

# Statistical Thermodynamics (Classical and Quantum statistics): Part-2

- ❖ Heat capacity of solids
- ❖ Equilibrium constant and partition functions
- ❖ Quantum statistics
- ❖ Fermi-Dirac and Bose-Einstein statistics



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## Statistical Thermodynamics: Part-2

- ❖ **The heat capacity of a solid:** Heat capacity is defined as the increase in the internal energy ( $E$ ) as the temperature of that substance is raised by one unit. The standardized unit could be a unit of mass (e.g., gram or kg, etc,) but the standardized unit for comparison between different substances is a *mole*.

$$C = \delta E / \delta T$$

- ❖ **Classical Approach:** For a solid we can also consider it being made of several harmonic oscillators. The average energy of a harmonic oscillator in one dimension is  $kT$ , where  $k$  is Boltzmann's constant. In all the 3 dimensions the average energy will be 3 times of  $kT$  e.g.,  $3kT$ . If there are  $N$  atoms in the lattice then the internal energy is  $E(\text{mole}) = N(3kT)$ .

For one mole  $E = 3RT$

$$C_p = (\partial E(\text{mole}) / \partial T)$$

and thus from the above

$$C_p = (\partial 3RT(\text{mole}) / \partial T)$$

$$C_p = 3R$$

The value for  $C_p$  of  $3R$  is about 6 calories per degree Kelvin. This is also known as the Dulong and Petit value.

# Statistical Thermodynamics: Part-2

## ❖ Equilibrium Constants in Terms of Partition Functions:

The equilibrium constant  $K$  of a reaction is related to the standard Gibbs energy of reaction by  $\Delta G^0 = -RT \ln K$  and molar partition function,  $q_m = q/n$

To calculate the equilibrium constant, we need to combine these two equations.

The equilibrium constant for the reaction  $a A + b B \rightarrow c C + d D$  is given by the following equation;

$$K = \left[ \left( q_{C,m} \frac{1}{N_A} \right)^c \left( q_{D,m} \frac{1}{N_A} \right)^d / \left( q_{A,m} \frac{1}{N_A} \right)^a \left( q_{B,m} \frac{1}{N_A} \right)^b \right] e^{-\Delta E_0 / RT}$$

Where  $\Delta E_0$  is the difference in molar energies of the ground states of the products and reactants

*Note: Students are requested to also see the Atkins' Physical chemistry book Chapter 17 for a more in-depth analysis*

# Statistical Thermodynamics: Part-2

❖ **What is statistics:** Statistics are usually defined as the collection of numerical data, it is a field of mathematics that deals with the collection, tabulation and interpretation of the numerical data.

There are two main types of statistics in thermodynamics:

**(1) Classical statistics (Maxwell-Boltzmann's statistics or MB statistics):** Here each particle of the system has an individuality and thus can be distinguishable. If we have only 2 cells and 2 particles, then each particle has equal probability of occupying either of the cell. A total of 4 possible arrangements thus exist in this system. Ideal gas molecules follow MB statistics)

**(2) Quantum statistics: (1) Fermi-Dirac (FD statistics):** In quantum statistics the particles are considered to be indistinguishable, so we have to consider only cells where particles can be placed. For a 2 particles and 2 cells system, we can have only one combination in Fermi-Dirac statistics because the filling of cells will be as per the Pauli's exclusion principle and therefore each cell can only contain one particle. Particles that follow FD statistics are known as Fermions (e.g., electron)

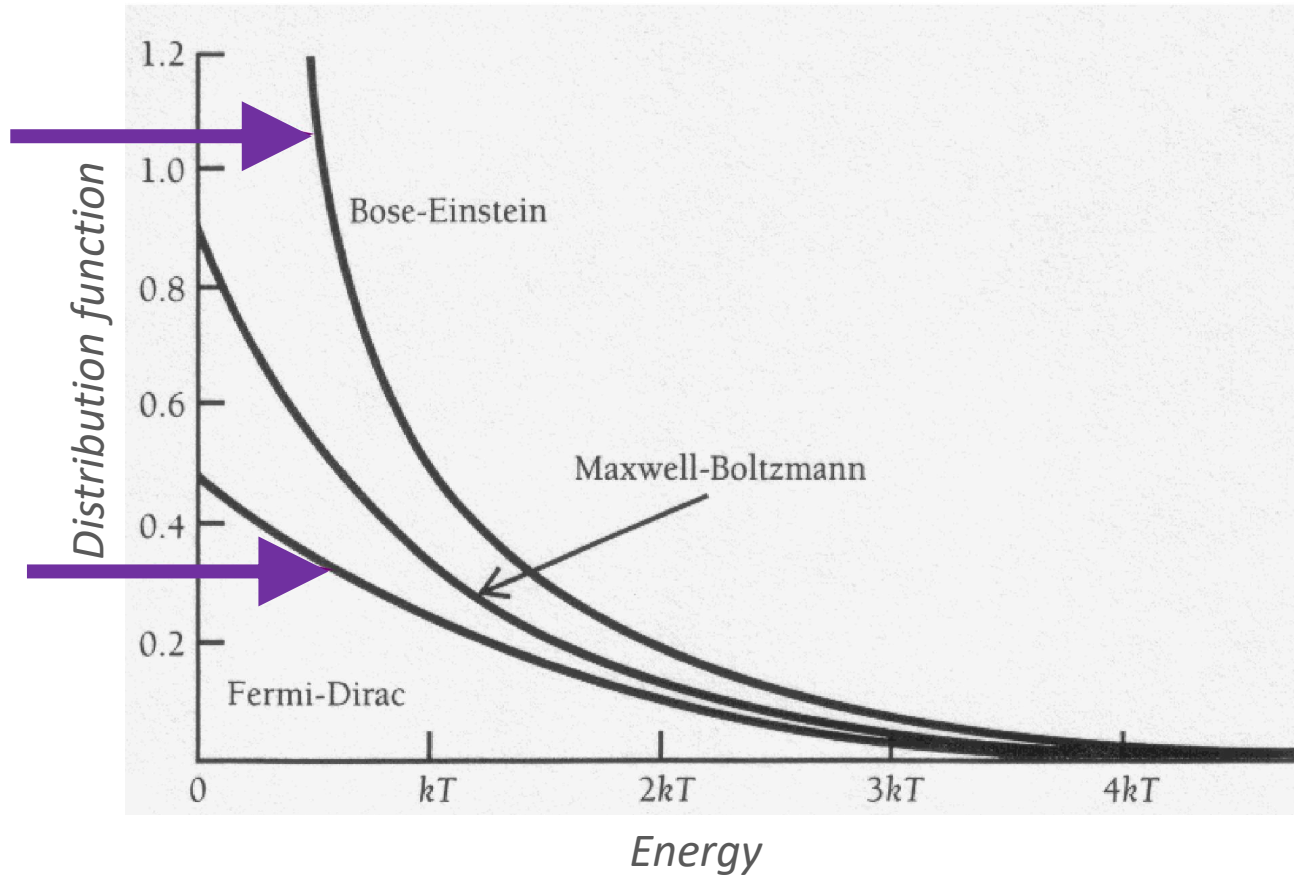
*[According to the Pauli exclusion principle: two or more identical fermions (particles with half-integer spin) cannot occupy the same quantum state within a quantum system simultaneously]*

**(1) Quantum statistics: (1) Bose-Einstein (BE statistics):** The main feature of the quantum statistics is that the particles of the system lose their individuality that is a postulate from quantum mechanics. Now since the particles are indistinguishable, therefore we can only consider about the cell. Again, if we have 2 particles and 2 cells then we can have three possible arrangements as the particles are indistinguishable. Particles that follow BE statistics are known as Bosons (e.g., photon)

# Statistical Thermodynamics: Part-2

Bosons like to be in same energy state, so many bosons are possible to fit in one place

Fermions do not like to be in same energy state, so many Fermions are not possible to fit in one place, so probability is low



# Statistical Thermodynamics: Part-2

## ❖ Quantum statistics

### ❖ (1) Fermi-Dirac (or FD) statistics:

Let us consider the total probability sum for a system of particles that follows Fermi-Dirac statistics.

Consider

$\epsilon_1, \epsilon_2, \dots, \epsilon_i, \dots$  are the energies of the successive energy levels,

$g_1, g_2, \dots, g_i, \dots$  are the degeneracies of these levels,

And  $N_1, N_2, \dots, N_i, \dots$  are the number of particles in all of the degenerate quantum states of a given energy level.

The probability of finding a particle in a quantum state depends on the number of particles in the system; we have  $p(N_i, \epsilon_i)$  rather than  $p(\epsilon_i)$ . Consequently, we cannot generate the total probability sum by expanding an equation like

$$1 = (P_1 + P_2 + \dots + P_i + \dots)^N$$

Three assumptions to make

(1) At constant  $T$ : A finite subset of the population sets available to the system accounts for nearly all of the probability.

(2) At isolated system: Essentially the same finite subset of population sets accounts for nearly all of the probability.

(3) All of the microstates with a given energy have the identical probability. We let this probability be  $\rho_{MS,N,E}^{FD}$ .

## Statistical Thermodynamics: Part-2

The total probability sum will be of the form

$$1 = \sum W^{FD}(N_i, \epsilon_i) \rho^{FD}_{MS,N,E}$$

It reflects the fact that there are  $W^{FD}(N_i, \epsilon_i)$  ways to put  $N_i$  particles in the  $g_i$  quantum states of energy level  $\epsilon_i$ . Here the probabilities are different for successive particles, so the coefficient  $W^{FD}$  is different from the polynomial coefficient, or thermodynamic probability. Instead, we must discover the number of ways to put  $N_i$  indistinguishable particles into the  $g_i$ -fold degenerate quantum states of energy  $\epsilon_i$  when a given quantum state can contain at most one particle.

These conditions can be satisfied only if  $g_i \geq N_i$ . If we put  $N_i$  of the particles into quantum states of energy  $\epsilon_i$ , there are  $g_i$  ways to place the first particle, but only  $g_i - 1$  ways to place the second, and  $g_i - 2$  ways to place the third, and  $g_i - (N_i - 1)$  ways to place the last one of the  $N_i$  particles.

This means that there are  $g_i! / (g_i - N_i)!$  ways to put  $N_i$  particles.

## Statistical Thermodynamics: Part-2

Because the particles cannot be distinguished from one another, we must exclude assignments which differ only by the way that the  $N_i$  particles are permuted. To do so, we must divide by  $N_i!$ . The number of ways to put  $N_i$  indistinguishable particles into  $g_i$  quantum states with no more than one particle in a quantum state is  $g_i! / (g_i - N_i)! N_i!$

$$W^{FD}(N_i, g_i) = [g_1! / (g_1 - N_1)! N_1!] \times [g_2! / (g_2 - N_2)! N_2!] \times \cdots \times [g_i! / (g_i - N_i)! N_i!] \times \cdots = \prod [g_i! / (g_i - N_i)! N_i!]$$

Now the total probability sum for a Fermi-Dirac system becomes

$$1 = \sum_{\{N_j\}} \prod_{i=1}^{\infty} \left[ g_i! / (g_i - N_i)! N_i! \right] [\rho^{FD}(\epsilon_i)]^{N_i}$$

*Note: Students are requested to also see the following freely available course online*  
[https://chem.libretexts.org/Bookshelves/Physical\\_and\\_Theoretical\\_Chemistry\\_Textbook\\_Maps/Book%3A\\_Thermodynamics\\_and\\_Chemical\\_Equilibrium\\_\(Ellgen\)/25%3A\\_Bose-Einstein\\_and\\_Fermi-Dirac\\_Statistics/25.01%3A\\_Quantum\\_Statistics](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Book%3A_Thermodynamics_and_Chemical_Equilibrium_(Ellgen)/25%3A_Bose-Einstein_and_Fermi-Dirac_Statistics/25.01%3A_Quantum_Statistics)



# Statistical Thermodynamics: Part-2

## ❖ Quantum statistics

### ❖ (1) Bose-Einstein statistics:

Particles that follow Bose-Einstein or (BE) statistics, we let the probability of a microstate of energy  $E$  in an  $N$ -particle system be  $\rho^{\text{BE}}_{\text{MS},N,E}$ . For an isolated system of BE particles, the total probability sum is given by the following equation:

$$1 = \sum W^{\text{BE}}(N_i, g_i) \rho^{\text{BE}}_{\text{MS},N,E}$$

We need to find  $W^{\text{BE}}(N_i, g_i)$ , that is the number of ways to assign indistinguishable particles to the quantum states, if any number of particles can occupy the same quantum state.

First considering the number of ways that  $N_i$  particles can be assigned to the  $g_i$  quantum states associated with the energy level  $\epsilon_i$ . Here the fewest number of quantum states that can be used is one. Also, we can not use more than  $N_i$  quantum states while giving each particle a quantum state.

## Statistical Thermodynamics: Part-2

**gi boxes around Ni points:** Consider having a linear frame on which there is a row of locations. Each location can hold one particle. The frame is closed at both ends. Between each successive pair of particle-holding locations, there is a slot, into which a wall can be inserted. This frame is shown below.

When we try inserting  $(g_i - 1)$  walls into these slots, the frame contains  $g_i$  boxes. We need to insert walls in such a way that Ni particles are distributed in  $g_i$  boxes and we can also have any number of particles in any desired boxes.

We do this by making frame to have  $(N_i + g_i - 1)$  particles placement locations. One such case is when all Ni particles are in one box (see Figure below). Here we require  $N_i$  occupied and  $(g_i - 1)$  unoccupied locations.

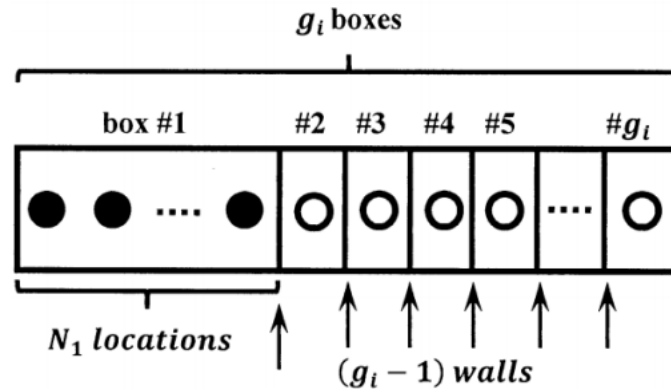


Figure: Maximum possible size frame  
For Ni BE particles in  $g_i$  locations

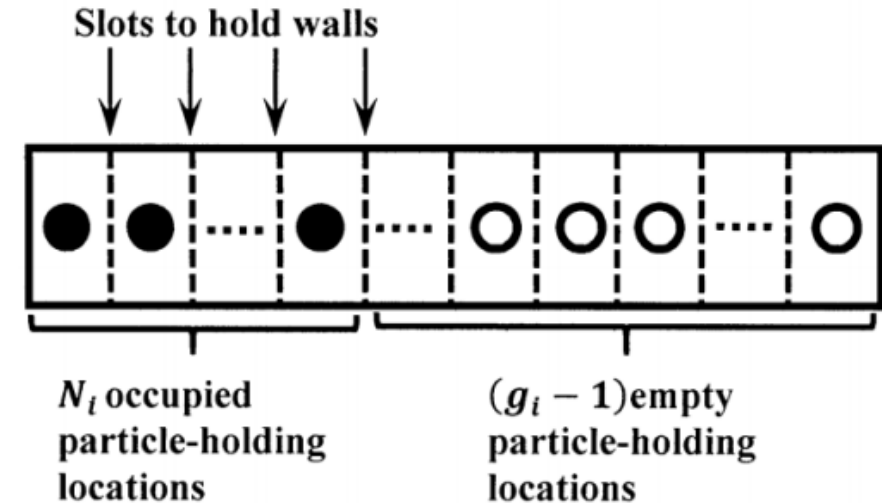


Figure: Assigning BE particles to degenerate energy levels

## Statistical Thermodynamics: Part-2

**Number of ways that we can place  $(g_i-1)$  walls into the  $(N_i+g_i-1)$  slots:** Here the first wall can go into any available  $(N_i+g_i-1)$  slots and second can go to any available  $(N_i+g_i-2)$  slots. Last wall will go to  $(N_i+g_i-1)-(g_i-2) = (N_i+1)$  slots. Thus the total number of ways of inserting the  $(g_i-1)$  walls is as follows;

$$(N_i+g_i-1)(N_i+g_i-2)\dots(N_i+1) = (N_i+g_i-1)(N_i+g_i-2)\dots(N_i+1)(N_i)\dots(2)(1) / N_i! = (N_i+g_i-1)! / N_i!$$

Total includes all permutations of the walls and it does not matter if 1<sup>st</sup>, 2<sup>nd</sup>, or the final wall occupies a slot. Based on this the expression is over counted by  $(g_i-1)!$  walls so finally the  $N_i$  particles can be assigned to the  $g_i$  quantum states in  $(N_i+g_i-1)! / N_i! (g_i-1)!$  ways.

$$W^{BE}(N_i, g_i) = [(N_1+g_1-1)! / (g_1-1)! N_1!] \times [(N_2+g_2-1)! / (g_2-1)! N_2!] \times \dots \times [(N_i+g_i-1)! / (g_i-1)! N_i!] \times \dots \\ = \prod [(N_i+g_i-1)! / (g_i-1)! N_i!]$$

And the total probability sum for a Bose-Einstein (BE) system is

$$1 = \sum_{\{N_j\}} \prod_{i=1}^{\infty} \left[ (N_i+g_i-1)! / (g_i-1)! N_i! \right] [\rho^{BE}(\epsilon_i)]^{N_i}$$

## References

- 1) Atkins' physical chemistry
- 2) Statistical thermodynamics by C. L. Tien and J. H. Lienhard
- 3) <https://chem.libretexts.org/> [*especially for quantum statistics FD and BE statistics*]