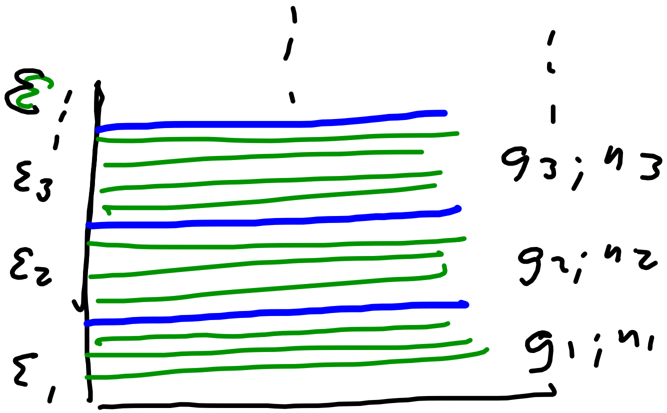
11/7

Statistics dependent density of states and particle distributions.

V, N, E $\Omega(N, V, E) = ?$ microcanonical

free particles



$\{n_i\}$ distribution of particles among the cells.

Constraints:

$$\sum_i n_i = N \qquad \sum_i n_i \varepsilon_i = E$$

number of microstates

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

$$W\{n_i\} = \omega(1)\,\omega(2)\ldots = \prod_i \omega(i)$$

# of microstates in cell 1

$\omega(i)$: # of ways in which n_i particles can be accommodated in g_i states with total energy $n_i \varepsilon_i$.

Bose - Einstein case:

- symmetric wave function
- indistinguishable particles
- unlimited # of particles per state.

We need to accommodate n_i indistinguishable particles in g_i distinguishable "boxes". This is similar to the calculation done for the harmonic oscillator distributing R indistinguishable quanta of energy among N distinguishable oscillators. The result was:

$$\binom{n_i + g_i - 1}{n_i} = \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!}$$

$$w_{B.E.}(i) = \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!}$$

and

$$\boxed{W_{B-E}\{n_i\} = \prod_i \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!}}$$

Fermi-Dirac:
- The wave function is antisymmetric
- Particles are undistinguishable.
- Only one or zero particles can populate a state.

Since n_i of the g_i levels will be occupied we need to find in how many ways we can select n_i states among g_i - This gives:

$$W_{FD}(i) = \binom{g_i}{n_i} = \frac{g_i!}{n_i!\,(g_i - n_i)!}$$

$$\therefore \boxed{W_{F.D.}\{n_i\} = \prod_i \frac{g_i!}{n_i!\,(g_i - n_i)!}}$$

Let's also do Maxwell-Boltzmann:

- Wave function is not symmetrized.
- Particles are distinguishable.
- No restriction on # of particles per state.

Each of the n_i particles can go into g_i states so we have $g_i^{n_i}$ possibilities.

But each $\{n_i\}$ distribution can be obtained in

$\frac{N!}{n_1!\, n_2! \cdots}$ ways then:

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

Gibbs correction

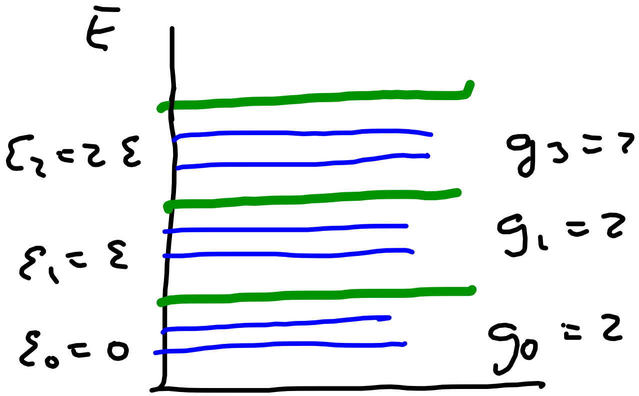
Gibbs did not correct for $\prod_i n_i!$

Now we will have:

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

(we will see that this reproduces the MB weights with the Gibb's correction)

Example: $N = 3$ $\quad E = 3\varepsilon$



B.E.: $\quad n_0 = n_1 = n_2 = 1$

$W_{B.E}(1,1,1) = 2^3 = 8$ possible arrangements

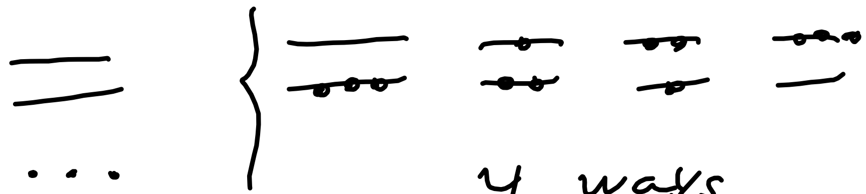
Using the expression:

$$W_{B.E} = \prod_i \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!} = \left[\frac{(1+2-1)!}{1!\;1!}\right]^3 = 2^3 = 8.$$

$n_0 = n_2 = 0 \qquad n_1 = 3$

$\omega_0 = 1 \qquad \omega_1 = ?$

$\omega_2 = 1$



4 ways

$W_{B.E}(0,3,0) = 4$

using the expression:

$$\omega_{BE}(0) = \omega_{BE}(2) = \frac{(n_i + g_i - 1)!}{n_i!\,(g_i-1)!} = \frac{(0+2-1)!}{0!\;1!} = 1$$

$$\omega_{BE}(1) = \frac{(3+2-1)!}{3!\;1!} = \frac{4!}{3!} = 4$$

$\therefore\ W_{B.E}(0,3,0) = 4.$

F.D: Now $(0,3,0)$ is not allowed and only $(1,1,1)$ can be considered.

We see that $\omega(0) = \omega(1) = \omega(2) = 2$

$$\therefore W_{F\text{-}D}(1,1,1) = 2^3 = 8$$

Using the expression:

$$W_{FD}\{n_i\} = \prod_i \frac{g_i!}{n_i!\,(g_i - n_i)!} = \left[\frac{2!}{1!\;1!}\right]^3 = 2^3 = 8.$$

M. B: Now both (1,1,1) and (0,3,0) are possible. We still have to correct by $\frac{1}{N!} = \frac{1}{3!} = \frac{1}{6}$.

By hand: (1,1,1)

$w_i = 2$ ⇝ # of ways in which we can get the $\{n_i\}$

$$W_{MB} = \frac{2^3 \times 6}{6} = 8$$

⇝ Gibbs

Expression

$$W_{MB} = \prod_i \frac{g_i^{n_i}}{n_i!} = \left(\frac{2^1}{1!}\right)^3 = 2^3 = 8.$$

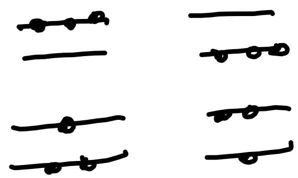
$n_0 = n_2 = 0 \quad n_1 = 3 \quad (0,3,0)$

By hand

$\omega_0 = 1 \quad \omega_2 = 1$

$\omega_1 = 8$

$\omega_1 :$



3 ways 3 ways

8 configurations

$$W(0,3,0) = \frac{8}{3!} = \frac{8}{6} = \frac{4}{3}$$

Gibbs

Expression:

$$W_{BB}(0,3,0) = \prod_i \frac{g_i^{n_i}}{n_i!} = \frac{2^0}{0!} \frac{2^3}{3!} \frac{2^0}{0!} = \frac{8}{6} = \frac{4}{3} \checkmark$$

Entropy:

$$S(N,V,E) = k \ln \Omega(N,V,E) = k \ln \left[\sum_{\{n_i\}}' W\{n_i\} \right]$$

As in Problem 3.4 (Problem 2 in HW #4)

$$S(N,V,E) \approx k \ln W\{n_i^*\}$$

only the weight of the distribution with the maximum weight will be relevant.

To find $\{n_i^*\}$ we will ask $\delta \ln W = 0$ using Lagrange multipliers to enforce the constraints.

$$\delta \ln W\{n_i\} - \left[\alpha \sum_i \delta n_i + \beta \sum_i \varepsilon_i \delta n_i\right] = 0 \qquad (*)$$

Notice that

$$\ln W_{B.E} = \sum_i \left[\ln (n_i + g_i - 1)! - \ln n_i! - \ln (g_i - 1)!\right]$$

$$\ln W_{F.D} = \sum_i \left[\ln g_i! - \ln n_i! - \ln (g_i - n_i)!\right]$$

$$\ln W_{MB} = \sum_i \left[n_i \ln g_i - \ln n_i!\right]$$

Assume that $g_i \gg 1$ and $n_i \gg 1$ and we will use that $\ln x! \simeq x \ln x - x$ (Stirling's).

$$\ln W_{B\cdot E} = \sum_i \left[(n_i + g_i) \ln (n_i + g_i) - (\cancel{n_i + g_i}) - n_i \ln n_i + \cancel{n_i} - g_i \ln g_i + \cancel{g_i}\right] =$$

$$= \sum_i \left[n_i \ln\left(\frac{n_i+g_i}{n_i}\right) + g_i \ln\left(\frac{n_i+g_i}{g_i}\right)\right] =$$

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

$$\ln W_{F.D} \simeq \sum_i \Big[g_i \ln g_i - \cancel{g_i} - n_i \ln n_i + \cancel{n_i} -$$

$$- (g_i - n_i)\ln(g_i - n_i) + \cancel{g_i} - \cancel{n_i} \Big] =$$

$$= \sum_i \left[n_i \ln\left(\frac{g_i - n_i}{n_i}\right) + g_i \ln \frac{g_i}{g_i - n_i}\right] =$$

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

and

$$\ln W_{MB} \approx \sum_i \left[n_i \ln g_i - n_i \ln n_i + n_i \right] =$$

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

We see that: 1

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

with $a = -1$ for BE

$a = 1$ for FD

$a = 0$ for MB

since $\lim_{a \to 0} \left[- \frac{g_i}{a} \ln \left(1 - a \frac{n_i}{g_i} \right) \right] \approx - \frac{g_i}{a} \left(- a \frac{n_i}{g_i} \right) \to n_i$

Now

$$\boxed{\delta \ln W} = \sum_i \delta m_i \left[\left(\ln\left(\frac{g_i}{m_i} - a\right) + \frac{m_i\left(-\frac{g_i}{m_i^2}\right)}{\frac{g_i}{m_i} - a} + \right.\right.$$

$$\left. + \frac{g_i}{a}\,\frac{a}{g_i}\cdot\frac{1}{1 - \frac{a m_i}{g_i}} \right] =$$

$$= \sum_i \delta m_i \left[\ln\left(\frac{g_i}{m_i} - a\right) - \underbrace{\frac{g_i}{m_i\left(\frac{g_i}{m_i} - a\right)}}_{\frac{g_i}{g_i - m_i a}} + \frac{g_i}{g_i - a m_i} \right]$$

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

with $a = -1$ (B.E), 1 (F.D), 0 (M.B).

Going back to (*):

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

The δn_i are independent here:

$$\therefore \ln\left(\frac{g_i}{n_i^*} - a\right) - \alpha - \beta \varepsilon_i = 0$$

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

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

Notice that:

$$\frac{n_i^*}{g_i} = \frac{1}{e^{\alpha+\beta\varepsilon_i}+a} \qquad (2)$$

most probable # of particles per energy level in the ith cell

We interpret this as the most probable # of particles in a single level with energy ε_i.

If g_i is large enough the result should be independent of the way in which the cells were defined.

Then

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

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

$\alpha + \beta\varepsilon_i$ because

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

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

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

$$= \frac{e^{\alpha+\beta\varepsilon_i}}{e^{\alpha+\beta\varepsilon_i} + a} = \frac{1}{1 + a e^{-\alpha-\beta\varepsilon_i}}$$

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

$$\therefore \quad \frac{S}{k} - \alpha N - \beta E = \frac{1}{a}\sum_i g_i \ln\left(1 + a e^{-\alpha - \beta \varepsilon_i}\right) \quad (3)$$

as before $\alpha = -\frac{\mu}{kT}$ $\quad \beta = \frac{1}{kT}$

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

(3) is

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

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