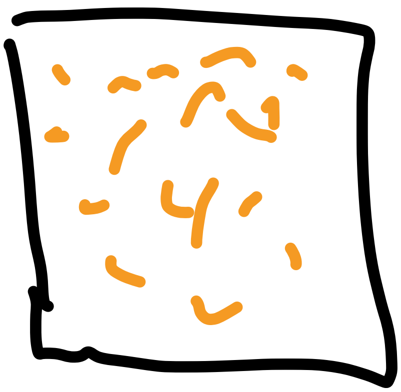
Lecture 3: Microcanonical, Pt 2

Last time:

Isolated system, assume molecules/particles follow Newton's laws



Conserve N, V, E

future class

How many states? Said

$$\Omega\,\cancel{Z}(N,V,E) = C\int d\vec{x}\;\delta(\mathcal{H}[x]-E)$$

actually not =, constant prefactor later. if indisting $\propto \frac{1}{N!}$

What is probability of a microstate?

$$P(X) = \begin{cases} \dfrac{1}{\Omega(N,V,E)} & \text{if } \mathcal{H}(x) = E \\ 0 & \text{if not} \end{cases}$$

$\Rightarrow$ really $P(x) = \dfrac{C\,\delta(\mathcal{H}(x) - E)}{\Omega(N,V,E)}$

Equal a-priori probability

$$\int dX\, P(x) = \frac{C}{\Omega(N,V,E)} \int dx\, \delta(\mathcal{H}(x) - E)$$

$= 1$, ✓

[will compute for ideal gas later]

Said a system will follow a "trajectory" and if we knew

$X(t_1) \to x(t_2) \to \cdots x(t_N)$ then

$$\langle A \rangle_{time} = \frac{1}{N} \sum_{i=1}^{N} A(X(t_i))$$

$\{X(t_i)\}$ are representative samples of $P(X)$ if system is <u>ergodic</u>

i.e. all states accessible and eventually reached.

If so $\langle A \rangle_t \xrightarrow{t \to \infty} \langle A \rangle_{ens}$
<u>assume</u>

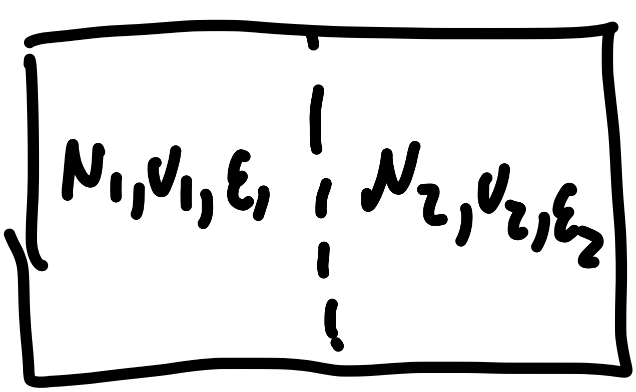
$$= \int dx \, P(x) A(x)$$

Note – no $P(x)$ needed in time average because each X comes up with correct prob already
→ called "sampling" distribution

Return to main point of stat mech which is to compute macro quantities from averages of micro

Start to explore connection w/ thermodynamics, which we will recap more later

Thermodynamics is the study of movement of heat/energy, and that is what we will consider first



- 2 systems so Energy can flow

Now $\mathcal{E}$ still conserved but
$\mathcal{E}_{tot} = \mathcal{E}_1 + \mathcal{E}_2$ is constant while
$\mathcal{E}_1$ could be $0 \leftrightarrow \mathcal{E}_{tot}$
and same for $\mathcal{E}_2$, so what value does it take? can ask what value is most probable.
ie maximize $\Omega(N_{tot}, V_{tot}, \mathcal{E}_{tot})$

what is Ω?

$$\Omega(N_{tot}, V_{tot}, \mathcal{E}_{tot}) = \Omega(N_1, V_1, \mathcal{E}_1) \times \Omega(N_2, V_2, \mathcal{E}_2)$$

maximize, find $\frac{d\Omega}{d\mathcal{E}_1} = 0$

Instead of Ω, maximize $\log \Omega$, often easier, equivalent

$$\log \Omega(N, V, E) = \log \Omega(N_1, V_1, E_1) + \log \Omega(N_2, V_2, E_2)$$

$$0 = \frac{\partial \log \Omega(N_1, V_1, E_1)}{\partial E_1} + \frac{\partial \log \Omega(N_2, V_2, E_2)}{\partial E_2}$$

$$E = E_1 + E_2 \Rightarrow E_1 = E - E_2$$

$$\frac{\partial X}{\partial E_2} = \frac{\partial X}{\partial E_1}\frac{\partial E_1}{\partial E_2} = -\frac{\partial X}{\partial E_1}$$

$$\Rightarrow \frac{\partial \log \Omega(N_1, V_1, E_1)}{\partial E_1} = \frac{\partial \log \Omega(N_2, V_2, E - E_1)}{\partial E_1}$$

[const N_1, V_1, N_2, V_2]

Thermo - heat flows until temp equal, so maybe related to temp

Will see from thermo that

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$$ so this

motivates us to associate

$$S(N,V,E) = k_B \log \Omega(N,V,E)$$

in which case,

(1) 2 bodies at equilibrium equalize $\frac{1}{k_B T} = \beta$

(2) Entropy is maximized for a closed system at equilibrium

Why this definition of entropy? It has one key property, extensivity

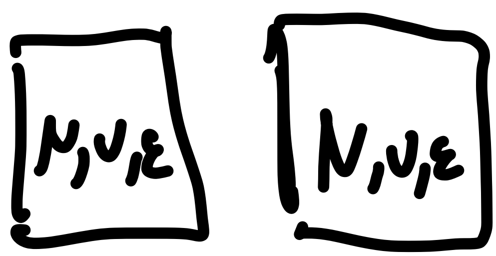
An extensive quantity is one that scales with the size of the system

$N, V, E, S \leftarrow$ examples

<u>Intensive</u> does not depend on system size - eg T, P

Divide extensive quantities to get intensive one, eg $\rho = N/V$

Why S extensive - duplicate system



$\Omega = \Omega_1 \Omega_2$

$S_{tot} = k_B \log \Omega = k_B \log \Omega_1 + k_B \log \Omega_2$

if doubled $S_{tot} = 2S_1$