PHYS4006: Thermal and Statistical Physics

Lecture Notes
Part – 2 (Unit-III & IV)

Classical and Quantum Statistics: MB, BE & FD Statistics

Dr. Neelabh Srivastava
(Assistant Professor)
Department of Physics
Mahatma Gandhi Central University
Motihari-845401, Bihar
E-mail: neelabh@mgcub.ac.in

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Need for Quantum Statistics

Classical statistics due to Maxwell-Boltzmann explained the energy and velocity distribution of the molecules of an ideal gas but it failed to explain the observed energy distribution of electrons in the so called '*electron gas*' and that of photons in the '*photon gas*'.

Moreover, M-B distribution function suffers from the following two major objections –

i. First the particles are assumed to be distinguishable though electrons or other elementary particles are indistinguishable.
ii. Any number of particles was allowed to occupy the same quantum state while many particles particularly electrons, obey Pauli's exclusion principle which does not allow a quantum state to accept more than one particle.

In classical statistics, $$\frac{n_i}{g_i} << 1$$

So, the probability of a cell containing two or more particles is negligible and the particles thus can be treated as distinguishable.

But, all natural systems obey uncertainty principle and minimum size of a cell in phase space in such a case is h^3 so that number of cells g_i is limited by the value of h^3.

When occupation index $\frac{n_i}{g_i} \approx 1$, the particles cannot be treated as distinguishable and thus classical statistics cannot therefore be applied.

These difficulties were resolved by the use of Quantum statistics and can be divided as:

i. **Bose-Einstein (BE) statistics**
ii. **Fermi-Dirac (FD) statistics**

Fermi-Dirac (FD) Statistics

The basic assumptions of FD statistics are:

- It is applicable for *identical* and *indistinguishable* particles.
- Total energy and total number of the particles of the entire system is constant.
- Spin of the particles should be half integral spin i.e. $\frac{1}{2}\hbar, \frac{3}{2}\hbar, \ldots\ldots\ldots$
- Particles must obey Pauli's exclusion principle, the number of particles in each sublevel will be one or more i.e. $g_i \geq n_i$.
- Functions associated with the particles should be anti-symmetric.
- All particles which obey F.D. statistics are known as *Fermions (electron, proton, neutron, ^{3}He, neutrino, muons, all hyperons (Λ, Σ, Ξ, Ω)* etc*)*.

Fermi-Dirac distribution law

Consider a system of Fermions having total number of particles N. We assume that these particles can be divided into different quantum groups or levels having energies ε_1, ε_2…….. ε_k and the number of particles in these levels are n_1, n_2, ………. n_k, respectively and let g_i represent the degeneracy of the energy level ε_i.

Since the particles are indistinguishable and only one fermion can accommodate in one cell.

So, the number of meaningful ways in which n_i particles are arranged in g_i quantum states is given by - ${}^{g_i}C_{n_i}$

$$\frac{(g_i)(g_i - 1)\ldots(g_i - n_i + 1)}{n_i!} \quad \text{or} \quad \frac{g_i!}{n_i!(g_i - n_i)!}$$

Thus, the total thermodynamic probability for an assembly of fermions (or particular macrostate) is

$$W(n_1, n_2 \cdots n_k) = \prod_{i=1}^{k} \frac{g_i!}{n_i!(g_i - n_i)!}$$

Most probable state:

taking natural logarithms

$$\ln(W) = \sum_{i=1}^{k} \ln(g_i!) - \sum_{i=1}^{k} \ln(n_i!) - \sum_{i=1}^{k} \ln((g_i - n_i)!)$$

Using Stirling's approximation in above equation, we get

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

Differentiating on both sides, we get

$$d(\ln(W)) = -\sum_{i=1}^{k} dn_i \ln(n_i) + \sum_{i=1}^{k} (dn_i)\ln(g_i - n_i)$$

For the most probable state, $d(\ln(W)) = 0$

$$d(\ln(W)) = \sum_{i=1}^{k} \ln\left(\frac{g_i - n_i}{n_i}\right)(dn_i)$$

In addition, the system must satisfy two auxiliary conditions:

i. Conservation of total number of particles: $dn = \sum_{i=1}^{k} dn_i = 0$

ii. Conservation of total energy of the system: $dU = \sum_{i=1}^{k} \varepsilon_i dn_i = 0$

Applying Lagrange's method of undetermined multipliers

$$\sum_{i=1}^{k} \ln\left(\frac{g_i - n_i}{n_i}\right)(dn_i) - \alpha\sum_{i=1}^{k}(dn_i) - \beta\sum_{i=1}^{k}\varepsilon_i(dn_i) = 0$$

$$\sum_{i=1}^{k}\left[\ln\left(\frac{g_i - n_i}{n_i}\right) - \alpha - \beta\varepsilon_i\right](dn_i) = 0$$

Proceeding as before

$$\ln\left(\frac{g_i - n_i}{n_i}\right) - \alpha - \beta\varepsilon_i = 0 \quad \Rightarrow \ln\left(\frac{g_i - n_i}{n_i}\right) = \alpha + \beta\varepsilon_i$$

$$\frac{g_i}{n_i} - 1 = e^{\alpha+\beta\varepsilon_i} \quad \Rightarrow \quad \boxed{f(\varepsilon_i) = \frac{n_i}{g_i} = \frac{1}{e^{\alpha+\beta\varepsilon_i} + 1}}$$

FD distribution function

Now, as we know that $\beta = \dfrac{1}{kT}$

The other multiplier, α is related to the chemical potential μ

$$\alpha = \frac{-\mu}{kT} = \frac{-E_F}{kT}$$

where E_F is Fermi energy

Bose-Einstein (BE) Statistics

The basic assumptions of BE statistics are:

- It is applicable for *identical* and *indistinguishable* particles.
- Any number of particles can occupy a single cell in the phase space.
- The size of cell can not be less than h^3 where h is Planck's constant.
- The number of phase space cells is comparable with the number of particles i.e., occupation index, $n_i/g_i=1$.

- It is applicable to particles with integral spin angular momentum in units of h/2π. All particles which obey B.E. statistics are known as *Bosons (*photon, phonon, all mesons etc*)*.

- The wave function of the system is symmetric under the positional exchange of any two particles.

- Total energy and total number of particles of the entire system is constant.

Bose-Einstein distribution law

Let us consider a system of bosons having total number of particles N. Suppose these identical, indistinguishable and non-interacting particles are to be distributed among g_i different quantum states each having energy ε_i.

So, the number of meaningful arrangements for which n_i indistinguishable particles are to be distributed among g_i cells without any restriction on the number of particles is given by -

$$\text{Number of ways} = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

So, the thermodynamic probability for a macrostate is then:

$$W(n_1, n_2, \ldots n_k) = \prod_{i=1}^{k} \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

Taking natural logarithm:

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

Using Stirling's approximations, we get

$$\ln(W)=\sum_{i=1}^{k}(n_i+g_i-1)\ln(n_i+g_i-1)-\sum_{i=1}^{k}(n_i+g_i-1)-\sum_{i=1}^{k}n_i\ln(n_i)$$

$$+\sum_{i=1}^{k}n_i-\sum_{i=1}^{k}(g_i-1)\ln(g_i-1)+\sum_{i=1}^{k}(g_i-1)$$

On further solving, we get $d(\ln(W))=-\sum_{i=1}^{k}\ln\left(\frac{n_i}{n_i+g_i}\right)dn_i$

Using Lagrange's method of undetermined multipliers wherein we multiply with two constraints α and β, respectively, one get

$$\sum_{i=1}^{k}\ln\left(\frac{n_i}{n_i+g_i}\right)dn_i+\alpha\sum_{i=1}^{k}dn_i+\beta\sum_{i=1}^{k}\varepsilon_i\,dn_i=0$$

Proceeding as before:

$$\ln\left(\frac{n_i}{n_i + g_i}\right) + \alpha + \beta\varepsilon_i = 0 \quad \sin ce\, dn_i \neq 0$$

Since, n_i and g_i are very large therefore, $n_i+g_i-1 = n_i+g_i$

$$\ln\left(\frac{n_i}{n_i + g_i}\right) = \exp\left[-\left(\alpha + \beta\varepsilon_i\right)\right]$$

$$\frac{g_i + n_i}{n_i} = \exp\left(\alpha + \beta\varepsilon_i\right)$$

$$\frac{g_i}{n_i} = e^{\alpha+\beta\varepsilon_i} - 1 \quad \Rightarrow \quad \frac{n_i}{g_i} = \frac{1}{e^{\alpha+\beta\varepsilon_i} - 1}$$

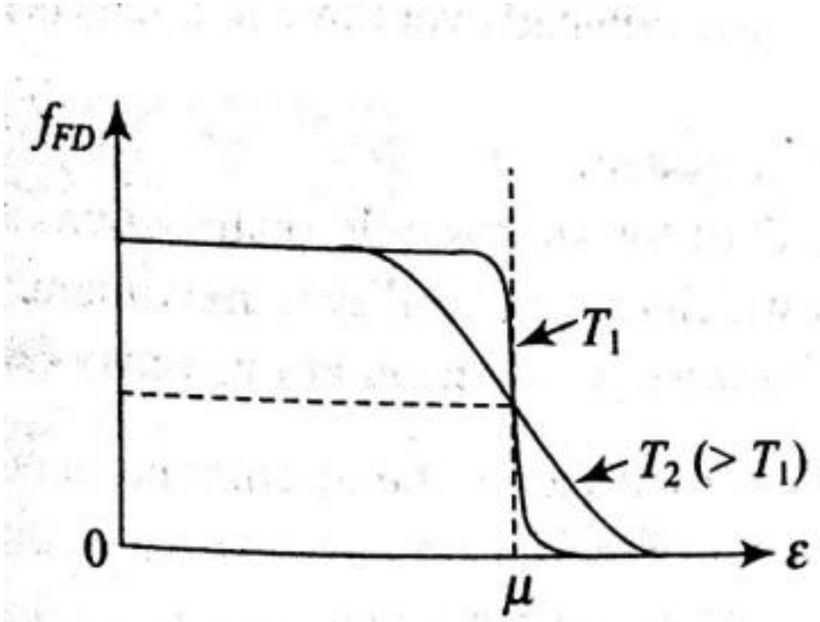
Hence, expression for the most probable distribution of particles among various energy levels of a system obeying B-E statistics is given by -

$$\boxed{n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i} - 1}} \quad (Bose-Einstein\ \ distribution\ \ law)$$

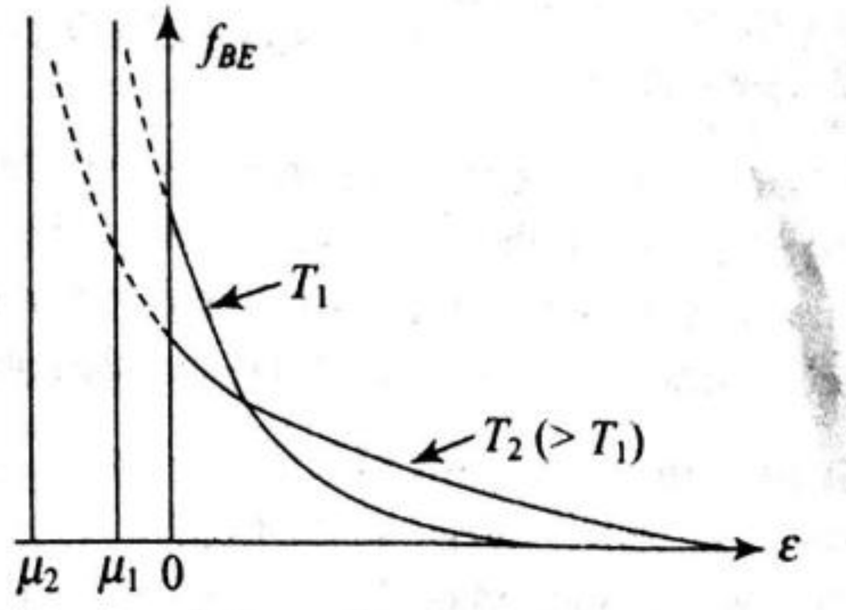
In general, combining all the three statistics, we can write the expression as

$$f(\varepsilon) = \frac{n_i}{g_i} = \frac{1}{e^{(\varepsilon_i - \mu)/kT} + \kappa}$$

where, constant κ takes values 0, -1 and 1 for M-B (classical), B-E and F-D statistics.



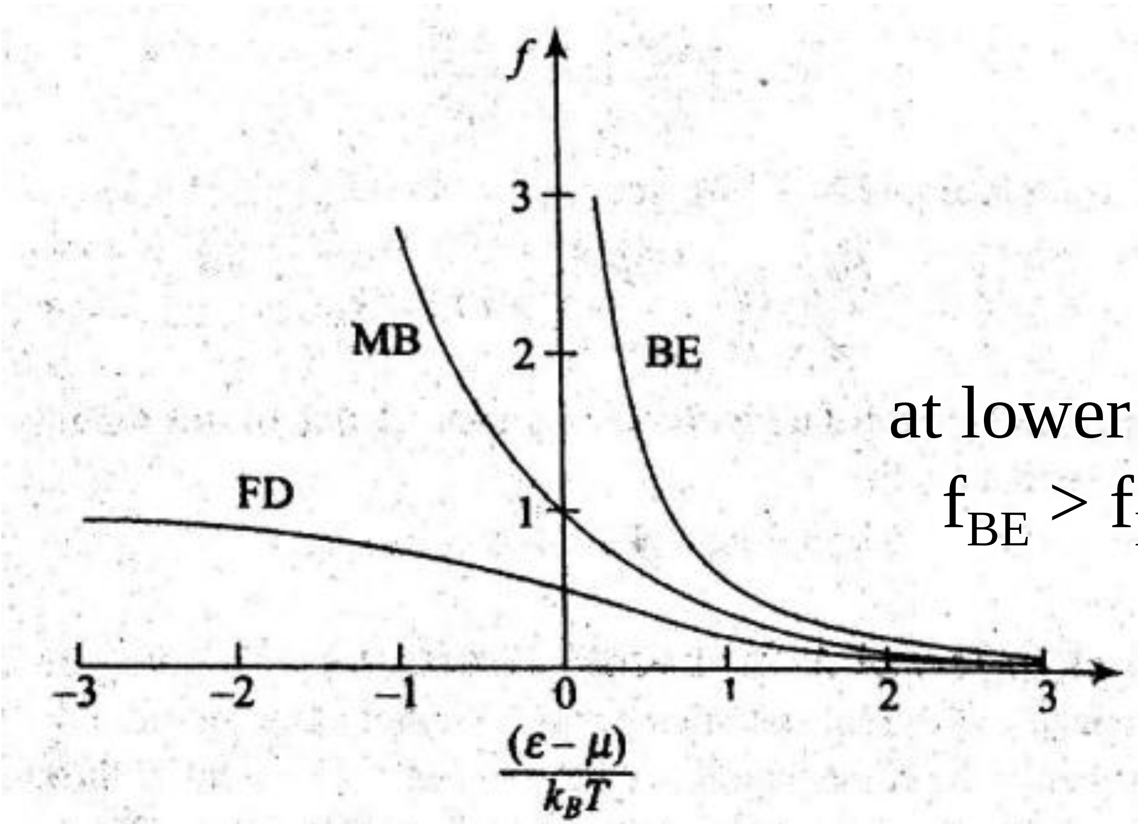
Plot of f_{FD} versus ε for fermions at two temperatures T_1 and T_2 (> T_1)



Plots of f_{BE} versus ε for bosons at two different temperatures T_1 and T_2 (> T_1)

For $\varepsilon_i=\mu$, $f_{FD}=1/2$ whereas $f_{BE}\rightarrow\infty$.

At low temperatures, when the f(ε) is *nearly a step function*, the distribution function is said to be *strongly degenerate*. At very high temperatures, when the *step like character is lost*, it is said to be *nearly non-degenerate*.



at lower energies,
$f_{BE} > f_{MB} > f_{FD}$

1. Distribution of Bosons is skewed towards lower energy states, whereas fermions are skewed towards higher energy states, i.e. higher probability of finding bosons in low level energy states and fermions in higher energy states.
2. At sufficiently high energies, classical and quantum results are identical.

- Thus, it is obvious that the quantum statistics (B-E and F-D) will tend to classical one (M-B) only when $e^{(\varepsilon_i-\mu)/kT} >> 1$

then $$\frac{n_i}{g_i} << 1$$

- Under high temperature and low particle density, quantum statistics tend to classical statistics.

Degeneracy

A system is said to be –

- Strongly degenerate when $\frac{n_i}{g_i} >> 1$
- Weakly degenerate when $\frac{n_i}{g_i} > 1$
- Non-degenerate when $\frac{n_i}{g_i} << 1$

References: Further Readings

1. *Statistical Mechanics* by R.K. Pathria
2. *Statistical Mechanics* by K. Huang
3. *Statistical Mechanics* by B.K. Agrawal and M. Eisner
4. *Thermal Physics (Kinetic theory, Thermodynamics and Statistical Mechanics)* by S.C. Garg, R.M. Bansal and C.K. Ghosh
5. *Heat, Thermodynamics and Statistical Physics* by C.L. Arora

Assignment

1) Calculate the number of different arrangements of 10 indistinguishable particles in 15 cells of equal a priori probability considering that one cell contains only one particle.

2) A system has 7 particles arranged in two compartments. The first compartment has 8 cells and the second has 10 cells (all cells are of equal size). Calculate the number of microstates in the macrostate (3, 4) when particles obey F-D statistics.

3) The molar mass of lithium is 0.00694 and its density is 0.53×10^3 kg/m^3. Calculate the Fermi energy and Fermi temperature of the electrons.

4) In a system of two particles, each particle can be in any one of three possible quantum states. Find the ratio of the probability that the two particles occupy the same state to the probability that the two particles occupy different states for MB, BE and FD statistics.

5) Three spin-1/2 fermions are to be distributed in two levels having energies E_1 & E_2, respectively. Each level can accommodate a maximum of two fermions with opposite spins, +1/2 and -1/2. Determine the number of microstates and macrostates.

6) Show that if f is the FD distribution function $-\left(\frac{\partial f}{\partial E}\right)$ is a maximum at the Fermi level. Also, show that $-\left(\frac{\partial f}{\partial E}\right)$ is symmetric about the Fermi level.

Thank You

For any questions/doubts/suggestions and submission of assignment
write at E-mail: neelabh@mgcub.ac.in