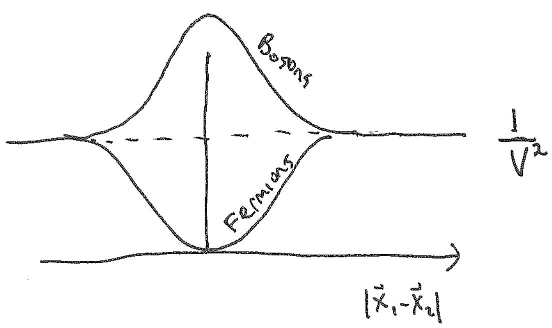
Pre-Discusion : Quantum Gases | Fluids

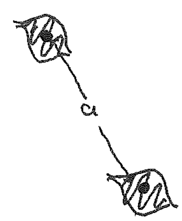
Two particle density matrix

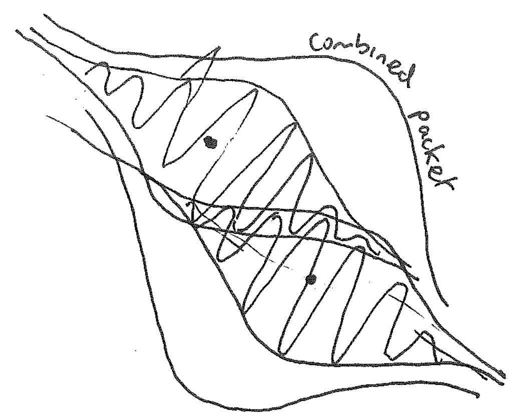
$$\langle x_1, x_2 | \hat{\rho} | x_1, x_2 \rangle = \frac{1}{V^2}\left(1 \pm e^{-\frac{2\pi (x_1 - x_2)^2}{\lambda_T^2}} \right)$$



Fermions : correlation hole.

Bosons : correlation bump – tendency to condense.





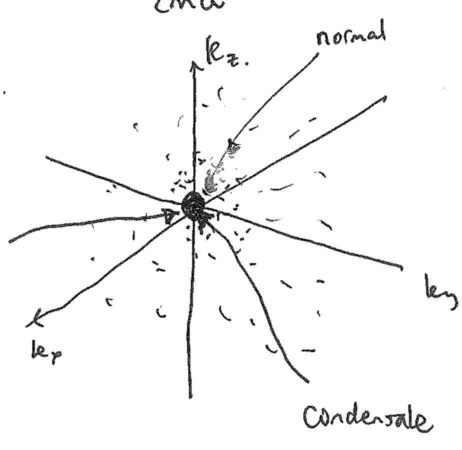
$$\frac{N}{V} = \frac{1}{a^3} \qquad \lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}$$

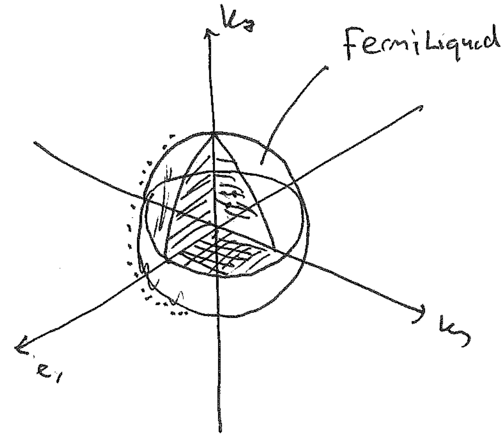
$\lambda_T \ll a$

$\lambda_T \gtrsim a$

$$\Rightarrow \quad k_B T \lesssim \frac{h^2}{2ma^2} = k_B T_0$$

BEC





6. THEORY OF SIMPLE GASES

6.1 Ideal Gas in the Grand Canonical Ensemble

The easiest way to treat the ideal quantum gas is to write the density matrix in the occupation number basis

$$|\{n_{k\sigma}\}\rangle = |n_{k_1\sigma_1}, n_{k_1\sigma_2} \ldots n_{k_r\sigma_r} \ldots \rangle$$

where

$$n_{k\sigma} = \begin{cases} 0, 1 & \text{Fermions} \\ 0, 1, 2 \ldots & \text{Bosons} \end{cases}$$

The energy of this state is

$$E[\{n_{k\sigma}\}] = \sum_{k,\sigma} E_k n_{k\sigma}$$

Now the easiest way forward is to work in the Grand Canonical Ensemble, Writing

$$\hat{\rho} = \frac{1}{Z} e^{-\beta(\hat{H}-\mu\hat{N})}$$

where

$$Z = \sum e^{-\beta(\epsilon_i - \mu N_i)} = \mathrm{Tr}\left[e^{-\beta(\hat{H}-\mu\hat{N})}\right]$$

and

$$\hat{H} - \mu\hat{N} = \sum_{k,\sigma} (\epsilon_k - \mu) n_{k\sigma}$$

Now the wonderful thing about the non-interacting problem, is that the Fock space can be considered to be a product of the individual spaces for each one particle state $|\vec{k}\sigma\rangle$. Thus

$$|n_{k_1}, n_{k_2} \dots n_{k_r} \dots\rangle = \prod_{\otimes} |n_{\vec{k}_r \sigma_r}\rangle$$

$$\hat{\rho} = \prod_{\otimes} \hat{\rho}_{\vec{k}_r \sigma_r} \qquad \rho_{k_r,\sigma_r} = e^{-\beta(\epsilon_{k_r}-\mu) n_{k_r \sigma_r}} / Z_{k_r \sigma_r}$$

$$\mathrm{Tr}\, e^{-\beta(\hat{H}-\mu\hat{N})} = \sum_{\{\}} e^{-\beta\sum_{\vec{k}}(\epsilon_k - \mu) n_{k\sigma}} = \prod_{k_r,\sigma_r} \overbrace{\left(\sum_{n_{k\sigma}} e^{-\beta(\epsilon_k-\mu)n_{k\sigma}}\right)}^{Z_{k_r\sigma_r}}$$

$$= \prod_{k_r,\sigma_r} Z_{k_r \sigma_r}$$

6.2 Fermions

$$Z^F_{k\sigma} = \left(1 + e^{-\beta(\epsilon_k - \mu)}\right) \qquad \hat{\rho} = \prod_{k,\sigma}^{\otimes} \frac{1}{Z^F_{k\sigma}} \begin{pmatrix} 1 & 0 \\ 0 & e^{-\beta(\epsilon_k - \mu)} \end{pmatrix}$$

$$F^F_{k\sigma} = -k_B T \ln\left(1 + e^{-\beta(\epsilon_k - \mu)}\right)$$

$$\mathcal{Z} = \prod_{k,\sigma} Z_{k\sigma} \iff F = \sum_{k,\sigma} F_{k\sigma}$$

$$= -g_s k_B T \sum_k \ln\left(1 + e^{-\beta(\epsilon_k - \mu)}\right)$$

$$= -g_s V \int \frac{d^3k}{(2\pi)^3} \ln\left(1 + e^{-\beta(\epsilon_k - \mu)}\right)$$

$$= -PV$$

$$\boxed{\begin{aligned} P[\mu] &= \int \frac{d^3k}{(2\pi)^3} \ln\left(1 + e^{-\beta(\epsilon_k - \mu)}\right) \\ N[\mu] &= \frac{-\partial F}{\partial \mu} = \sum_{k,\sigma} \frac{-\partial F_{k\sigma}}{\partial \mu} = \sum_{k,\sigma} \left(\frac{1}{e^{\beta(\epsilon_k - \mu)} + 1}\right) \\ n_{k\sigma} &= \frac{-\partial F_{k\sigma}}{\partial \mu} = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1} \end{aligned}}$$

6.3 Bosons

$$\hat{\rho} = \prod_{\otimes\, k,\sigma} \frac{1}{Z_{k}^{BE}} \begin{pmatrix} 1 & & & & \\ & e^{-\beta(E_k-\mu)} & & & \\ & & \ddots & & \\ & & & e^{-\beta(E_k-\mu)n_k} & \\ & & & & \ddots \end{pmatrix}$$

$$Z_k^{BE} = \sum_{n_k=0,\infty} e^{-\beta(E_k-\mu)n_k} = \frac{1}{1-e^{-\beta(E_k-\mu)}} = n_F(E_k)$$

$$F_k^{BE} = -k_B T \ln Z_k^{BE} = k_B T \ln\left(1-e^{-\beta(E_k-\mu)}\right)$$

$$F^{BE} = \sum_{\vec{k}} k_B T \ln\left(1-e^{-\beta(E_k-\mu)}\right) = k_B T V \int \frac{d^3k}{(2\pi)^3} \ln\left(1-e^{-\beta(E_k-\mu)}\right)$$

$$\Rightarrow \quad P = -k_B T \int \frac{d^3k}{(2\pi)^3} \ln\left(1-e^{-\beta(E_k-\mu)}\right)$$

$$\langle n_k \rangle = -\frac{\partial F_k^{BE}}{\partial \mu} = +\frac{e^{-\beta(E_k-\mu)}}{1-e^{-\beta(E_k-\mu)}} = \frac{1}{e^{\beta(E_k-\mu)}-1} = n_{BE}(E_k)$$

Summarizing

$$\begin{cases} \langle n_{k\sigma} \rangle = \dfrac{1}{e^{\beta E_k} z^{-1} \pm 1} \\ F = \mp \sum_{k,\sigma} k_B T \ln\left(1 \pm z e^{-\beta E_k}\right) \end{cases}$$

$+$ F
$-$ BE

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

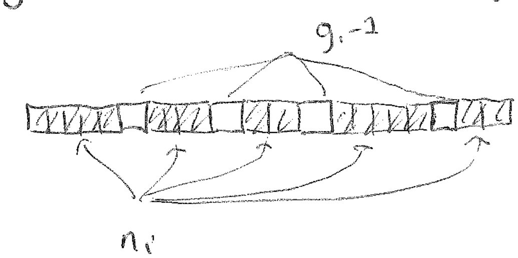
6.4 Quantum Particles — Microcanonical Ensemble.

$$\Omega(N,V,E) = \sum_{\{n_i\}} W[\{n_i\}]$$

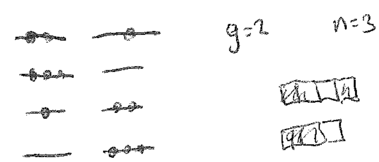
where

$$W[n_i] = \prod_{i \atop \text{levels}} w[i]$$

Now for bosons, we can multiply occupy each state. $w_{BE}(i)$ is equivalent to arranging n_i boxes amongst $g_i - 1$ dividers:

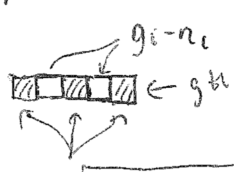


$$\boxed{w_{BE}[i] = \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!}}$$



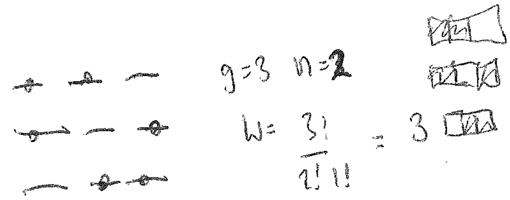
$W = \frac{4!}{3!\,1!} = 4$

For fermions we have n_i occupied boxes and $g_i - n_i$ unoccupied



So

$$\boxed{w_{FD}(i) = \frac{g_i!}{n_i!\,(g_i - n_i)!}}$$



$W = \frac{3!}{2!\,1!} = 3$

For completeness, let us include MB statistics. n_i particles into g_i states independently of each other.

No degeneracy, $W_{MB}(i) = \dfrac{N!}{\prod_i n_i!}$

With degeneracy, we add a degenercy factor $(g_i)^{n_i}$ to each state to obtain:

$$W_{MB}[i] = \frac{(g_i)^{n_i}}{n_i!}$$

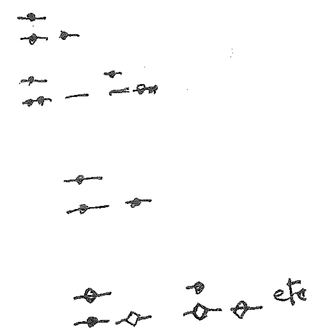
$$W_{MB} = N! \prod_i W_{MB}(i).$$

e.g $g=1$, $g=2$ 3 particles

$$W_{BE} = \left(\frac{1!}{1!\,0!}\right)\left(\frac{3!}{2!\,1!}\right) = 3$$

$$W_F = \left(\frac{1!}{1!\,0!}\right)\left(\frac{2!}{2!\,0!}\right) = 1$$

$$W_{MB} = \frac{3!}{2!\,1!} \times 1 \times 2^2 = 12$$



Need to maximize

$$S = k_B \ln \Omega = k_B \ln \sum_{\{n_i\}} W[\{n_i\}]$$

$$\simeq k_B \ln W[\{n_i^*\}]$$

where $\{n_i^*\}$ is the distribution that maximizes $W[\{n_i^*\}]$ subject to $\sum n_i = N$ & $\sum n_i \epsilon_i = E$.

$$\delta \ln W[\{n_i\}] - \left[\alpha \sum \delta n_i + \beta \sum \delta n_i \epsilon_i\right] = 0$$

Now

$$\ln w_{BE} \simeq (n_i + g_i - 1) \ln \frac{n_i + g_i - 1}{e} - n_i \ln \frac{n_i}{e} - (g_i - 1) \ln\left(\frac{g_i - 1}{e}\right)$$

$$= n_i \ln\left(\frac{g_i}{n_i} + 1\right) + g_i \ln\left(1 + \frac{n_i}{g_i}\right)$$

$$\ln W_{FD} = g_i \ln \frac{g_i}{e} - n_i \ln \frac{n_i}{e} - (g_i - n_i) \ln\left(\frac{g_i - n_i}{e}\right)$$

$$= n_i \ln\left(\frac{g_i}{n_i} - 1\right) - g_i \ln\left(1 - \frac{n_i}{g_i}\right)$$

$$\boxed{\ln W = n_i \ln\left(\frac{g_i}{n_i} - a\right) - \frac{g_i}{a} \ln\left(1 - \frac{a n_i}{g_i}\right)}$$

$a = +1$ FD
$= -1$ BE
$= 0$ MB !

$$\delta \ln W = \frac{n_i \left(\frac{-g_i}{n_i^2}\right)}{\left(\frac{g_i}{n_i} - a\right)} - \frac{g_i}{a} \frac{\left(\frac{-a}{g_i}\right)}{\left(1 - \frac{a n_i}{g_i}\right)} + \ln\left(\frac{g_i}{n_i} - a\right)$$

$$= \ln\left(\frac{g_i}{n_i} - a\right)$$

Where $a = +1$ FD, -1 BE.

$$\delta \ln W - \left[\alpha \left[\sum \delta n_i\right] + \beta \sum \delta n_i \epsilon_i\right]$$

$$= \sum_i \delta n_i \left[\ln\left[\frac{g_i}{n_i} - a\right] - \alpha - \beta \epsilon_i\right] = 0$$

$$\Rightarrow \quad \ln\left[\frac{g_i}{n_i} - a\right] = \alpha + \beta \epsilon_i$$

$$\frac{g_i}{n_i} - a = e^{\alpha + \beta \epsilon_i}$$

$$\frac{g_i}{n_i} = e^{\alpha + \beta \epsilon_i} + a \quad \Rightarrow \quad \boxed{\langle n_i^p \rangle = \frac{g_i}{e^{\alpha + \beta \epsilon_i} + a}}$$

$a = +$ FD $\quad a = -1$ BE $\quad a = 0$ MB

$$1 - a\frac{n_i^*}{g_i} = 1 - \frac{a}{e^{\beta\epsilon+\alpha}+a} = \frac{1}{1+ae^{-\alpha-\beta\epsilon}}$$

$$\frac{S}{k_B} \simeq \ln W[\{n_i^*\}] = \sum_i n_i^* \ln\left(\frac{g_i}{n_i^*} - a\right) - \frac{g_i}{a}\ln\left(1 - \frac{a n_i^*}{g_i}\right)$$

$$= \sum_i n_i^* (\alpha + \beta\epsilon_i) + \frac{g_i}{a}\ln\left(1 + a e^{-\alpha-\beta\epsilon_i}\right)$$

$$= \alpha N + \beta E + \frac{1}{a}\sum g_i \ln\left(1 + a e^{-\alpha-\beta\epsilon_i}\right)$$

But $\quad S = \frac{E}{T} - \frac{\mu}{T}N - \frac{F}{T} \iff F = (E - ST - \mu N)$

$\Rightarrow \quad \beta = \frac{1}{k_B T} \qquad \alpha = -\frac{\mu}{k_B T} = -\mu\beta.$

& $\quad \boxed{F = -\frac{1}{a}\sum g_i k_B T \ln\left(1 + a e^{-\beta(\epsilon_i-\mu)}\right) = -PV}$

Finally M.B case

$$\ln W_{MB} = n_i \ln g_i - n_i \ln(n_i/e)$$

$$\delta \ln W_{MB} = \delta n_i (\ln g_i - \ln n_i) = \delta n_i \ln\left(\frac{g_i}{n_i}\right)$$

Corresponds to $a \to 0$

$$F_{MB} = -PV = -\sum g_i k_B T e^{-\beta(\epsilon_i-\mu)} \Rightarrow \underline{PV = \sum k_B T n_i^* = N k_B T}$$