

Ideal Quantum Gas - Grand canonical ensemble

$$\ln Z = \pm \sum_i \ln(1 \pm e^{-\beta(\epsilon_i - \mu)}) \quad + \text{FD}, - \text{BE}$$

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

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

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

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

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

$g(\epsilon) = \# \text{ states with energy } \epsilon \text{ per unit energy per volume}$

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

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

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

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

Density of States

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

$$g \sim \sqrt{\epsilon}$$

pressure

$$g(\epsilon) = \frac{2g_s}{\sqrt{\pi} \lambda^3} \frac{1}{k_B T} \sqrt{\epsilon}$$

$$\text{using } \lambda = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2}$$

$$\frac{P}{k_B T} = \frac{1}{V} \ln \mathcal{Z} = \pm \frac{1}{V} \sum_i \ln(1 \pm z e^{-\beta \epsilon_i}) \quad z = e^{\beta \mu}$$

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

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

substitute variables $y = \beta \epsilon$

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

integrate by parts

$$\lambda = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2} \text{ thermal wavelength}$$

$$\frac{P}{k_B T} = \pm \frac{2g_s}{\sqrt{\pi} \lambda^3} \left\{ \frac{2}{3} y^{3/2} \ln(1 \pm z e^{-y}) \Big|_0^\infty - \int_0^\infty dy \frac{2}{3} y^{3/2} \frac{(\mp z e^{-y})}{1 \pm z e^{-y}} \right\}$$

$$\boxed{\frac{P}{k_B T} = \frac{4g_s}{3\sqrt{\pi} \lambda^3} \int_0^\infty dy \frac{y^{3/2}}{z^{-1} e^y \pm 1}}$$

+ FD
- BE

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

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

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

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

$$\boxed{\frac{N}{V} = \frac{2g_s}{\sqrt{\pi} \lambda^3} \int_0^\infty dy \frac{y^{1/2}}{z^{-1} e^y \pm 1}}$$

+ FD
- BE

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

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

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

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

$$\Rightarrow \frac{E}{V} = \frac{3}{2} P \quad \text{or} \quad \boxed{P = \frac{2}{3} \frac{E}{V}} \quad \text{both fermions and bosons}$$

(same result as for classical, ideal gas!!) nonrelativistic only

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

$$\begin{aligned} f_n(z) &\equiv \frac{1}{\Gamma(n)} \int_0^\infty dy \frac{y^{n-1}}{z^{-1} e^y + 1} = \sum_{\ell=1}^\infty (-1)^{\ell+1} \frac{z^\ell}{\ell^n} \\ g_n(z) &= \frac{1}{\Gamma(n)} \int_0^\infty dy \frac{y^{n-1}}{z^{-1} e^y - 1} = \sum_{\ell=1}^\infty \frac{z^\ell}{\ell^n} \end{aligned} \quad \left\{ \begin{array}{l} \Gamma(n+1) = n \Gamma(n) \\ \Gamma(1/2) = \sqrt{\pi} \\ \Rightarrow \Gamma(3/2) = \frac{1}{2} \sqrt{\pi} \\ \Gamma(5/2) = \frac{3}{4} \sqrt{\pi} \end{array} \right.$$

In terms of these:

Fermions

$$\frac{P}{k_B T} = \frac{g_s}{\lambda^3} f_{5/2}(z)$$

$$\frac{N}{V} = \frac{g_s}{\lambda^3} f_{3/2}(z)$$

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

$$\frac{E}{N} = \frac{3}{2} k_B T \frac{f_{5/2}(z)}{f_{3/2}(z)}$$

Bosons

$$\frac{P}{k_B T} = \frac{g_s}{\lambda^3} g_{5/2}(z)$$

$$\frac{N}{V} = \frac{g_s}{\lambda^3} g_{3/2}(z)$$

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

$$\frac{E}{N} = \frac{3}{2} k_B T \frac{g_{5/2}(z)}{g_{3/2}(z)}$$

Equation of state: low densities - virial expansion

$$z \ll 1$$

"non-degenerate"

keep lowest terms in series expansion

$$\frac{p}{k_B T} = \frac{g_s}{\lambda^3} \left\{ \frac{f_{5/2}}{g_{5/2}} \right\} = \frac{g_s}{\lambda^3} \left(z \mp \frac{z^2}{2^{5/2}} + \dots \right) \quad \begin{array}{l} - \text{FD} \\ + \text{BE} \end{array}$$

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

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

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

$$\frac{1}{2^{3/2}} - \frac{1}{2^{5/2}} = \frac{2}{2^{5/2}} - \frac{1}{2^{5/2}} = \frac{1}{2^{5/2}}$$

$$pV = Nk_B T \left(1 \pm \frac{z}{2^{5/2}} + \dots \right)$$

↑ 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

→ small z limit is the low density limit $n \lambda^3 \ll 1$

$$pV = Nk_B T \left(1 \pm \frac{1}{2^{5/2} g_s} \frac{N}{V} \lambda^3 + \dots \right) \quad \equiv \text{high } T$$