Motivation

- What is heat, and how do I distinguish it from macroscopic work?

- Essentially heat is energy which is shared amongst <u>many</u> constituents

- So what we will try to do is to count the ways that the particles can share the total energy.

  For instance one particle could have all the energy and the rest none. Or every particle could have exactly the same amount of energy. These are two possibilities out of many. As we will see there are of order 10^{N_A} number of configurations.

- In the process we will derive the Boltzmann factor, and prove the relation

$$U = \frac{3}{2} N k_B T$$

and define temperature precisely.

Equilibrium as Maximum Probability

- We will describe how to count the number of configurations (ways to share the energy) next.
  A microstate is a complete specification of the coordinates and momenta of the system,
  $\vec{r}_1, \vec{p}_1, \ldots \vec{r}_N, \vec{p}_N$

- The number of microstates with energy between E and $E + \delta E$ is $\Omega(E)$, this is the number of ways to share the total energy E, or the number of accessible (or possible) states

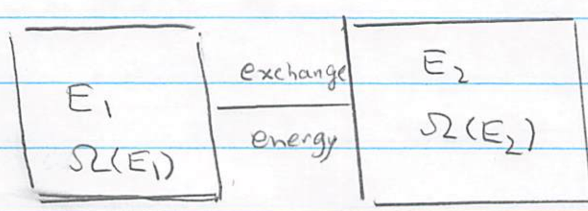
- Since there are of order 10^{N_A} states. Which one should be preferred? Boltzmann's answer was that they are <u>all equally likely</u>: $\boxed{P_{\substack{\text{micro}\\\text{state}}} = \frac{1}{\Omega(E)}}$

- The entropy is (up to a constant) the log of Ω

  $\hat{S} \equiv \log \Omega$ $\qquad\qquad$ entropy $= S$

  $$\hat{S} = \ln \Omega(E) \qquad\qquad \hat{S} \equiv S/k_B$$

- Why do we care? Take two systems



System 1, has energy E_1 and can be in any of its $\Omega(E_1)$ possible microstates. Ditto for system 2

The total energy $E = E_1 + E_2$ is partitioned between the two systems. The partition of E into E_1 and E_2 describes the macrostate of the system, i.e. we are just specifying two macroscopic quantities, instead of the microstate (6N quantities)

- The number of micro states with E_1 in ① and E_2 in ② (i.e. with a specified macrostate) is:

$$\Omega_{TOT} \equiv \Omega(E_1)\,\Omega(E_2)$$

In terms of logs

$$\log \Omega_{TOT} = \log \Omega_1 + \log \Omega_2$$

or

$$\hat{S}_{TOT} = \hat{S}_1 + \hat{S}_2$$

- Since each microstate is equally likely the probability of having E_1 in ① and E_2 in ② is proportional to $\Omega(E_1)\,\Omega(E_2)$, i.e. $\boxed{P_{\substack{macro\\state}} = \Omega(E_1)\,\Omega(E_2)\,/\,\Omega(E)}$

- Lets ask how $P_{macro}(E_1, E_2)$ will change as E_1 is changed, or equivalently how Ω_{TOT} or S_{TOT} changes as E_1 changes in time:

$$\frac{d\hat{S}_{TOT}}{dt} = \frac{dS_1}{dE_1}\frac{dE_1}{dt} + \frac{dS_2}{dE_2}\frac{dE_2}{dt}$$

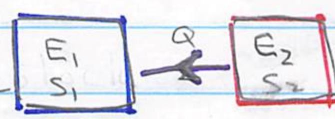
Since $\underbrace{E_1 + E_2}_{\text{Energy is shared!}} = E = \text{const}$, $\dfrac{dE_2}{dt} = -\dfrac{dE_1}{dt}$ and so

$$\frac{d\hat{S}_{TOT}}{dt} = \left(\frac{\partial \hat{S}_1}{\partial E_1} - \frac{\partial \hat{S}_2}{\partial E_2}\right)\frac{dE_1}{dt}$$

- Now $P \propto \Omega_{TOT}$ and $\hat{S}_{TOT} = \ln \Omega_{TOT}$. So if the system evolves towards its most probable configuration then we must have $\hat{S}_{TOT}$ increase in time:

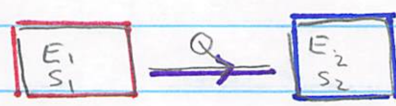
$$\boxed{\frac{d\hat{S}_{TOT}}{dt} = \left(\frac{\partial \hat{S}_1}{\partial E_1} - \frac{\partial \hat{S}_2}{\partial E_2}\right)\frac{dE_1}{dt} > 0}$$

- So if:



$\dfrac{\partial \hat{S}_1}{\partial E_1} - \dfrac{\partial \hat{S}_2}{\partial E_2} > 0$ then energy will flow to Left, $dE_1/dt > 0$, $\underline{\underline{T_2 > T_1}}$

But if



$\dfrac{\partial \hat{S}}{\partial E_1} - \dfrac{\partial \hat{S}}{\partial E_2} < 0$ then energy will flow to right, $dE_1/dt < 0$, $\underline{\underline{T_1 > T_2}}$

- So it is very natural to <u>define</u>

$$\left(\frac{\partial \hat{S}}{\partial E}\right) \propto \frac{1}{T}$$

The constant is the Boltzman constant

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

or since $\hat{S} \equiv S/k_B$ we have

$$\boxed{\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T} \qquad \text{and} \qquad S = k_B \ln \Omega(E)}$$

- In the next section we will show that for an ideal gas:

$$\Omega = C V^N E^{3N/2} \qquad \text{with } C \text{ a constant}$$

So

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

- Substituting Ω we have $\ln \Omega = 3N/2 \ln E + \text{const}$ leading to

$$k\left(\frac{3N}{2E}\right) = \frac{1}{T} \qquad \text{or} \qquad \boxed{E = \frac{3}{2} N k_B T}$$