Quantum Statistics

Maxwell - Bolzmann

$$f_{MB}(E) = C\, e^{-E/kT}$$

1. particles are distinguishabe
2. Any number of particles are allowed to have energy E

can be taken to be distinguishable if

$$\ell \gg \lambda \qquad \text{for an ideal gas}$$

$$\ell \approx \left(\frac{V}{N}\right)^{1/3} \qquad \text{at STP} \quad V = .0224\ m^3 \text{ for 1 mole}$$

$$\ell = \left(\frac{.0224\ m^3}{6.02\times10^{23}}\right)^{1/3} \sim 3\ nm$$

$$\lambda = \frac{h}{p} \qquad \frac{\langle p^2\rangle}{2m} = \frac{3}{2}kT$$

$$\lambda = \frac{h}{\sqrt{3mkT}} = \frac{hc}{\sqrt{3mc^2kT}} \sim 0.03\ nm$$ for O_2 molecules at $T = 300\,K$

so $\ell \gg \lambda$ is satisfied for idea gas at room temperature distinguishable particles

$$\psi_D = \psi_{\vec{a}}(\vec{r}_1)\,\psi_{\vec{b}}(\vec{r}_2)$$

$\vec{a}, \vec{b}$ - all quantum numbers

$\vec{r}_1, \vec{r}_2$ - coordinates

$$\int d^3\vec{r}_1 \int d^3\vec{r}_2 \; \psi_D^* \psi_D = 2$$

If they are indistinguishable, must take into account proper exchange symmetry

for bosons

$$\psi_s(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_{\vec{a}}(\vec{r}_1)\,\psi_b(\vec{r}_2) + \psi_b(\vec{r}_1)\,\psi_{\vec{a}}(\vec{r}_2)\right]$$

symmetric under particle exchange

for 3 particles

$$\psi_s(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \frac{1}{\sqrt{3!}}\Big[\psi_a(\vec{r}_1)\,\psi_{\vec{b}}(\vec{r}_2)\,\psi_{\vec{c}}(\vec{r}_3) +$$

$$\psi_{\vec{a}}(\vec{r}_1)\,\psi_{\vec{c}}(\vec{r}_2)\,\psi_{\vec{b}}(\vec{r}_3) +$$

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- - - $\Big]$ four other permutations

rohlf 12.10

2 distinguishable particles

$$\psi_D^* \psi_D = \psi_{\vec{a}}^2(\vec{r}_1)\, \psi_{\vec{a}'}^2(\vec{r}_2)$$

for 2 bosons

$$\psi_S^* \psi_S = \frac{1}{2}\left[\psi_{\vec{a}}(\vec{r}_1)\, \psi_{\vec{a}}(\vec{r}_2) + \psi_{\vec{a}}(\vec{r}_1)\, \psi_{\vec{a}}(\vec{r}_1) \right]$$

$$= 2\, \psi_D^* \psi_D$$

for 3 bosons

$$\psi_S^* \psi_S = 6\, \psi_D^* \psi_D$$

$n!$ greater than distinguishable particles

$$W^{boson}_{a \to b} = (n_b + 1)\, W_{a \to b}$$

2 state system

$$\frac{n_a}{n_b} = \frac{W_{b \to a}}{W_{a \to b}} = \frac{e^{-E_a/KT}}{e^{-E_b/KT}}$$ distinguishable

$$\frac{n_a}{n_b} = \frac{(n_a + 1)\, W_{b \to a}}{(n_b + 1)\, W_{b \to a}} = \frac{(n_a + 1)\, e^{-E_a/KT}}{(n_b + 1)\, e^{-E_b/KT}}$$

Bose Distribution

$$W^{boson}_{a\to b} = (n_b+1)\, W_{a\to b}$$

↑ for distinguishable particles

for a two state system

$$\frac{n_a}{n_b} = \frac{(n_a+1)\, W_{a\to b}}{(n_b+1)\, W_{b\to a}} = \frac{(n_a+1)\, e^{-E_a/kT}}{(n_b+1)\, e^{-E_b/kT}}$$

$$\frac{(n_a+1)\, e^{-E_a/kT}}{n_a} = \frac{(n_b+1)\, e^{-E_b/kT}}{n_b} = A(T)$$

$$n_a = \frac{1}{A e^{E_a/kT} - 1}$$

↑ needed for particle conservation

for photons, don't need to conserve number

$A = 1$ (photons)

$$f_{BE}(E) = \frac{1}{e^{E/kT} - 1} \qquad \text{(photons)}$$

Fermi Distribution

2 state system

$$w^{\text{fermion}}_{a\to b} = (1-n_b)\, W_{a\to b}$$

$$w_{b\to a} = (1-n_a)\, W_{b\to a}$$

$$\frac{(1-n_a)\, e^{-E_a/kT}}{n_a} = \frac{(1-n_b)\, e^{-E_b/kT}}{n_b} = A(T)$$

$$n_a = \frac{1}{A\, e^{E_a/kT} + 1}$$

$$A = e^{-E_F/kT}$$ E_F · fermi energy

$$f_{FD} = \frac{1}{e^{(E-E_F)/kT} + 1}$$

Density of States

$$n_s(E) = \frac{N(E)}{V}$$ number of possible states per volume

$$\rho(E) = \frac{dn_s}{dE}$$ - density of states

Non-Relativistic electrons in a box

$$E = \frac{h^2}{8mL^2}\left(n_1^2 + n_2^2 + n_3^2\right)$$

$$R^2 = \left(n_1^2 + n_2^2 + n_3^2\right)^{1/2}$$

$$E = \frac{h^2 R^2}{8mL^2}$$

$$R = \frac{2\sqrt{2mE}\,L}{h}$$

$$N = (2)\left(\frac{1}{8}\right)\left(\frac{4}{3}\right)\pi R^3 = \left(\frac{8\pi}{3}\right)(2mE)^{3/2}\left(\frac{L}{h}\right)^3$$

$$n_s = \frac{N}{L^3} = \left(\frac{8\pi}{3}\right)\frac{(2mE)^{3/2}}{h^3}$$

$$\rho = \frac{dn_s}{dE} = \frac{4\pi(2m)^{3/2}}{h^3}\sqrt{E}$$ (electrons)

Phase Space

Volume in phase space (PS)

$$V_{PS} = \int dx \int dy \int dz \int dp_x \int dp_y \int dp_z$$

a particle occupies a fixed volume in phase space

$$p\lambda = h$$

volume is h^3

$$N(p) = g \frac{V_{PS}}{h^3} = g \frac{V V_p}{h^3}$$

number of intrinsic spin states

$$n_s(p) = \frac{N(p)}{V} = g \frac{V_p}{h^3} = g \frac{4}{3}\pi \frac{p^3}{h^3}$$

$$\rho(E) = \frac{dn_s}{dE} = \frac{dn_s}{dp} \frac{dp}{dE}$$

$$p = \frac{1}{c}\sqrt{E^2 - (mc^2)^2} \quad \text{from } E = \sqrt{(pc)^2 + (mc^2)^2}$$

$$E^2 = (mc^2)^2 + (pc)^2$$

$$2E\,dE = 2pc^2\,dp \qquad \frac{dp}{dE} = \frac{E}{pc^2}$$

$$\rho(E) = \frac{4\pi g p^2}{h^3} \frac{E}{pc^2} = \frac{4\pi g p^2}{h^3 v}, \qquad v = \frac{pc^2}{E}$$

In Class problem

Using $\rho(E) = \dfrac{4\pi g\, p^2}{h^3 V}$

find $\rho(E)$ for photons and electrons.

photons:

$g = 2$ ~ for the two polarization states

$E = pc$

$v = c$

$$\rho(E) = \left(\frac{4\pi}{h^3}\right)(2)\left(\frac{E}{c}\right)^2\cdot\left(\frac{1}{c}\right) = \frac{8\pi}{h^3c^3}E^2$$

electrons

$$p = mv = \sqrt{2mE}$$

$$\rho(E) = \left(\frac{4\pi}{h^3}\right)\underset{\substack{\uparrow \\ \text{2 spin states}}}{(2)}(2mE)\cdot\frac{m}{\sqrt{2mE}} = \frac{4\pi(2m)^{3/2}}{h^3}\sqrt{E}$$

Bose Einstein Condensation

for bosons

$$\frac{dn}{dE} = p(E) \frac{1}{e^{(E-\mu)/kT} - 1}$$

for a spin 0 bose gas

$$p(E) = \frac{4\pi g p^2}{h^3 V}$$

$$g = 1$$

$$p(E) = \frac{4\pi m p^2}{h^3 p} = \frac{4\pi m \sqrt{2mE}}{h^3} = \frac{2\pi (2m)^{3/2}}{h^3} \sqrt{E}$$

$$\frac{dn}{dE} = \frac{2\pi (2m)^{3/2}}{h^3} \frac{\sqrt{E}}{e^{(E-\mu)/kT} - 1}$$

μ - chemical potential - needed to conserve particle number

$$\frac{N}{V} = \frac{2\pi (2m)^{3/2}}{h^3} \int_0^\infty \frac{\sqrt{E}}{e^{(E-\mu)/kT} - 1} dE$$

$\mu < 0$ or $\frac{N}{V}$ can be negative at low E

If Temperature is lowered at constant $\frac{N}{V}$

at some T_0, $\mu = 0$

$$T_0 = 3.31 \frac{\hbar^2}{Km} \left(\frac{N}{V}\right)^{2/3}$$

Integral expression for $\frac{N}{V}$ doesn't treat $E = 0$ properly.

for $T < T_0$

$$N_{E>0} = \frac{V\, 2\pi\, (2m)^{3/2}}{h^3} \int_0^\infty \frac{\sqrt{E}}{e^{E/kT} - 1} = N \left(\frac{T}{T_0}\right)^{3/2}$$

$$N_{E=0} = N\left(1 - \left(\frac{T}{T_0}\right)^{3/2}\right)$$

steady increase of $N_{E=0}$ as $T \to 0$ is Bose Einstein Condensation.

Examples

Superfluid helium

^4He spin = 0

liquifies at 4 K - Von der Walls

$\rho \approx 125 \ kg/m^3$

from $T_0 = 3.31 \frac{\hbar^2}{km} \left(\frac{N}{V}\right)^{2/3}$

$T_0 \sim 3K$

transition to 'superfluid' at 2.2 K

Strong van-der-walls interactions reduce

$N_{E=0}$ to 10 % even at $T = 0$

Rubidium gas

^{87}Rb

Cooled to 170 nK

laser cooling

magnetic cooling

BEC signature