SM: $\left.\frac{\partial S}{\partial V}\right|_{N,E} = \frac{P}{T}$

CLASSICAL MECHANICS

$p_m = \frac{\Delta E}{\Delta V}$

CALCULATE $\Delta E = W = \int \vec{F} d\vec{s}$

Mech: Trajectory

$Q(t), P(t), V(t)$

Assumption: slow change → adiabatic

→ Ensemble average

$= \int \frac{FA}{A} ds$

Area

$= -\int p_m dV$

$p\uparrow \rightarrow V\downarrow$

CAN'T CALCULATE ΔE FOR A ARBITRARY SYSTEM →

LOOK AT RATE OF CHANGE

$\frac{\Delta E}{\Delta t} \rightarrow \frac{dE}{dt}$

$\frac{dE}{dt} = p_m(t) \frac{dV}{dt}$

$\frac{dE}{dt} = \frac{dH}{dt}$

classical Hamiltonian of system

$H = H(P(t), Q(t), V(t))$

$$\frac{dH}{dt} = \frac{\partial H}{\partial Q}\frac{\partial Q}{\partial t} + \frac{\partial H}{\partial P}\frac{\partial P}{\partial t} + \frac{\partial H}{\partial V}\frac{\partial V}{\partial t}$$

$$H(P,Q) = \frac{1}{2}\frac{P^2}{m} + U(Q)$$

$$\frac{\partial H}{\partial P} = \frac{P}{m} = \dot{Q} \quad ; \quad \frac{\partial H}{\partial Q} = \frac{\partial U}{\partial Q} = -\dot{P}$$

$$\frac{dH}{dt} = \underbrace{-\dot{P}\dot{Q} + \dot{Q}\dot{P}}_{=0} + \frac{\partial H}{\partial V}\frac{\partial V}{\partial t}$$

$\rightarrow$ Adiabatic assumption, $\frac{\partial V}{\partial t}$ is slow enough for the system to be always in equilibrium.

$\Rightarrow$ CAN AVERAGE AT EACH TIME t OVER ENSEMBLE OF ALL TRAJECTORIES

$$\frac{\partial \langle E \rangle}{\partial t} = \frac{\partial \langle H \rangle}{\partial t} = \left\langle \frac{\partial H}{\partial V} \right\rangle \frac{\partial \langle V \rangle}{\partial t}$$

$$\stackrel{!}{=} -p_m \frac{dV}{dt}$$

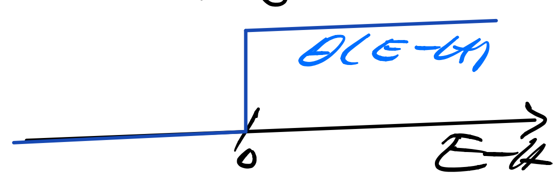
$$\Rightarrow -p_m = \frac{1}{\Omega(E)} \int \delta(E - H) \frac{\partial H}{\partial V} \, dP \, dQ \qquad (1)$$

$$\left(\frac{\partial S}{\partial V}\right)_{N,E} = \frac{\partial\, k_B \ln \Omega}{\partial V}\Big|_{N,E} = k\,\frac{1}{\Omega}\,\frac{\partial \Omega}{\partial V}\Big|_{N,E}$$

$$\Rightarrow \frac{\partial \Omega}{\partial V}\Big|_{N,E} = \frac{\partial}{\partial V}\int \delta(E-H)\, dP\, dQ$$

$$= \frac{\partial}{\partial V}\int \frac{\partial}{\partial E}\,\Theta(E-H)\, dP\, dQ$$

↳ step function



$$= \frac{\partial}{\partial E}\int \frac{\partial}{\partial V}\,\Theta(E-H(P,Q,V))\, dP\, dQ$$

$$= \frac{\partial}{\partial E}\int \delta(E-H)\,\underbrace{\frac{\partial(E-H)}{\partial H}}_{-1}\cdot\frac{\partial H}{\partial V}\, dP\, dQ$$

$$\frac{\partial S}{\partial V}\Big|_{N,E} = -\frac{k_B}{\Omega(E)}\,\frac{\partial}{\partial E}\int \delta(E-H)\,\frac{\partial H}{\partial V}\, dP\, dQ \qquad (2)$$

(1), (2)

$$\Rightarrow \frac{\partial S}{\partial V}\Big|_{N,E} = +\frac{k_B}{\Omega(E)}\,\frac{\partial}{\partial E}\left(\Omega(E)\cdot p\ldots\right)$$

$$= k_B \underbrace{\frac{1}{\Omega(E)} \frac{\partial \Omega(E)}{\partial E}}_{} \cdot p_m + k_B \cdot \frac{\partial p_m}{\partial E}$$

$$= \frac{\partial k_B \ln \Omega}{\partial E} = \frac{\partial S}{\partial E}\Big|_{V,N} = \frac{1}{T}$$

$$\Rightarrow \boxed{\frac{\partial S}{\partial U}\Big|_{E,N} = \frac{p_m}{T}} + k_B \frac{\partial p_m}{\partial E}$$

$\gtrsim = \Delta p$

$$\downarrow \qquad \frac{O(1)}{O(1)} \qquad\qquad \downarrow \qquad \frac{O(1)}{O(N)} \to 0$$

$N \to \infty$

CALCULATE $k_B \frac{\partial p_m}{\partial E}$ FOR IDEAL GAS:

$$pV = NkT$$
$$E = \frac{3}{2} NkT$$

$$\to \partial p_{i.g.} = \frac{2}{3} \frac{P}{T} \frac{1}{N}$$

→ IDEAL GAS

$$\Omega_{\text{CRUDE}}(E,V,N) = \frac{V^N \left(\frac{3N}{2E}\right) \pi^{\frac{3N}{2}} (2mE)^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}$$

WHAT'S WRONG:

1) ANNOYING → $\cancel{\frac{3N}{2E}}$ → does not matter

2) WRONG → UNITS $[\Omega] = [(q \cdot p)^{3N}]$

2) NOT RIGHT FOR IDEAL GAS —

GAS PARTICLES ARE INDISTINGUISHABLE $\to \frac{1}{N!}$

$\hookrightarrow [h^{3N}] \to$ QM STAT MECH

WILL SHOW THAT h^{3N} GIVES THE CORRECT $T=0$ LIMIT FOR THE ENTROPY

$$\lim_{T \to 0} S(T) = \text{const} = 0$$

$$\Rightarrow \Omega(E) = \int_{E<H<E+\delta E} \frac{dP\, dQ}{N!\, h^{3N}}$$

IDEAL GAS

$$\Omega(E) = \frac{V^N}{N!} \frac{\pi^{\frac{3N}{2}} (2mE)^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!\, h^{3N}}$$

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

$$= N k_B \left(\frac{V}{h^3} (2\pi m E)^{3/2} \right) - k \ln\left(N! \left(\frac{3N}{2}\right)!\right)$$

large N $\quad N! \approx N \ln N - N$

$$= \frac{5}{2} Nk + Nk \ln\left(\frac{V}{N} \left(\frac{1}{h} \left(\frac{4\pi m E}{3N} \right)^{\frac{1}{2}} \right)^3 \right)$$

$$S(E,V,N) = Nk\left(\frac{5}{2} - \ln\left(n\,\lambda_{th}^3\right)\right)$$

$n = \frac{N}{V}$ density

$$\lambda_{th} = \frac{h}{\sqrt{4\pi m \, E/3N}} \qquad \lambda_{th}^3 = \frac{1}{n_Q}$$

Quantum density

$= \frac{1}{2}kT$

$$\lambda_{th} = \frac{h}{\sqrt{2\pi m kT}}$$

thermal de Broglie wavelength,
in analogy with ~~the~~ de Broglie wavelength in QM: $\lambda_{dB} = \frac{h}{p}$

$E = \frac{p^2}{2m} \rightarrow \lambda_{th} = \frac{h}{p\sqrt{2\pi}}$