

**CLASSICAL LIMIT**  
**(Review and free reading)**

In classical mechanics we can specify simultaneously both  $q_i$  and  $p_i$  for a particle. In quantum mechanics the uncertainty principle prevents this. A classical description is a reasonable approximation only when the effect of  $h$  is negligible, i.e.

$$\Delta q \Delta p \gg h$$

Consider the motion of a molecule in a gas. If  $p_{av}$  denotes the mean momentum and  $r_{av}$  its mean separation from other identical molecules, then a classical description is valid when

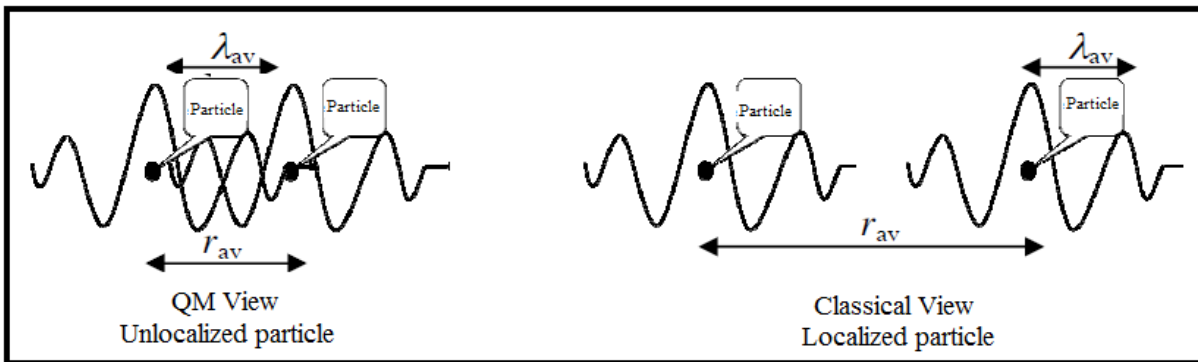
$$r_{av} p_{av} \gg h$$

or, Using De Broglie wavelength,  $p = h / \lambda$ , when

$$r_{av} \gg \lambda_{av} \quad (\text{classical limit});$$

$$r_{av} \ll \lambda_{av} \quad (\text{quantum limit});$$

Since  $\lambda_{av}$  is a measure of the spread of molecule in space, it means that when  $r_{av} \gg \lambda_{av}$  holds, the molecular wave functions do not overlap and therefore they are distinguished by their position.



To give a physical content to  $r_{av} \gg \lambda_{av}$ , we imagine that each particle occupies a tiny cube of side  $r_{av}$  and these cubes fill the volume  $V$ ,

$$r_{av}^3 N = V, \quad r_{av} = \left( \frac{V}{N} \right)^{1/3}$$

If we anticipate and relate the temperature  $T$  with the average energy  $\bar{\epsilon}$  by:

$$\frac{p_{av}^2}{2m} \approx \bar{\epsilon} = \frac{3}{2} k_B T, \quad p_{av} \approx (3mk_B T)^{1/2}$$

Where  $k_B$  is the Boltzmann constant, then

$$\lambda_{av} \approx \frac{h}{(3mk_B T)^{1/2}}$$

Therefore, the classical condition becomes

$$\left( \frac{V}{N} \right)^{1/3} \gg \frac{h}{(3mk_B T)^{1/2}}$$

This means the classical description is valid when:

- 1-  $N$  is small (dilute gas),
- 2-  $T$  is large, and
- 3-  $m$  is not too small.

For an ideal (Boltzmaan) gas consisting of  $N$  indistinguishable molecules of mass  $m$ , we have

$$E = \sum_{i=1}^{3N} \varepsilon_i, \quad \varepsilon_i = \frac{p_i^2}{2m}$$

And

$$e^{-\beta E} = e^{-\beta \sum_{i=1}^{3N} \varepsilon_i} = e^{-\beta \varepsilon_1} e^{-\beta \varepsilon_2} e^{-\beta \varepsilon_3} \dots = \prod_i e^{-\beta \varepsilon_i},$$

The single-particle partition function (for  $N = 1$ ) is

$$Z_{\text{sp}} = \sum_i e^{-\beta \frac{p_i^2}{2m}} = \frac{1}{h^3} \left[ \int_{-\infty}^{\infty} e^{-\beta E(p_i)} d\Gamma_i \right]^3 = V \left( \frac{2\pi m}{h^2 \beta} \right)^{3/2} = V n_Q = \frac{n_Q}{n}, \quad d\Gamma_i = dp_i dq_i$$

where we replaced the sum over discrete states by an integral over the phase space.  $n_Q = \frac{1}{\lambda^3} = \left( \frac{2\pi m}{h^2 \beta} \right)^{3/2}$  is

called the “quantum concentration” and  $n = \frac{1}{V}$  is the concentration. The  $n_Q$  is the concentration associated with

one particle in a cube of side  $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ .

### Examples:

(i) Molecules in a gas at NTP

Using  $\rho_{\text{molecules}} = 10^{25} \text{ molecules m}^{-3}$ ,

We have the available volume  $V_{\text{molecule}} = 10^{-25} \text{ m}^3$ ,

Using  $r_{\text{molecule}} = 10^{-10} \text{ m}$

We have the actual volume  $V_{\text{molecule}} = 10^{-30} \text{ m}^3$

So, in gases, the volume of a molecule is usually being much smaller than the volume available to it, we can, in principle, identify each molecule in the gas. Therefore, the molecules are localized and distinguishable.

(iii) Conduction electrons in metal

Using  $\rho_{\text{electrons}} = 10^{28} \text{ electrons m}^{-3}$ ,

We have the available volume  $V_{\text{electron}} = 10^{-28} \text{ m}^3$ ,

Using  $r_{\text{electron}} = \frac{h}{p} = \frac{h}{\sqrt{2mE(1\text{eV})}} = 10^{-9} \text{ m}$

We have the actual volume  $V_{\text{electron}} = 10^{-27} \text{ m}^3$

So, in metals, the volume of the electron is larger than the available volume. Hence the electron wave functions overlap considerably. We can not localize the electrons, they are indistinguishable, and quantum statistics must be applied.

## QS\_examples

- (iii) We can also use the above analysis to estimate a transition temperature for the onset of quantum effects. For example we take He atoms in a fluid phase and conduction electrons in an alkali metal.

From  $\left(\frac{V}{N}\right)^{1/3} \gg \frac{h}{(3mk_B T)^{1/2}}$  we get:

$$T = \left(\frac{h^2}{3mk_B}\right)\left(\frac{N}{V}\right)^{2/3}$$

$$= \begin{cases} 1.2 \times 10^{-14} (N/V)^{2/3} \text{ K m}^2, \text{ electrons} \\ 1.6 \times 10^{-18} (N/V)^{2/3} \text{ K m}^2, \text{ He atoms} \end{cases}$$

for He atoms  $\frac{V}{N} \approx 5 \times 10^{-29} \text{ m}^3 \text{ atom}^{-1} \Rightarrow \underline{T \approx 10 \text{ K}}$

for electrons  $\frac{V}{N} \approx 1 \times 10^{-29} \text{ m}^3 \text{ electron}^{-1} \Rightarrow \underline{T \approx 3 \times 10^5 \text{ K}}$

So we can see that at room temperature a classical treatment of atomic fluids is allowable whereas we must use a quantum description of electrons in a metal up to a very high temperature. Gases at room temperature have a density 1000 times less than a fluid and so will have a transition temperature even lower than 10 K. They can clearly be treated as classical under most conditions.

QS\_examples

**Symmetry of wave functions:** Matter waves are described by a complex valued wave function  $\Psi(\mathbf{r}, t)$  obeying the Schrodinger equation

$$\hat{H}\Psi(\mathbf{r}, t) = E\Psi(\mathbf{r}, t), \quad \hat{H} = \left[-\frac{\hbar}{2m}\nabla^2 + V(\mathbf{r})\right], \quad E = i\hbar\frac{\partial}{\partial t}$$

which is the fundamental equation in quantum mechanics. The simplest of  $N$  identical noninteracting particles could be described by the Schrodinger equation

$$\hat{H}\Psi = E\Psi, \quad \hat{H} = \sum_{i=1}^N \frac{p_i^2}{2m}, \quad \Psi = \Psi(r_1, r_2, \dots, r_N) \quad \#$$

where  $p_i^2 = \mathbf{p}_i \cdot \mathbf{p}_i$ , and  $\mathbf{p}_i$  is the momentum operator of the  $i$ th particle. The Hamiltonian is independent of the positions of the particles or any other coordinates. e.g., spin, if any.

Introduce the *permutation operator*  $\hat{P}$ , which interchanges particle  $i$  with particle  $j$ , i.e.  $r_i \leftrightarrow r_j$ . For example:

$$\hat{P}_{12}\Psi_a(1)\Psi_b(2) = \Psi_a(2)\Psi_b(1) \text{ or } \hat{P}_{12}\Psi(1, 2) = \Psi(2, 1)$$

The Hamiltonian  $\hat{H}$  is invariant under all permutation of the identical particles:

$$\hat{P}\hat{H}\hat{P}^{-1} = \hat{H} \Rightarrow \hat{P}\hat{H}\hat{P}^{-1}\hat{P} = \hat{H}\hat{P} \Rightarrow [\hat{H}, \hat{P}] = 0$$

The eigenstates of  $\hat{H}$  should also be eigenstates of  $\hat{P}$ . In general, the single product wave function

$$\Psi = \Psi(r_1, r_2, \dots, r_N) = \prod_i^N \Psi_k(r_i)$$

is not an eigenstate of  $\hat{P}$ . An eigenstate must satisfy

$$\hat{P}\Psi(r) = p\Psi(r) \Rightarrow \hat{P}^2\Psi(r) = p\hat{P}\Psi(r) = p^2\Psi(r)$$

$$\hat{P}^2 = \hat{1} \Rightarrow p^2 = 1 \Rightarrow p = \pm 1$$

then

$$\hat{P}\Psi(r) = \Psi(r) \Rightarrow \text{Symmetric wavefunction}$$

$$\hat{P}\Psi(r) = -\Psi(r) \Rightarrow \text{Antisymmetric wavefunction}$$

It is a *law of nature* that the symmetry ( $S$ ) or antisymmetric ( $A$ ) under the interchange of two particles is a property of the particles themselves.

**Example**, for two-particle system we have

$$\Psi(1, 2) = \Psi_a(1)\Psi_b(2) \quad (\text{classical}) \quad \#$$

$$\Psi^{(S)}(1, 2) = \Psi^{(S)}(2, 1) = \frac{1}{\sqrt{2}}[\Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1)] \quad (\text{symmetric}) \quad \#$$

$$\Psi^{(A)}(1, 2) = -\Psi^{(A)}(2, 1) = \frac{1}{\sqrt{2}}[\Psi_a(1)\Psi_b(2) - \Psi_a(2)\Psi_b(1)] \quad (\text{antisymmetric}) \quad \#$$

For  $N$  fermions, we have the Slater's determinant

$$\Psi^{(A)}(1, 2) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_a(1) & \Psi_a(2) & \dots & \dots & \Psi_a(N) \\ \Psi_b(1) & \Psi_b(2) & \dots & \dots & \Psi_b(N) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \dots \\ \Psi_z(1) & \Psi_z(2) & \dots & \dots & \Psi_z(N) \end{vmatrix}. \quad \#$$

Due to Pauli, with interchanges all the coordinates of the particles, then identical particles could be divided into two groups, Bose gas and Fermi gas. The following table shows the main properties of each system plus the unnatural gas, Boltzmann gas.

**Quantum Statistics with examples**

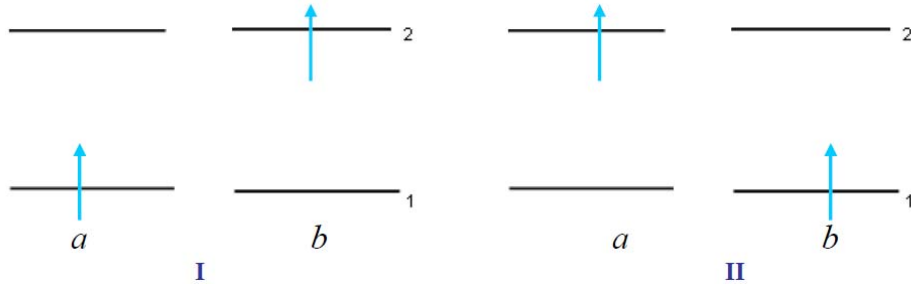
Let us consider a system consisting of non-interacting molecules, denoted by  $a, b, c \dots$ , whose energy levels are given by  $E_a, E_b, E_c, \dots$ . In the classical statistical mechanical treatment of ideal gases, the particles/molecules/atoms are assumed to be *distinguishable*. Therefore, every possible occupation of energy levels by particles is admissible. Hence the following decomposition of the Hamiltonian, total energy and the partition function holds good.

$$H = H_a + H_b + H_c + \dots$$

$$E = E_a + E_b + E_c + \dots$$

$$q_a = \sum_a e^{-\beta E_a}, \quad q_b = \sum_b e^{-\beta E_b}$$

$$Q = q_a q_b q_c \dots \quad \text{where } a, b, c \text{ etc are the particle indices.}$$



Owing to the distinguishability of the particles 'a' and 'b', arrangements I and II are different and each should be counted separately.

However, when particles are *indistinguishable*, the arrangements I and II are one and the same and hence should be counted only as one arrangement. Evaluating the total partition function as

$$Q = q_a q_b q_c \dots$$

is incorrect as it has those extra terms.

**Justification:**

I. Take five balls that are distinguishable.



The total number of ways in which the balls can be arranged in three levels such that  
 2 balls in level 1  
 2 balls in level 2  
 1 ball in level 3

are  $\frac{5!}{2!2!1!} = 30$

Generically,  $\frac{N!}{n_1!n_2!n_3! \dots}$  where  $n_1, n_2, n_3, \dots$  are the numbers of balls occupying levels 1, 2, 3.. etc respectively.

QS\_examples

II. Supposing the balls were indistinguishable,



Then the number of ways in which the above arrangement can be done is just 1!

Supposing an arrangement with only one ball occupying each level is desired, then again there only one possible way to obtain it in the indistinguishable balls case. Whereas with distinguishable balls there are  $N!$  possible ways of obtaining this arrangement.

Therefore, classical statistics vastly over-estimates the number of configurations. In classical statistical mechanics, this is of course taken into account by the  $1/N!$  terms (Boltzmann factor) in front of the partition function. This method does not work at low temperature where quantum nature of the particles become important that impose further restrictions on the occupancy of the energy levels of the system. In a system of Bose particles, any number of particles can occupy any given energy level. On the other hand, particles obeying Fermi-Dirac statistics, maximum of one particle can occupy a given energy level. That is, the occupation number of a given energy level can be 1 or 0.

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**High Temperature Limit**

When the temperature is high, a system has a large number of accessible energy states such as translational, rotational, electronic.... The number of states is much more than the number of atoms/molecules. At high temperatures, a large number of states become accessible, especially the translational states. In such a case, the possibility of multiple occupancy of a state will be greatly reduced. *Thus the occupied energy levels are mostly non-degenerate.* Thus, the occupation due to quantum statistics is not important and classical Boltzmann statistics works well. This is exactly like case II in justification. So the surplus contributions that will feature for the indistinguishable particles in the expression

$$Q = q_a q_b q_c \dots$$

$N!$  compared to distinguishable particles.

For an ideal gas the atoms/molecules are independent (negligible intermolecular forces) and indistinguishable. In the expression

$$Q = q^N$$

there are  $N!$  surplus contributions in the thermodynamic limit for an ideal gas. Thus the exact partition function for an ideal gas in this limit is

$$Q = \frac{q^N}{N!} \rightarrow (1)$$

In the thermodynamic limit,  $n\lambda^3 \ll 1$  (where  $n$  is the number density,  $\lambda$  is the de-Broglie wavelength,  $\lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{1}{2}}$  and  $n\lambda^3$  is a dimensionless quantity) because  $m \gg 1$ ,  $T \gg 1$  and  $n \ll 1$ . This is the classical regime where Maxwell-Boltzmann statistics holds good and indistinguishability can be exactly accounted for. But as we go on to *low temperatures and high densities* multiple occupancy of states increases.  $n\lambda^3 \approx 1$  is in this limit. Under such conditions, the indistinguishability of particles becomes much more significant. This is where the quantum effects creep in and there is need for a revised statistics.

-----( **End the free reading** )-----

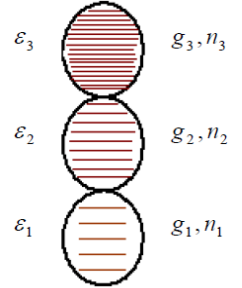
## Quantum Statistics (Chapter 6\_Pathria)

All known indistinguishable particles, fall in to the class of either *Fermions* or *Bosons*. These two statistics or distributions lay different constraints on the occupancy of a particular state but under the conservation of two quantities, the total number of particles and the total energy.

$$\sum_i n_i = N, \quad \sum_i n_i \epsilon_i = E$$

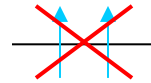
These constraints become very significant when there is degenerate/multiple occupancy of energy levels.

To understand the effects of these statistics on the distribution of energy levels, we first group the energy levels with energy within a small interval together and assign a degeneracy factor to each group according to the number of energy levels in each group. Let us denote the energy and degeneracy of *i*-th group by  $\epsilon_i$  and  $g_i$ , respectively. The picture aside illustrates the grouping.



**Ideal Fermi-Dirac Gas (Fermions):** Fermions obey the condition on the occupation of a state is that: a state can have 1 particle or 0 particle in it, but never two or more (i.e.  $n_i = 0,1$ ). So,  $n_i$  is always less than or equal to  $g_i$ . This is because they obey the Pauli exclusion principle.

$$n_i = 0,1$$



Let  $n_i$  be the number of particles occupying an energy level  $\epsilon_i$  in a particular configuration. If  $g_i$  is the degeneracy of  $\epsilon_i$ , ( $g_i \geq n_i$ ), then the number of possible arrangements amongst the degenerate levels of  $\epsilon_i$  is

$$w_{FD}^{(i)} = \binom{g_i}{n_i} = \frac{g_i!}{n_i!(g_i - n_i)!} \quad \rightarrow (2)$$

(This is exactly like picking ‘*n*’ white balls out of ‘*g*’ white balls.)

**Partition function:** That is, a particular possible state will be either occupied or unoccupied, so that  $n_i = 0,1$ .

$$\begin{aligned} Z_{\text{Fermions}} &= \sum_{n_1=0}^1 \sum_{n_2=0}^1 \dots e^{-\beta \sum_s n_s \epsilon_s} = \sum_{n_1=0}^1 \sum_{n_2=0}^1 \dots e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)} \\ &= \left\{ \sum_{n_1=0}^1 e^{-\beta N_1 \epsilon_1} \right\} \left\{ \sum_{n_2=0}^1 e^{-\beta N_2 \epsilon_2} \right\} \dots = \prod_{s=0}^{\infty} \{1 + e^{-\beta \epsilon_s}\}, \\ \ln Z &= \sum_{s=0}^{\infty} \ln \{1 + e^{-\beta \epsilon_s}\} \end{aligned}$$

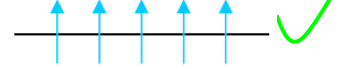
It follows that, the mean energy and the mean occupation number of a given state are:

$$\langle u \rangle = -\frac{\partial \ln Z}{\partial \beta} = \sum_{s=0}^{\infty} \frac{\epsilon_s e^{-\beta \epsilon_s}}{1 + e^{-\beta \epsilon_s}}, \quad \langle n_s \rangle = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_s} = \frac{1}{e^{+\beta \epsilon_s} + 1}$$

**Ideal Bose-Einstein Gas (Bosons):** Bosons obey this statistics. There is no constraint on the occupation of a particular state in an energy level as these particles do not obey the Pauli principle. Any number of particles can occupy a state in an energy level.

$$n_i = 0, 1, 2, 3, \dots$$

$$n_i^{\max} = \infty$$

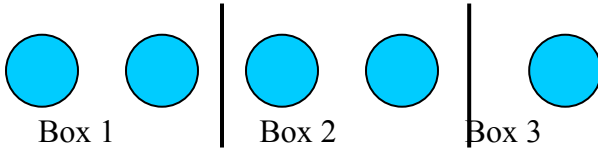


Let  $n_i$  be the number of particles occupying an energy level  $\epsilon_i$  in a particular configuration. If  $g_i$  is the degeneracy of  $\epsilon_i$ , then the number of possible arrangements amongst the degenerate levels of  $\epsilon_i$  are

$$w_{BE}^{(i)} = \binom{n_i + g_i - 1}{n_i} = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \rightarrow (3)$$

**Justification:**

Suppose we take five indistinguishable balls (bosons,  $n_i$ ) and arrange them into three distinct boxes (degenerate levels,  $g_i = 3$ ) with no restriction on the occupation numbers in each box.



Here there are five balls and two sticks (the number of sticks will always be one lesser than the number of degenerate levels). The total number of possible arrangements for the balls in the boxes is

$$\frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} = \frac{(5 + 3 - 1)!}{5!2!} = \frac{7!}{5!2!} = 21$$

We are justified in doing  $(g_i - 1)!$  because only the boxes are distinct, the sticks are not. The sticks are indistinguishable.

**Partition function:** Consider the situation where the mean occupation number of a given state is independent on the mean occupation numbers of the other states. That is, each occupation number may range from zero to infinity, so that  $N_s = 0, 1, 2, \dots$

We have  $E_N(n_1, n_2, n_3, \dots) = \sum_i n_i \epsilon_i$

However, the normalisation,  $N = \sum_i n_i$ , is no longer required because the number of photons is fluctuating. The partition function can therefore be rewritten as:

$$Z_N = \sum_{n_1, n_2, n_3, \dots} e^{-\beta \sum_i n_i \epsilon_i} \equiv \sum_{n_1} \sum_{n_2} \sum_{n_3} \dots e^{-\beta \sum_i n_i \epsilon_i}$$

Where  $n_i = 0, 1, 2, \dots, \infty$ . So,

$$Z_{\text{Bosons}} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots e^{-\beta \sum_s n_s \epsilon_s} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots e^{-\beta (n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)}$$

$$= \left\{ \sum_{n_1=0}^{\infty} e^{-\beta n_1 \epsilon_1} \right\} \left\{ \sum_{n_2=0}^{\infty} e^{-\beta n_2 \epsilon_2} \right\} \dots = \prod_{i=1}^{\infty} \sum_{n_{ij}=0}^{\infty} e^{-\beta n_{ij} \epsilon_i},$$



Now,

$$\sum_{n_{ij}=0}^{\infty} e^{-\beta n_{ij} \epsilon_i} \equiv e^0 + e^{-\beta \epsilon_i} + e^{-2\beta \epsilon_i} + \dots = \frac{1}{1 - e^{-\beta \epsilon_i}} \quad (\text{sum of a geometric series})$$

So,

$$Z_{\text{Bosons}} = \prod_{i=0}^{\infty} \frac{1}{1 - e^{-\beta \epsilon_i}}$$

and

$$\ln Z = -\sum_{s=0}^{\infty} \ln \{1 - e^{-\beta \epsilon_s}\}$$

It follows that, the average occupation number

$$\begin{aligned} \langle n_i \rangle &= -\frac{1}{\beta} \left( \frac{\partial \ln Z_N}{\partial \epsilon_i} \right)_{T, \epsilon_j \neq \epsilon_i} = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \sum_r \ln \left( \frac{1}{1 - e^{-\beta \epsilon_r}} \right) = \frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \sum_r \ln(1 - e^{-\beta \epsilon_r}) \\ &= \frac{1}{\beta} \frac{\beta e^{-\beta \epsilon_i}}{1 - e^{-\beta \epsilon_i}} = \frac{1}{e^{\beta \epsilon_i} - 1} \end{aligned}$$

the mean energy of a given state are:

$$\langle u \rangle = -\frac{\partial \ln Z}{\partial \beta} = \sum_{s=0}^{\infty} \frac{\epsilon_s e^{-\beta \epsilon_s}}{1 - e^{-\beta \epsilon_s}},$$

the *mean occupation number* of a single-particle state with energy  $\epsilon_s$  is given by

$$\langle n_s \rangle = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_s} = \frac{1}{e^{\beta \epsilon_s} - 1}$$

**Example:** Compare the Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac statistics when four particles are arranged in two energy levels. Three particles are at energy level  $\epsilon_1$  having a degeneracy  $g_1 = 4$  and one particle at energy level  $\epsilon_2$  having a degeneracy  $g_2 = 2$ .

**Solution:**

Note that:  $n_1 = 3, g_1 = 4, n_2 = 1, g_2 = 2$

$$w_{MB} = N! \prod_{i=1}^m \frac{g_i^{n_i}}{n_i!} = 4! \frac{4^3 \times 2^1}{3!1!} = 512$$

$$w_{BE} = \prod_{i=1}^m \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} = \frac{(3 + 4 - 1)! (1 + 2 - 1)!}{3!3! 1!1!} = 40$$

$$w_{FD} = \prod_{i=1}^m \frac{g_i!}{n_i! (g_i - n_i)!} = \frac{4! 2!}{3!1! 1!1!} = 4$$

## Classification

**Maxwell-Boltzmann statistics** This is the classical statistics and is applicable for a system of independent, distinguishable (or indistinguishable) and identical particles. No restriction about the symmetry, spins, etc.

**Bose-Einstein statistics** is applicable for a system of independent, indistinguishable and identical particles of integral spin (like photons). There is no restriction on the number of particles present in any given quantum state.

**Fermi-Dirac statistics** is applicable for a system of independent, indistinguishable and identical particles of half-integral spin (like electrons). In this statistics, a given energy state can be occupied at best by one particle only.

	B.E. (Bosons)	F.D. (Fermions)	M.B
Particles	Indistinguishable	Indistinguishable	Distinguishable
Wave-functions	Symmetric	Antisymmetric	Any
Spin	$0, \hbar, 2\hbar, \dots$	$\frac{1}{2}\hbar, \frac{3}{2}\hbar, \dots$	Any
Examples	photons, $\pi$ -meson, ${}^4\text{He}$	electron, proton, ${}^3\text{He}$	Any
$n_i$	0, 1, 2, .....	0, 1	0, 1, 2, .....
$\omega(i)$	$\omega_{BE} = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$	$\omega_{FD} = \frac{g_i!}{n_i!(g_i - n_i)!}$	$\omega_{MB} = \frac{g_i^{n_i}}{n_i!}$ (*)
$\Omega$	$\Omega_{BE} = \prod_{i=1}^r \omega_{BE}$	$\Omega_{FD} = \prod_{i=1}^r \omega_{FD}$	$\Omega_{MB} = \prod_{i=1}^r \omega_{MB}$
$f(\epsilon_i) = \frac{N_i}{g_i}$	$\frac{1}{e^{-\alpha + \beta \epsilon_i} - 1}$	$\frac{1}{e^{-\alpha + \beta \epsilon_i} + 1}$	$e^{-\alpha - \beta \epsilon_i}$
Applications	Photons of radiation, gas molecules at very low temperature.)	Free electrons in metal and semiconductor (except at very High temperature.)	Gas molecules (except near 0 K), electrons at Extremely High temperature.

(\*) corrected by "correct Boltzmann counting" i.e. divided by  $N!$ . This correction does not correspond to any physical property of the particles in the system. It is just a rule that defines the mathematical model for indistinguishable particles.

\*\* Define the dilute gas, dilute means that for all energy levels, the occupation numbers are very small compared with the available number of quantum states (i.e. most quantum states are empty). We assume that

$$N_j \ll g_j \quad \text{for all } j.$$

**This condition holds for real gases except at very low temperatures.**

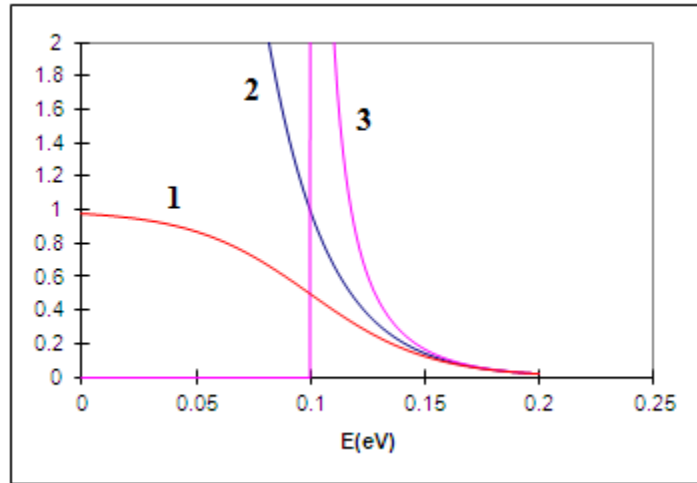
For dilute gas one finds

$$\omega_{FD} = \omega_{BE} = \omega_{MB} = \prod_{i=1}^r \frac{g_i^{N_i}}{N_i!}$$

Simply we can have

$$f_j \equiv \frac{n_j}{g_j} = \frac{1}{e^{\beta(\epsilon_j - \mu)} + a}, \quad a = \begin{cases} +1 & \text{for FD statistics} \\ -1 & \text{for BE statistics} \\ 0 & \text{for MB statistics} \end{cases}$$

**Three Distributions**



The mean occupation number  $\langle n_s \rangle$  of a single-particle energy state  $\mathcal{E}_s$  in a system of noninteracting particles: curve 1 is for fermions, curve 2 for bosons, and curve 3 for the Maxwell–Boltzmann particles.

**See Partia Page 150 for the comments**

- i- In the Fermi–Dirac case ( $a = 1$ ), the mean occupation number never exceeds unity, for the variable  $n_s$  itself cannot have a value other than 0 or 1.
- ii- In the Bose–Einstein case ( $a = -1$ ), the occupancy of that particular level becomes infinitely high. As in the case of Bose–Einstein *condensation*.

**Example:** Consider the case of  $N = 3$ ,  $n_1 = 2$  in  $\epsilon_1$ ,  $n_2 = 1$  in  $\epsilon_2$ ,  $g_1 = 2$  and  $g_2 = 1$ . Compare the Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac statistics.

**Solution:**

$$w_{MB} = N! \prod_{i=1} \frac{g_i^{n_i}}{n_i!} = 3! \frac{2^2 \times 1^1}{2! \times 1!} = 12$$

$$w_{BE} = \prod_{i=1} \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} = \frac{(2 + 2 - 1)!}{2! \times 1!} \times \frac{(1 + 1 - 1)!}{1! \times 0!} = 3;$$

$$w_{FD} = \prod_{i=1} \frac{g_i!}{n_i! (g_i - n_i)!} = \frac{2!}{2! \times 0!} \times \frac{1!}{1! \times 0!} = 1;$$



QS\_examples

**Example:** Consider a system of *two* non-interacting, and identical particles in a volume  $V$ . Each particle has three accessible energy levels  $\epsilon_1 = 0$ ,  $\epsilon_2 = 1\epsilon$ , and  $\epsilon_3 = 2\epsilon$ . The lowest energy level is doubly degenerate. Determine the partition function and the mean energy of the system if:

- A. the particles are distinguishable and obey the classical Maxwell-Boltzmann statistics.
- B. the particles obey Fermi-Dirac statistics.
- C. the particles obey Bose-Einstein statistics.
- D. Determine the high temperature limit of the mean energy of the above three cases. Comparing the results what can you conclude about the behavior of fermions and bosons in this limit?

**Solution:**

**A- Maxwell-Boltzmann Statistics:** We have the following distributions:

Energy	Macrostates			
	1	2	3	4
$2\epsilon$	0	0	0	0
$\epsilon$	0	0	0	0
0	ab	0	0	ab
Total Energy =	0	0	0	0

Energy	Macrostates			
	5	6	7	8
$2\epsilon$	0	0	0	0
$\epsilon$	b	a	b	a
0	a	0	b	0
Total Energy =	$\epsilon$	$\epsilon$	$\epsilon$	$\epsilon$

Energy	Macrostates			
	9	10	11	12
$2\epsilon$	b	a	b	a
$\epsilon$	0	0	0	0
0	a	0	0	a
Total Energy =	$2\epsilon$	$2\epsilon$	$2\epsilon$	$2\epsilon$

Energy	Macrostates			
	14	15	16	
$2\epsilon$	b	a	ab	
$\epsilon$	a	b	0	
0	0	0	0	0
Total Energy =	$3\epsilon$	$3\epsilon$	$4\epsilon$	

The total number of macrostates =  $g^N = 4^2 = 16$ .

The partition function is:

QS\_examples

$$Z_{MB} = \sum_i g_i e^{-\beta \epsilon_i} = 4e^{-\beta \epsilon_0} + 4e^{-\beta \epsilon_1} + 5e^{-\beta \epsilon_2} + 2e^{-\beta \epsilon_3} + e^{-\beta \epsilon_4} = 4 + 4e^{-\beta \epsilon} + 5e^{-2\beta \epsilon} + 2e^{-3\beta \epsilon} + e^{-4\beta \epsilon}$$

$$U_{MB} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{4\epsilon e^{-\beta \epsilon} + 10\epsilon e^{-2\beta \epsilon} + 6\epsilon e^{-3\beta \epsilon} + 4\epsilon e^{-4\beta \epsilon}}{4 + 4e^{-\beta \epsilon} + 5e^{-2\beta \epsilon} + 2e^{-3\beta \epsilon} + e^{-4\beta \epsilon}} \rightarrow \frac{3}{2} \epsilon \quad (\text{as } T \rightarrow \infty)$$

**B- Fermi-Dirac Statistics:** We have the following distributions:

Energy	Macrostates									
	1	2	3	4	5	6				
2ε	0	0	0	a	a	a				
ε	0	a	a	0	0	a				
0	a	a	a	0	0	a	0	a	0	0
Total Energy =	0	ε	ε	2ε	2ε	3ε				

The partition function is:

$$Z_{FD} = \sum_i g_i e^{-\beta \epsilon_i} = e^{-\beta \epsilon_0} + 2e^{-\beta \epsilon_1} + 2e^{-\beta \epsilon_2} + e^{-\beta \epsilon_3} = 1 + 2e^{-\beta \epsilon} + 2e^{-2\beta \epsilon} + e^{-3\beta \epsilon}$$

$$U_{FD} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{2\epsilon e^{-\beta \epsilon} + 4\epsilon e^{-2\beta \epsilon} + 3\epsilon e^{-3\beta \epsilon}}{1 + 2e^{-\beta \epsilon} + 2e^{-2\beta \epsilon} + e^{-3\beta \epsilon}} \rightarrow \frac{3}{2} \epsilon \quad (\text{as } T \rightarrow \infty)$$

**C- Bose-Einstein Statistics:** We have the following distributions:

Energy	Macrostates									
	1	2	3	4	5					
2ε	0	0	0	0	0					
ε	0	0	0	a	a					
0	aa	0	0	aa	a	a	0	0	a	
Total Energy =	0	0	0	ε	ε					

Energy	Macrostates									
	6	7	8	9	10					
2ε	a	2	0	a	aa					
ε	0	0	aa	a	0					
0	a	0	0	0	0	0	0	0	0	
Total Energy =	2ε	2ε	2ε	3ε	4ε					

The partition function is:

$$Z_{BE} = \sum_i g_i e^{-\beta \epsilon_i} = 3e^{-\beta \epsilon_0} + 2e^{-\beta \epsilon_1} + 3e^{-\beta \epsilon_2} + e^{-\beta \epsilon_3} + e^{-\beta \epsilon_4} = 3 + 2e^{-\beta \epsilon} + 3e^{-2\beta \epsilon} + e^{-3\beta \epsilon} + e^{-4\beta \epsilon}$$

$$U_{BE} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{2\epsilon e^{-\beta \epsilon} + 6\epsilon e^{-2\beta \epsilon} + 3\epsilon e^{-3\beta \epsilon} + 4\epsilon e^{-4\beta \epsilon}}{3 + 2e^{-\beta \epsilon} + 3e^{-2\beta \epsilon} + e^{-3\beta \epsilon} + e^{-4\beta \epsilon}} \rightarrow \frac{3}{2} \epsilon \quad (\text{as } T \rightarrow \infty)$$

d- In the high ( $T \rightarrow \infty, \beta \rightarrow 0$ ) temperature limit fermions and bosons behave as classical Boltzmann particles.

## QS\_examples

**Example:** Consider a system of *two* particles in a volume  $V$ , each of which can be in any one of three quantum states of respective energy  $\epsilon_1 = 0$ ,  $\epsilon_2 = 1\epsilon$ , and  $\epsilon_3 = 3\epsilon$ . The system is in contact with a heat reservoir at temperature  $T = (k\beta)^{-1}$ . Write an expression for the **partition function** if the particles obey:

- 1- the classical Maxwell-Boltzmann statistics and are consider *distinguishable*.
- 2- the classical Maxwell-Boltzmann statistics and are consider *undistinguishable*.
- 3- the particles obey Fermi-Dirac statistics.
- 4- the particles obey Bose-Einstein statistics.

**Solution:**

Configuration				Number of states		
0	1 $\epsilon$	3 $\epsilon$	total	MB	BE	FD
xx			0	1	1	--
	xx		2 $\epsilon$	1	1	--
		xx	6 $\epsilon$	1	1	--
x	x		1 $\epsilon$	2	1	1
x		x	3 $\epsilon$	2	1	1
	x	x	4 $\epsilon$	2	1	1

$$Z_{MB} = \sum_{\{n_i\}} e^{-\beta \sum_s n_s \epsilon_s} = \sum_{i(\text{energy levels})} g_i e^{-\beta \epsilon_i}$$

$$= 1 + e^{-2\beta\epsilon} + e^{-6\beta\epsilon} + 2e^{-\beta\epsilon} + 2e^{-3\beta\epsilon} + 2e^{-4\beta\epsilon}$$

$$Z_{BE} = \sum_i g_i e^{-\beta \epsilon_i} = 1 + e^{-2\beta\epsilon} + e^{-6\beta\epsilon} + e^{-\beta\epsilon} + e^{-3\beta\epsilon} + e^{-4\beta\epsilon}$$

$$Z_{FD} = \sum_i g_i e^{-\beta \epsilon_i} = e^{-\beta\epsilon} + e^{-3\beta\epsilon} + e^{-4\beta\epsilon}$$

The total number of arrangements possible for a particular configuration for both F-D as well as B-E are (this is over all the energy levels of a particular configuration)

$$W\{n_i\} = \prod_i w^{(i)}(n_i) \rightarrow \quad (4)$$

The total number of arrangements possible over all configurations is

$$\Omega(N, V, E) = \sum_{\{n_i\}} W(\{n_i\}) \rightarrow \quad (5)$$

where  $\Omega(N, V, E)$  is the partition function in microcanonical ensemble.

Thus the entropy is

$$S = k_B \ln \Omega \cong k_B \ln W(\{n_i^*\}) \rightarrow \quad (6)$$

Maximizing the entropy and **finding out the maximum term by Lagrange's method of undetermined multipliers.**

$$\delta \ln W(\{n_i\}) - \left[ \alpha \sum_i \delta n_i - \beta \sum_i \varepsilon_i \delta n_i \right] = 0 \rightarrow \quad (7)$$

$$W\{n_i\} = \prod_i w^{(i)}(n_i)$$

$$\ln[W\{n_i\}] = \ln\left[\prod_i w^{(i)}(n_i)\right] = \sum_i \ln w^{(i)}(n_i)$$

$$\delta \ln W(\{n_i\}) = \sum_i \delta \ln w^{(i)}(n_i) \rightarrow \quad (8)$$

**For F-D statistics,**

$$w^{(i)} = \frac{g_i!}{n_i!(g_i - n_i)!}$$

$$\ln w^{(i)} = \ln g_i! - \ln n_i! - \ln(g_i - n_i)!$$

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

$$= g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln(g_i - n_i)$$

$$= g_i \ln \left( \frac{g_i}{g_i - n_i} \right) + n_i \left( \frac{g_i - n_i}{n_i} \right) = -g_i \ln \left( 1 - \frac{n_i}{g_i} \right) + n_i \ln \left( \frac{g_i}{n_i} - 1 \right) \rightarrow (9)$$

**For B-E statistics,**

$$w^{(i)} = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

$$\ln w^{(i)} = \ln(n_i + g_i - 1)! - \ln n_i! - \ln(g_i - 1)!$$

$$= (n_i + g_i - 1) \ln(n_i + g_i - 1) - \cancel{n_i} - \cancel{g_i} + \cancel{1} - n_i \ln n_i + \cancel{n_i} - (g_i - 1) \ln(g_i - 1) + \cancel{g_i} - \cancel{1}$$

$$= (n_i + g_i - 1) \ln(n_i + g_i - 1) - n_i \ln n_i - (g_i - 1) \ln(g_i - 1)$$

$$= n_i \ln \frac{(n_i + g_i - 1)}{n_i} + (g_i - 1) \ln \frac{(n_i + g_i - 1)}{(g_i - 1)} \cong n_i \ln \left( 1 + \frac{g_i}{n_i} \right) + g_i \ln \left( 1 + \frac{n_i}{g_i} \right) \rightarrow \quad (10)$$

**General form of  $\ln w^{(i)}$  for F-D and B-E statistics is**

$$\ln w^{(i)} = n_i \ln \left( \frac{g_i}{n_i} - a \right) - \frac{g_i}{a} \ln \left( 1 - a \frac{n_i}{g_i} \right) \rightarrow \quad (11)$$

where  $a = -1$  for BE  
 $a = 1$  for FD  
 $a = 0$  for MB

$$(12)$$

$$\begin{aligned} \delta \ln w^{(i)} &= \left[ \ln \left( \frac{g_i}{n_i} - a \right) + n_i \frac{\left( \frac{-g_i/n_i^2}{g_i - a} \right)}{\left( \frac{g_i}{n_i} - a \right)} - \frac{g_i}{a} \frac{\left( \frac{-a/g_i}{1 - a \frac{n_i}{g_i}} \right)}{\left( 1 - a \frac{n_i}{g_i} \right)} \right] \delta n_i = \left[ \ln \left( \frac{g_i}{n_i} - a \right) - \frac{g_i}{n_i} \left( \frac{1}{\frac{g_i}{n_i} - a} \right) + \left( \frac{1}{1 - a \frac{n_i}{g_i}} \right) \right] \delta n_i \\ &= \left[ \ln \left( \frac{g_i}{n_i} - a \right) - \left( \frac{1}{1 - a \frac{n_i}{g_i}} \right) + \left( \frac{1}{1 - a \frac{n_i}{g_i}} \right) \right] \delta n_i = \left[ \ln \left( \frac{g_i}{n_i} - a \right) \right] \delta n_i \rightarrow \quad (13) \end{aligned}$$

From eqns (7) and (8),

$$\delta \ln W(\{n_i\}) - \left[ \alpha \sum_i \delta n_i - \beta \sum_i \varepsilon_i \delta n_i \right] = 0 \quad \Rightarrow \quad \delta \ln W(\{n_i\}) = \sum_i \delta \ln w^{(i)}(n_i)$$

Thus,

$$\begin{aligned} \sum_i \left[ \ln \left( \frac{g_i}{n_i} - a \right) - \alpha - \beta \varepsilon_i \right] \delta n_i &= 0 \quad \Rightarrow \quad \ln \left( \frac{g_i}{n_i^*} - a \right) - \alpha - \beta \varepsilon_i = 0 \\ n_i^* &= \frac{g_i}{e^{\alpha + \beta \varepsilon_i} + a} \rightarrow \quad (15) \end{aligned}$$

$n_i^*$  is the distribution that maximizes the entropy. Hence

$$\frac{S}{k_B} \cong \ln W(\{n_i^*\}) = \sum_i \ln w^{(i)}(n_i^*)$$

From eqn (11)

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

$$\frac{S}{k_B} = \sum_i \left[ n_i^* (\alpha + \beta \varepsilon_i) + \frac{g_i}{a} \ln(1 + a e^{-\alpha - \beta \varepsilon_i}) \right] \rightarrow (15)$$

$$\sum_i n_i^* = N \quad ; \quad \sum_i n_i^* \varepsilon_i = E$$

$$\frac{S}{k_B} - \alpha N - \beta E = \frac{1}{a} \sum_i g_i \ln(1 + a e^{-\alpha - \beta \varepsilon_i})$$



$$\alpha = -\frac{\mu}{k_B T} ; \quad \beta = \frac{1}{k_B T}$$

Thus,

$$\frac{S}{k_B} + \frac{\mu N}{k_B T} - \frac{E}{k_B T} = \frac{1}{a} \sum_i g_i \ln(1 + a e^{-\alpha - \beta \epsilon_i})$$

From thermodynamics,

$$\frac{S}{k_B} + \frac{\mu N}{k_B T} - \frac{E}{k_B T} = \frac{G - (E - TS)}{k_B T} = \frac{PV}{k_B T} \rightarrow (16)$$

**Equation of state for a quantum ideal gas is**

$$PV = \frac{k_B T}{a} \sum_i g_i \ln(1 + a e^{-\alpha - \beta \epsilon_i}) \rightarrow (17)$$

In the high temperature limit,

$$\alpha, \beta \approx 0$$

Hence Taylor expansion can be done,  $\ln(1+x) \approx x$

$$\frac{PV}{k_B T} = \frac{1}{a} \sum_i g_i a e^{-\alpha - \beta \epsilon_i} = \sum_i g_i e^{-\alpha - \beta \epsilon_i} \rightarrow (18)$$

For an ideal gas with Maxwell-Boltzmann distribution, the equation of state is

$$\frac{PV}{k_B T} = \sum_i n_i^* = N \quad (\text{Ideal gas law})$$

But from eqn (14)

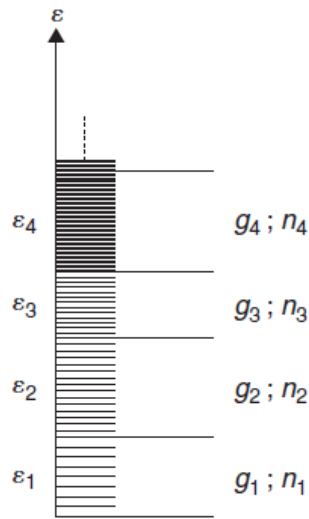
$$n_i^* = \frac{g_i}{e^{\alpha + \beta \epsilon_i}}$$

Thus,

$$\frac{PV}{k_B T} = \sum_i g_i e^{-\alpha - \beta \epsilon_i} \rightarrow (19)$$

(Compare eqn (18) and (19)). Irrespective of whether it is a Bose gas or a Fermi gas, in the thermodynamic limit it goes over to Maxwell-Boltzmann distribution.

## Bose-Einstein



The grouping of the single-particle energy levels into “cells.”

At energy  $\varepsilon_j$  there are  $N_j$  particles divided among  $g_i$  states. How many ways can they be distributed? Consider  $N_j$  particles and  $g_j - 1$  barriers between states, a total of  $N_j + g_j - 1$  objects to be arranged. How many arrangements?

### Bose-Einstein

$$w_j = \frac{(N_j + g_j - 1)!}{N_j!(g_j - 1)!}$$

$$w_{BE}(N_1, N_2, \dots, N_n) = \prod_{j=1}^n \frac{(N_j + g_j - 1)!}{N_j!(g_j - 1)!}$$

$$\begin{aligned} \ln w_{BE} &= \sum_{j=1}^n \ln(N_j + g_j - 1)! - \sum_{j=1}^n \ln N_j! - \sum_{j=1}^n \ln(g_j - 1)! \\ &= \sum_{j=1}^n [(N_j + g_j - 1) \ln(N_j + g_j - 1) - (N_j + g_j - 1)] - \sum_{j=1}^n [N_j \ln N_j - N_j] \\ &\quad - \sum_{j=1}^n [(g_j - 1) \ln(g_j - 1) - (g_j - 1)] \end{aligned}$$

$$\ln w_{BE} = \sum_{j=1}^n [(N_j + g_j - 1) \ln(N_j + g_j - 1) - N_j \ln N_j - (g_j - 1) \ln(g_j - 1)]$$

$$\delta \ln w_{BE} = \sum_{j=1}^n \delta N_j \left[ \ln(N_j + g_j - 1) + \frac{(N_j + g_j - 1)}{(N_j + g_j - 1)} - \ln N_j - \frac{N_j}{N_j} \right]$$

$$\delta \ln w_{BE} = \sum_{j=1}^n \delta N_j \left[ \ln \left( \frac{N_j + g_j}{N_j} \right) \right]$$

### Constraints (Lagrange Multipliers)

$$\delta \left( \ln w_{BE} - \alpha \sum_{j=1}^n N_j - \beta \sum_{j=1}^n \varepsilon_j N_j \right) = 0$$

$$\sum_{j=1}^n \delta N_j \left[ \ln \left( \frac{N_j + g_j}{N_j} \right) - \alpha - \beta \varepsilon_j \right] = 0$$

$$\ln \left( 1 + \frac{g_j}{N_j} \right) - \alpha - \beta \varepsilon_j = 0$$

$$1 + \frac{g_j}{N_j} = e^{\alpha + \beta \varepsilon_j} \quad \frac{g_j}{N_j} = e^{\alpha + \beta \varepsilon_j} - 1 \quad \Rightarrow \quad f_j = \frac{N_j}{g_j} = \frac{1}{e^{\alpha + \beta \varepsilon_j} - 1}$$

### Boltzmann Distribution

$$\ln \left( \frac{N_j}{g_j} \right) = -\alpha - \beta \varepsilon_j \quad \Rightarrow \quad \frac{N_j}{g_j} = e^{-\alpha - \beta \varepsilon_j} = f_j = \frac{1}{e^{\alpha + \beta \varepsilon_j}}$$

### Fermi-Dirac

At energy  $\varepsilon_j$  there are  $N_j$  particles divided among  $g_j$  states, but only one per state.  $g_j \geq N_j$ . How many ways can the  $N_j$  occupied states be selected from the  $g_j$  states?

$$w_j = \frac{g_j!}{N_j!(g_j - N_j)!}$$

$$w_{FD}(N_1, N_2, \dots, N_n) = \prod_{j=1}^n \frac{g_j!}{N_j!(g_j - N_j)!}$$

$$\begin{aligned} \ln w_{FD} &= \sum_{j=1}^n \ln g_j! - \sum_{j=1}^n \ln N_j! - \sum_{j=1}^n \ln(g_j - N_j)! \\ &= \sum_{j=1}^n [g_j \ln g_j - g_j - N_j \ln N_j + N_j - (g_j - N_j) \ln(g_j - N_j) + (g_j - N_j)] \\ &= \sum_{j=1}^n [g_j \ln g_j - N_j \ln N_j - (g_j - N_j) \ln(g_j - N_j)] \end{aligned}$$

$$\delta \ln w_{FD} = \sum_{j=1}^n \delta N_j \left[ -\ln N_j - \frac{N_j}{N_j} + \ln(g_j - N_j) + \frac{(g_j - N_j)}{(g_j - N_j)} \right] = \sum_{j=1}^n \delta N_j \left[ \ln \left( \frac{g_j - N_j}{N_j} \right) \right]$$

QS\_examples

$$\delta \left( \ln w_{FD} - \alpha \sum_{j=1}^n N_j - \beta \sum_{j=1}^n \varepsilon_j N_j \right) = 0$$

$$\sum_{j=1}^n \delta N_j \left[ \ln \left( \frac{g_j - N_j}{N_j} \right) - \alpha - \beta \varepsilon_j \right] = 0 \Rightarrow \frac{g_j}{N_j} - 1 = e^{\alpha + \beta \varepsilon_j} \quad \frac{g_j}{N_j} = e^{\alpha + \beta \varepsilon_j} + 1 \Rightarrow f_j = \frac{N_j}{g_j} = \frac{1}{e^{\alpha + \beta \varepsilon_j} + 1}$$

$$\ln \left( \frac{g_j}{N_j} - 1 \right) - \alpha - \beta \varepsilon_j = 0$$

**Distributions**

$$f_j \equiv \frac{n_j}{g_j} = \frac{1}{e^{\beta(\varepsilon_j - \mu)} + a}, \quad a = \begin{cases} +1 & \text{for FD statistics} \\ -1 & \text{for BE statistics} \\ 0 & \text{for MB statistics} \end{cases}$$

## Quantum Statistics

When taken to classical limit quantum results must agree with classical. B-E and F-D must approach Boltzmann in classical limit. What is that limit?

Low particle density! Then distinguishability is not a factor.

### Classical limit

$$\frac{N_j}{g_j} = f_j = \frac{1}{e^{\alpha + \beta \epsilon_j} \pm 1}, \quad \beta = \frac{1}{kT}$$

For  $f_j \ll 1$ ,  $e^{\alpha + \beta \epsilon_j} \gg 1$

$$f_j \cong \frac{1}{e^{\alpha + \beta \epsilon_j}} \quad \text{Same as Boltzmann}$$

### Quantum Results

$$\frac{N_j}{g_j} = f_j = \frac{1}{e^{\alpha} e^{\frac{\epsilon_j}{kT}} \pm 1}$$

– Bose-Einstein

+ Fermi-Dirac

### Chemical Potential

$$\frac{N_j}{g_j} = f_j = \frac{1}{e^{\alpha} e^{\frac{\epsilon_j}{kT}} \pm 1} = \frac{1}{e^{\frac{\epsilon_j - \mu}{kT}} \pm 1}, \quad \alpha = -\frac{\mu}{kT}$$

– Bose-Einstein

+ Fermi-Dirac