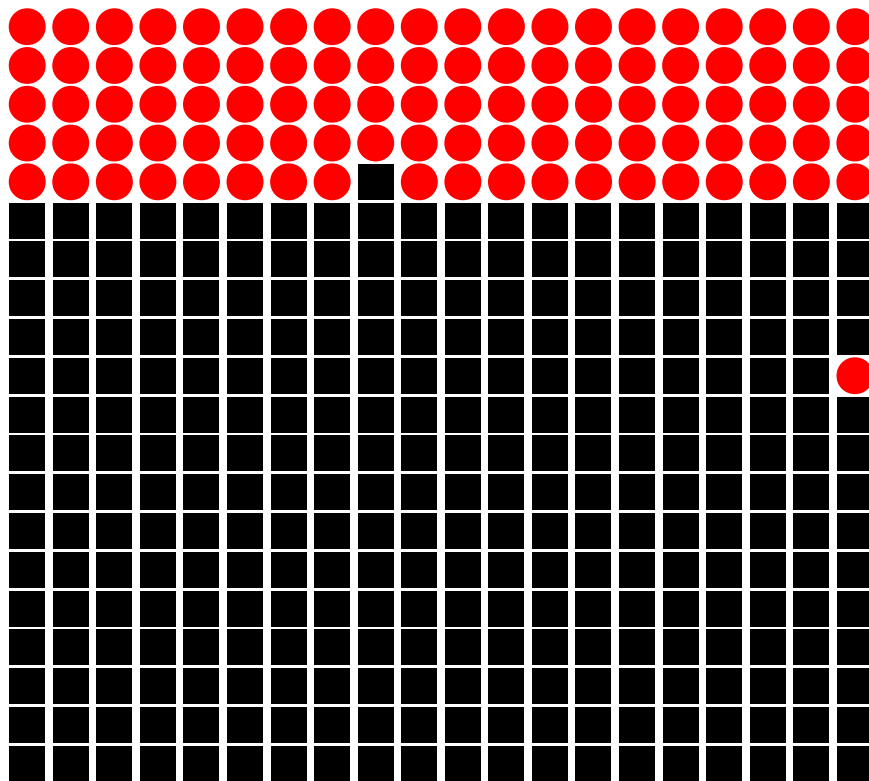
a typical state: the
energy is still, $E = 100 \Delta$

- After two hops the system is in one of about 800,000,000 microstates. After three hops the system is in about 25 trillion states, and so on. Each hop increases the # of possible states. We call this an increase in entropy
(see slides)
- The number of possibilities can not increase indefinitely. After a large number of hops the system can be in any of its $\Omega = e^{225}$ states with equal probability. This is the state of maximum number of possibilities (given the overall energy constraint) that we call the thermal equilibrium, i.e. maximal entropy
- Our goal is to use this idea of maximizing possibilities to understand temperature better; as we will see two systems have maximum # of possibilities when their temperatures are equal.
- We will show that the temperature here is related to the mean energy per site in this case

$$k_B T = \frac{\Delta}{\ln 3} \quad \text{or} \quad \beta \Delta = \ln 3$$

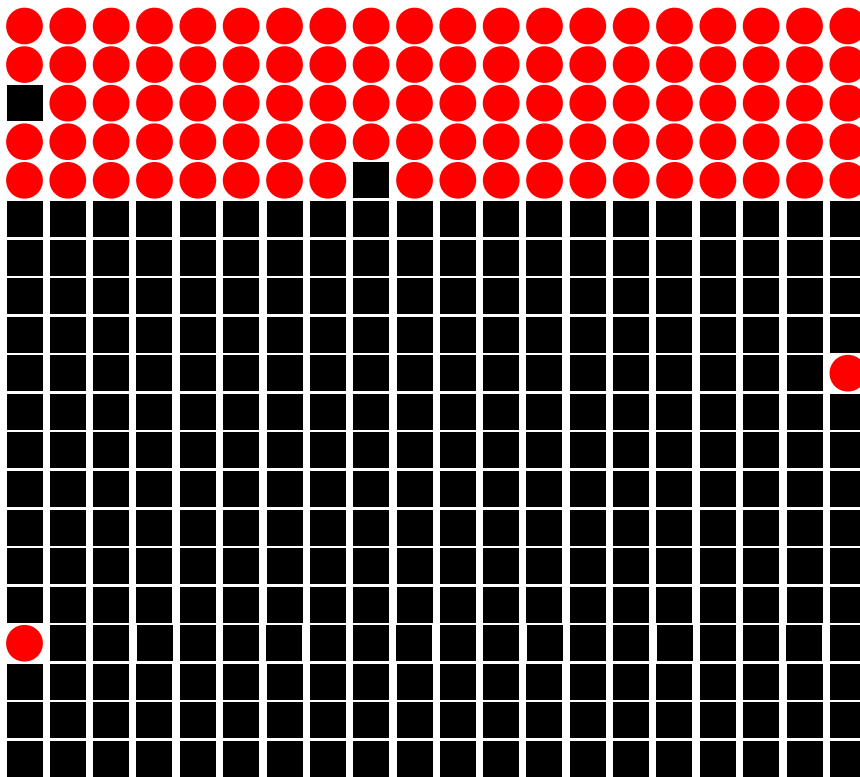
by counting the number of states.

Possible states after one “hop”



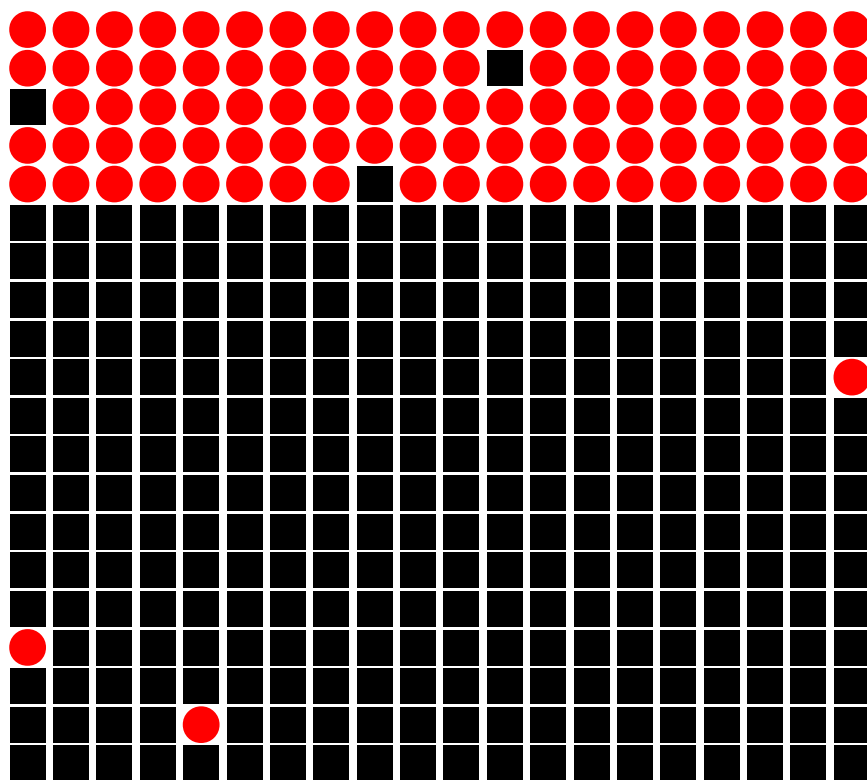
The system can now be in one of 30,000 micro states.

Possible states after two “hops”



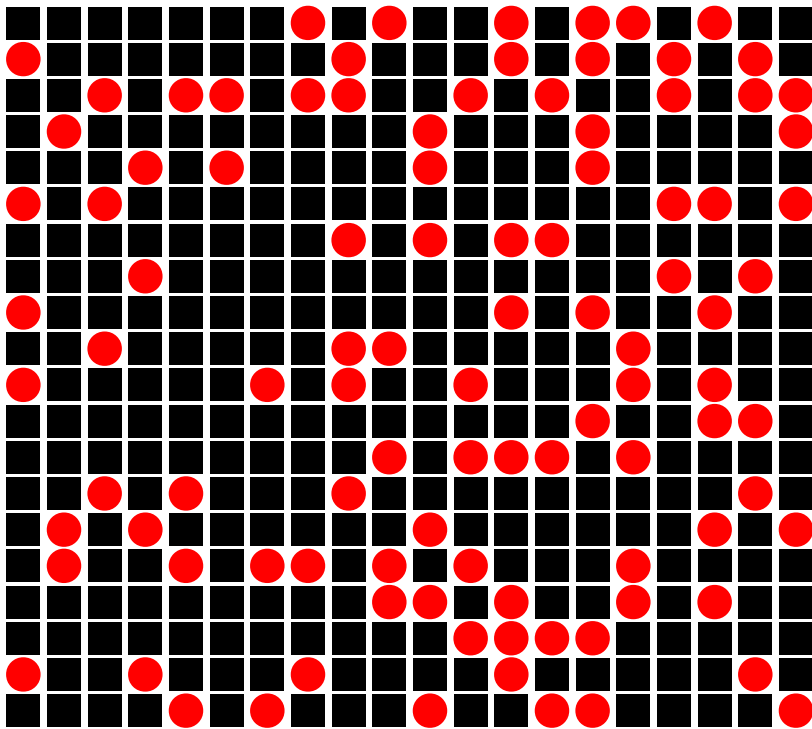
The system can now be in one of approximately 800 million states.

Possible states after three “hops”



The system can now be in one of approximately 25 trillion micro states.

After many “hops”, the system has “thermalized”



With the partition gone the system explores many new configurations

“thermalized” means that the system is equally likely to be in any of its e^{225} microstates

Micro canonical Ensemble

- First we have to count the number of microstates with energy in an interval $[E, E + \delta E]$ (This is hard and can only be done in three cases at this level)

$$\Omega(E) \equiv \text{number of microstates in interval } [E, E + \delta E]$$

In the homework problem we took $\delta E = \Delta$
And found $\Omega(E) = e^{225}$ for N two state systems

- In equilibrium, each state is equally likely.
So the probability to be in a microstate is:

$$P_m = \frac{1}{\Omega(E)}$$

For example for a six sided die there are six outcomes $\Omega = 6$ and the probability to roll any one of them is $1/6$.

- The entropy of the system is the log of the number of states up to a constant

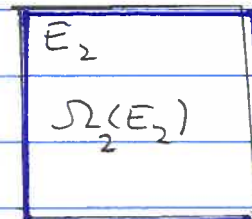
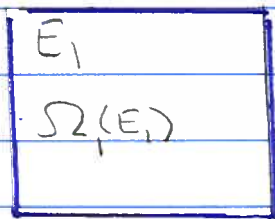
$$S \equiv k_B \ln \Omega(E) = -k_B \ln P_m$$

The constant k_B is a historical artifact of the Celsius scale. We will often quote S/k_B which is unitless

$$[S/k_B] = \text{unitless}$$

$$[S] = \text{J/K}$$

- Why do we care? Take two systems initially separated



System 1 has energy E_1 and can be in any of its $\Omega_1(E_1)$ micro-states; ditto for system 2.

- The total energy $E_1 + E_2 = E_{\text{tot}}$ is partitioned between the two subsystems. The partition of E_{tot} into E_1 and E_2 describes the macrostate of the total system, i.e. we are just specifying two macroscopic quantities E_1 and E_2 not the full state

- The number of microstates with E_1 in system 1 and E_2 in system 2 (i.e. with a specified macro state) is;

$$\Omega_{\text{Tot}}(E_1, E_2) = \Omega_1(E_1) \Omega_2(E_2)$$

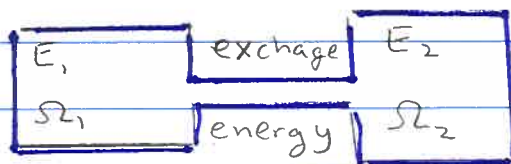
(Think about two six sided die the number of micro states of outcomes is 6×6)

- In terms of logs

$$\log \Omega_{\text{Tot}} = \log \Omega_1(E_1) + \log \Omega_2(E_2)$$

or
$$S_{\text{Tot}} = S_1(E_1) + S_2(E_2)$$

- Now imagine that the two systems exchange energy



The "hops" will increase the number of possible states since E_1 and E_2 can change. Only the sum is fixed, $E = E_1 + E_2$. The probability for a partition of E_{Tot} into E_1 and E_2 is

$$P_{\text{macro}}(E_1, E_2) = \Omega_1(E_1) \Omega_2(E_2) / \Omega(E)$$

$$= \frac{\text{\# of states with partition } E_1 \text{ and } E_2}{\text{Total \# of states with } E_{\text{Tot}}}$$

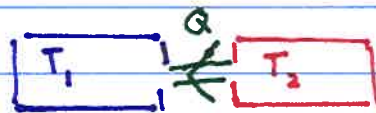
• As E_1 and E_2 change due to the leaks, the probability will increase as $\Omega_1(E_1) \Omega_2(E_2)$ increases or equivalent. In Ω_{TOT} or S_{TOT} increases ($\Omega(E)$ is fixed since $E = \text{const}$)

$$\frac{dS_{TOT}}{dt} = \frac{\partial S_1}{\partial E_1} \frac{dE_1}{dt} + \frac{\partial S_2}{\partial E_2} \frac{dE_2}{dt}$$

Since $E_1 + E_2 = E = \text{const}$, $\frac{dE_1}{dt} = -\frac{dE_2}{dt}$ and so

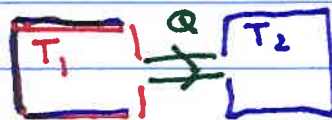
$$\frac{dS_{TOT}}{dt} = \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) \frac{dE_1}{dt} > 0$$

So if:



$\left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) > 0$ then energy will flow from right to left, $dE_1/dt > 0$. This corresponds to $T_2 > T_1$ or $\frac{1}{T_1} > \frac{1}{T_2}$

But if



$\left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) < 0$ then energy will flow from left to right, $dE_1/dt < 0$, $T_1 > T_2$
 $1/T_1 < 1/T_2$

Energy stops flowing when $\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$, i.e.

when entropy is maximized $S_{\text{Tot}} = S_1 + S_2$

$$dS_{\text{Tot}} = \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) dE_1 = 0$$

Thus it is very natural to define

$$\frac{\partial S}{\partial E} = k_B \frac{\partial \ln \Omega}{\partial E} = \frac{1}{T}$$

The state of maximal entropy (thermal equilibrium) is then when $T_1 = T_2$

- Further, we identify dE_1 as the energy absorbed and rethermalized as heat dQ , (aka energy shared amongst many constituents) thus we have

The second
Law

$$dS_1 = \frac{dQ_1}{T_1}$$

energy absorbed
by system 1
and rethermalized

Change of entropy
in system one

Thus measurements of heat flow can determine changes in entropy experimentally.