10/20

Last time:

$$\langle n_s \rangle_{B\text{-}E} = \frac{1}{e^{\beta(\varepsilon_s-\mu)}-1} \qquad \frac{\overline{\Delta n_s^2}}{\bar{n}_s^2} = \frac{1}{\bar{n}_s} + 1 \quad \text{(broad distribution)}$$

$$\langle n_s \rangle_{F\text{-}D} = \frac{1}{e^{\beta(\varepsilon_s-\mu)}+1} \qquad \frac{\overline{\Delta n_s^2}}{\bar{n}_s^2} = \frac{1}{\bar{n}_s} - 1 \quad \text{sharper distribution}$$

Let's find $\overline{\Delta n_s^2}$ for F-D:

$$\overline{(\Delta n_s)^2} = -\frac{1}{\beta}\frac{\partial \bar{n}_s}{\partial \varepsilon_s} = +\frac{1}{\beta}\frac{\beta e^{\beta(\varepsilon_s-\mu)}}{\left[e^{\beta(\varepsilon_s-\mu)}+1\right]^2} = \frac{e^{\beta(\varepsilon_s-\mu)}+1-1}{\left[e^{\beta(\varepsilon_s-\mu)}+1\right]^2} =$$

$$= \bar{n}_s - (\bar{n}_s)^2 = \bar{n}_s(1-\bar{n}_s) \quad *$$

Classical limit of quantum distributions.

We found that:

① $\bar{n}_r = \dfrac{1}{e^{\alpha+\beta\varepsilon_r} \pm 1}$ $\quad$ + FD $\quad$ − BE $\qquad \alpha = -\beta\mu$

② $\sum_r \bar{n}_r = \sum_r \dfrac{1}{e^{\alpha+\beta\varepsilon_r} \pm 1} = N$

Classical limit:

If $e^{\alpha+\beta\varepsilon_r} \gg 1 \qquad \bar{n}_r \to e^{-\alpha-\beta\varepsilon_r}$ ③ $\quad$ for both distributions

But $N = \sum_r \bar{n}_r = e^{-\alpha} \sum_r e^{-\beta \varepsilon_r}$

$$\therefore \quad e^{-\alpha} = \frac{N}{\sum_r e^{-\beta \varepsilon_r}} \qquad (4)$$

then replacing (4) in (3):

$$\bar{n}_r \rightarrow \frac{N e^{-\beta \varepsilon_r}}{\sum_r e^{-\beta \varepsilon_r}}$$ Maxwell-Boltzmann's distribution.

When $e^{\alpha + \beta \varepsilon_r} \gg 1$ FD = BE = MB.

When is $e^{\alpha + \beta \varepsilon_r} \gg 1$?

1) If $\frac{N}{V} << 1$ then $\bar{n}_r << 1$ and $e^{\alpha+\beta\varepsilon_r} >> 1$ $\forall r$.

2) If $T >> 1$ (very large T). Now all the levels will have the same probability or the same occupancy. Then $\bar{n}_r << 1$ $\forall r$. Then $e^{\alpha+\beta\varepsilon_r} >> 1$.

This means that for $\frac{N}{V} << 1$ and $T >> 1$ we do not need to use quantum statistics. This is the so-called non-degenerate case.

Partition function for ideal gas in classical limit of quantum mechanical distributions:

$\pm$ FD/BE

We found that

$$\ln Z = \alpha N \pm \sum_r \ln\left(1 \pm e^{-\alpha-\beta\varepsilon_r}\right) \xrightarrow{e^{\alpha+\beta\varepsilon_r} \gg 1}$$

$\ln(1\pm x) \simeq \pm x$ if $x \ll 1$.

$$\simeq \alpha N \pm \sum_r \pm e^{-\alpha-\beta\varepsilon_r} =$$

$$= \alpha N + \underbrace{\sum_r e^{-\alpha-\beta\varepsilon_r}}_{\sum_r \bar{n}_{r\,M-B}} = \alpha N + \sum_r \bar{n}_r =$$

$$= \alpha N + N \qquad (5)$$

But we found in 4 that

$$e^{-\alpha} = \frac{N}{\sum_r e^{-\beta\varepsilon_r}}$$

$$\therefore \; -\alpha = \ln N - \ln \sum_r e^{-\beta\varepsilon_r}$$

or $$\alpha = -\ln N + \ln \sum_r e^{-\beta\varepsilon_r} \qquad (6)$$

Then putting 6 in 5:

$$\ln Z = -N\ln N + N \ln \overbrace{\sum_r e^{-\beta\varepsilon_r}}^{z_{MB}\ \text{(partition function for one M-B single particle)}} + N =$$

$$= -(\underbrace{N\ln N - N}_{\ln N!}) + N \ln z_{MB} \simeq$$

$$= -\ln N! + \ln z_{MB}^N = \ln \frac{z_{MB}^N}{N!}$$

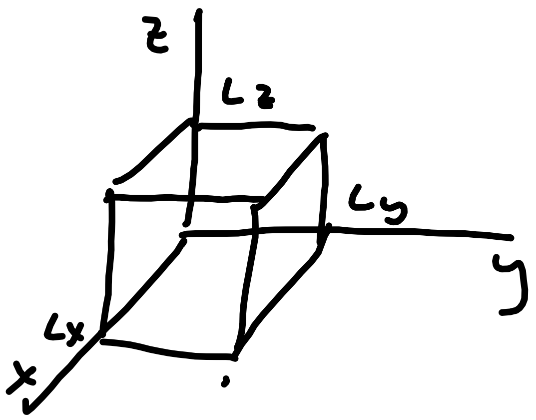
Then we find that

$$Z \to \frac{Z_{MB}}{N!}$$

Now the Gibbs' paradox has been solved without having to add $N!$ by hand.

Note: If $e^{\alpha+\beta\varepsilon_r} \ll 1$ then the gas is called "degenerate" and quantum statistics are needed.

Ideal gas in the classical limit from a quantum mechanical treatment (as opposed to the classical treatment with p_i and q_i independent that we used before):



Particle in a box (quantum mechanical).

Free boundary conditions:

$\psi = 0$ for $x_i = 0$ or L_i.

① $i\hbar \frac{\partial \psi}{\partial t} = \mathcal{H} \psi$ Schrödinger

② $\mathcal{H} = \frac{1}{2m} \vec{p}^{\,2} = \frac{1}{2m} \left(\frac{\hbar}{i} \nabla\right)^2 = -\frac{\hbar^2}{2m} \nabla^2$

If $\psi = \phi \, e^{-i\omega t} = \phi \, e^{-\frac{i \varepsilon}{\hbar} t}$ (3)

since $\varepsilon = \hbar \omega$ and also $\bar{p} = \hbar \bar{k}$

Plugging (3) in (1):

$$i\hbar \left(-\frac{i \varepsilon}{\hbar}\right) \phi \, e^{-i\omega t} = -\frac{\hbar^2}{2m} \nabla^2 \psi =$$

$$= -\frac{\hbar^2}{2m} \nabla^2 \phi \, e^{-i\omega t}$$

or

$$\nabla^2 \phi + \frac{2m\varepsilon}{\hbar^2} \phi = 0 \quad (4)$$

time independent eq.

$$\phi \propto e^{\pm i \bar{k} \cdot \bar{r}} = e^{\pm i (k_x x + k_y y + k_z z)}$$

$$\phi = A \sin k_x x \sin k_y y \sin k_z z \qquad (5)$$

satisfies the b.c. of $\phi(0) = 0$ $\phi(L_i) = 0$

if $k_i = \dfrac{\pi n_i}{L_i}$ $(*)$ $n_i = 1, 2, 3, \ldots$

So only positive values of k_i occur

(see in the book the case of periodic boundary conditions).

Plugging (5) in (4) we find that:

$$\varepsilon = \frac{\hbar^2 k^2}{2m} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \quad (7)$$

Density of states:

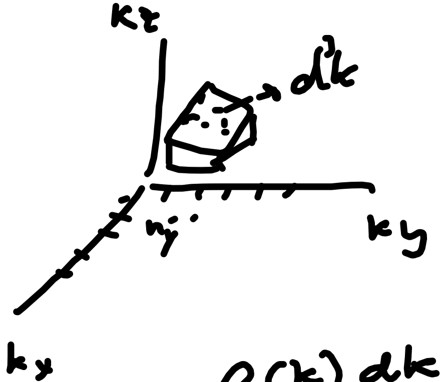
The degeneracy or the number of accessible state in terms of (n_x, n_y, n_z) for a certain interval dk or $d\varepsilon$ is very difficult to calculate if we consider that k is discrete. But the energy levels are so close to each other at room temperature $(\Delta\varepsilon \ll kT)$ that we can consider k and ε as continuous.

How many n_i state do we have in a Δk interval?

From (*) $k_i = \frac{\pi n_i}{L_i} \Rightarrow \Delta k_i = \frac{\pi \Delta n_i}{L_i}$

$$\rho(\bar{k})\, d^3k = \Delta n_x \Delta n_y \Delta n_z = \frac{L_x L_y L_z}{\pi^3} d^3k =$$

$$= \frac{V}{\pi^3} d^3k = \frac{V}{\pi^3} k^2 dk \sin\theta\, d\theta\, d\varphi$$



Now I integrate over θ and φ because ε only depends on k:

$$\rho(k)\, dk = \frac{V}{\pi^3} k^2 dk \underbrace{\int_0^{\pi/2} \sin\theta\, d\theta}_{1} \underbrace{\int_0^{\pi/2} d\varphi}_{\pi/2} = \frac{V}{\pi^3} k^2 \frac{\pi}{2} dk$$

$$\rho(k)\,dk = \frac{V k^2}{2\pi^2}\,dk$$

Density of states in terms of k.

Since $\varepsilon = \frac{\hbar^2 k^2}{2m} \Rightarrow k^2 = \frac{2m\varepsilon}{\hbar^2}$

$$dk = \frac{\cancel{2}m\,d\varepsilon}{\cancel{2}k\hbar^2} = \frac{m\cancel{\hbar}}{\sqrt{2m\varepsilon}}\frac{d\varepsilon}{\hbar^2} \qquad 2k\,dk = \frac{2m\,d\varepsilon}{\hbar^2}$$

$$\rho(\varepsilon)\,d\varepsilon = \frac{V\,2m\varepsilon}{2\pi^2\,\hbar^2}\,\frac{m}{\sqrt{2m\varepsilon}\,\hbar}\,d\varepsilon = \frac{Vm\sqrt{2m\varepsilon}}{2\pi^2\hbar^3}\,d\varepsilon =$$

$$= \frac{V}{4\pi^2}\frac{(2m)^{3/2}}{\hbar^3}\,\varepsilon^{1/2}\,d\varepsilon$$

(density of states with the same $\varepsilon^{1/2}$ dependence that we found in all classical case)

Partition Function

We found that

$$\ln Z = N(\ln z - \ln N + 1) \qquad z = \sum_r e^{-\beta \varepsilon_r}$$

and $$Z = \frac{z^N}{N!}$$

Let's find z:

$$z = \sum_{k_x, k_y, k_z} e^{-\frac{\beta \hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)} =$$

$$= \left(\sum_{k_i} e^{-\frac{\beta \hbar^2}{2m} k_i^2} \right)^3 \qquad \text{and } k_i = \frac{\pi n_i}{L_i}$$

But since $\Delta\varepsilon << kT$ at room temperature we can replace the sum over k_i by an integral assuming k continuous.

$$\sum_{k_i=0}^{\infty} e^{-\frac{\beta\hbar^2 k_i^2}{2m}} \longrightarrow \int_0^{\infty} e^{-\frac{\beta\hbar^2 k^2}{2m}} \underbrace{\frac{L_i}{\pi} dk}_{\substack{\#\text{ of } N_i \\ \text{points in} \\ dk}} =$$

$$= \frac{L_i}{2\pi}\left(\frac{2\pi m}{\beta\hbar^2}\right)^{1/2} = \frac{L_i}{2\pi\hbar}\left(\frac{2\pi m}{\beta}\right)^{1/2} = \frac{L_i}{h}\left(\frac{2\pi m}{\beta}\right)^{1/2}$$

$$\therefore\ z = \frac{V}{h^3}(2\pi m k T)^{3/2}$$

same as before but $h_0 \equiv h$!

Then

$$\ln Z = N(\ln \zeta - \ln N + 1) =$$

$$N\left(\ln \frac{V}{N} + \frac{3}{2}\ln kT + \frac{3}{2}\ln(2\pi m) - 3\ln h + 1\right)$$

$$= N\left(\ln \frac{V}{N} - \frac{3}{2}\ln\beta + \frac{3}{2}\ln\left(\frac{2\pi m}{h^2}\right) + 1\right)$$

$$\therefore \quad \bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2}NkT \quad \text{(as expected)}$$

$$S = k(\ln Z + \beta\bar{E}) = Nk\left(\ln\frac{V}{N} + \frac{3}{2}\ln T + \sigma_0\right)$$

$$\sigma_0 = \frac{3}{2}\ln\frac{2\pi m k}{h^2} + 5/2$$ σ_0 it is <u>NOT</u> arbitrary.