

Equilibrium & The Micro-Canonical Ensemble (Intro)

- Consider an ensemble of N quantum harmonic oscillators with frequency ω_0



- For definiteness take $N=400$ and assume that the energy is $E = q \hbar \omega_0$ with $q = 400$,
 $\bar{n} = q/N = 1$ (energy per site.)
- One way to share the q units of energy amongst the oscillators is shown on the next slide (a). It is not the typical configuration, a more typical way to share the energy is shown in panel (b). They have the same energy, and \bar{n}

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

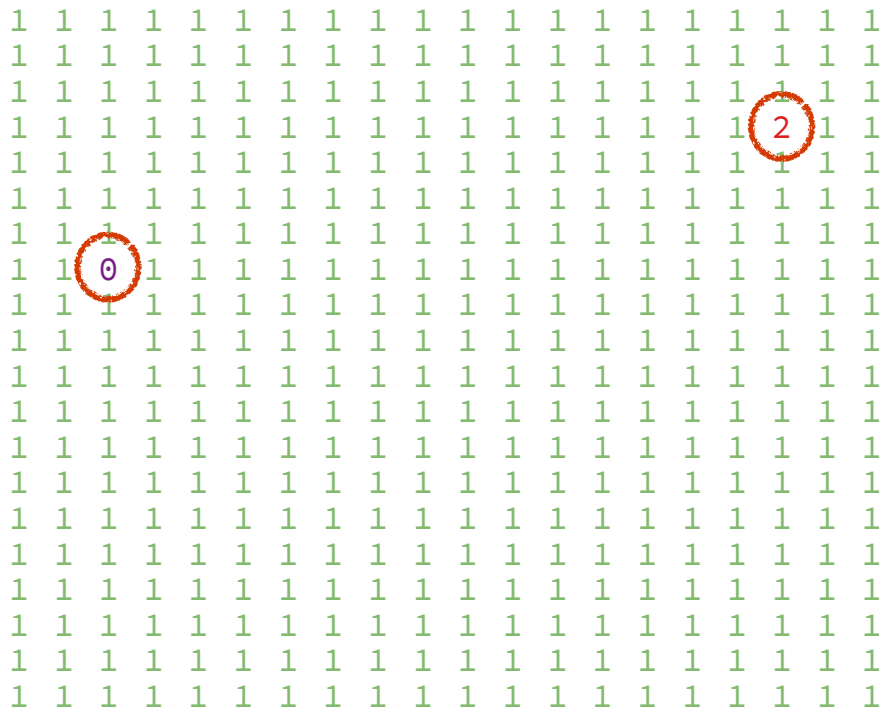
- Suppose at time $t=0$, I have an ordered macro-state as shown (a). Then suppose I make a "hop" taking one site at random and placing its energy in another (different) site chosen at random. The system can now be in one of $\frac{N(N-1)}{2} = 159,600$ states

- After two hops the system is in one of 25,472,160,000 microstates. After three hops the system is in 4000 trillion states, and so on. Each hop increases the # of possible states. We call this an increase in entropy
- The number of possibilities can not increase indefinitely. After a large number of hops the system can be in any of its $\Omega = e^{555}$ 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

$$k_B T = \frac{t w_0}{\ln 2} \quad \text{or} \quad \beta t w_0 = \ln 2$$

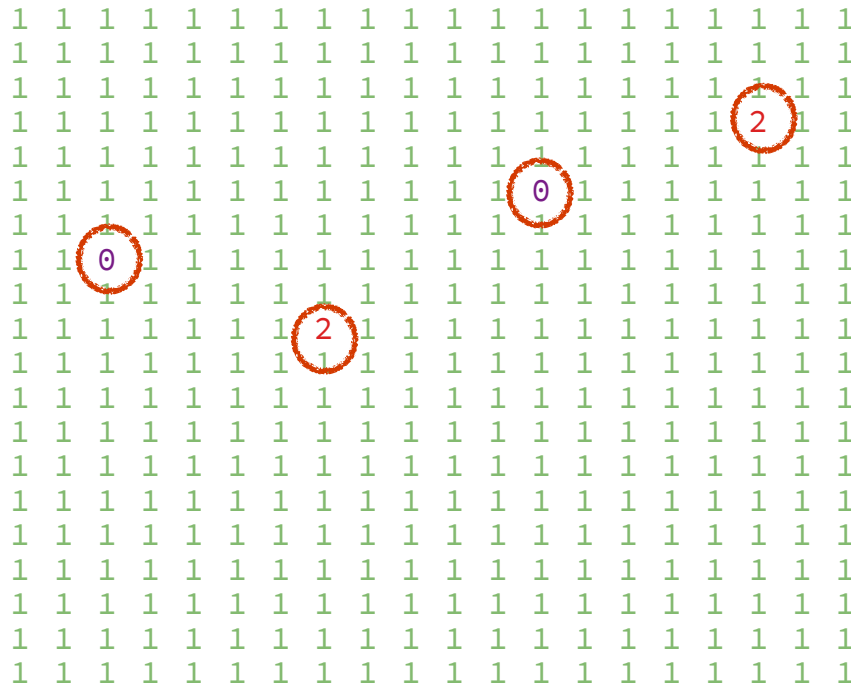
by counting the number of states.

Possible states after one “hop”



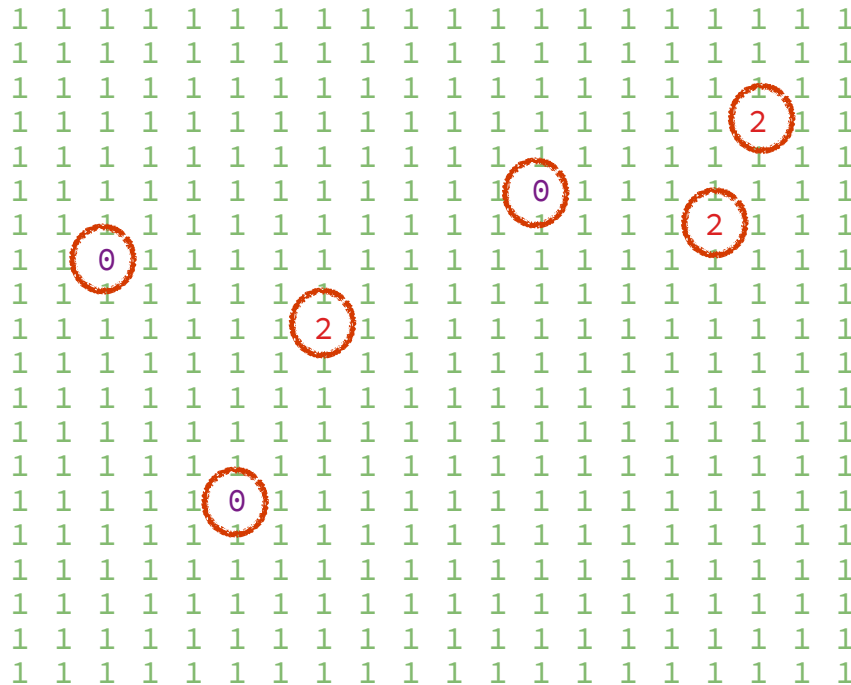
The system can now be in one of 159,600 micro states.

Possible states after two “hops”



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

Possible states after three “hops”



The system can now be in one of approximately 4000 trillion micro states.

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

1	0	1	0	2	1	0	0	2	1	3	1	1	1	0	0	0	0	1	0
1	2	2	2	0	0	0	0	0	1	1	0	0	3	5	1	0	0	0	0
0	0	1	1	0	2	0	0	6	1	1	0	1	1	1	0	2	0	0	0
0	3	3	0	0	2	0	0	3	0	1	3	0	2	0	0	0	3	0	0
2	0	0	1	0	6	0	4	1	0	0	0	2	1	0	0	1	1	1	0
1	0	6	0	4	0	1	2	1	0	0	0	1	0	0	0	0	3	4	1
0	0	0	1	2	4	0	0	1	0	0	2	0	1	2	1	1	2	0	6
1	3	0	0	2	0	1	0	1	0	0	3	0	4	0	2	1	0	6	1
1	1	1	0	0	0	0	1	0	3	1	2	0	0	0	0	1	0	0	0
0	0	0	0	0	2	0	3	1	0	0	0	0	0	3	0	0	2	2	1
9	1	0	1	1	0	2	1	0	1	0	0	0	3	7	3	0	2	3	0
2	2	0	0	0	0	0	1	0	1	7	1	3	1	0	1	3	0	1	0
0	5	3	0	1	2	4	8	1	0	4	0	3	0	1	0	0	0	4	0
0	0	0	0	1	0	0	0	0	1	0	1	0	0	2	3	0	2	0	0
0	1	1	0	0	2	0	4	0	1	0	4	0	1	1	1	1	8	5	1
0	0	0	0	1	0	0	0	2	0	1	0	1	1	2	0	0	1	1	1
3	0	0	0	4	0	0	1	0	1	2	0	0	1	2	0	2	0	1	0
0	0	1	2	1	0	0	0	0	0	1	0	0	0	2	0	1	1	0	0
1	0	1	0	0	0	1	0	3	1	0	0	0	0	0	2	9	0	0	5
0	0	1	2	3	0	1	2	0	2	4	0	0	0	1	2	0	0	0	1

“thermalized” means that the system is equally likely to be in any of its e^{555} 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 $\delta E = \hbar \omega_0$
And found $\Omega(E) = e^{555}$ for N harmonic oscillators

- 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

$$\begin{array}{c} E_1 \\ \Omega_1(E_1) \end{array}$$

$$\begin{array}{c} E_2 \\ \Omega_2(E_2) \end{array}$$

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 $E_1 + E_2 = E$ is partitioned between the two subsystems. The partition of E 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;

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

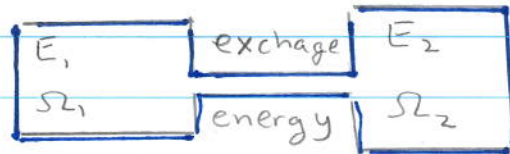
(Think about two six sided die the number of micro states of outcomes is 6×6)

- 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 into E_1 and E_2 is

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

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

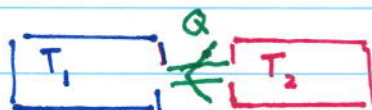
• As E_1 and E_2 change due to the hops, the probability will increase as $\Omega_1(E_1)\Omega_2(E_2)$ increases or equivalently $\ln \Omega_{\text{TOT}}$ or S_{TOT} increases ($\Omega(E)$ is fixed since $E = \text{const}$)

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

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

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

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_1 (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.

For this formula to apply the system one should be in equilibrium at temperature T , and the added heat should then be thermalized, i.e. shared in all possible ways. These requirements are written that $dS = dQ_{\text{rev}}/T$. Here "rev" is short for reversible, since if I have two equilibrated systems at the same temperature, heat can flow both ways reversibly without increasing entropy.