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Now let's look at the diagonal elements of $\hat{\rho}$:

$$\langle \bar{r}_1, \bar{r}_2 | \hat{\rho} | \bar{r}_1, \bar{r}_2 \rangle = \frac{1}{Z_2} \langle \bar{r}_1, \bar{r}_2 | e^{-\beta \hat{H}} | \bar{r}_1, \bar{r}_2 \rangle \cong$$

$$\cong \frac{1}{2\lambda^6} \frac{1 \pm e^{-2\pi r_{12}^2/\lambda^2}}{\frac{1}{2}\left(\frac{V}{\lambda^3}\right)^2} = \frac{1}{V^2}\left[1 \pm e^{-\frac{2\pi r_{12}^2}{\lambda^2}}\right]$$

$\neq \frac{1}{V^2}$ for fermions or bosons.

Now if $r_{12} \approx \lambda$ $\langle \hat{\rho} \rangle$ is very different than in the classical case.

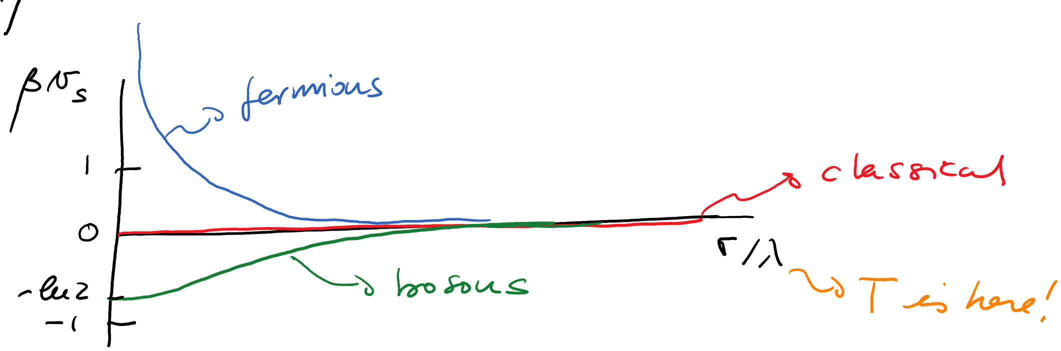
For bosons: $1 + e^{-\frac{2\pi r_{12}^2}{\lambda^2}} \longrightarrow 2$ if $r_{12} \to 0$ positive spatial correlations

For fermions: $1 - e^{-\frac{2\pi r_{12}^2}{\lambda^2}} \longrightarrow 0$ if $r_{12} \to 0$ negative spatial correlation

We can define an statistical potential:

$$v_s(r) = -kT \ln\left(1 \pm e^{-\frac{2\pi r^2}{\lambda^2}}\right)$$

$$\langle \bar{r}_1 \bar{r}_2 | \hat{\rho} | \bar{r}_1, \bar{r}_2 \rangle = e^{-\beta v_s}$$



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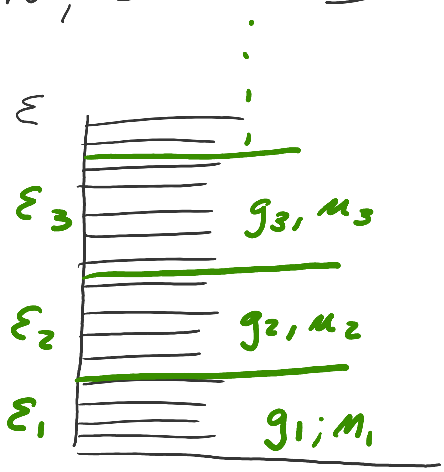
Theory of simple gases

- Non-interacting systems but with quantum effects.
- Ideal gas:

Let's work in the microcanonical ensemble.

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



We divide the energy range into arbitrary cells containing g_i states with energy ε_i (because $\delta\varepsilon$ inside the cell is negligible).

Assume $g_i \gg 1 \;\forall i$.

We want to distribute the N particles into the ε_i cells and find configurations $\{n_i\}$ that satisfy that:

$$\left.\begin{aligned} \sum_i n_i &= N \\ \sum_i n_i \varepsilon_i &= E \end{aligned}\right\} \text{ constraints.} \quad (*)$$

Then

$$\Omega(N, V, E) = \underbrace{\sum_{\{n_i\}}}_{\text{satisfying } (*)} \underbrace{W\{n_i\}}_{\text{\# of distinct microstates for each } \{n_i\}}$$

with

$$W\{n_i\} = w_1(1)\, w_2(2) \ldots = \prod_i w(i)$$

# of microstates in cell 1

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

- To find $w(i)$ and $W\{n_i\}$ we need to consider the statistics of the particles.

- Bosons: indistinguishable particles with no restrictions regarding placement. This will provide Bose-Einstein (BE) statistics. The wave-function is symmetric. Particles are called bosons. Particles with integer spin.

$w(i)$: # of ways in which we can place n_i indistinguishable particles in g_i distinguishable levels. We found this # for the harmonic oscillator and it is:

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

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

and

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

$n_i!\,(g_i-1)!$

Fermions:

Now $W_{F.D}(i)$ is the # of ways in which the g_i's can be divided into 2 groups: one with 0 particles and one with one fermion each.

We see that n_i of the g_i levels will have 1 fermion and $g_i - n_i$ levels will be empty. Then

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

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

Fermions have half-integer spin. They have an antisymmetric wave-function and satisfy Pauli's exclusion principle: one or zero fermions per level.

- Maxwell-Boltzmann (or classical) case:

  Unsymmetrized wave-function and $1/N!$ Gibbs correction. In fact, the particles are distinguishable and then we correct by $1/N_i!$.

We can accommodate n_i particles in g_i levels in

$$g_i^{n_i} \quad \text{ways.}$$

levels in

$$g_i^{n_i} \quad \text{ways.}$$

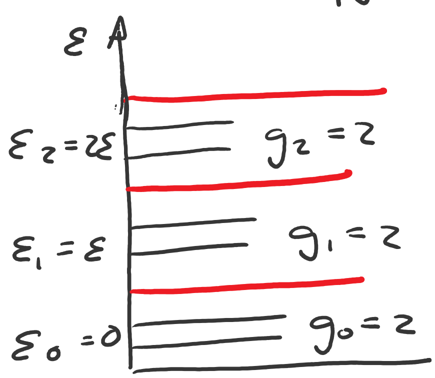
But each $\{n_i\}$ set can be obtained in $\dfrac{N!}{n_1!\, n_2! \cdots}$ ways. Then

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

Gibbs

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

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



a) B.E: There are 2 $\{n_i\}$ configurations satisfying the constraint.

i) $n_0 = n_1 = n_2 = 1$

$$W_{B.E}(1,1,1) = 2^3 = 8 \qquad \text{(by hand)}$$

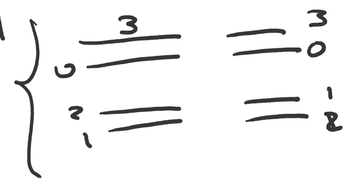
$n_i = 1;\ g_i = 2 \ \forall i$

$$w_{BE}(i) = \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!} = \frac{(1+2-1)!}{1!\ 1!} = 2$$

$$W_{BE} = \prod_i w_{BE}(i) = 2^3 = 8. \qquad (\text{formula}).$$

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

By hand: $\quad w_0 = w_2 = 1 \quad$ and $\quad w_1 = 4$



$$\therefore \; W_{B.E}(0,3,0) = w_0 w_1 w_2 = 4$$

Formula:

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

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

$$\therefore \; W_{BE}\{0,3,0\} = 4 .$$

F, D. case:

Now $\quad n_0 = n_1 = n_2 = 1 \quad$ (only possible)

$n_0 = n_2 = 0$ and $n_1 = 3$ is not allowed because only up to two fermions can be there.

$$\therefore \; W_{F.D}(1,1,1) = 2^3 = 8 \qquad (\text{by hand})$$

$$w_{F.D}(i) = \frac{g_i!}{n_i!\,(g_i - n_i)!} = \frac{2!}{1!\,(2-1)!} = 2$$

$$\therefore \; W_{F.D}(1,1,1) = \prod_i w_{F.D}(i) = 2^3 = 8.$$

M-B: Now both (1,1,1) and (0,3,0) are allowed. Now the particles are distinguishable and we "correct" with $\frac{1}{N!} = \frac{1}{3!} = \frac{1}{6}$ to fix overcounting.

By hand: (1,1,1)

$n_0 = n_1 = n_2 = 1$ We can chose n_i in $3! = 6$ ways.

$w_i = 2$

$$\therefore\ W = \frac{\overset{w_0 \times w_1 \times w_2}{2^3} \times 6!}{\underset{\text{Gibbs}}{6!}} = 8$$

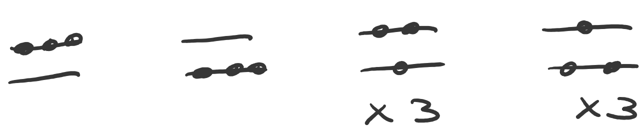
Formula:

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

(0,3,0): $n_0 = n_2 = 0$ $n_1 = 3$

$w_0 = w_2 = 1$

But $w_1 = 8$



$$W_{MB}(0,3,0) = \frac{1 \times 8 \times 1}{\underset{\text{Gibbs}}{3!}} = \frac{8}{6} = \frac{4}{3}$$

Formula:

Formula:

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

—— x ——

Entropy

$$S(N,V,E) = k \ln \Omega(N,V,E) =$$

$$= k \ln \left[\sum_{\{n_i\}}' W\{n_i\} \right] \approx$$

$$\approx k \ln W\{n_i^*\}$$

only the term with $\{n_i^*\}$ the configuration with the maximum weight contributes (see Problem 2 in HW#4).

To find $\{n_i^*\}$ we ask that $\delta \ln W = 0$ using Lagrange multipliers to take care of the constraints.

$\therefore$

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

Notice that:

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

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

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

We assume that $n_i >> 1$ and $g_i >> 1$ so we can use Stirling's approximation: $\ln x! \approx x \ln x - x$.

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

$$\ln W_{F.D} \approx \sum_i \left[n_i \ln \left[\frac{g_i}{n_i} - 1 \right] - g_i \ln \left(1 - \frac{n_i}{g_i}\right) \right]$$

$$\ln W_{M-B} \approx \sum_i \left[n_i \left(\ln \left(\frac{g_i}{n_i}\right) + 1 \right) \right]$$

Notice that:

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

with $a = -1$ for B.E.

$a = 1$ for F.D.

$a = 0$ for M.B.

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

Then

$$\ln W \Big|_{a=0} \approx \sum_i \left[n_i \ln \left(\frac{g_i}{n_i} \right) + n_i \right] =$$

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

Now we can obtain $\delta \ln W$ using $(**)$:

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

Then going back to ⊛ :

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

Since δn_i are independent $\Rightarrow$

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

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

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

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

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

this can be interpreted as the most probable # of particles in a single level with energy ε_i.

Notice that if g_i is very large the result for $\frac{n_i^*}{g_i}$ should not depend on the way in which we chose the cells.