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 $k_\mu = \frac{2\pi n_\mu}{L}$, $n_\mu = 0, 1, \ldots$
due to periodic boundary conditions. volume $V = L^3$

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

s: spin polarizations

g_s: # 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 $\epsilon = \frac{\hbar^2 k^2}{2m}$, $k = \sqrt{\frac{2m\epsilon}{\hbar^2}}$

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

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

Density of States

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

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

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 $y = \beta\epsilon$

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

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

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

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

+ FD
− BE

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

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

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

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

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

+ FD
− BE

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

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

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

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

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

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

Equation of state: low densities - virial expansion

$z \ll 1$ "non-degenerate"

keep lowest terms in series expansion

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

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

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

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

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

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

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 $n\lambda^3 \ll 1$

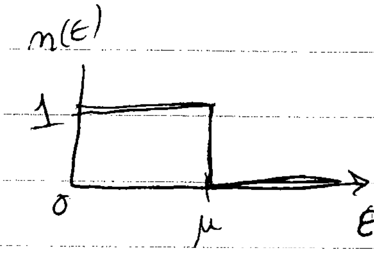
$$pV = Nk_B T\left(1 \pm \frac{1}{2^{5/2} g_s}\frac{N}{V}\lambda^3 + \cdots\right)$$

or high T

Sommerfeld model of electrons in a conductor

Fermi gas - high density / low temperature limit
"degenerate" fermi gas

Consider first $T \to 0$



$$\langle n(\epsilon) \rangle = \frac{1}{e^{\beta(\epsilon-\mu)}+1}$$

as $T \to 0$ $\quad e^{\beta(\epsilon-\mu)} \to \begin{cases} \infty & \epsilon > \mu \\ 0 & \epsilon < \mu \end{cases}$

$$\Rightarrow \langle n(\epsilon) \rangle \to \begin{cases} 0 & \epsilon > \mu \\ 1 & \epsilon < \mu \end{cases}$$

$\Rightarrow$ all states with $\epsilon < \mu$ are filled, all states with $\epsilon > \mu$ are empty. This is the $T=0$ ground state of the Fermi gas. We therefore see that $\mu(T=0)$ is the energy of the highest energy single particle state that is occupied in the ground state. One calls this energy the Fermi-energy

$$\epsilon_F \equiv \mu(T=0)$$

at $T=0$

$$N = g_s \sum_{\vec{k} \,\leftarrow\, \text{s.t. } \frac{\hbar^2 k^2}{2m} \le \epsilon_F} 1 \qquad \text{count occupied states}$$

$$= g_s \frac{V}{(2\pi)^3} 4\pi \int_0^{k_F} dk\, k^2 = \frac{g_s V}{6\pi^2} k_F^3 \qquad \text{where } \frac{\hbar^2 k_F^2}{2m} = \epsilon_F$$

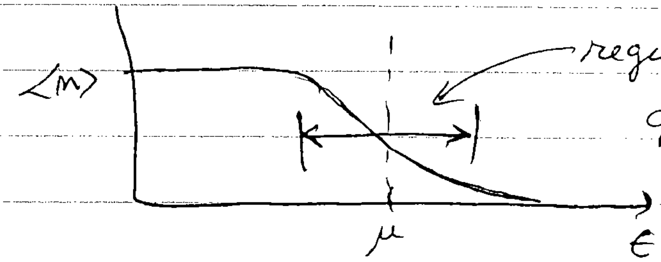
$$n \equiv \frac{N}{V} = \frac{g_s}{6\pi^2} k_F^3 = \frac{g_s}{6\pi^2} \left(\frac{2m\epsilon_F}{\hbar^2} \right)^{3/2}$$

or

$$\epsilon_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2 n}{g_s} \right)^{2/3}, \quad k_F = \left(\frac{6\pi^2 n}{g_s} \right)^{1/3}$$

relation between $\mu(T=0)$ and density $n = N/V$

Now at finite T



region of energy where $\langle n \rangle$ differs from ground state ($T=0$) is a region of order $k_B T$ about μ.

So the $T \approx 0$ approx is good when $k_B T \ll \mu$

~~Since $\mu(T) > \mu(0) = \epsilon_F$ we have~~

Using $\mu \approx \mu(0) = \epsilon_F$ we have

$$k_B T \ll \frac{\hbar^2}{2m}\left(\frac{6\pi^2 n}{g_s}\right)^{2/3} \Rightarrow \frac{2\pi m k_B T}{h^2} \ll \frac{1}{4\pi}\left(\frac{6\pi^2 n}{g_s}\right)^{2/3}$$

$$\Rightarrow \lambda^2 \gg 4\pi\left(\frac{g_s}{6\pi^2 n}\right)^{2/3}$$

$$\Rightarrow n\lambda^3 \gg \frac{(4\pi)^{3/2}}{6\pi^2} g_s = \frac{4}{3\sqrt{\pi}} g_s$$

so this is equivalent to a low T or a high density limit $n\lambda^3 \gg 1$ – called the "degenerate" limit.

(just as the classical limit $z \approx n\lambda^3 \ll 1$ was a high T low density limit)

Fermi temperature $T_F = \epsilon_F / k_B$. Degenerate limit is $T \ll T_F$

For electrons in a metal, $T_F \approx 10000\,°K$.

So electrons in a metal are always in the degenerate limit.

Energy in the degenerate limit $T=0$

$$\frac{E}{V} = \int_0^{\epsilon_F} d\epsilon \; g(\epsilon)\,\epsilon \qquad g(\epsilon) = C\sqrt{\epsilon}$$

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

density of states

$$n = \frac{N}{V} = \int_0^{\epsilon} d\epsilon \; g(\epsilon)$$

$$\left.\begin{aligned} \Rightarrow \frac{E}{V} &= C\int_0^{\epsilon_F} d\epsilon \; \epsilon^{3/2} = \frac{2}{5} C \epsilon_F^{5/2} \\ n = \frac{N}{V} &= C\int_0^{\epsilon_F} d\epsilon \; \epsilon^{1/2} = \frac{2}{3} C \epsilon_F^{3/2} \end{aligned}\right\} \Rightarrow \frac{E}{V} = \frac{3}{5}\frac{N}{V}\epsilon_F$$

$$\frac{E}{V} = \frac{3}{5} n \epsilon_F \qquad \text{or} \qquad \boxed{\frac{E}{N} = \frac{3}{5}\epsilon_F}$$

energy per volume — energy per particle

Above gives $T=0$ results. To get behavior at low $T>0$, or to get quantities such as $C_V = \left(\frac{\partial E}{\partial T}\right)_V$, we need to get the next order terms in a low temperature expansion.

In general we need to do integrals of the form

$$\int d\epsilon \frac{\tilde{\phi}(\epsilon)}{z^{-1}e^{\beta\epsilon}+1} = \int d\epsilon \; \tilde{\phi}(\epsilon)\, n(\epsilon), \qquad \tilde{\phi}(\epsilon) \text{ some function}$$

ex: to compute n, $\tilde{\phi}(\epsilon) = g(\epsilon)$; to compute $\frac{E}{V}$, $\tilde{\phi}(\epsilon) = g(\epsilon)\,\epsilon$