Lecture 5 - Ideal Gas

Last time:

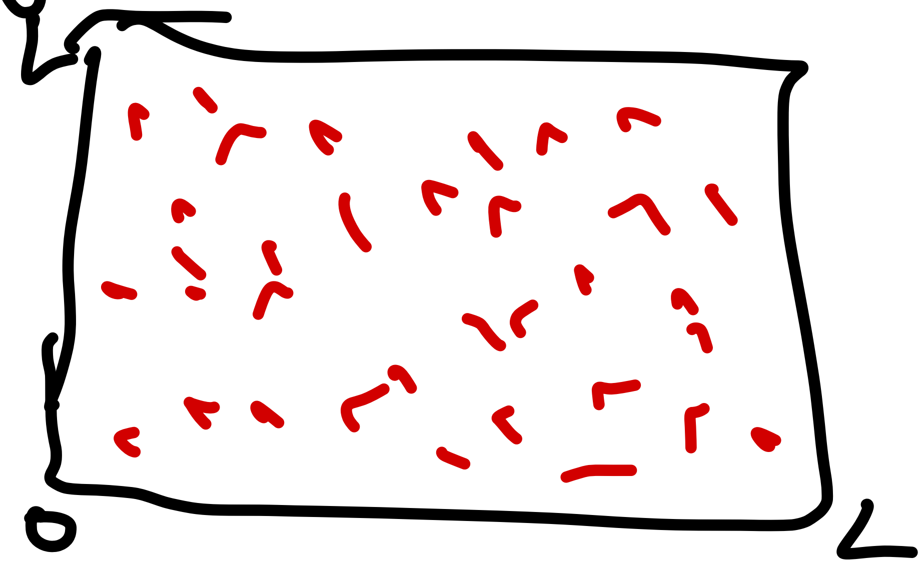
Entropy: state function

- doesn't decrease (on average)

For an isolated system

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

Ideal gas:



const N, V, E

$V = L^d$

density: $\rho = N/V$ low

molecules don't "feel" eachother

$$U(x) = \begin{cases} 0 & \text{if } x_i \in (0, L) \quad i = 1 \ldots 3N \\ \infty & \text{otherwise} \end{cases}$$

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

$$\Omega(N, V, E) = \frac{E_0}{h^{3N} N!} \int \delta(\mathcal{H}(\vec{x}) - E)\, d\vec{x}$$

$$d\vec{x} = dx_1 dx_2 \ldots dx_{3N}\, dp_1 dp_2 \ldots dp_{3N}$$

$$\int_{\underset{\leftarrow 0}{-\infty}}^{\overset{L}{\infty}} dx_1 \; \ldots \; \int_{-\infty}^{\infty} dp$$

$$\mathcal{H}(\vec{x}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

Prefactor $\frac{\mathcal{E}_0}{h^{3N} N!}$

- $\mathcal{E}_0$! $\delta(x)$ has units of $\frac{1}{[x]}$

$$\int_{-\infty}^{\infty} dx\, \delta(x) = 1$$

eg $\int_a^b dx \cdot 2 = 2 \cdot (b-a)$

$$S = k_B \log \Omega = k_B \log \mathcal{E}_0 + k_B \log (\ \ )$$

• $N!$

a b

c

1	2	3
a	b	c
	c	b
b	a	c
	c	a
c	b	a
	a	b

$[N_A!\, N_B! \ldots]$

how many ways can we label these molecules?

$$N \cdot (N-1) \cdot (N-2) \cdots 1$$

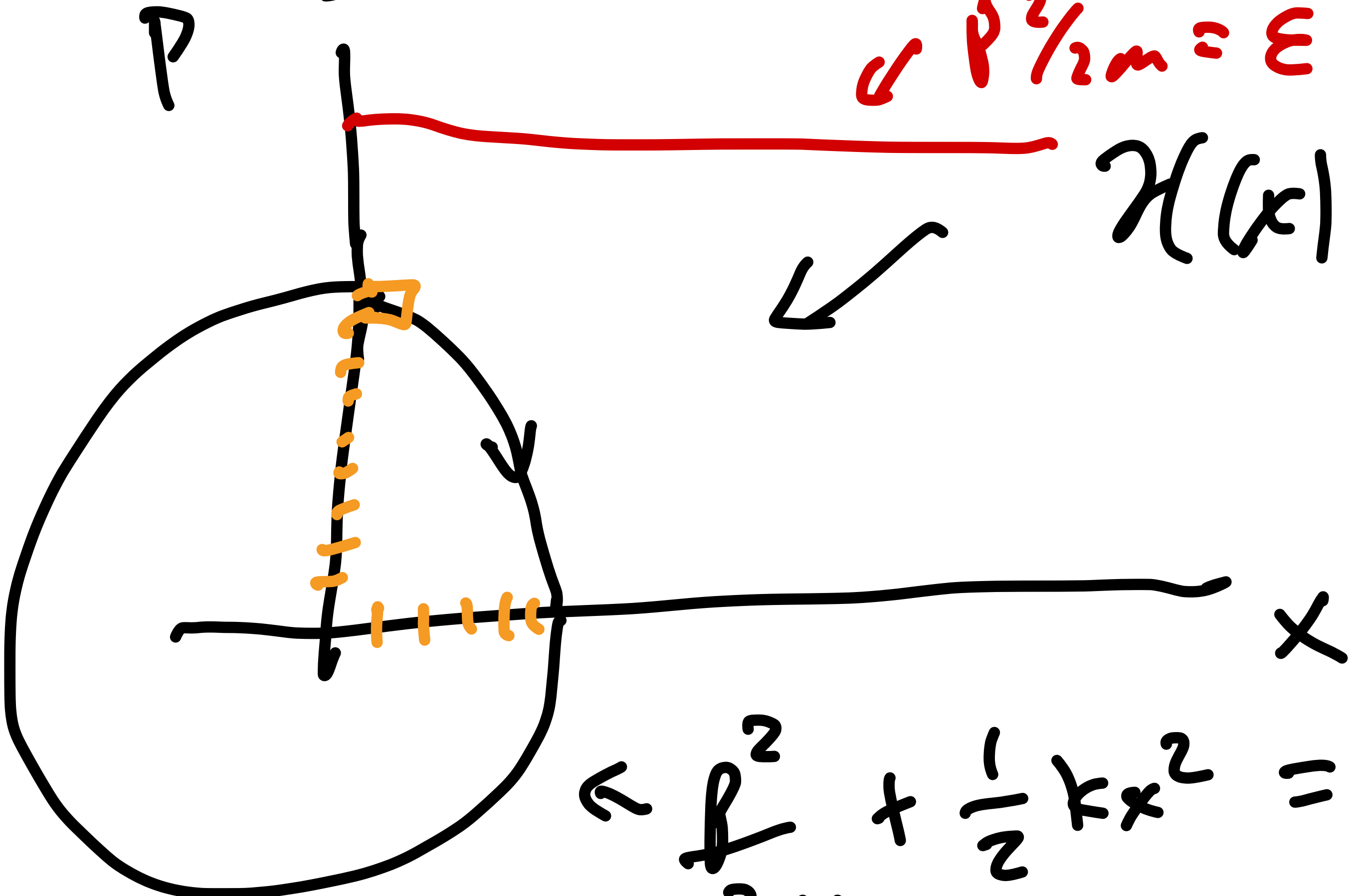
• h^{3N}

$$\int dx_1 \ldots \int dp_1 \ldots dp_{3N}$$

$$x \cdot p$$

how many states does this have

$p^2/2m = E$



$\mathcal{H}(x) = E$

$\frac{p^2}{2m} + \frac{1}{2}kx^2 = E$

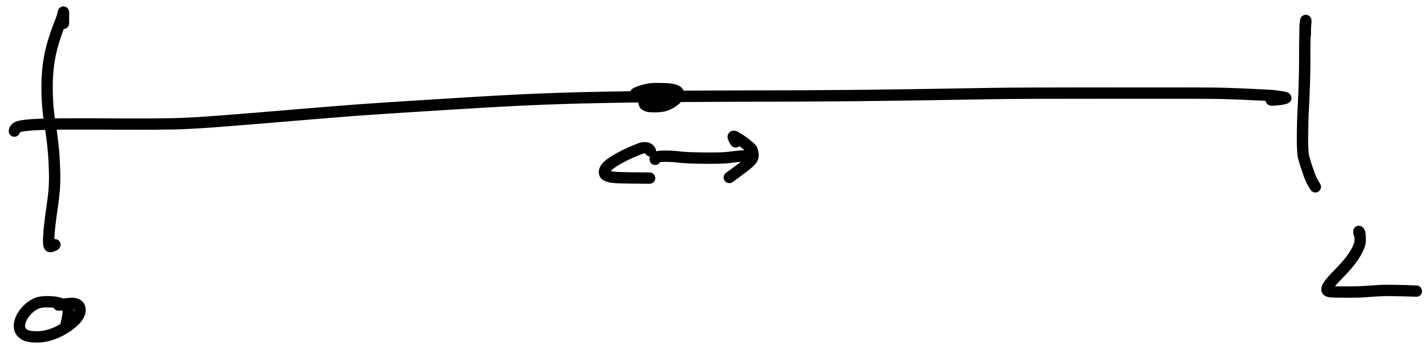
can't know x_i, p_i simultaneously

$\Delta x \Delta p \geq \frac{\hbar}{2}$

$x \cdot p \sim h$

Ω for an ideal gas

consider 1 particle in 1d



$$\Omega = \frac{\varepsilon_0}{h\cdot(1!)} \underbrace{\int_0^L dx}_{L} \int_{-\infty}^{\infty} dp \, \delta\Big(\underbrace{\frac{p^2}{2m}}_{\mathcal{H}(\vec{x})} - \varepsilon\Big)$$

$$y = \frac{1}{\sqrt{2m}}\, p \qquad dy = \frac{1}{\sqrt{2m}}\, dp$$

$$= \varepsilon_0/h \cdot \sqrt{2m}\, L \cdot \int_{-\infty}^{\infty} dy \; \delta(y^2 - \varepsilon)$$

$$\delta(y^2 - \varepsilon) = \delta\left((y-\sqrt{\varepsilon})(y+\sqrt{\varepsilon})\right)$$

$$\rightarrow \quad = \frac{1}{2\sqrt{\varepsilon}}\left[\delta(y-\sqrt{\varepsilon}) + \delta(y+\sqrt{\varepsilon})\right]$$

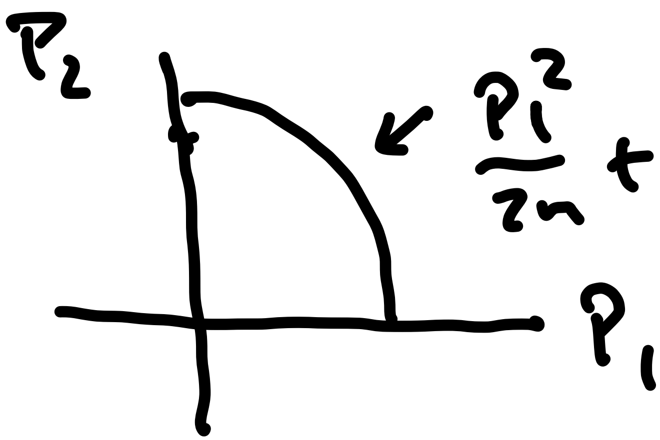
$$\left[\ \delta(f(x)) = \sum_{\text{roots}} \delta(\quad) \ .\right.$$

$$\Omega_{1d} = \frac{L\,\varepsilon_0}{h}\sqrt{2m}\int_{-\infty}^{\infty} dy \cdot \frac{1}{2\sqrt{\varepsilon}} \cdot \left[\delta(y-\sqrt{\varepsilon}) + \delta(y+\sqrt{\varepsilon})\right]$$

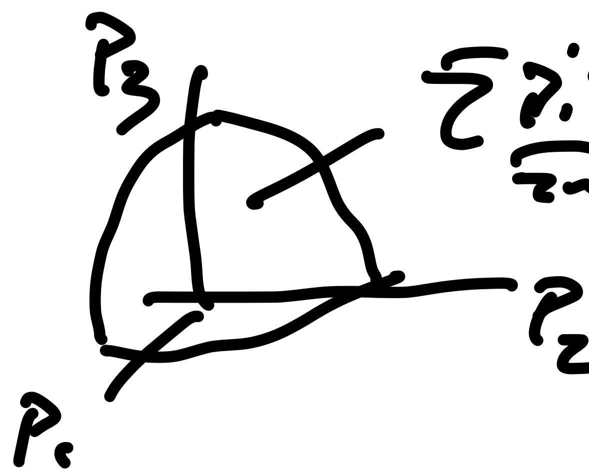
$$= \frac{L\,\varepsilon_0}{h}\sqrt{\frac{2m}{\varepsilon}}$$

$$\Omega(N,V,E) = \frac{\varepsilon_0}{h^{3N} N!} \underbrace{\int_0^L dx_1 \cdots}_{L^{3N} = V^N} \int_{-\infty}^{\infty} dp_1 \ldots dp_{3N} \cdot \delta\left(\sum_{i=1}^{3N} \frac{p_i^2}{2m} - E\right)$$

$$= \frac{\varepsilon_0 V^N}{h^{3N} N!} \int dp^{3N}\, \delta\left(\underbrace{\sum_{i=1}^{3N} \frac{p_i^2}{2m}} - E\right)$$



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



$$\sum \frac{p_i^2}{2m} = E$$

$$x^2 + y^2 + z^2 = r^2 \qquad \int d\theta\, d\varphi$$

$$dx\,dy\,dz = r^2 \sin\theta\, dr\, \underbrace{d\theta\, d\varphi}$$

$$\underbrace{4\pi r^2}_{\text{surface area of the sphere}} dr$$

$$p_1^2 + p_2^2 + \dots + p_{3N}^2 = r^2$$

$$dp_1\, dp_2 \dots dp_{3N} = \underbrace{S_{3N-1}}\, r^{3N-1}\, dr$$

$$\Omega \overset{\text{large } N}{\approx} \frac{E_0}{N!}\left(\frac{V}{h^3}\left(\frac{4\pi m E e}{3N}\right)^{3/2}\right)^N$$

$\uparrow$ depends on N, V, E

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

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

$$\ln \Omega = \ln\left[E^{3/2 N} \cdot \text{stuff}\right]$$
$$= \frac{3}{2} N \ln E + \ln(\text{stuff})$$

$$\frac{1}{T} = k_B \cdot \frac{3}{2} N \cdot \frac{1}{E} \Rightarrow E = \frac{3}{2} N k_B T \checkmark$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,E}$$

$$\ln S = \underbrace{\ln V^N}_{N \ln V} + \ln(\text{stuff})$$

$$\frac{P}{T} = k_B \frac{\partial (N \ln V)}{\partial V} + 0$$

$$\frac{P}{T} = k_B \frac{N}{V} \Rightarrow PV = N k_B T \checkmark$$

$$= nRT$$

$$\Omega = \frac{\varepsilon_0}{N!}\left(\frac{V}{h^3}\left(\frac{4\pi m E e}{3N}\right)^{3/2}\right)^N$$

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

$$= \frac{\varepsilon_0}{N!}\left(\frac{V}{h^3}\left(2\pi m\ k_B T\right)^{3/2}\right]^N e^{3N/2}$$

$$= \frac{\varepsilon_0}{N!}\left(V \cdot \underbrace{\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}}\right]^N e^{3N/2}$$

$$\Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}} \qquad = \frac{\varepsilon_0}{N!}\left(\frac{V}{\Lambda^3}\right]^N e^{3N/2}$$

$$S = k_B \ln \Omega \qquad \Omega = \frac{\epsilon_0}{N!}\left(\frac{V}{\Lambda^3}\right)^N e^{3N/2}$$

$$= Nk_B \ln\left(\frac{V}{\Lambda^3}\right) - k_B \ln(N!) + \frac{3}{2}Nk_B + \text{const}$$

$$\therefore$$

$$\ln(N!) \approx \underline{N}\ln N - N$$

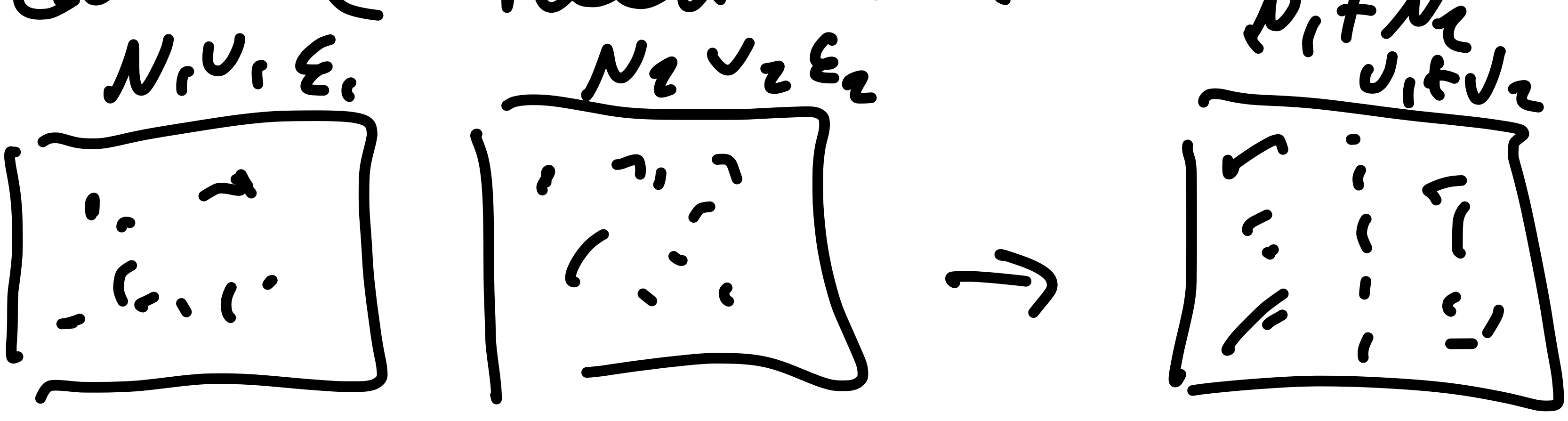
$$= Nk_B \ln\left(\frac{V}{\Lambda^3 N}\right) + \frac{5}{2}Nk_B + \_\_$$

$$= \boxed{Nk_B \ln\left[\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right] + \frac{5}{2}Nk_B} + \_\_$$

Sackur - Tetrode

Why do we need $N!$

$\frac{N}{V} \sim$



Gibbs' Paradox

HW: $S_{combined} - S_1 - S_2$