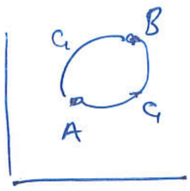
Finishing with TD

~~dasc~~

$$\oint \frac{dQ}{T}\Big|_{rev} = 0 \qquad \oint \frac{dQ}{T}\Big)_{gen} \leq 0$$



$$\int_A^B \frac{dQ}{T}\Big)_{rev,\,c_1} = \int_A^B \frac{dQ}{T}\Big)_{rev,\,c_2}$$

$$\frac{dQ}{T}\Big)_{rev} = dS \qquad \int_A^B dS = S_B - S_A$$

$$\int_A^B \frac{dQ}{T}\Big)_{rev} + \int_B^A \frac{dQ}{T}\Big)_{gen} \leq 0$$

$S(B) - S(A)$

$$\int_B^A \frac{dQ}{T}\Big)_{gen} \leq S(A) - S(B)$$

$$\boxed{\frac{dQ}{T} \leq dS}$$

$$dU = dQ - PdV$$

$$dQ = dU + PdV \leq dS\, T$$

$$dU = TdS - PdV \quad (rev)$$

$$\frac{\partial U}{\partial S}\Big)_V = T \qquad \frac{\partial S}{\partial U}\Big)_V = \frac{1}{T} \qquad \frac{\partial U}{\partial V}\Big)_S = -P$$

TD. Potential Helmholtz Free Energy

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

$$TdS = dU - dA - SdT \geq dQ$$

$$\cancel{dQ} - PdV - SdT \geq dA$$

(*) Derivatives give useful relations

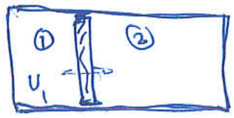
(*) We will obtain A from statistical physics.

Eqn. of state

$$\boxed{\frac{\partial A}{\partial V}\Big)_T = -P} \qquad \frac{\partial A}{\partial T}\Big)_V = -S$$

if $dV=0$, $dT=0$ then $dA \leq 0$

A reaches a minimum at equilibrium



T

$$A = A_1(V_1, T) + A_2(V_2, T)$$

$$\frac{\partial A}{\partial V_1}\Big)_{V,T} = 0 \qquad \frac{\partial}{\partial V_1}\left[A_1(V_1,T) + A_2(V - V_1, T)\right] = 0$$

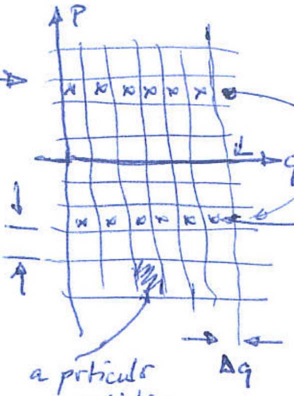
$$P_1 = P_2 \Longleftarrow \qquad \frac{\partial A_1}{\partial V_1}\Big)_T - \frac{\partial A_2}{\partial V_2}\Big)_T \qquad \frac{\partial A_2}{\partial V_2}\frac{\partial V_2}{\partial V_1}$$

μ-States of a system

Classical: position $\vec{q}$, momentum $\vec{p}$

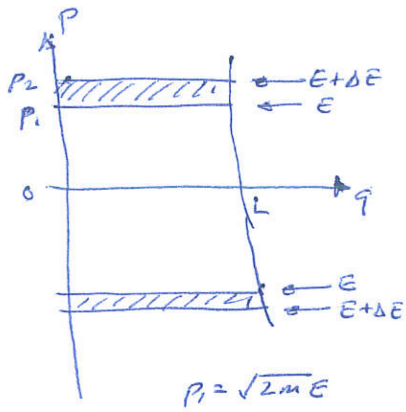
e.g. in one dimension, one particle

Phase space Γ →



constant energy E

divide into pieces such that $\Delta q \cdot \Delta p \sim h$



$p_1 = \sqrt{2mE}$

$p_2 = \sqrt{2m(E+\Delta E)} = \sqrt{2mE}\sqrt{1+\frac{\Delta E}{E}}$

$p_2 - p_1 = \sqrt{2mE}\,\frac{\Delta E}{2E}$ $\quad \left(1+\frac{\Delta E}{2E}\right)$

# of states

$\frac{\sqrt{2mE}}{2E}\,\frac{\Delta E \cdot L}{h} \times 2$

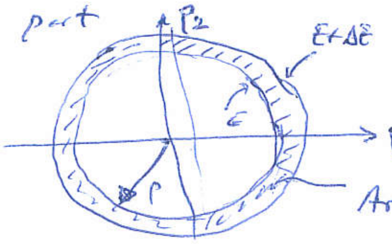
$\pm p$ states

$\Omega(E)\,\Delta E$ = # of states that satisfy $E < H < E+\Delta E$

2 particles in 1-D

position space simple $0 < q_1 < L$, $0 < q_2 < L$

momentum part



$E < \frac{p_1^2 + p_2^2}{2m} < E + \Delta E$

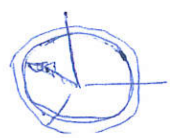
← Too much algebra - just motivate

Area $(\pi p^2) = \underbrace{\pi \cdot 2m(E+\Delta E) - \pi \cdot 2mE}_{2m\pi\,\Delta E}$

$\frac{p^2}{2m} = E \Rightarrow p = \sqrt{2mE}$

~~Volume~~ ~~Area~~ Number of all possible μ states for this system $\frac{(\pi\, 2m\Delta E)\cdot L^2}{h^2}$

3 particles in 1D



$\frac{4}{3}\pi\left(2m(E+\Delta E)\right)^{3/2} - \frac{4}{3}\pi(2mE)^{3/2}$

$4\pi(2mE)$

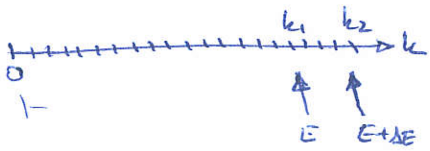
$\frac{4}{2}\pi(2mE)^{1/2}\,\Delta E\, 2m$

$\frac{4}{3}\pi(r+dr)^3 - \frac{4}{3}\pi r^3$

$= 4\pi r^2 dr$ ✓

QM case

$k = \frac{2\pi}{\lambda} = \frac{\pi}{\lambda/2} = \frac{\pi}{L/n} = \frac{n\pi}{L}$



$E + \Delta E = \frac{\hbar^2 k_2^2}{2m}$ $\quad k_2^2 = \frac{2m(E+\Delta E)}{\hbar^2}$

$E = \frac{\hbar^2 k_1^2}{2m}$ $\quad k_1^2 = \frac{2mE}{\hbar^2}$

$k_2 - k_1 = \sqrt{\frac{2m}{\hbar^2}}\left(\sqrt{E+\Delta E} - \sqrt{E}\right)$

$= \sqrt{\frac{2m}{\hbar^2}}\left(\sqrt{E}\sqrt{1+\frac{\Delta E}{E}} - \sqrt{E}\right)$

$= \sqrt{\frac{2m}{\hbar^2}}\sqrt{E}\left(+\frac{\Delta E}{2E}\right) = \frac{\sqrt{2mE}}{\hbar}\frac{\Delta E}{2E}$

of μ states: $\frac{k_2 - k_1}{\pi/L} = \frac{\sqrt{2mE}}{2E\hbar}\frac{L}{\pi}\Delta E$

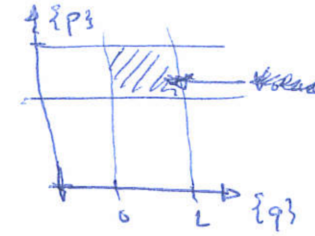
A system with N particles

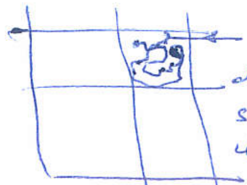
Classical: $\underbrace{q_{1x}, q_{1y}, q_{1z}, \cdots q_{Nz}}_{\substack{3N \\ \text{coordinates}}}, \; \underbrace{p_{1x}, p_{1y}, p_{1z}, \cdots p_{Nz}}_{\substack{3N \\ \text{momenta}}}$

Quantum mechanical, E.g. $k_x = \frac{n_x \pi}{L}$, $k_y = \frac{n_y \pi}{L}$, $k_z = \frac{n_z \pi}{L}$

μ-state: Specify k_x, k_y, k_z for all N particles.

Spectrally

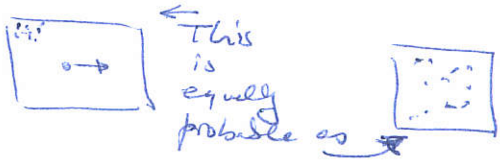




Discuss ergodicity

Postulate of equal a-priori probability:

All μ-states that satisfy the macroscopic constraints are equally probable

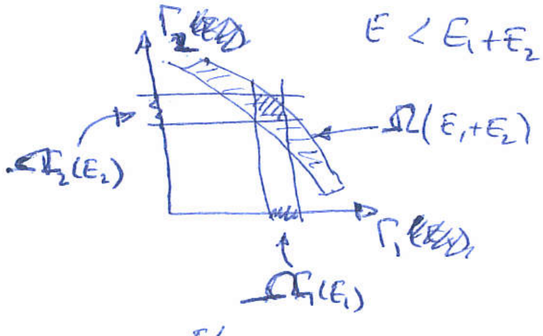


But there are a lot more "random looking" configurations

Let's see what happens when we put two systems in contact with one another

So, the total energy constraint is now

$$E < E_1 + E_2 < E + \Delta$$



Change notation
$\Gamma(E) \to \Omega(E)$
to avoid confusion between Γ and $\Gamma(E)$

$$\Omega(E) = \sum_{i=0}^{E/\Delta E} \Omega_1(E_i)\,\Omega_2(E - E_i)$$

One of them will contribute the most: max term $= \Omega_1(\bar{E}_1)\,\Omega_2(E_1 - \bar{E}_1)$

$$\frac{\partial}{\partial E_1}\left(\Omega_1(E_1)\,\Omega_2(\overset{E_2}{E - E_1})\right) = 0$$

$$\frac{\partial \Omega_1}{\partial E}\,\Omega_2 - \Omega_1 \frac{\partial \Omega_2}{\partial E_2} = 0 \;\longrightarrow\; \frac{\frac{\partial \Omega_1}{\partial E_1}}{\Omega_1} = \frac{\frac{\partial \Omega_2}{\partial E_2}}{\Omega_2}$$

$$\frac{\partial}{\partial E_1} \ln \Omega_1 = \frac{\partial}{\partial E_2} \ln \Omega_2$$

We can show that the maximum term $\Omega_1(\bar{E}_1)\Omega_2(\bar{E}_2)$ dominates the summation

$$\Omega(E) = \sum_{i=0}^{E/\Delta E} \Omega_1(E_i)\Omega_2(E-E_i)$$

$$\Omega_1(\bar{E}_1)\Omega_2(\bar{E}_2) \leq \Omega(E) \leq \frac{E}{\Delta}\Omega_1(\bar{E}_1)\Omega_2(\bar{E}_2)$$

$\Omega(E)$ contains additional terms

This would be the case if all terms were equal to this

$$\ln\left[\Omega_1(\bar{E}_1)\Omega_2(\bar{E}_2)\right] \leq \ln\Omega(E) \leq \underbrace{\ln\frac{E}{\Delta}}_{\text{order } \ln N} + \ln\left[\Omega_1(\bar{E}_1)\Omega_2(\bar{E}_2)\right]$$

Again, all energy distributions are equally probable but the one for $\max(\Omega_1(E_1)\Omega_2(E_2))$ dominates!

What is the significance of

$$\underbrace{\frac{\partial}{\partial E_1}\ln\Omega_1(E_1)}_{\sim T_1 \to \sim \frac{1}{T_1}} = \underbrace{\frac{\partial}{\partial E_2}\ln\Omega_2(E_2)}_{\sim T_2 \to \sim \frac{1}{T_2}} \;?$$

Remember

$$dU = dQ - PdV$$

$$= TdS - PdV$$

$$dS = \frac{dU}{T} + \frac{P}{T}dV$$

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$$

$$\ln\Omega(E) \propto S(E)$$

"Logarithm of the number of possibilities"

What does this signify?

If I have two possible states

①
② $S \sim \ln 2$. All logarithms are proportional to one another!

$$y = \ln x \Rightarrow x = e^y = 2^{(\log_2 e)y}$$

$$(\log_2 e)y = \log_2 x$$

$$(\log_2 e)\ln x = \log_2 x$$

Let us use base 2 for this problem

①
② $S = \log_2 2 = 1$ bit ← convention for $\log_2$ 1 bit sufficient

①②③④ → $S = \log_2 4 = 2$ bits ← 2 bits necessary to specify

Information content in a probabilistic event

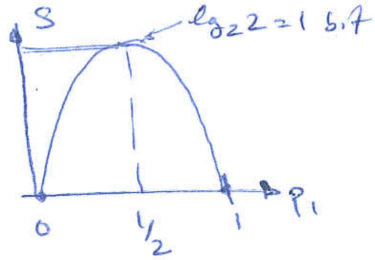
Missing information, entropy

$$S = -\sum_i p_i \log_2 p_i \quad \text{bits}$$

Give examples – Info in messages
– Noise
– Compression

Two possibility case

$$S = -p_1 \log_2 p_1 - (1-p_1)\log_2(1-p_1)$$



General case, maximum entropy

$$\text{Consider} \quad F = -\sum_i p_i \log p_i + \lambda\Big(\underbrace{\sum_i p_i - 1}_{\text{constraint}}\Big)$$

Lagrange multiplier

$\frac{\partial F}{\partial \lambda} = 0 \Rightarrow$ constraint

$\frac{\partial F}{\partial p_i} = 0 \Rightarrow$ maximise

$$\frac{\partial F}{\partial p_i} = 0 \Rightarrow -\log \bar{p}_i - 1 + \lambda = 0 \;=\; \log \bar{p}_i = \lambda - 1$$

$\Rightarrow$ all $\bar{p}_i$'s equal

constraint $\Rightarrow \bar{p}_i = 1/N$

$$\text{Max } S = -\sum_i \frac{1}{N}\log_2 \frac{1}{N} = \log_2 N$$

Equal probability $\longleftrightarrow$ Max Entropy $= \log(\#\text{ of states})$