Equation of state: low densities - virial expansion

$z \ll 1$ "non-degenerate"
near the classical limit

keep lowest terms in series expansion

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

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

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

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

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

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 $z = \left(\frac{N}{V}\frac{\lambda^3}{g_s}\right) = \frac{N}{Q_1}$ - same result we had classically

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

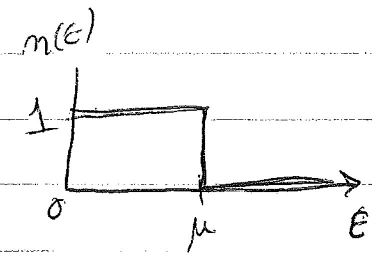
$$pV = Nk_BT\left(1 \pm \frac{1}{2^{5/2}g_s}\frac{N}{V}\lambda^3 + \cdots\right)$$

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

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

$T=0$

$$N = g_s \sum_{\vec{k}} 1 \qquad \text{count occupied states}$$

$\vec{k}$ $\leftarrow$ such that $\frac{\hbar^2 k^2}{2m} < \mathcal{E}_F$ $\qquad \frac{\hbar^2 k_F^2}{2m} \equiv \mathcal{E}_F$

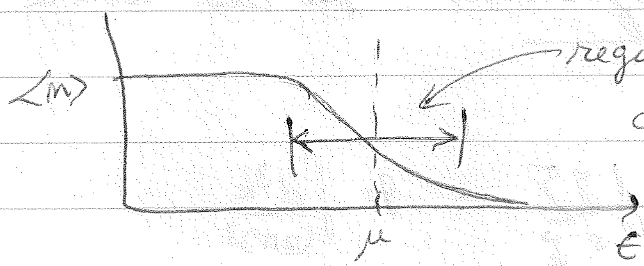
density $\quad n = \frac{N}{V} = \frac{1}{V} g_s \sum_{\vec{k}} 1 = \int_0^{\mathcal{E}_F} d\mathcal{E}\, g(\mathcal{E})$

$$= \frac{2g_s}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2}\right)^{3/2} \int_0^{\mathcal{E}_F} d\mathcal{E}\, \sqrt{\mathcal{E}} = \frac{2g_s}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2}\right)^{3/2} \frac{2}{3} \mathcal{E}_F^{3/2}$$

$$= \frac{2g_s}{\sqrt{\pi}} \left(\frac{2\pi m}{4\pi^2 \hbar^2}\right)^{3/2} \frac{2}{3} \mathcal{E}_F^{3/2} = \frac{2g_s}{\sqrt{\pi}\, 8\pi^{3/2}} \frac{2}{3} \left(\frac{2m}{\hbar^2}\right)^{3/2} \mathcal{E}_F^{3/2}$$

$$= \frac{g_s}{6\pi^2} \Big(\underbrace{\frac{2m\,\mathcal{E}_F}{\hbar^2}}_{=k_F}\Big)^{3/2} \Rightarrow \boxed{\mathcal{E}_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 n}{g_s}\right)^{3/2}}$$

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.

$$g(\varepsilon) = C\sqrt{\varepsilon}$$

$$g(\varepsilon_F) = C\sqrt{\varepsilon_F}$$

$$n = \int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon) = \int_0^{\varepsilon_F} d\varepsilon\, C\, \varepsilon^{1/2} = \frac{2}{3} C \varepsilon_F^{3/2}$$

$$\Rightarrow C = \frac{3}{2} \frac{n}{\varepsilon_F^{3/2}}$$

$$\boxed{g(\varepsilon_F) = \frac{3}{2} n \frac{\varepsilon_F^{1/2}}{\varepsilon_F^{3/2}} = \frac{3}{2} \frac{n}{\varepsilon_F}}$$

$$g(\varepsilon) = g(\varepsilon_F) \frac{g(\varepsilon)}{g(\varepsilon_F)} = \frac{3}{2} \frac{n}{\varepsilon_F} \sqrt{\frac{\epsilon}{\epsilon_F}}$$

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

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

$$\Rightarrow \frac{E}{V} = C\int_0^{\epsilon_F} d\epsilon \; \epsilon^{3/2} = \frac{2}{5} C \epsilon_F^{5/2}$$

$$n = \frac{N}{V} = C\int_0^{\epsilon_F} d\epsilon \; \epsilon^{1/2} = \frac{2}{3} C \epsilon_F^{3/2}$$

$$\Rightarrow \frac{E}{V} = \frac{3}{5}\frac{N}{V}\epsilon_F$$

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

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

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

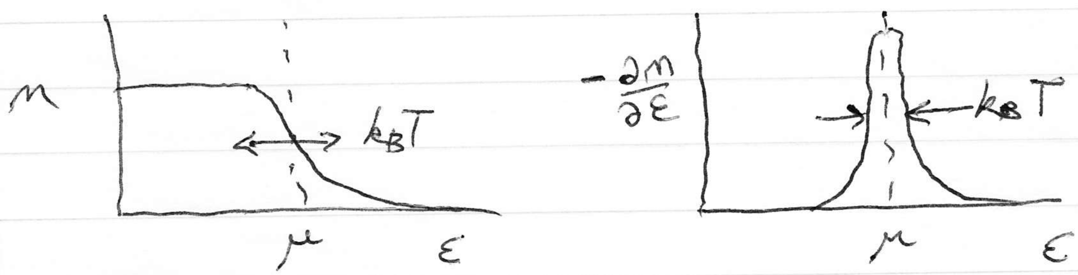
ex: to compute n, $\tilde{\phi}(\epsilon) = g(\epsilon)$; to compute $\frac{E}{V}$, $\tilde{\phi}(\epsilon) = g(\epsilon)\,\epsilon$

To evaluate integrals of the form $\int_0^\infty d\varepsilon \frac{\tilde{\phi}(\varepsilon)}{z^{-1}e^{\beta\varepsilon}+1}$ one uses the Sommerfeld expansion

$$n(\varepsilon) = \frac{1}{z^{-1}e^{\beta\varepsilon}+1} \qquad \phi(\varepsilon) = \int_0^\varepsilon d\varepsilon' \, \tilde{\phi}(\varepsilon')$$

Then

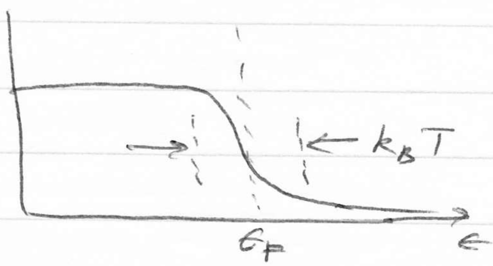
$$\int_0^\infty d\varepsilon \; \tilde{\phi}(\varepsilon) n(\varepsilon) = \Big[\phi(\varepsilon) n(\varepsilon) \Big]_0^\infty + \int_0^\infty d\varepsilon \, \phi(\varepsilon) \left(-\frac{\partial n}{\partial \varepsilon} \right)$$



Integral is only non-zero within region of width $k_B T$ around $\mu \simeq \varepsilon_F = k_B T_F$ and $T \ll T_F$

so expand integrand about $\varepsilon = \mu$ in a Taylor series in $(\varepsilon - \mu)$. Only even powers in this expansion are non-zero. The result is a power series in $\left(\frac{T}{T_F}\right)^{2n}$. This is the Sommerfeld expansion. Since for metals $T \ll T_F$, we only need the lowest terms in this expansion

Simple estimate of C_V



when increase temperature to $k_B T$, the electrons near the fermi energy ϵ_F will increase their energy by an amount $\sim k_B T$. The number of such electrons ~~is roughly~~ per unit volume is roughly

$$\underbrace{g(\epsilon_F)}_{\text{density of states at } \epsilon_F}\underbrace{(k_B T)}_{\text{energy interval about } \epsilon_F \text{ of states which } \cancel{\text{increase}} \text{ get excited}}$$

$\Rightarrow$ increase in energy per unit volume is

$$\Delta u \sim \underbrace{(g(\epsilon_F) k_B T)}_{\#\text{ electrons excited}} \underbrace{(k_B T)}_{\text{excitation energy per excited electron}} \sim g(\epsilon_F)(k_B T)^2$$

$$\Rightarrow c_V = \frac{d\Delta u}{dT} \sim g(\epsilon_F) k_B^2 T \underbrace{=}_{\text{for free electrons}} \frac{3}{2}\frac{n}{\epsilon_F} k_B^2 T = \frac{3}{2} n k_B \left(\frac{T}{T_F}\right)$$

The Sommerfeld expansion gives the <u>precise</u> numerical coefficient

$$\frac{C_V}{V} = c_V = \frac{\pi^2}{2}\left(\frac{k_B T}{\epsilon_F}\right) n k_B = \frac{\pi^2}{2}\left(\frac{T}{T_F}\right) n k_B$$