Quantum Statistical Mechanics (contd.)

Equation of state

Fermi-Dirac :

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

$$\lambda^3 n = f_{3/2}(z)$$

Bose Einstein :

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

$$\lambda^3 n = g_{3/2}(z)$$

$$\left.\begin{matrix} f_k(z) \\ g_k(z) \end{matrix}\right\} = \frac{2^{2k-1}}{\sqrt{\pi}} \frac{\Gamma(k-\frac{1}{2})}{\Gamma(2k-1)} \int_0^\infty dx \, \frac{x^{2k-1}}{z^{-1}e^{x^2} \pm 1} .$$

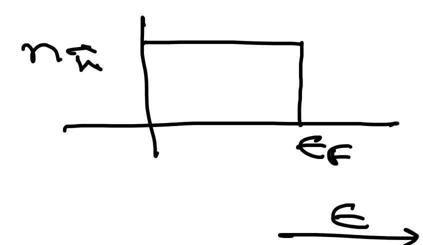
Fermi gas

Low temperature limit

$$n_{\vec{k}} = \frac{1}{e^{\beta(\epsilon_{\vec{k}} - \mu)} + 1} \xrightarrow[T \to 0]{} \begin{cases} 0 & \text{if } \epsilon_{\vec{k}} > \mu \\ 1 & \text{if } \epsilon_{\vec{k}} < \mu \end{cases}$$

$$\Theta(x) = \begin{cases} 1 & \text{if } x > 0 \\ 0 & \text{if } x < 0 \end{cases}$$

$$n_{\vec{k}} \xrightarrow[T \to 0]{} \Theta(\mu - \epsilon_{\vec{k}}).$$



Define Fermi energy,

$$\epsilon_F = \mu(n, 0).$$

" Quantum Degenerate limit "

We know, $N = \sum_{\substack{\text{states} \\ \epsilon < \epsilon_F}} 1$

For fermions of spin S

$$N = (2S+1) \sum_{\substack{\text{states} \\ \epsilon < \epsilon_F}} 1 = \frac{V(2S+1)}{(2\pi)^3} \int_{|\vec{k}| < \vec{k}_F} d^3\vec{k}$$

$$= \frac{V(2S+1)}{(2\pi)^3} \frac{4\pi}{3} k_F^3 .$$

$$\therefore n = \frac{N}{V} = \frac{(2S+1)}{6\pi^2} k_F^3 .$$

$$k_F = \left(\frac{6\pi^2 n}{(2S+1)} \right)^{1/3}$$

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

Ground State

At absolute zero,

$$U_0 = \sum_{|\vec{k}|<k_F} \epsilon_{\vec{k}} = \frac{V}{(2\pi)^3}(2S+1)\int_0^{k_F} 4\pi k^2 dk \left(\frac{\hbar^2 k^2}{2m}\right).$$

$$= \frac{V(2S+1)}{(2\pi)^3}\left(\frac{\hbar^2}{2m}\right)\frac{4\pi}{5}k_F^5.$$

$$= \left\{\frac{V(2S+1)}{(2\pi)^3}\frac{4\pi}{3}k_F^3\right\}\frac{3}{5}\frac{\hbar^2 k_F^2}{2m}$$

$$= N\left(\frac{3}{5}\epsilon_F\right)$$

$$\boxed{\frac{U_0}{N} = \frac{3}{5}\epsilon_F} \leftarrow \text{Internal energy per fermion at } T=0.$$

independent of S.

Recall, $PV = \frac{2}{3}U$.

$\therefore$ At absolute zero,

$$\boxed{P_0 = \frac{2}{5}n\epsilon_F} \neq 0.$$

"zwitterbewegung"

Quantum mechanical fluctuations.

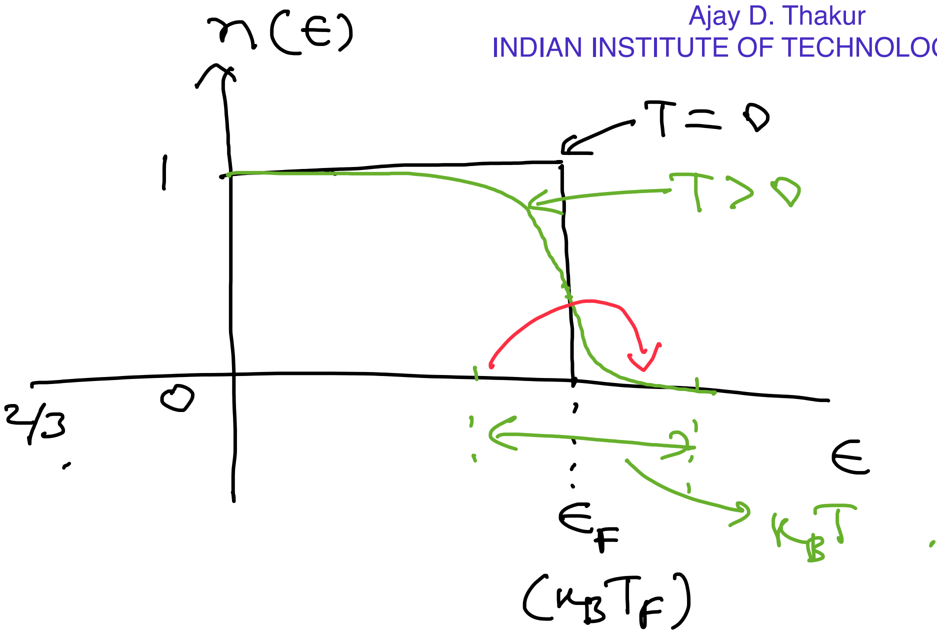
e.g., for a Fermi gas with $n = 10^{22}\ \mathrm{cm}^{-3}$,

$P_0 \approx 10^4$ atm. Huge!.

Fermi temperature, T_F

$$T_F = \left(\frac{\epsilon_F}{k_B}\right).$$

$$= \left(\frac{\hbar^2}{2 m k_B}\right)\left[\frac{6\pi^2 n}{(2S+1)}\right]^{2/3}.$$



Typical metals, $\epsilon_F \approx 2\,eV$

& $T_F \sim 20{,}000\,K$.

99.985 % of Fermions are "frozen" below ϵ_F at room temperatures.

Fraction excited $\propto \left(\frac{T}{T_F}\right)$.

~ 0.015

Avg. excitation energy per particle $\sim k_B T$.

Internal energy $\sim \left(\frac{T}{T_F}\right) N k_B T$.

$$\therefore \boxed{\frac{C}{N k_B} \sim \left(\frac{T}{T_F}\right).}$$

Low temperature properties of a Fermi Gas

$T \ll T_F$ corresponds to $n\lambda^3 \gg 1$.
(Degenerate limit)

Recall, $n\lambda^3 = \underbrace{f_{3/2}(z)}$.
$\hookrightarrow$ low temperature limit
(Asymptotic expansion)

$$f_n(z) = \sum_{l=1}^{\infty} (-1)^{l+1} \frac{z^l}{l^n}.$$

$$f_{3/2}(z) = \frac{4}{\sqrt{\pi}} \int_0^{\infty} dx \frac{x^2}{z^{-1}e^{x^2}+1}.$$

; Let $y = x^2$
$z = e^{\beta\mu} = e^{\xi}$.
$\therefore \xi = \ln z$.
$2x\,dx = dy$

$\left\{ \begin{array}{l} \text{as } x \to 0,\ y \to 0. \\ \& \ x \to \infty,\ y \to \infty. \end{array} \right.$

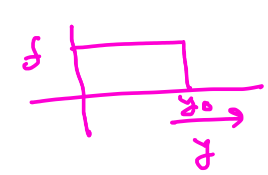
$$= \frac{2}{\sqrt{\pi}} \underbrace{\int_0^{\infty} dy \frac{\sqrt{y}}{e^{y-\xi}+1}}_{\int dy\,(u\,v)}.$$

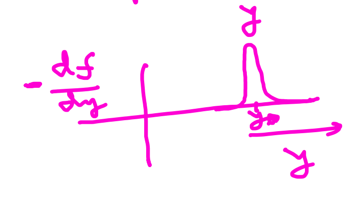
$$\int u\,v\,dy = u \int v\,dy + \int \left(\frac{du}{dy} \int v\,dy\right) dy$$

$$= \frac{2}{\sqrt{\pi}} \left[\frac{2}{3} \left[\frac{y^{3/2}}{e^{y-\xi}+1} \right]_0^{\infty} - \frac{2}{3} \int_0^{\infty} dy\, y^{3/2} \frac{\partial}{\partial y} \left\{ \frac{1}{e^{y-\xi}+1} \right\} \right]$$

$v = \sqrt{y}$
$u = \frac{1}{e^{y-\xi}+1}.$

$$= \frac{4}{3\sqrt{\pi}} \int_0^{\infty} dy\, y^{3/2} \underbrace{\frac{e^{y-\xi}}{(e^{y-\xi}+1)^2}}_{\text{peaked at } y=\xi}.$$





$$= \frac{4\xi^{3/2}}{3\sqrt{\pi}} \int_{-\xi}^{\infty} dt \left(1 + \frac{t}{\xi}\right)^{3/2} \frac{e^t}{(e^t+1)^2}.$$

Let, $y = \xi + t$.
$\xi = \beta\mu = \frac{\mu}{k_B T}$.

$$= \frac{4\xi^{3/2}}{3\sqrt{\pi}} \int_{-\infty}^{\infty} dt \left(1 + \frac{t}{\xi}\right)^{3/2} \frac{e^t}{(e^t+1)^2} + O(e^{-\xi})$$

$\left\{ \begin{array}{l} T \to 0 \\ \Rightarrow \xi \to \infty. \end{array} \right.$

$$= \frac{4\xi^{3/2}}{3\sqrt{\pi}} \int_{-\infty}^{\infty} dt \left(1 + \frac{3}{2}\frac{t}{\xi} + \frac{3}{8}\frac{t^2}{\xi^2} + \cdots\right) \frac{e^t}{(e^t+1)^2} + O(e^{-\xi}).$$

$$\approx \frac{4\xi^{3/2}}{3\sqrt{\pi}} \left(I_0 + \frac{3}{8\xi^2} I_2 \right) \; ; \quad \text{where, } I_n = 2\int_0^{\infty} dt \frac{t^n e^t}{(e^t+1)^2}.$$

$$I_0 = 2\int_0^{\infty} dt \frac{e^t}{(e^t+1)^2} = 1.$$

$$\& \quad I_2 = 2\int_0^{\infty} dt \frac{t^2 e^t}{(e^t+1)^2} = \frac{\pi^2}{3}$$

Exercise

$$f_{3/2}(z) \approx \frac{4\xi^{3/2}}{3\sqrt{\pi}} \left[1 + \frac{\pi^2}{8\xi^2} \right]$$

$$\approx \frac{4}{3\sqrt{\pi}} \left[\xi^{3/2} + \frac{\pi^2}{8} \frac{1}{\xi^{1/2}} \right]$$

$$\approx \frac{4}{3\sqrt{\pi}} \left[(\ln z)^{3/2} + \frac{\pi^2}{8} \frac{1}{\sqrt{\ln z}} \right].$$

$\xi = \beta\mu$

$z = e^{\beta\mu}$.

$\therefore \xi = \beta\mu = \ln z$.

Recall $n\lambda^3 = f_{3/2}(z)$.

To first term in the above expansion,

$$\ln z \approx \left(\frac{3\sqrt{\pi}}{4} n\lambda^3 \right)^{2/3} = \left(\frac{T_F}{T}\right).$$

$$\left\{ \ln z = \beta\mu = \frac{\epsilon_F}{k_B T} = \frac{k_B T_F}{k_B T}. \right.$$

To next order,

$$n\lambda^3 \approx \frac{4}{3\sqrt{\pi}} \left[(\ln z)^{3/2} + \frac{\pi^2}{8} \frac{1}{\sqrt{\ln z}} \right].$$

$$\Rightarrow (\ln z)^{3/2} \approx \frac{3\sqrt{\pi}}{4} n\lambda^3 - \frac{\pi^2}{8} \frac{1}{\sqrt{\ln z}}.$$

Substituting the first approximation, $\ln z = \frac{T}{T_F}$,

$$\ln z \approx \frac{T_F}{T} \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right]$$

$$\Rightarrow \mu \approx \epsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{T}{T_F}\right)^2\right].$$

Bose-Einstein Condensation

Rb^{87}

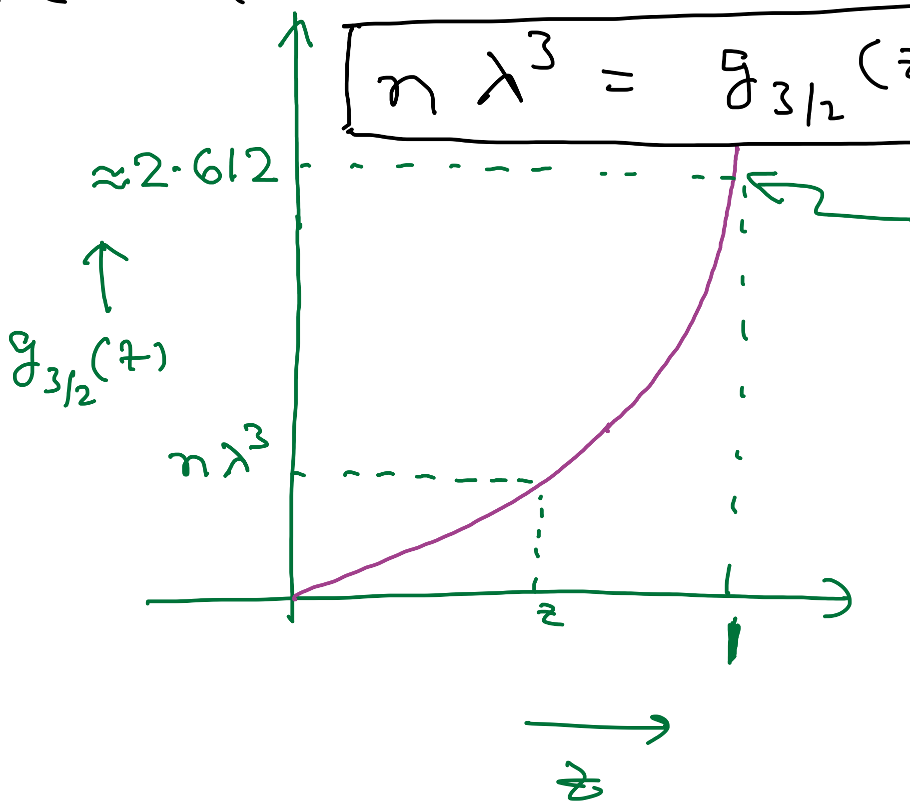
(Eric Cornell & Carl Wieman, "The Bose-Einstein Condensate", Scientific American 278, 26 (1998)).

Na^{23} BEC

W. Ketterle

Recall: For a gas of Bosons whose total number is conserved, we had obtained

$$\boxed{n\lambda^3 = g_{3/2}(z); \qquad z = e^{\beta\mu}, \quad \mu = \frac{G}{N}}$$



$$z\frac{d}{dz}g_{3/2}(z) = g_{1/2}(z) = \sum_{l=1}^{\infty}\frac{z^l}{l^{1/2}} \longrightarrow \text{diverges as } z \to 1.$$

This is bounded by $g_{3/2}(1)$.

$$g_{3/2}(1) = \sum_{l=1}^{\infty}\frac{1}{l^{3/2}} = \zeta\left(\tfrac{3}{2}\right)$$

Riemann-zeta f^n.

$n\lambda^3 = g_{3/2}(z)$ has solutions only when, $n\lambda^3 \leq g_{3/2}(1)$.

This condition can be violated by increasing n or increasing λ (or lowering T).

During Bose-Einstein condensation, the fugacity z is 1.

$$z = \begin{cases} \text{solution of } n\lambda^3 = g_{3/2}(z) & \text{if } n\lambda^3 < g_{3/2}(1) \text{ (Gas phase)} \\ 1 & \text{if } n\lambda^3 \geq g_{3/2}(1) \text{ (condensed phase)} \end{cases}$$

The critical values at which this happens,

$$n\lambda^3 = g_{3/2}(1)\Big|_{T=T_c}$$

i.e., $$n\left(\frac{2\pi\hbar^2}{mk_BT_c}\right)^{3/2} = \zeta\left(\tfrac{3}{2}\right) \approx 2.612$$

$$\therefore T_c \approx \frac{2\pi\hbar^2}{mk_B\left[\zeta(3/2)\right]^{2/3}} n^{2/3}.$$

e.g., for Rb^{87}, $m \approx 86.9092 \text{ amu} = 86.9092 \times 1.661 \times 10^{-27}$ kg

$$\therefore T_c \approx \left(\frac{2\pi \times (1.058 \times 10^{-34})^2 \, n^{2/3}}{86.9092 \times 1.661 \times 10^{-27} \times 1.38 \times 10^{-23} \times (2.612)^{2/3}}\right.$$

$$\approx 1.8611 \times 10^{-20} \, n^{2/3}.$$

Note

1. Can we derive this estimate from Heisenberg uncertainty principle?

Let $\epsilon_0 = k_B T_c$ be the zero point energy.

The atom is localized to a region of volume $\left(\frac{V}{N}\right)$, s.t., $\Delta x \sim \left(\frac{V}{N}\right)^{1/3}$.

We have, $\Delta x \cdot \Delta p_x \sim \frac{\hbar}{2}$; $\Delta p_x = \frac{\hbar}{2\Delta x}$

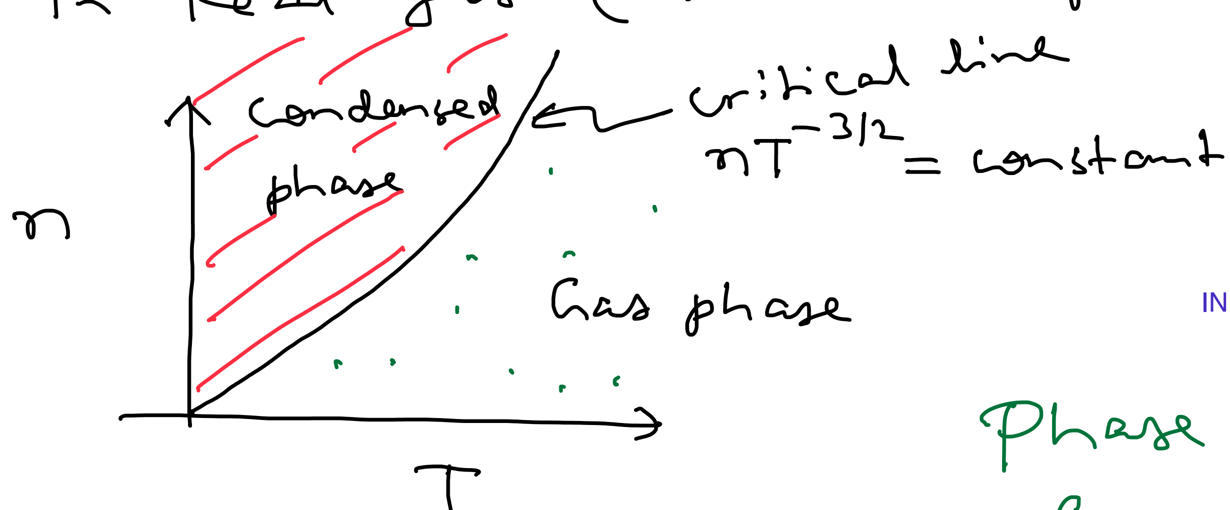
$$\Delta p_x \sim \frac{\hbar}{2}\left(\frac{V}{N}\right)^{-1/3}$$

$$\epsilon_0 = k_B T_c = \frac{1}{2m}(\Delta p_x)^2 = \frac{\hbar^2}{8m}\left(\frac{V}{N}\right)^{-2/3}.$$

$$\Rightarrow T_c = \left(\frac{\hbar^2}{8 m k_B}\right) n^{2/3}.$$

This gives a similar order of magnitude estimate.

2. In BEC, there does not exist a pair potential $V(r_{ij})$ as we considered in the case of interaction between particles in Real gas (Virial expansion)

3. 

Phase diagram for BEC.

Statistical Physics
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