

# 1. Outline of Statistical Mechanics

- The objective of statistical mechanics is to treat the behavior of a very large assembly of identical particles or systems in a statistical or probabilistic fashion, deriving the most probable values of the properties of the ensemble without inquiring in detail what are the values of these properties for any particular particle at any given time.
- We will limit ourselves to assembly of identical systems that are independent of each other and can only interact via instantaneous processes that conserve energy and momentum (Free particle ideal monoatomic gas).
- Phase space: The behavior of any system and its members is described using a six-dimensional phase space whose coordinates are  $(x, y, z, p_x, p_y, p_z)$ .
- The basic postulate of statistical mechanics is that the A PRIORI probability for a system to be in any given quantum state is the same for all quantum states of the system. This is only true when there are no dynamical restrictions. The a priori probabilities in any given ensemble of systems will be modified by external constraints, such as the requirements that the total number and the total energy of all the systems belonging to the ensemble remain constant.
- We will consider different types of systems (particles that are treated as billiard balls):
  - (a) distinguishable particles that are allowed to occupy arbitrary quantum state
  - (b) indistinguishable particles that obey Pauli exclusion principle
  - (c) The role of the indistinguishability of the elementary particles.

Therefore, we will find out that the form of the distribution function depends upon:

- whether the total number of particles is constant or not
- whether particles are indistinguishable
- whether particles are quantum-line or not.

## 1.1 The Distribution function and the DOS

- To compute average properties of an ensemble of particles, it is necessary to know how those particles are, on the average, distributed in energy.

$f(E)$  → average number of particles that occupy a single quantum state  $E$

$g(E)dE$  → number of quantum states of the system whose energy is in a range  $dE$  about  $E$

The number of particles with energy between  $E$  and  $(E+dE)$  is, then, given by:

$$N(E)dE = f(E)g(E)dE$$

distribution function  
(depends upon the probabilities associated with the distribution of particles of the system among the available quantum states)

density of states function  
(depends only upon how the quantum states are situated in energy).

- If both of these quantities are known, then the average value of any quantity  $d$  is given by:

$$\langle d \rangle = \frac{\int d(E)N(E)dE}{\int N(E)dE} = \frac{1}{N} \int d(E)f(E)g(E)dE$$

In general,  $d$  can be a function of the system coordinates  $q_i$  ( $x, y, z$  for  $i=1,2,3$ ) and  $p_i$  ( $=p_x, p_y, p_z$ ). For example, the Hamiltonian of the system is given by:

$$H = \frac{1}{2m} \sum_i [p_i^2 + 2mV(q_i)] = \sum_i \left[ \frac{p_i^2}{2m} + V(q_i) \right]$$

- To calculate the DOS function  $g(E)$ , we will solve the Schrödinger equation for free particles confined in a container with dimensions  $x_0, y_0, z_0$ . The TISE is then of the form:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + \frac{\hbar^2 k^2}{2m} \psi(x, y, z) = 0 \Rightarrow \nabla^2 \psi + k^2 \psi(x, y, z) = 0$$

for which valid solutions are plane waves of the form:

$$\psi(x, y, z) = A e^{i\vec{k} \cdot \vec{r}} = A e^{i(xk_x + yk_y + zk_z)}$$

- If we demand that the wave function on any one face of the container is equal to the wave function on the opposite face, we have:

$$\begin{aligned} \psi(0, y, z) &= \psi(x_0, y, z) \\ \psi(x, 0, z) &= \psi(x, y_0, z) \\ \psi(x, y, 0) &= \psi(x, y, z_0) \end{aligned} \quad \Rightarrow \quad \begin{aligned} k_x &= \frac{2\bar{u}n_x}{x_0} \\ k_y &= \frac{2\bar{u}n_y}{y_0} \\ k_z &= \frac{2\bar{u}n_z}{z_0} \end{aligned}$$

The above restriction leads to quantization of energy, i.e. only discrete values of energies, given by:

$$\begin{aligned} E(n_x, n_y, n_z) &= \frac{\hbar^2}{2m} 4\bar{u}^2 \left( \frac{n_x^2}{x_0^2} + \frac{n_y^2}{y_0^2} + \frac{n_z^2}{z_0^2} \right) \\ &= \frac{2\bar{u}^2 \hbar^2}{m} \left( \frac{n_x^2}{x_0^2} + \frac{n_y^2}{y_0^2} + \frac{n_z^2}{z_0^2} \right) \end{aligned}$$

are allowed. Now, if one plots the allowed values of the momentum that correspond to all possible integer values for  $(n_x, n_y, n_z)$  as points in an orthogonal momentum space, one would obtain simple orthogonal lattice with unit cell dimensions, or volume,

$$V_u = \frac{(2\bar{u})^3}{x_0 y_0 z_0} = \frac{(2\bar{u})^3}{V} \quad \leftarrow \text{physical volume of the container}$$

For particles of spin  $1/2$  like electrons, there will be two allowed momentum states per lattice point in momentum space, which leads to:

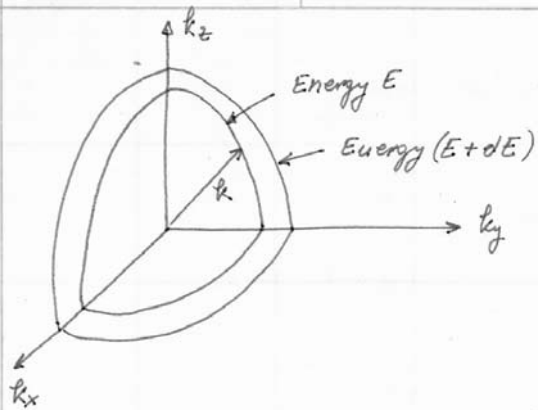
$$V_u' = \frac{1}{2} \frac{(2\bar{u})^3}{V}$$

- We now consider a surface in the momentum space, all points of which are at a constant energy  $E$ :

$$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 k^2}{2m}$$

If we draw additional sphere of energy  $(E+dE)$ , the spherical shell between these two spheres is:

$$dV = 4\bar{u} k^2 dk$$



The number of quantum states to be found in this volume of momentum space is then given by

$$g(E)dE = \frac{4\bar{u}k^2 dk}{(2\bar{u})^3} V = \frac{V}{2\bar{u}^2} k^2 dk$$

For free particle:  $E = \frac{\hbar^2 k^2}{2m}$  which gives  $dE = \frac{\hbar^2}{m} k dk$

Therefore:

$$g(E)dE = \frac{V}{2\bar{u}^2} \frac{m}{\hbar^2} \sqrt{\frac{2mE}{\hbar^2}} dE = \overset{\downarrow \text{spin}}{2 \times} \frac{V}{4\bar{u}^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E} dE$$

The DOS function, corrected for spin is, thus, of the form:

$$g(E) = \frac{V}{2\bar{u}^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E}$$

Note: Since only the volume of the container appears in the final result, it is intuitively clear that the same density of states would be obtained for a container of different shape.

## 1.2 MAXWELL-BOLTZMANN DISTRIBUTION

- The Maxwell-Boltzmann distribution function makes three assumptions:

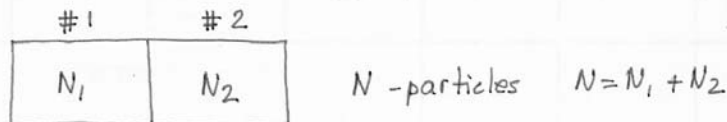
- (1) The particles are identifiable, distinguishable
- (2) The number of particles is constant  $\rightarrow N$
- (3) The total energy is constant  $\rightarrow U$

	$E_1$	$E_2$	...	$E_n$	(Energy levels)
# particles:	$N_1$	$N_2$	...	$N_n$	$\sum_i N_i = N$
energy :	$N_1 E_1$	$N_2 E_2$	...	$N_n E_n$	$\sum_i N_i E_i = U$

- The distribution which has the maximum probability of occurrence is that distribution of particles among levels which can be realized in a maximum number of statistically independent ways.

$\rightarrow$  This is the same problem as putting numbered objects into a set of numbered containers.

$\rightarrow$  Start with two containers (boxes)



Let denote by  $Q(N_1, N_2)$  the number of statistically independent ways of putting  $N_1 + N_2$  objects into these two containers:

$$Q(0, N) = 1$$

$$Q(1, N_2) = N, \quad N_2 = N - 1$$

$$Q(2, N_2) = N(N-1) \frac{1}{2!}, \quad N_2 = N - 2$$

$$Q(3, N_2) = \frac{1}{3!} N(N-1)(N-2)$$

$$\boxed{\textcircled{2} \textcircled{1} \mid N_2} = \boxed{\textcircled{1} \textcircled{2} \mid N_2}$$

Therefore:

$$Q(N_1, N_2) = \frac{1}{N_1!} N(N-1) \dots (N-N_1+1) = \frac{N(N-1) \dots (N_2+1)}{N_1!}$$

$$Q(N_1, N_2) = \frac{N!}{N_1! N_2!}$$

- Suppose now that the second container is divided into two compartments containing  $\nu_1$  and  $\nu_2$  objects, where

$$\nu_1 + \nu_2 = N_2 = N - N_1$$

The number of independent ways of realizing the distribution  $(\nu_1, \nu_2)$  among the sub-compartments of the second box is:

$$Q(\nu_1, \nu_2) = \frac{N_2!}{\nu_1! \nu_2!}$$

We may also think of this as having three distinct containers and the total # of ways of arranging the objects is:

$$Q(N_1, \nu_1, \nu_2) = Q(N_1, N_2) Q(\nu_1, \nu_2) = \frac{N!}{N_1! N_2!} \frac{N_2!}{\nu_1! \nu_2!} = \frac{N!}{N_1! \nu_1! \nu_2!}$$

- We can generalize the above result for  $n$ -containers to obtain the distribution:

$$Q(N_1, N_2, \dots, N_n) = \frac{N!}{\prod_{i=1}^n N_i!}$$

The actual probability associated with this distribution is obtained by dividing by a factor  $n^N$  (total number of ways of arranging  $N$  objects among  $n$  boxes).

- Now, if each of the ~~box~~ containers representing an energy state is actually a group of containers (this would correspond to degenerate levels in the system with degeneracy  $g_i$ ), there will be  $g_i^{N_i}$  ways of arranging the particles among the states or containers pertaining to that level. Therefore:

$$Q(N_1, N_2, \dots, N_n) = \frac{N!}{\prod_{i=1}^n N_i!} \prod_{i=1}^n g_i^{N_i}$$

- We now assume that the actual distribution  $(N_1, N_2, \dots, N_n)$  of particles is that which can be realized in a maximum number of statistically independent ways, and is subject to a restrictions:

$$N = \sum_{i=1}^n N_i = \text{const}$$

$$U = \sum_{i=1}^n N_i E_i = \text{const}$$

- Review of the method of Lagrangean multipliers:

If one wants to find maximum of  $f$  under the restriction that some other functions  $\phi(x_1, x_2, \dots, x_n)$  and  $\psi(x_1, x_2, \dots, x_n)$  remain constant, then

$$df + \alpha d\phi + \beta d\psi = 0$$

independent of the choice of the constants  $\alpha$  and  $\beta$ .  
In other words:

$$\left( \frac{\partial f}{\partial x_1} + \alpha \frac{\partial \phi}{\partial x_1} + \beta \frac{\partial \psi}{\partial x_1} \right) dx_1 + \left( \frac{\partial f}{\partial x_2} + \alpha \frac{\partial \phi}{\partial x_2} + \beta \frac{\partial \psi}{\partial x_2} \right) dx_2 + \dots = 0$$

i.e.  $\left. \begin{aligned} \frac{\partial f}{\partial x_i} + \alpha \frac{\partial \phi}{\partial x_i} + \beta \frac{\partial \psi}{\partial x_i} &= 0 && n \text{ - equations:} \\ \phi(x_1, x_2, \dots, x_n) &= \phi_0 = \text{const} \\ \psi(x_1, x_2, \dots, x_n) &= \psi_0 = \text{const} \end{aligned} \right\} \begin{array}{l} (n+2) \\ \text{equations for} \\ (n+2) \text{ unknowns.} \end{array}$

- We now apply this method to  $\ln Q(N_1, N_2, \dots, N_n)$  to get:

$$\ln Q = \ln N! + \sum_{i=1}^n N_i \ln g_i - \sum_{i=1}^n \ln N_i!$$

using Stirling's approximation that  $\ln x! \approx x \ln x - x$  we have:

$$\ln Q = \ln N! + \sum_{i=1}^n N_i \ln g_i - \sum_{i=1}^n (N_i \ln N_i - N_i)$$

Then:

$$\begin{aligned} \frac{\partial \ln Q}{\partial N_j} &= \frac{\partial}{\partial N_j} \sum_{i=1}^n N_i \ln g_i - \frac{\partial}{\partial N_j} \sum_{i=1}^n (N_i \ln N_i - N_i) \\ &= \ln g_j - [\ln N_j + 1 - 1] = \ln g_j - \ln N_j \end{aligned}$$

Making use of the method of Lagrangean multipliers gives:

$$\frac{\partial \ln Q}{\partial N_j} + \alpha \frac{\partial}{\partial N_j} \sum_{i=1}^n N_i + \beta \frac{\partial}{\partial N_j} \sum_{i=1}^n E_i N_i = 0$$

or:

$$\ln g_j - \ln N_j + \alpha + \beta E_j = 0$$

$$\ln \left( \frac{N_j}{g_j} \right) = \alpha + \beta E_j \Rightarrow N_j = g_j e^{\alpha + \beta E_j}$$

Therefore:

$$f(E_j) = \frac{N_j}{g_j} = e^{\alpha + \beta E_j} = e^{\alpha} e^{\beta E_j} = e^{\alpha} e^{-E_j/k_B T} \quad (\beta = -\frac{1}{k_B T})$$

average number of particles per quantum state

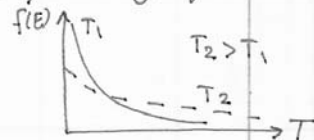
This particular energy distribution function obtained under the classical assumption of identifiable particles and without the use of the Pauli exclusion principle, is called the MAXWELL-BOLTZMANN distribution function.

The value of  $\alpha$  can be expressed in terms of the total number of particles, i.e.

$$N = \sum_{j=1}^n N_j = e^{\alpha} \sum_{j=1}^n g_j e^{-E_j/k_B T} \Rightarrow e^{\alpha} = \frac{N}{\sum_{j=1}^n g_j e^{-E_j/k_B T}}$$

If the energy levels are crowded very closely, then  $g_j$  may be regarded as  $g(E)dE$  and the quantity  $N_j$  as  $N(E)dE$ , which leads to:

$$N(E)dE = g(E) \underbrace{e^{\alpha} e^{-E/k_B T}}_{f(E)} dE$$



Since:  $N = \int N(E)dE = e^{\alpha} \int g(E) e^{-E/k_B T} dE$ , we get:

$$e^{\alpha} = \frac{N}{\int g(E) e^{-E/k_B T} dE}$$



### Example: Maxwell-Boltzmann statistics of ideal gas

- We now discuss the properties of an ideal gas of free particles, for which:

$$g(E) = \frac{V}{2\bar{u}^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E}$$

For this particular case:

$$e^{\omega} = \frac{N}{\int_0^{\infty} g(E) e^{-E/k_B T} dE} = \frac{N}{I}$$

where the integral  $I$  is of the form:

$$\begin{aligned} I &= \int_0^{\infty} g(E) e^{-E/k_B T} dE = \frac{V}{2\bar{u}^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\infty} \sqrt{E} e^{-E/k_B T} dE \\ &= \frac{V}{2\bar{u}^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} (k_B T)^{3/2} \int_0^{\infty} \sqrt{u} e^{-u} du = \frac{V}{2\bar{u}^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} (k_B T)^{3/2} \frac{\sqrt{\pi}}{2} \end{aligned}$$

$$\Gamma(3/2) = \frac{\sqrt{\pi}}{2}$$

$\Gamma$ -function whose general form is:  $\Gamma(n) = \int_0^{\infty} u^{n-1} e^{-u} du$

Therefore:

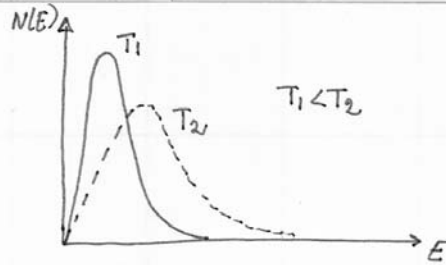
$$I = 2V \left(\frac{m k_B T}{2\pi \hbar^2}\right)^{3/2} \quad \text{or:} \quad e^{\omega} = \frac{N}{2V} \left(\frac{2\pi \hbar^2}{m k_B T}\right)^{3/2}$$

To summarize, the Maxwell-Boltzmann distribution function for an ideal gas is:

$$f(E) = \frac{N}{2V} \left(\frac{2\pi \hbar^2}{m k_B T}\right)^{3/2} e^{-E/k_B T}$$

- The distribution of the particle density with energy is then given by:

$$\begin{aligned} N(E) dE &= g(E) f(E) dE = \frac{V}{2\bar{u}^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{N}{2V} \left(\frac{2\pi \hbar^2}{m k_B T}\right)^{3/2} e^{-E/k_B T} \sqrt{E} dE \\ N(E) dE &= \frac{N}{4\bar{u}^2} \left(\frac{4\bar{u}}{k_B T}\right)^{3/2} \sqrt{E} e^{-E/k_B T} dE = \frac{2\bar{u} N}{(\bar{u} k_B T)^{3/2}} \sqrt{E} e^{-E/k_B T} dE \end{aligned}$$



- The total internal energy can be obtained in a similar manner, i.e.

$$\frac{U}{N} = \frac{\int N(E) E dE}{\int N(E) dE} = \frac{1}{N} \int_0^{\infty} \frac{2\bar{u}N}{(\bar{u}k_B T)^{3/2}} \sqrt{E} \cdot E e^{-E/k_B T} dE$$

$$= \frac{1}{N} \cdot \frac{2\bar{u}N}{(\bar{u}k_B T)^{3/2}} \sqrt{k_B T} (k_B T)^{3/2} \int_0^{\infty} u^{3/2} e^{-u} du$$

average energy per particle  $\Gamma(5/2) = \frac{3}{2} \Gamma(3/2) = \frac{3}{2} \frac{\sqrt{\pi}}{2} = \frac{3\sqrt{\pi}}{4}$

$$\frac{U}{N} = \frac{2\bar{u}}{\sqrt{\pi}} k_B T \cdot \frac{3\sqrt{\pi}}{4} = \frac{3}{2} k_B T$$

Therefore, the average internal energy per particle is:

$$\boxed{\frac{U}{N} = \frac{3}{2} k_B T} \quad \rightarrow \quad \frac{1}{2} k_B T \text{ per one degree of freedom}$$

- Our objective is to derive the equation of state for an ideal Boltzmann gas from the dynamical properties of the particles and from the distribution function. For this purpose, we need to convert the energy distribution into velocity distribution using:

$$E = \frac{mv^2}{2} = \frac{\hbar^2 k^2}{2m} \quad \text{free particles and parabolic dispersion.}$$

In this case:  $dE = mv dv$  and:

$$N(v)dv = \frac{2\bar{u}N}{(\bar{u}k_B T)^{3/2}} \sqrt{\frac{m}{2}} v e^{-mv^2/2k_B T} \cdot mv dv$$

$$= 4\bar{u}N \left(\frac{m}{2\bar{u}k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}} dv$$

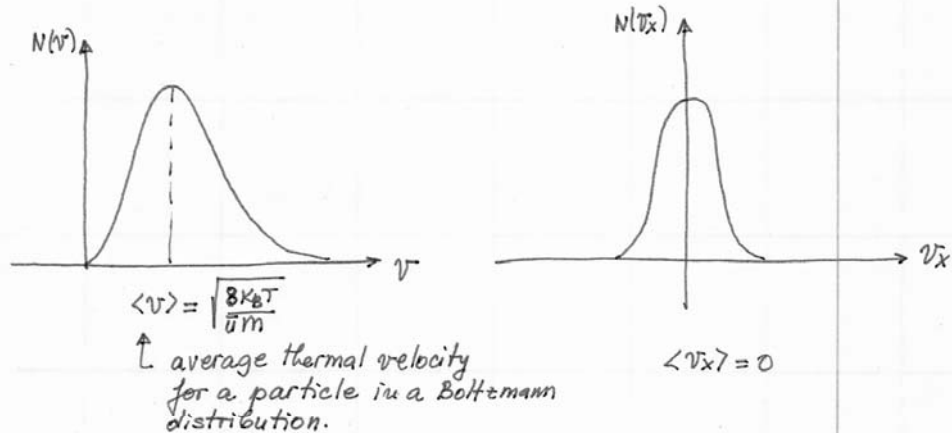
This function expresses the number of particles of the system whose speeds lie in a range  $dv$  about  $v$ , or the number of particles in a shell of thickness  $dv$ .

Since:  $4\bar{v}v^2dv = dv_x dv_y dv_z$ , we also get that:

$$N(v_x, v_y, v_z) dv_x dv_y dv_z = N \left( \frac{m}{2\bar{v}k_B T} \right)^{3/2} e^{-\frac{m}{2k_B T} (v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z$$

i.e.

$$N(v_x) dv_x = N \sqrt{\frac{m}{2\bar{v}k_B T}} e^{-\frac{mv_x^2}{2k_B T}} dv_x$$



Note: The above derived distributions are equilibrium distributions. If we apply external field (perturbation) these distributions will change shape.

### 1.3. FERMI-DIRAC DISTRIBUTION FUNCTION

• The differences between Maxwell-Boltzmann and Fermi-Dirac statistics are:

- (1) Particles are indistinguishable  $\rightarrow Q$  will be different because of this
- (2) Particles obey Pauli exclusion principle  $\rightarrow$  each quantum state can have only one particle in it

M.B.  $Q(N_1, N_2) = \frac{N!}{N_1! N_2!}$

F.D.  $Q(N_1, N_2) = 1 \rightarrow$  there is only one way of putting those particles

- Constraints:

$$\phi = \sum_j N_j = N \rightarrow \text{total \# of particles is constant}$$

$$\psi = \sum_j N_j E_j = U \rightarrow \text{total energy is constant}$$

- Consider now the  $i$ -th energy level with degeneracy  $g_i$ . For this level, the total # of ways of arranging the particles is:

$$g_i (g_i - 1) (g_i - 2) \dots (g_i - N_i + 1) = \frac{g_i!}{(g_i - N_i)!}$$

Since  $N_i$  particles have  $N_i!$  ways of permuting themselves (they are indistinguishable), we have to divide by  $N_i!$  to get:

$$Q(N_1, N_2, \dots, N_n) = \prod_{i=1}^n \frac{g_i!}{N_i! (g_i - N_i)!}$$

- We now use the method of Lagrange multipliers to maximize  $Q$  using that:

$$d \ln Q + \alpha d\phi + \beta d\psi = 0$$

or:

$$\frac{\partial}{\partial N_j} \ln Q + \alpha \frac{\partial}{\partial N_j} \phi + \beta \frac{\partial}{\partial N_j} \psi = 0$$

where:

$$\ln Q = \sum_i \ln g_i! - \sum_i \ln N_i! - \sum_i \ln (g_i - N_i)!$$

Now, using Stirling's formula, we get:

$$\ln Q = \sum_i (g_i \ln g_i - g_i) - \sum_i (N_i \ln N_i - N_i) - \sum_i [(g_i - N_i) \ln (g_i - N_i) - (g_i - N_i)]$$

Therefore:

$$-(\ln N_j + 1 - 1) - [-\ln (g_j - N_j) - 1 + 1] + \alpha + \beta E_j = 0$$

$$-\ln N_j + \ln (g_j - N_j) = -\alpha - \beta E_j$$

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

Solving for  $N_j/g_j$  gives:

$$g_j/N_j = 1 + e^{-\alpha} e^{-\beta E_j} \Rightarrow \frac{N_j}{g_j} = \frac{1}{1 + e^{-\alpha} e^{-\beta E_j}}$$

Again, if we take the value of  $\beta$  to be  $\beta = -1/k_B T$ , we get:

$$\frac{N_j}{g_j} = \frac{1}{1 + e^{\frac{E_j/k_B T - \alpha}{k_B T}}} = \frac{1}{1 + \exp\left(\frac{E_j - E_F}{k_B T}\right)}$$

$E_F \rightarrow$  Fermi energy, or the Fermi level of the system.

- Now, if the levels are assumed to crowd together in a continuum, so that

$$N_j \rightarrow N(E) dE \quad \text{and} \quad g_j = g(E) dE$$

we find:

$$N(E) dE = g(E) f(E) dE = \frac{g(E) dE}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}$$

and:

$$N = \int \frac{g(E) dE}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}$$

The Fermi energy is a function of temperature and also depends upon the DOS function of the system.

(a) 3D System: (free particles)

- The DOS function is given by:  $g(E) = \frac{V}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} \sqrt{E}$

- The electron density then equals to:

$$\begin{aligned} n = \frac{N}{V} &= \int_0^{\infty} g(E) f(E) dE = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} \int_0^{\infty} \frac{\sqrt{E} dE}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)} \\ &= \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} (k_B T)^{3/2} \underbrace{\int_0^{\infty} \frac{\sqrt{u} du}{1 + \exp(u - \eta_F)}}_{\text{Fermi integral of order } 1/2} \quad \text{where } \eta_F = \frac{E_F}{k_B T} \end{aligned}$$

Therefore:

$$n = \frac{N}{V} = \frac{1}{2\pi^2} \left(\frac{2m^* k_B T}{\hbar^2}\right)^{3/2} F_{1/2}(\eta_F)$$

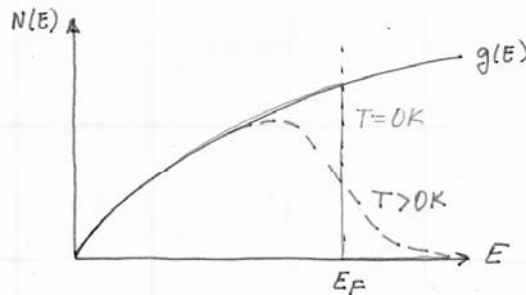
- The internal energy of the system is given by:

$$\begin{aligned}
 U &= \int_0^{\infty} E N(E) dE = \int_0^{\infty} E f(E) g(E) dE \\
 &= \frac{V}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} \int_0^{\infty} E^{3/2} \frac{dE}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)} = \frac{V}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} (k_B T)^{5/2} \int_0^{\infty} \frac{u^{3/2} du}{1 + \exp(u - \eta_F)} \\
 &= \frac{V}{2\pi^2} \frac{(2m^* k_B T)^{3/2}}{\hbar^3} k_B T F_{3/2}(\eta_F)
 \end{aligned}$$

- The average energy per particle is then given by:

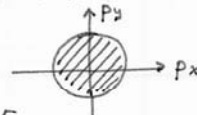
$$\langle E \rangle = \frac{U}{N} = k_B T \frac{F_{3/2}(\eta_F)}{F_{1/2}(\eta_F)}$$

- Plot of  $N(E)$ :



At low temperatures, the Fermi-Dirac distribution may be represented as a sphere in momentum space in which all or most of the quantum states of energy less than  $E_F$  are filled, while all or most of the states of energy greater than  $E_F$  are empty. The equation of the surface of this 'Fermi sphere' must be:

$$p_x^2 + p_y^2 + p_z^2 = 2m^* E_F$$



- For energies that are much greater than  $E_F$ , the Fermi-Dirac distribution might be written as:

$$f(E) \approx e^{-(E - E_F)/k_B T}$$

If all the energies available to the system satisfy the condition  $E - E_F \gg k_B T$ , i.e.  $E_F$  is many  $k_B T$  units smaller than any available energy of the system, the system is called non-degenerate and the FD reduces to MB statistics.

(b) 2D System:

- The DOS function is given by  $g(E) = A \frac{m^*}{\hbar^2}$ , where  $A$  is the area of the 2D container.
- The total electron number is given by:

$$N = \int_0^{\infty} N(E) dE = \int_0^{\infty} g(E) f(E) dE = A \frac{m^*}{\hbar^2} \int_0^{\infty} \frac{dE}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}$$

$$N = A \frac{m^*}{\hbar^2} \int_0^{\infty} \frac{e^{-\frac{E - E_F}{k_B T}}}{1 + e^{-\frac{E - E_F}{k_B T}}} dE = -A \frac{m^*}{\hbar^2} k_B T \ln \left[ 1 + \exp\left(-\frac{E - E_F}{k_B T}\right) \right] \Big|_0^{\infty}$$

$$N = A \frac{m^*}{\hbar^2} k_B T \ln \left( 1 + e^{E_F / k_B T} \right)$$

To summarize:  $\frac{N}{A} = \frac{m^*}{\hbar^2} k_B T \ln \left( 1 + e^{E_F / k_B T} \right)$

↳ sheet electron density

(c) Note on the Fermi energy:

- As  $T$  increases,  $E_F(T) \rightarrow -\infty$ . This means that under high temperature limit, the Fermi-Dirac statistics reduces to Maxwell-Boltzmann.
- At lower temperatures, the above will occur in gases where the mass is large.

For dense gas of very light particles (free electrons in a metal), the Fermi energy is very large and the condition:  $E - E_F \gg k_B T$  is practically never satisfied.

In semiconductors, due to the peculiar form of the DOS function, the MB distribution is virtually always a good approximation to the FD distribution.

### 1.3 The Bose - Einstein Distribution

→ Assumptions:

- particles are indistinguishable
- particles do not obey the Pauli exclusion principle (related to photons, phonons and any other particles that have integer spin). This means that any number of particles can appear in any quantum state.

→ Consider array of  $N_i$  particles and  $(g_i - 1)$  partitions needed to divide particles into  $g_i$  groups.

- The number of ways of permuting  $N_i$  particles among  $g_i$  levels equals the number of independent ways of permuting the objects + partitions, i.e.

$$(N_i + g_i - 1)!$$

- Since permutations of particles among themselves or of partitions among themselves do not count as independent arrangements, one has to divide by:

$$N_i! (g_i - 1)!$$

- Therefore, the number of statistically independent ways of achieving a distribution  $Q(N_1, N_2, \dots, N_n)$  is:

$$Q_{BE}(N_1, N_2, \dots, N_n) = \prod_{i=1}^n \frac{(N_i + g_i - 1)!}{N_i! (g_i - 1)!}$$

We will now find the maximum of  $Q_{BE}(N_1, N_2, \dots, N_n)$  considering the following two cases:

- Restrictions imposed on the total number of particles and total energy on the system
- Restriction imposed only on the total energy of the system:

Case (a):

$$\ln Q_{BE}(N_1, N_2, \dots, N_n) = \sum_{i=1}^n \ln(N_i + g_i - 1)! - \sum_{i=1}^n \ln N_i! - \sum_{i=1}^n \ln(g_i - 1)!$$



$$\sum_{i=1}^n N_i = N$$

$$\sum_{i=1}^n E_i N_i = U$$

Using the method of Lagrange multipliers, we get:

$$\frac{\partial}{\partial N_j} \ln Q_{BE}(N_1, N_2, \dots, N_n) + d \frac{\partial}{\partial N_j} \sum_{i=1}^n N_i + \beta \frac{\partial}{\partial N_j} \sum_{i=1}^n E_i N_i = 0$$

$$\begin{aligned} \frac{\partial}{\partial N_j} \ln Q_{BE}(N_1, N_2, \dots, N_n) &= \frac{\partial}{\partial N_j} \left\{ \sum_{i=1}^n [(N_i + g_i - 1) \ln(N_i + g_i - 1) - (N_i + g_i - 1)] \right. \\ &\quad \left. - \sum_{i=1}^n [N_i \ln N_i - N_i] - \sum_{i=1}^n [(g_i - 1) \ln(g_i - 1) - (g_i - 1)] \right\} = \\ &= \ln(N_j + g_j - 1) + \cancel{1} - \cancel{1} - (\ln N_j + \cancel{1} - \cancel{1}) = \ln \left( \frac{N_j + g_j - 1}{N_j} \right) \end{aligned}$$

To summarize:

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

$$\ln \left( \frac{N_j + g_j}{N_j} - \frac{1}{N_j} \right) = -d - \beta E_j$$

$$\frac{N_j + g_j}{N_j} - \frac{1}{N_j} = e^{-d - \beta E_j} \Rightarrow 1 + \frac{g_j}{N_j} = e^{-d - \beta E_j}$$

$$\frac{g_j}{N_j} = e^{-d - \beta E_j} - 1$$

$$\Rightarrow f(E_j) = \frac{N_j}{g_j} = \frac{1}{e^{-d - \beta E_j} - 1}$$

Therefore, under the constraints that the total number of particles is conserved and the total energy of the system is conserved, the Bose-Einstein distribution reduces to:

$$f(E_j) = \frac{N_j}{g_j} = \frac{1}{e^{-d - \beta E_j} - 1} = \frac{1}{e^{E_j/k_B T - d} - 1}$$

Case (b): Total energy of the system conserved, but not the total number of particles.

The distribution function for this case can simply be obtained by assuming  $\lambda=0$ , i.e.

$$f(E_j) = \frac{1}{\exp\left(\frac{E_j}{k_B T}\right) - 1}$$

Note: In the case of 2D and 3D independent particles Bose-Einstein gases, as the temperature goes to zero, all the particles of the system will tend to condense into the lowest energy state. This phenomena is known as Bose-Einstein condensation.