

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

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

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

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

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

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

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

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

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

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  $\frac{N}{V} = \frac{15}{V^2} \langle m \rangle$

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

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

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

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

+ FD

- BE

Energy density  $E = \sum_i \epsilon_i \langle m_i \rangle$

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

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

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

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

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

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

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

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

$$\left. \begin{array}{l} \Gamma(n+1) = n \Gamma(n) \\ \Gamma(1/2) = \sqrt{\pi} \\ \Rightarrow \Gamma(3/2) = \frac{1}{2} \sqrt{\pi} \\ \Gamma(5/2) = \frac{3}{4} \sqrt{\pi} \end{array} \right\}$$

In terms of these:

Fermions

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

Bosons

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

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

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

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

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

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

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

Equation of state: low densities - virial expansion

$$z \ll 1$$

"non-degenerate"

keep lowest terms in series expansion

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

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

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

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

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

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

↑ 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  $n \lambda^3 \ll 1$

$$PV = N k_B T \left( 1 \pm \frac{1}{2^{5/2} g_s} \frac{N}{V} \lambda^3 + \dots \right) \quad \begin{array}{l} \text{or high } T \\ \equiv \end{array}$$

# Sommerfeld model of electrons in a conductor

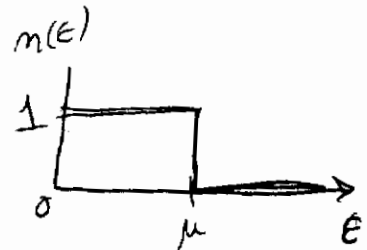
Fermi gas - high density / low temperature limit  
"degenerate" fermi gas

Consider first  $T \rightarrow 0$

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

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

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



$\Rightarrow$  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  $T=0$

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

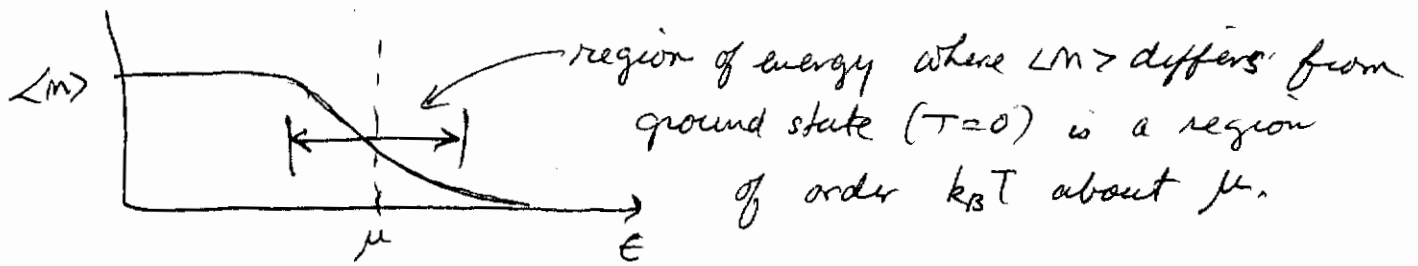
$$= g_s \frac{V}{(2\pi)^3} 4\pi \int_0^{k_F} dk k^2 = \frac{g_s V}{6\pi^2} k_F^3 \quad \text{where } \frac{\hbar^2 k_F^2}{2m} = \epsilon_F$$

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

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

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

Now at finite T



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

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

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

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

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

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

So this is equivalent to a low  $T$  or a high density limit  
 $m \lambda^3 \gg 1$  - called the "degenerate" limit.

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

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

For electrons in a metal,  $T_F \approx 10000 \text{ K}$ .

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