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Last time:

Find $\{n_i^*\}$ that maximizes S in microcanonical for an ideal gas (quantum).

$$\ln W \simeq \sum_i \left[n_i \ln \left(\frac{g_i}{n_i} - a \right) - \frac{g_i}{a} \ln \left(1 - a \frac{n_i}{g_i}\right)\right] \quad (1)$$

$$a = \begin{cases} -1 & B.E. \\ 1 & F.D \\ 0 & M.B \end{cases}$$

$$\delta \ln W = 0 = \sum_i \delta n_i \left[\left(\ln \left(\frac{g_i}{n_i} - a \right) + \right.\right.$$

$$\left.\left. + \frac{n_i \left(-\frac{g_i}{n_i^2} \right)}{g_i/n_i - a} + \frac{g_i}{a} \frac{a}{g_i} \frac{1}{1 - a n_i/g_i} \right] = \right.$$

$$= \sum_i \ln\left(\frac{g_i}{n_i} - a\right) \delta n_i = 0$$

Use Lagrange multipliers:

$$\sum_i \left[\ln\left(\frac{g_i}{n_i^*} - a\right) - \alpha - \beta \varepsilon_i\right]_{n_i = n_i^*} \delta n_i = 0$$

δn_i are independent then:

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

$$\frac{g_i}{n_i^*} = e^{\alpha + \beta \varepsilon_i} + a \Rightarrow \boxed{n_i^* = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} + a}}$$

Notice that

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

most probable number of particles per energy level in the ith cell.

For large enough g_i the results are independent of how we choose the cells.

Now:

$$\frac{S}{k} = \ln W\{n_i^*\} \overset{①}{=} \sum_i \Big[n_i^* \ln \Big(\underbrace{\frac{g_i}{n_i^*} - a}_{\alpha+\beta\varepsilon_i} \Big) -$$

$$- \frac{g_i}{a} \ln \Big(1 - a \frac{n_i^*}{g_i}\Big)\Big] =$$

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

$$= \bar{N}\alpha + \bar{E}\beta + \sum_i \frac{g_i}{a} \ln\left(1 + a\, e^{-\alpha - \beta \varepsilon_i}\right)$$

$$\therefore \quad \frac{S}{k} - \alpha N - \beta E = \frac{1}{a} \sum_i g_i \ln\left(1 + a\, e^{-\alpha - \beta \varepsilon_i}\right)$$

We know that $\alpha \equiv -\mu/kT$ and $\beta \equiv 1/kT$

$$\therefore \quad \frac{ST}{kT} + \frac{\mu N}{kT} - \frac{E}{kT} = \frac{PV}{kT}$$

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

Notice that for M.B:

$$PV = \lim_{a \to 0} \frac{kT}{a} \sum_i g_i \ln(1 + a e^{-\alpha - \beta \varepsilon_i}) \simeq$$

$$\simeq \frac{kT}{\cancel{a}} \sum_i \underbrace{g_i \cancel{a}\, e^{-\alpha - \beta \varepsilon_i}}_{M_i^{*}\,(M\text{-}B)} = kTN$$

ideal gas eq. of state.

Canonical ensemble: Ideal gas.

$$Z_N(V,T) = \sum_{\underbrace{E}_{\text{many body}}} e^{-\beta E}$$

no constraints.

$$* \begin{cases} E = \sum_{\varepsilon} n_\varepsilon \varepsilon \\ N = \sum_{\varepsilon} n_\varepsilon \end{cases}$$

ε : single particle energies

Notice that we can write:

$$Z_N(V,T) = \sum_{\{n_\varepsilon\}}{}' \underbrace{g\{n_\varepsilon\}}_{\text{what is this value?}} e^{-\beta \sum_\varepsilon n_\varepsilon \varepsilon}$$

$\rightsquigarrow *$

Now we have $g_i = 1$ since we are not using cells along the energy spectrum.

Now we can obtain $g\{n_r\}$ from $W_\alpha\{n_r\}$ setting $g_i = 1$:

$$W_{B.E}\{n_r\} = \prod_i \frac{(n_i + g_i - 1)!}{n_i!\,(g_i-1)!} \overset{g_i=1}{=} \prod_i \frac{(n_i)!}{n_i!\,0!} = 1$$

$$= g_{B.E.}\{n_r\}$$

$$W_{FD}\{n_r\} = \prod_i \frac{g_i!}{n_i!\,(g_i - n_i)!} \overset{g_i=1}{=} \prod_i \frac{1!}{n_i!\,(1-n_i)!} = \begin{cases} 1 & n_i = 0 \\ 1 & n_i = 1 \\ \text{not defined for } n_i > 1 \equiv 0. \end{cases}$$

$$= g_{F.D}\{n_r\}.$$

$$W_{MB}\{n_i\} = \prod_i \frac{g_i^{n_i}}{n_i!} \overset{g_i=1}{=} \prod_i \frac{1}{n_i!} = g_{M\text{-}B}(n_i)$$

Example: $N = 2$

single particle energies:

$E = 0,\ \varepsilon,\ 2\varepsilon$

2ε ———

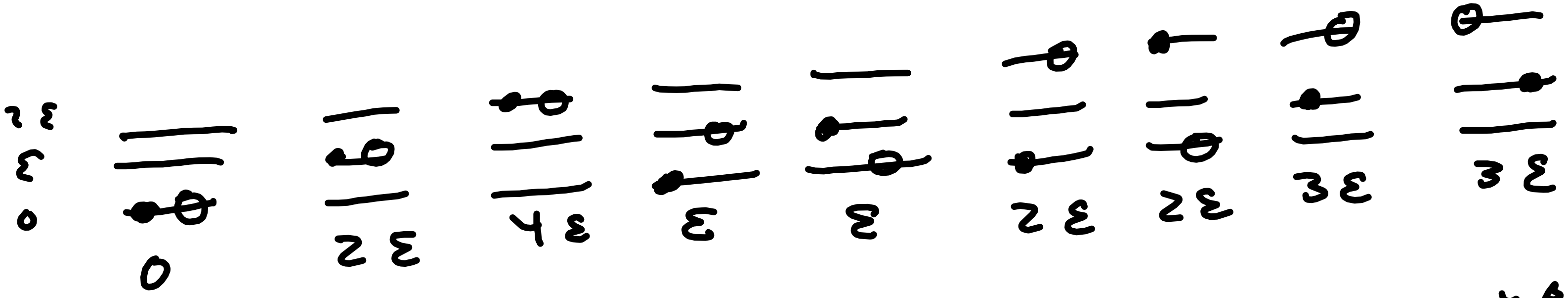
ε ———

0 ———

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

single particle partition function.

M - B: $3^2 = 9$ states for 2 particles:



$$Z_{2\,M.B} = \frac{1 + 2e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon} + 2e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon}}{2}$$

$2 \rightsquigarrow N! = 2!$ Gibbs.

From single particle:

$$Z_{2MB} = \frac{Z_1^2}{2!} = \frac{1}{2}\left(1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}\right)^2 =$$

From:

$$Z_{2MB} = \sum_{\{n_\varepsilon\}}{}' \, g_{MB}\{n_\varepsilon\} \, e^{-\beta \sum_\varepsilon n_\varepsilon \varepsilon} =$$

$$g_{MB}\{n_\varepsilon\} \to \frac{1}{\prod_\varepsilon n_\varepsilon!}$$

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

$$+ \frac{1}{1!\,0!\,1!} e^{-2\beta\varepsilon} + \frac{1}{0!\,1!\,1!} e^{3\beta\varepsilon} = \frac{Z_1^2}{2!}$$

For B.E : Indistinguishable only 6 states :

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

sum over all E.

$Z_{2B.E} =$ gives the same.

sum over $\{n_\varepsilon\}$ with $g\{n_\varepsilon\} = 1$

For F.D: only 3 of the states are allowed (no double occupation):

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

$$Z_{2FD} = \sum_{\{n_\varepsilon\}} g\{n_\varepsilon\}\, e^{-\beta\sum_\varepsilon n_\varepsilon \varepsilon} = e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon}$$

Maxwell-Boltzmann Z_N for ideal gas:

$$Z_N(V,T) = \sum_{\{n_{\varepsilon_s}\}}' \underbrace{\left[\prod_{\varepsilon_s} \frac{1}{n_{\varepsilon_s}!}\right]}_{g\{n_{\varepsilon_s}\}} \underbrace{\prod_{\varepsilon_s} \left(e^{-\beta \varepsilon_s}\right)^{n_{\varepsilon_s}}}_{e^{-\sum_{\varepsilon_s} \beta \varepsilon_s n_{\varepsilon_s}}} =$$

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

$$= \frac{1}{N!} \left[\sum_{\varepsilon_s} e^{-\beta \varepsilon_s}\right]^N = \frac{1}{N!} \left(Z_1(V,T)\right)^N$$

$$\sum k_s = N$$

$$\circledast \quad \left(\sum_r x_r\right)^N = \sum_{\{k_s\}}' \frac{N!}{\prod_s k_s!} \prod_s x_s^{k_s}$$

Notice that

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

Same that we had before for the ideal gas.

also

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

B-E and F-D:

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

since $g\{n_{\varepsilon_s}\}=1$

It is very hard to deal with the constraint now. But it will be easy to evaluate $\mathcal{Z}$ instead of Z_N.

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

$\sum_s n_s \varepsilon_s = E_r$
$\sum_s n_s = N_r$
$\langle E_r\rangle = \bar{E}$
$\langle N_r\rangle = \bar{N}$

$$= \underbrace{\sum_{N_r=0}^{\infty}}_{\text{sum over all possible } N_r.}\left[\underbrace{\sum_{\{n_{\varepsilon_s}\}}{}'}_{\text{sum over all } n_{\varepsilon_s} \text{ so that } \sum_{\varepsilon_s} n_{\varepsilon_s} = N_r} \prod_{\varepsilon_s}\left(z e^{-\beta\varepsilon_s}\right)^{n_{\varepsilon_s}}\right] =$$

equivalent to sum over all n_{ε_s} without restrictions - except the ones given by the statistics.

For B. E.:

$$\mathcal{Z} = \sum_{n_0, n_1, \dots}\left[\left(z e^{-\beta\varepsilon_0}\right)^{n_0}\left(z e^{-\beta\varepsilon_1}\right)^{n_1}\cdots\right]$$

$$= \underbrace{\sum_{n_0=0}^{\infty}\left(z e^{-\beta\varepsilon_0}\right)^{n_0}}_{\frac{1}{1-z e^{-\beta\varepsilon_0}}}\ \underbrace{\sum_{n_1=0}^{\infty}\left(z e^{-\beta\varepsilon_1}\right)^{n_1}}_{1/1-z e^{-\beta\varepsilon_1}}\cdots$$

$$\mathcal{Z}_{BE} = \prod_s \frac{1}{1 - z e^{-\beta \varepsilon_s}}$$

(Notice that in the book you have $\varepsilon_s \equiv \varepsilon$

$$\prod_\varepsilon \frac{1}{1 - z e^{-\beta\varepsilon}}$$

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

For F. D: $n_i = 0$ or 1

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

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

$$\mathcal{Z}_{F.D} = \prod_s \left(1 + z e^{-\beta \varepsilon_s}\right)$$

Note that the q-potential is given by:

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

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

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

Notice that (A) can be generalized to include M.B:

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

$a = -1 \Rightarrow$ B.E.

$a = 1 \Rightarrow$ F.D.

$a = 0 \Rightarrow$ M.B

D/

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

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

$$= z V f(T)$$

Then

$$\bar{N} \equiv z \frac{\partial q}{\partial z}\bigg|_{V,T} \overset{(1)}{=} \frac{z}{\cancel{a}} \sum_s \frac{\cancel{a}\, e^{-\beta \varepsilon_s}}{1 + a z e^{-\beta \varepsilon_s}} =$$

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

$$\bar{E} \equiv -\frac{\partial q}{\partial \beta}\bigg|_{z,V} = +\frac{1}{a} \sum_s \frac{a z \varepsilon_s e^{-\beta \varepsilon_s}}{1 + a z e^{-\beta \varepsilon_s}} =$$

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

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

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

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

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

$$= -\frac{1}{\beta} \frac{\partial \left[\frac{1}{a} \sum_s \ln\left(1 + a z e^{-\beta \varepsilon_s}\right) \right]}{\partial \varepsilon_r} \Bigg|_{z, T, \varepsilon_s \neq \varepsilon_r} =$$

$$\langle n_r \rangle = \frac{1}{z^{-1} e^{\beta \varepsilon_r} + a}$$

now we remember that

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

we see that $\langle n_r \rangle \equiv n_r^*$

if $g_i = 1$