Lecture 5 - Ideal Gas

Last time:

Entropy: state function which does not decrease in changing the state of a system

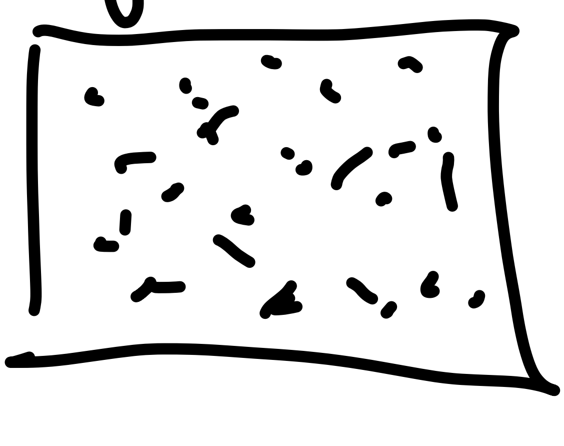
For isolated system, const N, V, E:

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

Now lets consider the properties of a gas:

generally: $\rho = N/V$ low

molecules don't "feel" eachother



Can say approximately,

$$U(\vec{x}) = \begin{cases} 0 & \text{if } x_i \in (0, L)\ \forall i \\ \infty & \text{otherwise} \end{cases}$$

$$\mathcal{H}(\vec{x}) = \sum_{i=1}^{N} \vec{p}_i^{\,2}/2m + \begin{cases} \infty & x_i \text{ outside box} \\ 0 & \text{otherwise} \end{cases}$$

$$\Omega = \varepsilon_0/h^{3N}N! \int dp^{3N}\, \delta\left(\sum \frac{p_i^2}{2m} - \varepsilon\right) \int dx^{3N}$$

$$\Omega = \frac{\varepsilon_0}{h^{3N}N!} V^N \int dp^{3N}\, \delta\left(\sum p_i^2/2m - \varepsilon\right)$$

What is this prefactor:

ε_0 : $\delta(x)$ has units $\frac{1}{x}$

otherwise $\int dx\, \delta(x) = 1$ would have units

$N!$: how many ways relabel N particles? $N(N-1)\ldots$

These arrangements indistinguishable

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

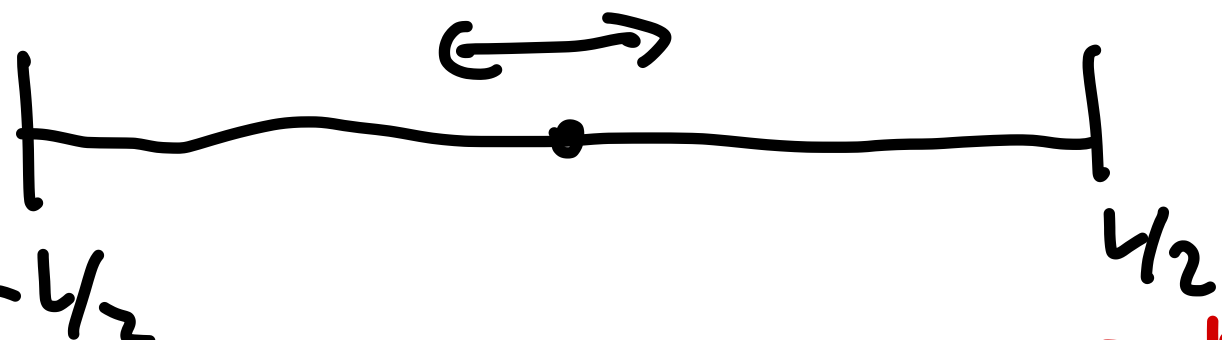
without $N!$, will get a paradox (later)

h^{3N}: • cancels units of $dx \cdot dp$

• hand wavy: enumerate all states, take all possible x & p, cannot know better than $\Delta x \Delta p \sim h$

• final result will connect to another QM concept

To see strategy, 1d first:



[Tuckerman 3.5

$$S = k_B \ln \Omega(1, L, \varepsilon)$$

$$\Omega = \frac{\varepsilon_0}{h} \int_{-\infty}^{\infty} dp \, \delta\left(\frac{p_1^2}{2m} - \varepsilon\right) \int_{-L/2}^{L/2} dx$$

$$\Omega_{1d} = \frac{L\varepsilon_0}{h}\int_{-\infty}^{\infty} dp\ \delta\left(p_i^2/_{2m} - \varepsilon\right)$$

$$\begin{cases} y^2 = p^2/_{2m} \\ dy = \frac{1}{\sqrt{2m}}\,dp \end{cases}$$

$$= \frac{L\varepsilon_0}{h}\sqrt{2m}\int_{-\infty}^{\infty} dy\ \delta\left(y^2 - \varepsilon\right)$$

$$\int \delta\left(y^2-\varepsilon\right) = \left(\delta\left(y-\sqrt{\varepsilon}\right) + \delta\left(y+\sqrt{\varepsilon}\right)\right)\cdot\frac{1}{2\sqrt{\varepsilon}}$$

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

✓

Now what happens for 3N?

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

first sub $y_i^2 = p_i^2/2m$

$$= \frac{\varepsilon_0}{h^{3N} N!} V^N \cdot (2m)^{3N/2} \int dy^{3N}\, \delta\Big(\underbrace{\sum y_i^2}_{r^2} - E\Big)$$

If 3d and we had $x^2+y^2+z^2=r^2$

Jacobian $= \int d\theta \int d\varphi\, r^2 \sin\theta\, dr\, d\theta\, d\varphi = \underbrace{4\pi}\, r^2 dr$

Here, 3N dimensional version of sphere S_{n-1}

$$dy^{3N} = r^{3N-1} S_{3N-1}\, dr$$

In HW, rest of details filled in

final result:

large N

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

note: depends on $N, V, \mathcal{E}$, and also m, but derivs will not count these

$$S = k_B \ln \Omega$$

$$\frac{1}{k_B T} = \frac{\partial \ln \Omega}{\partial \mathcal{E}} = \frac{3}{2} N \cdot \frac{1}{\mathcal{E}}$$

$$\Rightarrow \mathcal{E} = \frac{3}{2} N k_B T = \frac{3}{2} N R T$$ ✓

$$\frac{P}{T} = + k_B \frac{\partial \log \Omega}{\partial V} = N k_B \cdot \frac{1}{V}$$

$$PV = N k_B T = NRT$$ ✓

$$\Omega \approx \frac{\mathcal{E}_0}{N!}\left[\frac{V}{h^3}\cdot\left(\frac{4\pi m \mathcal{E} e}{3N}\right)^{3/2}\right]^N \quad {}^{3/2 N k_B}$$

[approx messes up units, but still ok]

$$\approx \frac{\mathcal{E}_0}{N!}\left[V\cdot\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right]^N \cdot e^{3N/2}$$

$\Lambda = \sqrt{h^2/2\pi m k_B T}$ – thermal wavelength

$\Omega_{1\,\text{particle}} \propto V/\Lambda^3$ ~ how many boxes

$\Omega_N \approx \frac{1}{N!}\Omega_1^N$

$$S = k_B \ln \Omega \approx N k_B \ln\left[V/\Lambda^3\right] - k_B \ln \underbrace{N!}_{\sim N\ln N - N} + \frac{3}{2} N k_B + C$$

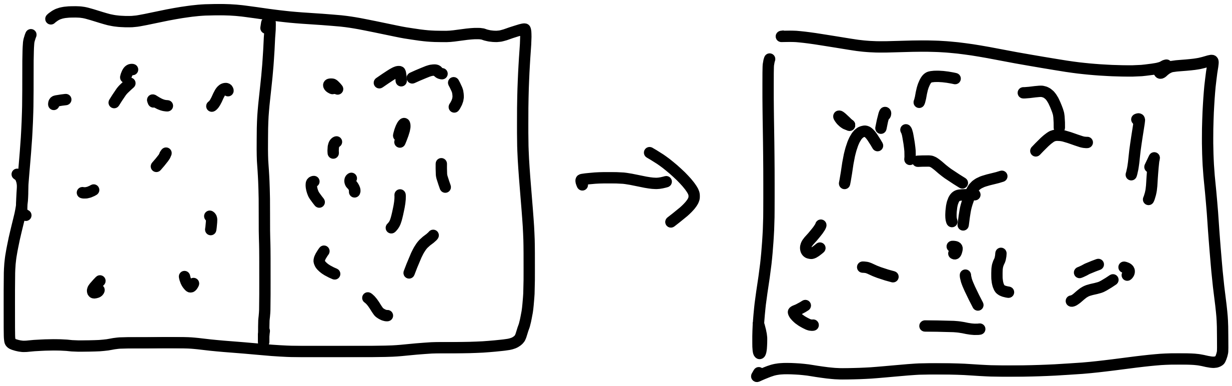
$$= N k_B \ln\left[\frac{1}{N} V/\Lambda^3\right] + \frac{5}{2} N k_B + C$$

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

Sackur-Tetrode equation

$V/N\Lambda^3 \gg 1$, classical regime is where valid

Why do we need $N!$? Gibbs paradox



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What is $S_2 - 2S_1$?

Compute with & without $N!$ factor (see HW)