

We consider N molecules whose energies are limited to the u_1, u_2, \dots, u_k arranged in order of increasing energy. They are either discrete energy state or, average energies with in a sequence of energy intervals. If there are n_i molecules of energy u_i and total energy of assembly is U then most probable distribution of molecule have two condition.

1. Conservation of particles, $\sum n_i = n_1 + n_2 + \dots + n_k = N$
 So $\sum \delta n_i = \delta n_1 + \delta n_2 + \dots + \delta n_k = \delta N \therefore \sum \delta n_i = 0$ — (1)
2. Conservation of energy, $\sum n_i u_i = n_1 u_1 + n_2 u_2 + \dots + n_k u_k = U$
 So $\sum u_i \delta n_i = u_1 \delta n_1 + u_2 \delta n_2 + \dots + u_k \delta n_k = \delta U$
 $\therefore \sum u_i \delta n_i = 0$ — (2)

Now most Probable distribution have the condition

$$-\sum \log_e n_i \delta n_i + \sum \log_e g_i \delta n_i = 0$$

Using the method of Lagrange multiplier, we multiply eq (1) by $-\alpha$ and eq (2) by $-\beta$ and add to this expression, α, β are independent of n_i

$$\sum (-\log_e n_i + \log_e g_i - \alpha - \beta u_i) \delta n_i = 0$$

$$\therefore -\log_e n_i + \log_e g_i - \alpha - \beta u_i = 0 \therefore \log_e \frac{n_i}{g_i} = \alpha - \beta u_i$$

$\therefore n_i = g_i e^{-(\alpha + \beta u_i)}$ This is Maxwell - Boltzmann distribution law.

To evaluate the value of α and β we consider the continuous distribution of molecular energies, rather than u_1, u_2, \dots, u_k so the eq becomes

$$n(u) du = g(u) e^{-\alpha} e^{-\beta u} du$$

In case of molecules of a gas, energy quantisation is inconspicuous because the total no. of molecules are very large.

$n(u) du =$ no. of molecules whose energies lies between u and $u+du$.

\therefore in terms of momentum, $n(p) dp = g(p) e^{-\alpha} e^{-\beta p^2/2m} dp$

The a priori probability $g(p)$ that a molecules have momentum betⁿ p and $p+dp$ is equal to the no. of cells in phase space with in which such a molecule may exist. Such cell of phase space have a volume h^3

$$\therefore g(p) dp = \frac{\iiint dx dy dz dp_x dp_y dp_z}{h^3}$$

The numerator is the phase space volume occupied by particles with the specified momenta

Now $\int \int \int dx dy dz = V$ and $\int \int \int dp_x dp_y dp_z = 4\pi p^2 dp$, it is the volume of a spherical shell of radius p and thickness dp in momentum space

$$\therefore n(p) dp = \frac{4\pi V p^2}{h^3} e^{-\alpha} e^{-\beta p^2/2m} dp$$

$$\text{Now } \int_0^\infty n(p) dp = N \text{ and } \int_0^\infty p^2 e^{-\alpha} e^{-\beta p^2/2m} dp = \frac{1}{4} \sqrt{\frac{\pi}{\beta}}$$

$$\therefore N = 4\pi e^{-\alpha} \frac{V}{h^3} \int_0^\infty p^2 e^{-\beta p^2/2m} dp = e^{-\alpha} \frac{V}{h^3} \left(\frac{2\pi m}{\beta}\right)^{3/2}$$

$$\therefore e^{-\alpha} = \frac{N h^3}{V} \left(\frac{\beta}{2\pi m}\right)^{3/2} \therefore n(p) dp = 4\pi N \left(\frac{\beta}{2\pi m}\right)^{3/2} p^2 e^{-\beta p^2/2m} dp$$

$$\text{Now } u = \frac{p^2}{2m} \therefore p^2 = 2mu \therefore 2p dp = 2m du \therefore dp = \frac{m du}{\sqrt{2mu}}$$

$$\therefore n(u) du = \frac{2N \beta^{3/2}}{\sqrt{\pi}} \sqrt{u} e^{-\beta u} du$$

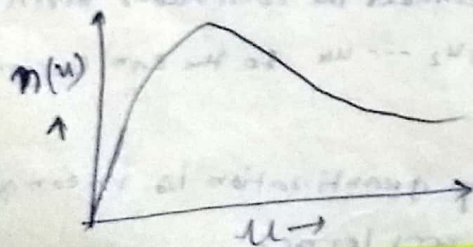
$$\therefore \text{Total energy } U = \int_0^\infty u n(u) du = \frac{2N \beta^{3/2}}{\sqrt{\pi}} \int_0^\infty u^{3/2} e^{-\beta u} du = \frac{3}{2} \frac{N}{\beta} \int_0^\infty x^{3/2} e^{-ax} dx = \frac{3}{4a} \sqrt{\frac{\pi}{a}}$$

From kinetic theory of gases, the total energy U of N molecules of an ideal gas at absolute temp T is $U = \frac{3}{2} NKT$

$$\therefore \beta = \frac{1}{kT} \quad k = \text{Boltzmann constant}$$

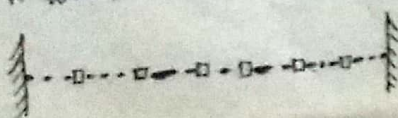
$$\therefore n(u) du = \frac{2N \beta^{3/2}}{(\pi kT)^{3/2}} \sqrt{u} e^{-u/kT} du$$

This equation gives the no. of molecules with energies between u and $u+du$ of an ideal gas containing a total N molecules at absolute temp T



Bose-Einstein Statistics

B.E statistics deals with identical particles which cannot be distinguished but can be counted. Here, all quantum states are assumed to have equal a priori probability, so that g_i represent the no. of states having some energy ϵ_i . Each quantum state corresponds to a cell in phase space and we find the no. of ways in which n_i particles can be distributed in g_i cells.



Here no. of cells $g_i = 7$

No. of partitions = $g_i - 1 = 6$

No. of indistinguishable particles $n_i = 16$

So in this system no. of object = $n_i + g_i - 1$

∴ Possible Permutation among the object = $\frac{(n_i + g_i - 1)!}{n_i! g_i!}$

also Particle Permutation among themselves = $n_i!$
and Partition Permutation among themselves = $g_i!$ do not affect the total distribution or irrelevant.

∴ Possible diffⁿ arrangement of n_i particles with i in g_i cells is

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

∴ Probability of the entire distribution of N particles is the

$$\text{Product } W = \prod \frac{(n_i + g_i - 1)!}{n_i! g_i!}$$

assume $n_i + g_i \gg 1$ ∴ $\frac{(n_i + g_i - 1)!}{n_i! g_i!} \approx \frac{(n_i + g_i)!}{n_i! g_i!}$

$$\begin{aligned} \therefore \log W &= \sum \left[\log_e \frac{(n_i + g_i)!}{n_i! g_i!} - \log_e n_i! - \log_e g_i! \right] \\ &= \sum \left[(n_i + g_i) \log_e (n_i + g_i) - n_i \log_e n_i - g_i \log_e g_i \right] \end{aligned}$$

Now $\delta \log_e W = \frac{1}{W} \delta W$

For most probable distribution $\delta \log_e W_{\max} = 0$

$$\log_e W = \sum \left[n_i \log_e (n_i + g_i) - n_i \log_e n_i - g_i \log_e g_i \right] \delta n_i = 0$$

$$\therefore \delta \log_e W_{\max} = \sum \left[\log_e (n_i + g_i) - \log_e n_i \right] \delta n_i = 0 \quad \text{--- (1)}$$

Now from conservation of particle $\sum \delta n_i = 0$ --- (2)

from conservation of energy $\sum u_i \delta n_i = 0$ --- (3)

We get from Lagrange multiplier ---

$$\sum \left[\log_e (n_i + g_i) - \log_e n_i - \alpha - \beta u_i \right] \delta n_i = 0$$

$$\therefore \log_e (n_i + g_i) - \log_e n_i - \alpha - \beta u_i = 0$$

$$\therefore \log_e \frac{n_i + g_i}{n_i} = \alpha + \beta u_i \quad \therefore 1 + \frac{g_i}{n_i} = e^{\alpha + \beta u_i}$$

$$\therefore \frac{g_i}{n_i} = e^{\alpha + \beta u_i} - 1$$

$$\therefore n_i = \frac{g_i}{e^{\alpha + \beta u_i} - 1} = \frac{g_i}{e^{\alpha} e^{\beta u_i / kT} - 1}$$

B.E Distribution law

$$\text{Total energy } U = \int_0^{\infty} U n(U) dU$$

Fermi-Dirac Statistics

F-D statistics apply for indistinguishable particles which are governed by exclusion principle. It is just like B-E statistics except that each cell can be occupied by particle.

If there are g_i cells having same energy U_i and n_i particles, then n_i cells are filled $g_i - n_i$ cells are empty.

g_i cells can be arranged in L^{g_i} different way. Permutation of n_i filled cell among themselves is irrelevant = L^{n_i} $L^{g_i - n_i}$ permutation of vacant cells among themselves are also irrelevant.

∴ The No. of distinguishable arrangement of particles n_i among the g_i cells is = $\frac{L^{g_i}}{L^{n_i}}$

∴ The probability W of the entire distribution of particles is the product $W = \prod \frac{L^{g_i}}{L^{n_i} L^{g_i - n_i}}$

Stirling formula $\log L^x = x \log L - x$

$$\log W = \sum [\log L^{g_i} - \log L^{n_i} - \log L^{g_i - n_i}]$$

$$= \sum [g_i \log L - n_i \log L + (g_i - n_i) \log L]$$

∴ for most probable distribution $\delta \log W_{max} = 0$

$$\therefore \sum [-\log L n_i + \log L (g_i - n_i)] \delta n_i = 0$$

New from conservation of particle $\sum \delta n_i = 0$ — (1)

From conservation of energy $\sum U_i \delta n_i = 0$ — (2)

Multiply the equat (1) by $-\alpha$ and equat (2) by $-\beta$ and using Lagrange multiplier method we get

$$\sum [-\log L n_i + \log L (g_i - n_i) - \alpha - \beta U_i] \delta n_i = 0$$

$$\therefore \log L \frac{g_i - n_i}{n_i} - \alpha - \beta U_i = 0$$

$$\therefore \frac{g_i - n_i}{n_i} = e^{\alpha + \beta U_i}$$

$$\therefore \frac{g_i}{n_i} = 1 + e^{\alpha + \beta U_i} \quad \therefore n_i = \frac{g_i}{1 + e^{\alpha + \beta U_i}} = \frac{g_i}{e^{\alpha} e^{\beta U_i / kT} + 1}$$

F-D-Distribution law

Comparison :-

- (1) M-B $n_i = \frac{g_i}{e^{\alpha} e^{\beta U_i / kT}}$ ✓
- (2) B-E $n_i = \frac{g_i}{e^{\alpha} e^{\beta U_i / kT} - 1}$ ✓
- (3) F-D $n_i = \frac{g_i}{e^{\alpha} e^{\beta U_i / kT} + 1}$ ✓

Bose-Einstein condensation

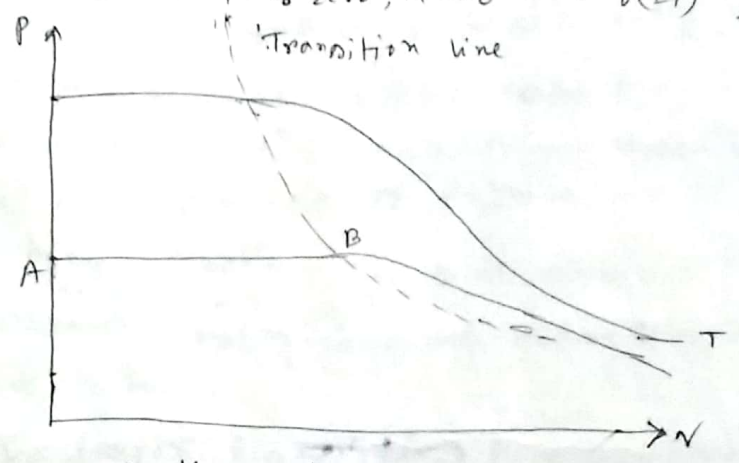
At absolute zero of tempⁿ the particle of a system tends to occupy the lowest energy state, this phenomenon is called B-E condensation. It is responsible for the superfluid state of liquid helium.

Bose-Einstein distribution function

$$n_o f(E_i) = \frac{1}{e^{-\alpha} e^{E_i/k_B T} - 1}$$

Here α = Lagrange undetermined multiplier.

As the tempⁿ approaches zero, $\alpha \rightarrow 0$ and $f(E_i) = \frac{1}{e^{E_i/k_B T} - 1}$



Graphs for the Bose gas. The dashed corresponds to the condensation.

At high tempⁿ B-E statistics looks like M-B Statistics

The B-E statistic distribution function

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{\alpha + \beta E_i} - 1} \quad \text{--- (1)}$$

At very high tempⁿ the particles are distributed over a wide energy range so that the number of particles in any energy range would be much smaller than the number of quantum states in that range. That is $g_i \gg N_i$ in this case.

$$\ln g_i - \ln N_i + \alpha + \beta E_i = 0 \quad \text{--- (2)}$$

which is the same as the equation for a Maxwell-Boltzmann system. Thus at high tempⁿ the BE distribution function reduces to the MB distribution function given by

$$f(E_i) = \frac{1}{e^{\alpha + \beta E_i}} \quad \text{--- (3)}$$

It is then easily appreciated that the quantity β must be identified as

$$\beta = + \frac{1}{k_B T}$$

Equation (1) is now written as

$$f(E_i) = \frac{1}{e^{\alpha} e^{E_i/k_B T}}$$

It is since that at high tempⁿ α is very large (number)

$$\therefore f(E_i) = e^{-(\alpha + \frac{E_i}{k_B T})} = e^{-(\alpha + \beta E_i)} = \text{M-B distribution function}$$

Specific heat of Solid :-

① Classical description

Solid have regular crystalline structure with the atom at the corner bound by elastic force capable of exhibiting simple harmonic motion.

Each atom of the solid have three S.H.M = Six degrees of freedom.

$$\therefore \text{Energy of 1 atom} = 6 \times \frac{1}{2} kT = 3kT$$

$$\therefore \text{Energy of 1 gm of atom of a solid} = 3kTN = 3RT$$

Now Specific heat at constant volume

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3R = \text{const for all solid}$$

where $Nk = R$
 $N = \text{Avogadro No}$
 $k = \text{Boltzmann const}$

\therefore We getulongy Petit law.

Stating that Specific heat of solid at constant volume is const and equal to $3R$. But the expt observation is different.

Einstein theory of Specific heat

In Einstein theory a solid containing N atoms can be represented by $3N$ one dimensional quantum harmonic oscillator having discrete energy value. The atoms vibrate independently of each other having same angular frequency the energy of an atomic oscillator given by

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega \quad \text{Here } \omega = \text{angular frequency}$$

$n = 0, 1, 2, \dots$ etc. When $n=0$ $E_0 = \frac{1}{2} \hbar \omega = \text{zero point energy}$

The average energy of an atomic oscillator

$$\bar{E} = \frac{\sum_{n=0}^{\infty} E_n e^{-E_n/k_B T}}{\sum_{n=0}^{\infty} e^{-E_n/k_B T}} = \frac{\hbar \omega \sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) e^{-\left(n + \frac{1}{2}\right) \alpha}}{\sum_{n=0}^{\infty} e^{-\left(n + \frac{1}{2}\right) \alpha}} \quad \text{--- (1)}$$

Where $\alpha = \frac{\hbar \omega}{k_B T}$ --- (2)

We can write Ser-(1) as-

$$\begin{aligned} \bar{E} &= \hbar \omega \frac{\left(\frac{1}{2}\right) e^{\alpha/2} + \left(\frac{3}{2}\right) e^{3\alpha/2} + \left(\frac{5}{2}\right) e^{5\alpha/2} + \dots}{e^{\alpha/2} + e^{3\alpha/2} + e^{5\alpha/2} + \dots} \\ &= \hbar \omega \frac{d}{d\alpha} \left[e^{\alpha/2} \left(1 + e^{-\alpha} + e^{-2\alpha} + \dots \right) \right] \\ &= \hbar \omega \frac{d}{d\alpha} \left[\frac{\alpha}{2} - \ln(1 - e^{-\alpha}) \right] = \hbar \omega \left[\frac{1}{2} + \frac{1}{e^{\alpha/k_B T} - 1} \right] \quad \text{--- (3)} \end{aligned}$$

The total internal energy in a system of N atoms

is obtained by multiplying the average energy of an oscillator \bar{E} by $3N$, so that

$$U = 3N \bar{E} = 3N \left[\frac{\hbar \omega}{2} + \frac{\hbar \omega}{e^{\hbar \omega/k_B T} - 1} \right]$$

At $T_0 = 0$ K, clearly $U = 3N (\hbar \omega/2)$, which is the zero point energy of N atoms.

At high tempⁿ $\frac{\hbar \omega}{k_B T}$ is small

So that $e^{\hbar \omega/k_B T} - 1 = 1 + \frac{\hbar \omega}{k_B T} + \frac{1}{2} \left(\frac{\hbar \omega}{k_B T}\right)^2 + \dots \approx 1 + \frac{\hbar \omega}{k_B T}$

$$\therefore U = 3N \left[\frac{\frac{1}{2} h\nu}{2} + \frac{\frac{1}{2} h\nu}{\left(\frac{h\nu}{k_B T}\right) + 1} \right] = 3N \left[\frac{\frac{1}{2} h\nu}{2} + \frac{\frac{1}{2} h\nu}{\frac{h\nu}{k_B T} \left(1 + \frac{h\nu}{k_B T}\right)} \right]$$

$$= 3N \left[\frac{\frac{1}{2} h\nu}{2} + \frac{k_B T}{-1} \left(1 - \frac{\frac{1}{2} h\nu}{k_B T}\right) \right]$$

$$= 3N \left[k_B T - \frac{\frac{1}{2} h\nu}{2} \right] \text{ which does not agree with classical value.}$$

For 1 mole of substance N is Avogadro no.

Hence the molar specific heat -

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3N k_B \left(\frac{\frac{1}{2} h\nu}{k_B T}\right) \frac{e^{-\frac{1}{2} h\nu/k_B T}}{\left(e^{-\frac{1}{2} h\nu/k_B T} - 1\right)^2}$$

$$= 3R \left(\frac{\Theta_E}{T}\right) \frac{e^{-\Theta_E/T}}{\left(e^{-\Theta_E/T} - 1\right)^2} \quad \left[\begin{array}{l} N k_B = R \\ = \text{gas const} \end{array} \right]$$

where $\Theta = \frac{h\nu}{k_B} = \text{Einstein temperature}$

The zero point energy is independent of tempⁿ and does not contribute to C_V .

At high tempⁿ when $T \gg \Theta_E$ the molar specific heat approaches classical Dulong Petit law.

$$\therefore \boxed{C_V = 3R}$$

At low tempⁿ $T \ll \Theta_E$

$$\therefore C_V = 3R \left(\frac{\Theta_E}{T}\right)^2 e^{-\Theta_E/T}$$

By a proper choice of Θ_E , Einstein theory may be fitted experimental value for most solid Θ_E ranges from $(100 - 300)K$

Statistical Mechanics

①

Calculate the Fermi energy at 0K of metallic silver containing one free electron per atom. The density and atomic weight of silver is 10.5 g/cm^3 and 108, respectively.

⇒ We have

$$E_F(0) = \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3}$$

The no. density of free electron is given by

$$\frac{N}{V} = \frac{6.02 \times 10^{23} \text{ atom/mole}}{108 \text{ g/mole}} \times 10.5 \text{ g/cm}^3$$

$$= 5.9 \times 10^{22} \text{ cm}^{-3} = 5.9 \times 10^{28} \text{ m}^{-3}$$

$$\therefore E_F(0) = \frac{(6.6 \times 10^{-34} \text{ J.s})^2 (3 \times 5.9 \times 10^{28} \text{ m}^{-3})^{2/3}}{8 \times 9.1 \times 10^{-31} \text{ kg} (3.14)}$$

$$= 8.8 \times 10^{-19} \text{ J} = \frac{8.8 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV} = 5.5 \text{ eV}$$

② Using the data of Prob. 1 determine the internal energy of the electron gas per unit volume at 0 K

⇒ The required internal energy is

$$u = \frac{3}{5} \left(\frac{N}{V} \right) E_F(0) = \frac{3}{5} \times 5.9 \times 10^{23} \times 8.8 \times 10^{-19} \text{ J/m}^3 \\ = 3.11 \times 10^{10} \text{ J/m}^3$$

③ Using the data of Prob. 1 calculate the molar specific heat due to free electron at constant volume in metallic Silver at 100 K.

Ans.:- We have $e_V^{(e)} = \frac{\pi^2}{2} N k_B \left(\frac{T}{T_F} \right)$

Here $N = 6.02 \times 10^{23}$ atoms/moles, $T = 100 \text{ K}$, $T_F = \frac{E_F(0)}{k_B}$

$$= \frac{8.8 \times 10^{-19} \text{ J}}{1.38 \times 10^{-23} \text{ J/K}} = 63768 \text{ K}$$

$$e_V^{(e)} = \frac{(3.14)^2}{2} \times 6.02 \times 10^{23} \times 1.38 \times 10^{-23} \times \left(\frac{100}{63768} \right) \\ = 0.69 \text{ J K}^{-1} \text{ mol}^{-1}$$

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 states to the probability that the two particles occupy different states for MB, BE and FD statistics.

Ans.:- Let w_1 be the desired ratio. w_1 is the no. of ways in which the two particles occupy the same state and w_2 is that in which they occupy different states then, $w = w_1/w_2$

For MB statistics, the particles are distinguishable and $w_1 = 3$. To calculate w_2 , we note that one particle can be in any one of the 3 quantum states and the remaining particle can be in any one of the 2

quantum states that are available to it. So, $w_2 = 3 \times 2 = 6$.

\therefore For MB statistics, $r = w_1/w_2 = 3/6 = 1/2$.

For FD and BE statistics, the particles are indistinguishable

In the case of FD, $w_1 = 0$ since the two particles cannot be in the same quantum state. Here $w_2 = 3 \times 2 = 6$.

So, for FD statistics $r = w_1/w_2 = 0/6 = 0$

For BE statistics $w_1 = 3$ and $w_2 = 3 \times 2 = 6$

So $r = w_1/w_2 = 3/6 = 1/2$.