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last time:

$$PV = \frac{kT}{a} \sum_i g_i \ln(1 + a\, e^{-\alpha - \beta \varepsilon_i})$$

$$a \begin{cases} -1 & BE \\ 1 & FD \\ 0 & M\text{-}B \end{cases}$$

For M-B (ideal gas)

$$PV \cong \lim_{a \to 0} \frac{kT}{\cancel{a}} \sum_i g_i\, \cancel{a}\, e^{-\alpha - \beta \varepsilon_i} = kT \sum_i n_i^*$$

$$= kTN$$

but $n_i^* = \dfrac{g_i}{e^{\alpha + \beta \varepsilon_i} + a} = \dfrac{g_i}{e^{\alpha + \beta \varepsilon_i}}$

eq. of state.

Ideal gas in the canonical ensemble:

$$Z_N(V,T) = \sum_{E} e^{-\beta E}$$

E: many body energies.

$$E = \sum_{\varepsilon} n_\varepsilon \varepsilon$$

$$N = \sum_{\varepsilon} n_\varepsilon$$

We can write:

here the particles are indistinguishable since we only look at occupation numbers

$$Z_N(V,T) = \sum_{\{n_\varepsilon\}}{}' \, g\{n_\varepsilon\} \, e^{-\beta \sum_{\varepsilon} n_\varepsilon \varepsilon}$$

Now we can see that if $g_i = 1$ (we no longer consider cells) then

$$g_{B.E}\{n_\varepsilon\} = 1$$

$$g_{F.D.}\{n_\varepsilon\} = \begin{cases} 1 & \text{if all } n_\varepsilon = 0 \text{ or } 1 \\ 0 & \text{otherwise} \end{cases}$$

$$g_{M-B}\{n_\varepsilon\} = \prod_\varepsilon \frac{1}{n_\varepsilon!}$$

$$W_{BE} = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

$$W_{FD} = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!}$$

$$=$$

$$W_{MB} = \prod_i \frac{(g_i)^{n_i}}{n_i!} =$$

$$= \prod_i \frac{1}{n_i!}$$

Examples:

$N = 2$

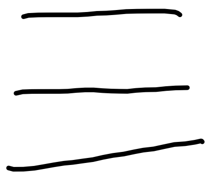
Single particle: E_i: $0, \varepsilon, 2\varepsilon$

$$Z_1 = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}$$

2ε

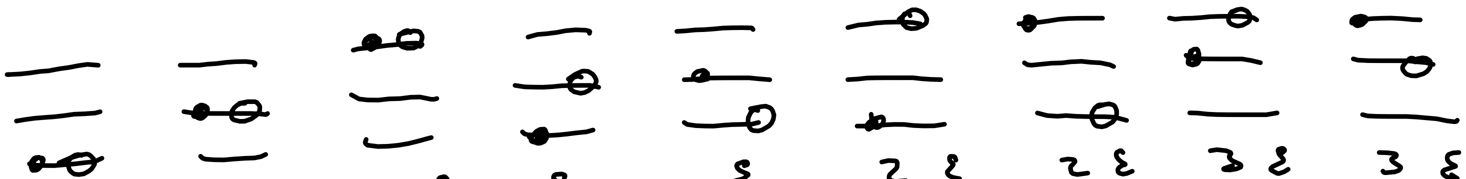
ε

0



M-B:

1) by hand 3^2 possibilities (9 states).



0 $\quad 2\varepsilon$ $\quad 4\varepsilon$ $\quad \varepsilon$ $\quad \varepsilon$ $\quad 2\varepsilon$ $\quad 2\varepsilon$ $\quad 3\varepsilon$ $\quad 3\varepsilon$

$$Z_{2,MB} = \frac{1 + 3e^{-2\beta\varepsilon} + 2e^{-\beta\varepsilon} + 2e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon}}{2 \; (N!) \; (\text{Gibbs})}$$

2) From single particle:

$$Z_{2,M.B} = \frac{Z_1^2}{2!} = \frac{1}{2}\left(1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}\right)^2$$ same as before.

same as in (1).

3) From quantum expression:

$$Z_{2,M.B} = \sum_{\{n_\varepsilon\}} g_{M.B}\{n_\varepsilon\}\, e^{-\beta\sum_\varepsilon n_\varepsilon \varepsilon} = \qquad g_{M.B} = \frac{1}{\prod_\varepsilon n_\varepsilon!}$$

$$= \frac{1}{2!}e^{-\beta 0} + \frac{1}{2!}e^{-\beta 2\varepsilon} + \frac{1}{2!}e^{-\beta 4\varepsilon} + e^{-\beta\varepsilon} +$$

$$+ e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon} =$$

$$= \frac{1}{2} + e^{-\beta\varepsilon} + \frac{3}{2}e^{-2\beta\varepsilon} + \frac{1}{2}e^{-\beta 4\varepsilon} + e^{-\beta 3\varepsilon}$$

same as in (1).

B-E: only 6 of the nine states should be considered.

$g_{BE}\{n_\varepsilon\} = 1 \quad \forall n_\varepsilon$

1) By hand.

$$Z_{2,B\text{-}E} = 1 + e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon}$$

2) From quantum expression.

$Z_{2,B\cdot E} \equiv Z_{2,B\cdot E}$ in (1) trivially.

F-D: only 3 of the nine states allowed because double occupancy is out:

By hand:

$$Z_{2,F\cdot D} = e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon}$$

From grandstar

$g_i\{n_\varepsilon\} = 1$ if $n_\varepsilon = 0$ or 1

$g_i\{n_\varepsilon\} = 0$ otherwise.

$$Z_{2FD} = e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon}$$

Maxwell-Boltzmann: (ideal gas).

$$Z_N(V,T) = \sum_{\{m_{\varepsilon_s}\}}' g_{MB}\{m_{\varepsilon_s}\}\, e^{-\beta \sum_s \varepsilon_s m_{\varepsilon_s}} =$$

$$= \sum_{\{m_{\varepsilon_s}\}}' \left[\left(\prod_{\varepsilon_s} \frac{1}{m_{\varepsilon_s}!} \right) \prod_{\varepsilon_s} \left(e^{-\beta \varepsilon_s}\right)^{m_{\varepsilon_s}} \right] =$$

$$= \frac{1}{N!} \sum_{\{m_{\varepsilon_s}\}}' \left[\frac{N!}{\prod_{\varepsilon_s} m_{\varepsilon_s}!} \prod_{\varepsilon_s} \left(e^{-\beta \varepsilon_s}\right)^{m_{\varepsilon_s}} \right] = \frac{1}{N!} \Big[\underbrace{\sum_{\varepsilon_s} e^{-\beta \varepsilon_s}}_{Z_1} \Big]^N$$

$$\left(\sum_r x_r\right)^N = \sum_{\substack{\{k_s\} \\ \sum k_s = N}} \frac{N!}{\prod_s k_s!} \prod_s x_s^{k_s}$$

(multinomial expansion)

We see that

$$Z_N(V,T) = \frac{Z_1^N}{N!} = \frac{V^N}{N!\,\lambda^{3N}}$$

correct expressions includes the Gibbs $\frac{1}{N!}$ correction

and

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N Z_N$$

grand-canonical.

However, for bosons or fermions is not easy to obtain Z_N, but we can find $\mathcal{Z}$ (grand-canonical)

$$Z_N(V,T) = \sum_{\{n_\varepsilon\}}{}' e^{-\beta \sum_s n_{\varepsilon_s} \varepsilon_s} \qquad \text{since } g_{\{n_s\}} = 1$$

with

$n_\varepsilon = 0 \to \infty$ for B.E.

$n_\varepsilon = 0, 1$ for F.D.

It is very hard to perform the sum with the constraint. However,

$$\mathcal{Z}(z, V, T) = \sum_{N_r=0}^{\infty} \left[z^{N_r} \sum_{\{m_{\varepsilon_s}\}}{}' e^{-\beta \sum_{\varepsilon_s} m_{\varepsilon_s} \varepsilon_s} \right] \longrightarrow \begin{array}{l} \sum_s m_s \varepsilon_s = \bar{\varepsilon} \\ \sum_s m_s = N \\ \langle E_r \rangle = \bar{E} \\ \langle N_r \rangle = N \end{array}$$

$$= \sum_{N_r=0}^{\infty} \left[\sum_{\{m_{\varepsilon_s}\}}{}' \prod_{\varepsilon_s} \left(z e^{-\beta \varepsilon_s} \right)^{m_{\varepsilon_s}} \right] =$$

$$= \sum_{\substack{m_0, m_1, \ldots \\ \text{(unrestricted)}}} \left[\left(z e^{-\beta \varepsilon_0} \right)^{m_0} \left(z e^{-\beta \varepsilon_1} \right)^{m_1} \cdots \right] =$$

This is valid for both B. E and F. D but the unrestricted sum depends on the quantum statistics.

$$\left(z e^{-\beta \varepsilon_1} \right)^{m_{\varepsilon_1}} \left(z e^{-\beta \varepsilon_2} \right)^{m_{\varepsilon_2}} \cdots = z^{\overbrace{m_{\varepsilon_1} + m_{\varepsilon_2} \cdots}^{N_r}} e^{-\beta(\varepsilon_1 m_{\varepsilon_1} + \varepsilon_2 m_{\varepsilon_2} \ldots)}$$

B. E:

$$\mathcal{Z}(z,V,T) = \sum_{n_0=0}^{\infty} \left(z e^{-\beta \varepsilon_0}\right)^{n_0} \sum_{n_1=0}^{\infty} \left(z e^{-\beta \varepsilon_1}\right)^{n_1} \cdots$$

$$= \frac{1}{1-z e^{-\beta \varepsilon_0}} \; \frac{1}{1-z e^{-\beta \varepsilon_1}} \cdots = \prod_s \frac{1}{1-z e^{-\beta \varepsilon_s}} =$$

geometric series

$$= \mathcal{Z}_{B.E}(z,V,T)$$

Notice that $z e^{-\beta \varepsilon_s} < 1$ for convergence.

For F.D:

$$\mathcal{Z}_{F.D}(z,V,T) = \sum_{n_0=0}^{1} (z e^{-\beta \varepsilon_0})^{n_0} \sum_{n_1=0}^{1} (z e^{-\beta \varepsilon_1})^{n_1} \cdots$$

$$= (1 + z e^{-\beta \varepsilon_0})(1 + z e^{-\beta \varepsilon_1}) \cdots =$$

$$= \prod_s (1 + z e^{-\beta \varepsilon_s})$$

Then now $q = \ln \mathcal{Z}(z,V,T)$ can be obtained.

$$q(z,V,T) \equiv \frac{PV}{kT} = \ln \mathcal{Z}(z,V,T) =$$

$$= \mp \sum_s \ln(1 \mp z e^{-\beta \varepsilon_s}) \begin{cases} - & \text{B.E.} \\ + & \text{F.D} \end{cases}$$

Remember that $z = e^{-\alpha} = e^{\mu/kT}$

We can include Z_{MB} in our definition of q:

$$q(z, V, T) = \frac{1}{a} \sum_s \ln(1 + a z e^{-\beta \varepsilon_s}) \quad (1)$$

$a = -1$ B.E

$a = 1$ F.D

$a = 0 \Rightarrow$ M.B

D/

$$q = \frac{PV}{kT} = \lim_{a \to 0} \left(\frac{1}{a} \sum_s \ln(1 + a z e^{-\beta \varepsilon_s}) \right) =$$

$$= \frac{1}{\cancel{a}} \sum_s \cancel{a} z e^{-\beta \varepsilon_s} = z \sum_s e^{-\beta \varepsilon_s} = z Z_1 \equiv$$

$$= z V f(T)$$

compare with 14.4.4) in book.

Then

$$\boxed{\bar{N} \equiv z \frac{\partial \mathcal{Z}}{\partial z}\Big|_{V,T}} = \frac{z}{\cancel{a}} \frac{\sum_s \cancel{a}\, e^{-\beta \varepsilon_s}}{1 + z e^{-\beta \varepsilon_s} a} =$$

$$= z \sum_s \frac{e^{-\beta \varepsilon_s}}{1 + z e^{-\beta \varepsilon_s} a} = \boxed{\sum_s \frac{1}{z^{-1} e^{\beta \varepsilon_s} + a}}$$

and

$$\boxed{\bar{E} = -\frac{\partial \mathcal{Z}}{\partial \beta}\Big|_{z,V}} = + \frac{1}{a} \sum_s \frac{a z \varepsilon_s e^{-\beta \varepsilon_s}}{1 + a z e^{-\beta \varepsilon_s}} =$$

$$= \boxed{\sum_s \frac{\varepsilon_s}{(z^{-1} e^{\beta \varepsilon_s} + a)}}$$

Since:

$$\mathcal{Z}(z,V,T) = \sum_{N_r=0}^{\infty}\left[z^{N_r}\sum_{\{n_s\}}{}' e^{-\beta\sum_s n_s \varepsilon_s}\right]$$

$$\langle n_r\rangle = \frac{1}{\mathcal{Z}}\sum_{N_i=0}^{\infty}\left[z^{N_i}\sum_{\{n_s\}}{}' n_r\, e^{-\beta\sum_s n_s \varepsilon_s}\right] =$$

$$= \frac{1}{\mathcal{Z}}\left[-\frac{1}{\beta}\frac{\partial \mathcal{Z}}{\partial \varepsilon_r}\bigg|_{z,T,\varepsilon_s\neq\varepsilon_r}\right] =$$

$$= -\frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \varepsilon_r}\bigg|_{z,T,\varepsilon_s\neq\varepsilon_r} = -\frac{1}{\beta}\frac{\partial q}{\partial \varepsilon_r}\bigg|_{z,T,\varepsilon_s\neq\varepsilon_r} =$$

but $q = q(a)$ then

$$\boxed{\langle n_r \rangle} = -\frac{1}{\beta}\frac{\partial \mathcal{J}}{\partial \varepsilon_r}\Big|_{z,T,\varepsilon_s \neq \varepsilon_r} = -\frac{1}{\beta}\frac{\partial\left(\frac{1}{a}\sum_s \ln\left(1+a z e^{-\beta\varepsilon_s}\right)\right)}{\partial \varepsilon_r}\Bigg|_{\substack{z,T,\\ \varepsilon_r\neq\varepsilon_s}}$$

$$= -\frac{1}{\beta}\frac{1}{a}\frac{a z(-\beta)e^{-\beta\varepsilon_r}}{1+a z e^{-\beta\varepsilon_r}} = \frac{z e^{-\beta\varepsilon_r}}{1+a z e^{-\beta\varepsilon_r}} =$$

$$= \boxed{\frac{1}{z^{-1}e^{\beta\varepsilon_r}+a}}$$

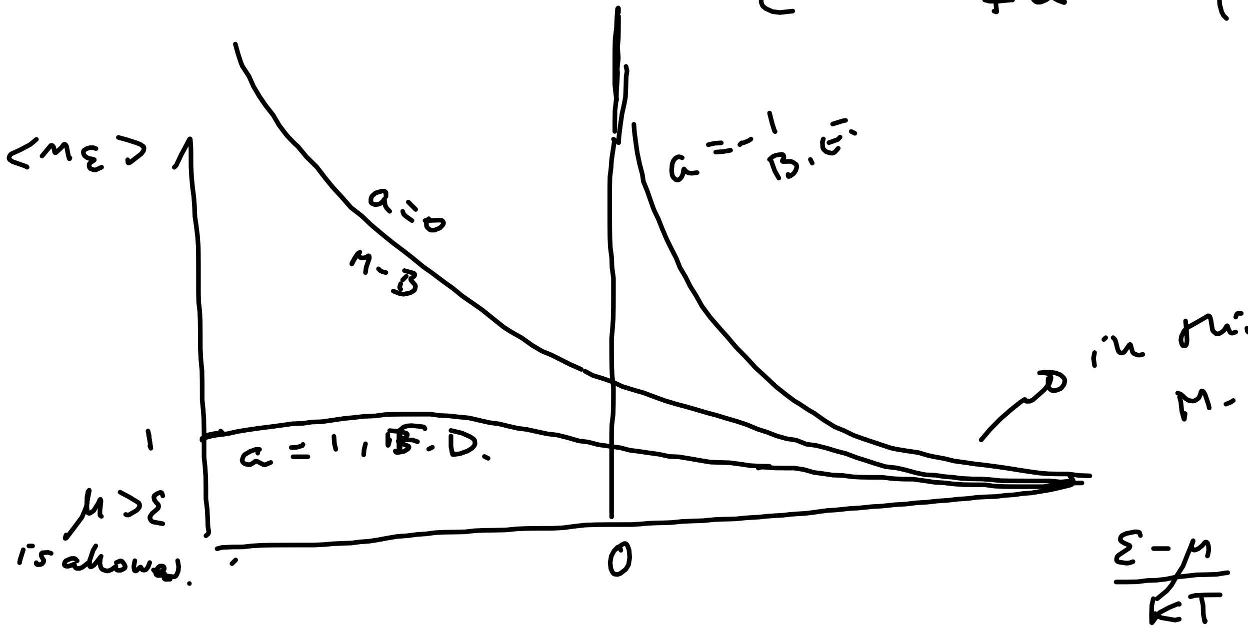
$\therefore$ comparing with $\frac{n_i^*}{g_i} = \frac{1}{e^{\alpha+\beta\varepsilon_i}+a}$ we obtain

that $n_i^* = n_r^* = \langle n_r \rangle$

Statistics of the occupation numbers:

We found that

$$\langle n_\varepsilon \rangle = \frac{1}{e^{(\varepsilon-\mu)/kT}+a} \qquad \begin{cases} a=-1 & \text{B E} \\ a=1 & \text{F D} \\ a=0 & \text{M. B.} \end{cases}$$



in this regime M-B is equivalent to B.E and F.D.

• For B.E: $\varepsilon - \mu > 0 \;\forall\; \varepsilon$.
If $\varepsilon_0 = 0 \Rightarrow \mu < 0$.