Ideal Quantum Gas - Grand canonical ensemble

$$\ln \mathcal{Z} = \pm \sum_i \ln\left(1 \pm e^{-\beta(\epsilon_i - \mu)}\right) \qquad +\text{FD}, \; -\text{BE}$$

for free particles, states can be labeled by ~~wavevector~~ wavevector $\vec{k}$ with $k_\mu = \frac{2\pi n_\mu}{L}$, $n_\mu = 0, \pm 1, \pm 2, \ldots$ due to periodic boundary conditions. volume $V = L^3$

$$\Rightarrow \sum_{\substack{i \\ \text{states}}} \rightarrow \sum_s \sum_{\vec{k}} \rightarrow g_s \frac{V}{(2\pi)^3} \int_0^\infty dk\, 4\pi k^2$$

spin polarizations

\# spin states for each $\vec{k}$

for free particles, ϵ depends only on $|\vec{k}|$. Define density of states $g(\epsilon)$ such that

$$\frac{g_s}{(2\pi)^3} \int dk\, 4\pi k^2 = \int g(\epsilon)\, d\epsilon$$

$g(\epsilon)$ = # states with energy ϵ per unit energy per volume

$$\Rightarrow g(\epsilon) = \frac{g_s 4\pi}{(2\pi)^3} k^2 \frac{dk}{d\epsilon}$$

For non-relativistic particles $\epsilon = \frac{\hbar^2 k^2}{2m}$, $k = \sqrt{\frac{2m\epsilon}{\hbar^2}}$

$$g(\epsilon) = \frac{g_s 4\pi}{(2\pi)^3} \frac{2m\epsilon}{\hbar^2} \sqrt{\frac{2m}{\hbar^2}} \frac{1}{2\sqrt{\epsilon}}$$

$$= \frac{2\pi g_s}{(2\pi)^3} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\epsilon} = \left(\frac{2\pi m}{h^2}\right)^{3/2} \frac{2^{3/2}(2\pi)^{3/2}}{(2\pi)^2} g_s \sqrt{\epsilon}$$

Density of States
$$\boxed{g(\epsilon) = \left(\frac{2\pi m}{h^2}\right)^{3/2} \frac{2 g_s}{\sqrt{\pi}} \sqrt{\epsilon}} \qquad g \sim \sqrt{\epsilon}$$

or $g(\epsilon) = \frac{2g_s}{\sqrt{\pi}\,\lambda^3}\frac{1}{k_BT}\sqrt{\frac{\epsilon}{k_BT}}$ using $\lambda = \left(\frac{h^2}{2\pi m k_BT}\right)^{1/2}$

pressure

$$\frac{P}{k_BT} = \frac{1}{V}\ln\mathcal{L} = \pm\frac{1}{V}\sum_i \ln\left(1 \pm z\, e^{-\beta\epsilon_i}\right) \qquad z = e^{\beta\mu}$$

$$= \pm\int_0^\infty d\epsilon\, g(\epsilon)\ln\left(1\pm z e^{-\beta\epsilon}\right)$$

$$= \pm\left(\frac{2\pi m}{h^2}\right)^{3/2}\frac{2g_s}{\sqrt{\pi}}\int_0^\infty d\epsilon\,\sqrt{\epsilon}\,\ln\left(1\pm z e^{-\beta\epsilon}\right)$$

substitute variables $y = \beta\epsilon$

$$\frac{P}{k_BT} = \pm\left(\frac{2\pi m k_BT}{h^2}\right)^{3/2}\frac{2g_s}{\sqrt{\pi}}\int_0^\infty dy\, y^{1/2}\ln\left(1\pm z e^{-y}\right)$$

integrate by parts $\qquad \lambda = \left(\frac{h^2}{2\pi m k_BT}\right)^{1/2}$ thermal wavelength

$$\frac{p}{k_BT} = \pm\frac{2g_s}{\sqrt{\pi}\,\lambda^3}\left\{\underbrace{\frac{2}{3}y^{3/2}\ln\left(1\pm z e^{-y}\right)\Big|_0^\infty}_{=0} - \int_0^\infty dy\,\frac{2}{3}y^{3/2}\frac{(\mp z e^{-y})}{1\pm z e^{-y}}\right\}$$

$$\boxed{\frac{p}{k_BT} = \frac{4g_s}{3\sqrt{\pi}\,\lambda^3}\int_0^\infty dy\,\frac{y^{3/2}}{z^{-1}e^{y}\pm 1}} \qquad \begin{matrix}+\ \text{FD}\\ -\ \text{BE}\end{matrix}$$

density of particles $\frac{N}{V} = \frac{1}{V}\sum_i \langle n_i\rangle$

$$\frac{N}{V} = \frac{1}{V}\sum_i\frac{1}{z^{-1}e^{\beta\epsilon_i}\pm 1} = \int_0^\infty d\epsilon\, g(\epsilon)\frac{1}{z^{-1}e^{\beta\epsilon}\pm 1}$$

$$= \left(\frac{2\pi m}{h^2}\right)^{3/2}\frac{2g_s}{\sqrt{\pi}}\int_0^\infty d\epsilon\,\frac{\sqrt{\epsilon}}{z^{-1}e^{\beta\epsilon}\pm 1}$$

$$= \left(\frac{2\pi m k_BT}{h^2}\right)^{3/2}\frac{2g_s}{\sqrt{\pi}}\int dy\,\frac{y^{1/2}}{z^{-1}e^{y}\pm 1}$$

$$\boxed{\frac{N}{V} = \frac{2g_s}{\sqrt{\pi}\,\lambda^3}\int_0^\infty dy\,\frac{y^{1/2}}{z^{-1}e^{y}\pm 1}} \qquad \begin{matrix}+\ \text{FD}\\ -\ \text{BE}\end{matrix}$$

energy density $\quad E = \sum_i \epsilon_i \langle n_i \rangle$

$$\frac{E}{V} = \frac{1}{V} \sum_i \frac{\epsilon_i}{z^{-1} e^{\beta \epsilon_i} \pm 1} = \int_0^\infty d\epsilon \, g(\epsilon) \frac{\epsilon}{z^{-1} e^{\beta\epsilon} \pm 1}$$

$$= \frac{2 g_s}{\sqrt{\pi}\,\lambda^3} k_B T \int_0^\infty dy \frac{y^{3/2}}{z^{-1} e^{y} \pm 1}$$

$$\frac{E}{V} = \frac{3}{2} k_B T \frac{4 g_s}{3\sqrt{\pi}\,\lambda^3} \int_0^\infty \frac{y^{3/2}}{z^{-1} e^{y} \pm 1} = \left(\frac{3}{2} k_B T\right)\left(\frac{p}{k_B T}\right)$$

$$\Rightarrow \frac{E}{V} = \frac{3}{2} p \quad \text{or} \quad \boxed{p = \frac{2}{3}\frac{E}{V}}$$

both fermions and bosons (same result as for classical, ideal gas!!) nonrelativistic only

Define "standard functions" (see Pathria Appendices D and E)

$$f_n(z) \equiv \frac{1}{\Gamma(n)} \int_0^\infty dy \frac{y^{n-1}}{z^{-1} e^{y} + 1} = \sum_{\ell=1}^{\infty} (-1)^{\ell+1} \frac{z^\ell}{\ell^n}$$

$$g_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty dy \frac{y^{n-1}}{z^{-1} e^{y} - 1} = \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^n}$$

$\Gamma(n+1) = n\,\Gamma(n)$

$\Gamma(\tfrac{1}{2}) = \sqrt{\pi}$

$\Rightarrow \Gamma(3/2) = \tfrac{1}{2}\sqrt{\pi}$

$\Gamma(5/2) = \tfrac{3}{4}\sqrt{\pi}$

In terms of these:

Fermions	Bosons
$\frac{p}{k_B T} = \frac{g_s}{\lambda^3} f_{5/2}(z)$	$\frac{p}{k_B T} = \frac{g_s}{\lambda^3} g_{5/2}(z)$
$\frac{N}{V} = \frac{g_s}{\lambda^3} f_{3/2}(z)$	$\frac{N}{V} = \frac{g_s}{\lambda^3} g_{3/2}(z)$
$\frac{E}{V} = \frac{3}{2} k_B T \frac{g_s}{\lambda^3} f_{5/2}(z)$	$\frac{E}{V} = \frac{3}{2} k_B T \frac{g_s}{\lambda^3} g_{5/2}(z)$
$\frac{E}{N} = \frac{3}{2} k_B T \frac{f_{5/2}(z)}{f_{3/2}(z)}$	$\frac{E}{N} = \frac{3}{2} k_B T \frac{g_{5/2}(z)}{g_{3/2}(z)}$

Equation of state: low densities - virial expansion

$z \ll 1$ "non-degenerate"

keep lowest terms in series expansion

$$\frac{p}{k_BT} = \frac{g_s}{\lambda^3}\begin{Bmatrix} f_{5/2} \\ g_{5/2}\end{Bmatrix} = \frac{g_s}{\lambda^3}\left(z \mp \frac{z^2}{2^{5/2}} + \cdots\right) \quad \begin{matrix} - \text{ FD} \\ + \text{ BE}\end{matrix}$$

$$\frac{N}{V} = \frac{g_s}{\lambda^3}\begin{Bmatrix} f_{3/2} \\ g_{3/2}\end{Bmatrix} = \frac{g_s}{\lambda^3}\left(z \mp \frac{z^2}{2^{3/2}} + \cdots\right)$$

$$\Rightarrow \frac{p}{k_BT} = \frac{N}{V}\frac{\left(z \mp \frac{z^2}{2^{5/2}} + \cdots\right)}{\left(z \mp \frac{z^2}{2^{3/2}} + \cdots\right)} = \frac{N}{V}\left(1 \mp \frac{z}{2^{5/2}} + \cdots\right)\left(1 \pm \frac{z}{2^{3/2}} + \cdots\right)$$

$$= \frac{N}{V}\left(1 \pm \frac{z}{2^{3/2}} \mp \frac{z}{2^{5/2}} + \cdots\right) \qquad \frac{1}{2^{3/2}} - \frac{1}{2^{5/2}} = \frac{2}{2^{5/2}} - \frac{1}{2^{5/2}} = \frac{1}{2^{5/2}}$$

$$pV = Nk_BT\left(1 \pm \frac{z}{2^{5/2}} + \cdots\right)$$

quantum correction to classical ideal gas law.

+ FD - p increases compared to classically
- effective repulsion due to Pauli exclusion

− BE - p decreases compared to classically
- effective attraction.

above is similar conclusion to what we saw from 2-particle density matrix.

for small z, the leading term gives $\frac{N}{V} = \frac{g_s}{\lambda^3} z$

or $z = \left(\frac{N}{V}\frac{\lambda^3}{g_s}\right)$ - same result we had classically

$\Rightarrow$ small z limit is the low density limit $n\lambda^3 \ll 1$ or high T

$$pV = Nk_BT\left(1 \pm \frac{1}{2^{5/2} g_s}\frac{N}{V}\lambda^3 + \cdots\right)$$