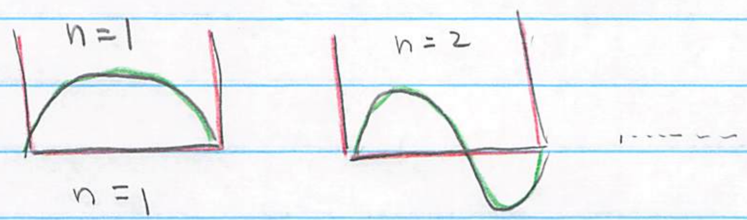
Why $\hbar$ in $d^3r\, d^3p/\hbar^3$?

- Now we will turn to why we have $\hbar^3$ in

$$\int \frac{d^3r\, d^3p}{\hbar^3}$$

- First consider a quantum mechanical "particle in a box" in 1d. The wave functions are shown below



$$\psi_n = \sqrt{\frac{2}{L}}\sin(k_n x)$$

$$\boxed{E_n = \frac{\hbar^2 k_n^2}{2m} \qquad k_n = \frac{\pi n}{L}}$$

- The energy eigenstates are super-position of waves with momentum $p = \pm \hbar k_n$

$$\sin k_n x = \frac{e^{ipx/\hbar} - e^{-ipx/\hbar}}{2i}$$

- Then

$$Z_1 = \sum_{n=1}^{\infty} e^{-E_n/kT}$$

Spacing between Energies is small.

Now

$$E_n = \frac{\hbar^2}{2m}\left(\frac{\pi n}{L}\right)^2 \propto \frac{1}{L^2}$$

So since L is big the spacing is small and the sum over n can be replaced by an integral

- The typical quantum number is when $E_n \sim k_B T$

$$\frac{\hbar^2}{2m}\frac{n^2}{L^2} \sim k_B T \quad \text{or} \quad n \sim L^2\left(\frac{2mT}{\hbar^2}\right) \sim \frac{L^2}{\lambda_{th}^2} \gg 1$$

typical n in sum over states is large!

- So since the typical n in the sum over states is large, we can replace the sum with an integral

$$Z_1 = \int_0^\infty dn\, e^{-E(n)/T}$$

now $k = \frac{\pi n}{L}$ so $dn = \frac{L\,dk}{\pi}$ and

$$\boxed{Z_1 = \int_0^\infty \frac{L\,dk}{\pi}\, e^{-E(k)/kT}}$$

- finally we can change the integration limits to $(-\infty, \infty)$ not $(0, \infty)$ and divide by two, calling $p = \pm\hbar k$, to find

$$Z_1 = \int_{-\infty}^\infty \frac{L\,dp}{2\pi\hbar}\, e^{-\mathcal{E}(p)/kT}$$

or

$$\boxed{Z_1 = \int \underbrace{\frac{dr\,dp}{h}}_{\text{phase space}}\, e^{-\mathcal{E}(p)/kT}}$$

To summarize:

- We are summing over state:

$$\sum_{k_n} e^{-E_n/k_B T}$$

The sum over states becomes an integral whenever $L/\lambda_{th} \gg 1$, i.e.

$$\boxed{\sum_{k_n} \longrightarrow \int_0^\infty \frac{L\,dk}{\pi} = \int_{-\infty}^{\infty} \frac{L\,dp}{2\pi\hbar} = \underbrace{\int \frac{dx\,dp}{h}}_{\text{phase space}}}$$

$p = \pm\hbar k$

extend

- In more dimensions (say 3D!)

$$E_n = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

$k_x = \frac{\pi n_x}{L}$

$k_y = \frac{\pi n_y}{L}$

$k_z = \pi n_z / L$

- And the sum over states becomes an integral over phase space with $1/h^3$

$$\boxed{\sum_{k_x}\sum_{k_y}\sum_{k_z} \longrightarrow \int_0^\infty \frac{L^3 dk_x\,dk_y\,dk_z}{\pi^3}}$$

$p = \hbar k$

$$= \int_{-\infty}^{\infty} \frac{L^3\,dk_x\,dk_y\,dk_z}{(2\pi)^3} = \underbrace{\int \frac{dx\,dp_x\,dy\,dp_y\,dz\,dp_z}{(2\pi\hbar)^3}}_{\text{phase space}}$$

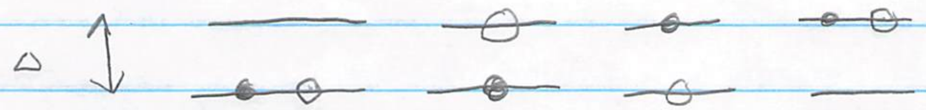
$$\boxed{= \underbrace{\int \frac{d^3\vec{r}\,d^3\vec{p}}{h^3}}_{\text{phase space}}}$$

Extend range from $(0,\infty)$ to $(-\infty,-\infty)$ for k_x, k_y and k_z and get $1/2^3$

Why N!

- Consider the same two level system (see slide) Composed of two distinguishable subsystems. For example, the two subsystems might be a different physical locations. When we considered N atoms forming a crystal this was the case, i.e. one atom per site:

- The states are



Dark circles atom A
Light circles atom B

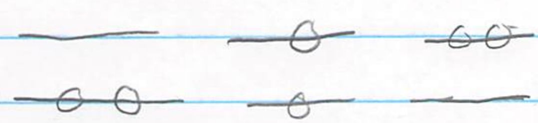
- Then the partition function

$$Z_{TOT} = e^{0} + e^{-\beta\Delta} + e^{-\beta\Delta} + e^{-2\beta\Delta}$$

$$= \sum_{i,j} e^{-\beta(\varepsilon_i^A + \varepsilon_j^B)} = \sum_i e^{-\beta\varepsilon_i^A} \sum_j e^{-\beta\varepsilon_j^B} = (Z_1)^2$$

With N particles, distinguishable, we get Z_1^N

- However in the gas the particles are indistinguishable

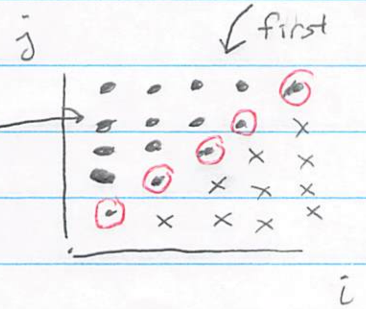


$$Z_{TOT} = e^{0} + e^{-\beta\Delta} + e^{-2\beta\Delta} = \sum_{i=0}^{\infty}\sum_{j=i}^{\infty} e^{-\beta(\varepsilon_i + \varepsilon_j)} \neq Z_1^2$$

- However consider the case when the number of accessible states is much greater than the number of particles (see slides)

$$Z_{TOT} = \sum_{i}^{\infty} \sum_{j=i}^{\infty} e^{-\beta(\varepsilon_i + \varepsilon_j)} = \frac{1}{2!} \underbrace{\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} e^{-\beta(\varepsilon_i + \varepsilon_j)}}_{\text{non-diagonal terms}} + \underbrace{\frac{1}{2} \sum_{i=j} e^{-\beta(\varepsilon_i + \varepsilon_{j=i})}}_{\text{diagonal terms}}$$

first



- States we sum over first

then

sum over • and ×, but put a factor of 1/2

diagonal terms
two particles in same state, ⊙

- Since the density is low two particles are rarely in the same quantum state and then we approximate

$$Z_{TOT} \simeq \frac{1}{2!} Z_1^2 + \text{neglected diagonal terms}$$

from when two particles are in same quantum state.

Then, for three indistinguishable atoms

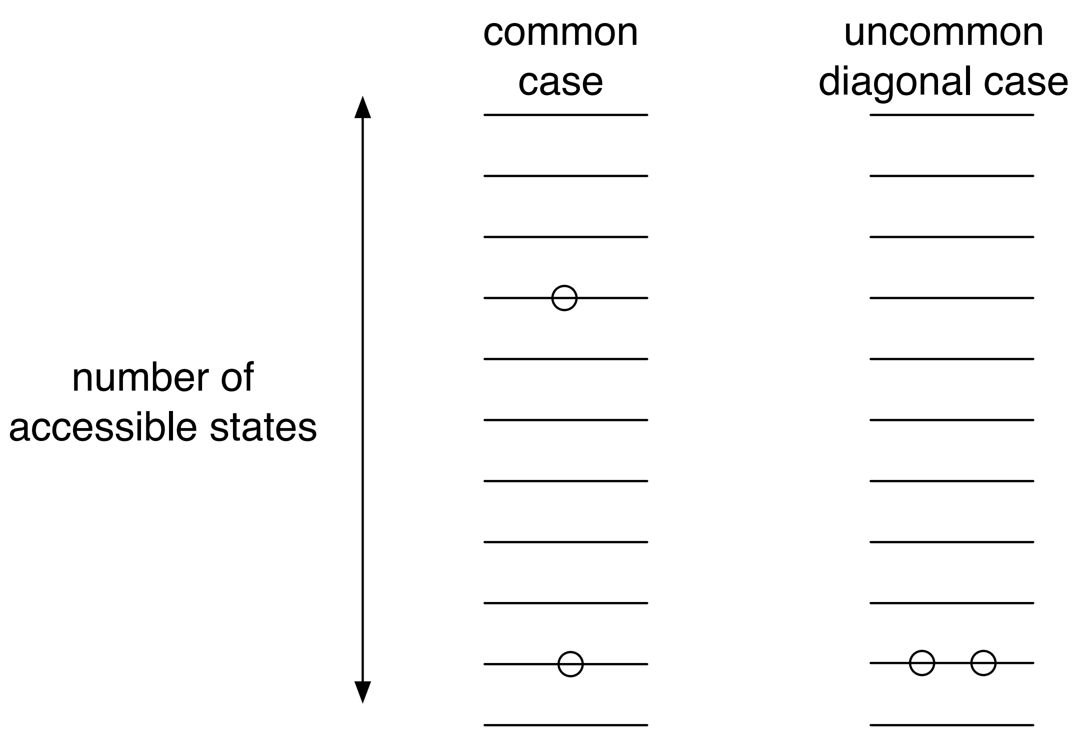
$$Z_{TOT} = \sum_{i}^{\infty} \sum_{j=i}^{\infty} \sum_{k=j}^{\infty} \simeq \frac{1}{3!} \sum_{i,j,k=1}^{\infty} e^{-\beta(\varepsilon_i + \varepsilon_j + \varepsilon_k)} + \text{diagonal} \simeq \frac{Z_1^3}{3!}$$

- So we need to require for this approximation that the Number of particles N to be less than the number of states, $n_{states} \sim \left(\frac{Lp}{h}\right)^3$, that is $n_{states} \sim V/\lambda_{th}^3$, so we need

$$\boxed{1 \ll (V/N)/\lambda_{th}^3}$$

Ideal Gas Limit:

The number of particles is much smaller than the number of quantum states



Usually the two particles are in different states when

$$n\lambda_{\mathrm{th}}^3 \ll 1$$

So in words we are requiring that the volume per particle is large compared to the (debroglie λ)^3

Then we have approximately

$$\boxed{\sum_{\substack{\text{states} \\ \text{of identical} \\ \text{indistinguishable} \\ \text{particles}}} e^{-\beta(\varepsilon_1 + \dots \varepsilon_N)/kT} \simeq \frac{1}{N!} Z_1^N}$$