Chapter 10

Identical Particles

8. Bose Einstein Condensation

For a Bose-Einstein gas, the chemical potential μ is always negative and therefore, $A \geq 1$. Further let us consider spinless particles, so that $g = 1$. With the decrease of temperature, A decreases and can attain the minimum value 1. The value of A is 1 at a critical temperature T_B called the Bose temperature. This Bose temperature can be determined from equation $N_e = 2g\pi V\left(\frac{2mk_B T_B}{h^2}\right)^{3/2}\int_0^\infty \frac{u^{1/2}}{Ae^u - 1}du = \frac{gV}{\lambda^3}g_{3/2}(A)$.

By putting $A = 1$. At this temperature, the number of particles in the ground states is negligible. Hence,

$N = V\left(\frac{2\pi mk_B T_B}{h^2}\right)^{3/2} g_{3/2}(1)$ where $g_{3/2}(1) = 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \frac{1}{4^{3/2}} + ... \equiv \varsigma(3/2)$

is the Riemann zeta function whose value is 2.612. Hence, the Bose temperature is given by

$$T_B = \left(\frac{h^2}{2\pi m k_B}\right)\left(\frac{N}{2.612V}\right)^{2/3}$$

Thus, the Bose temperature is the minimum temperature at which all the particles are in the exited states. For all known Bose-Einstein gases, value of Bose temperature is very low. For example for He^4, it is about 3.14 K. Through this value is very low, but there is a temperature $0 \le T \le T_B$ where Bose-Einstein gases show a specific behavior.

Bose-Einstein condensation (Bose-Einstein gas at $T < T_B$)

In this temperature range A = 1 and number of particles in the excited states is

$$N_e = N - N_0 = 2.612V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$

It shows that for the given values of V and T, when $N > 2.612V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$

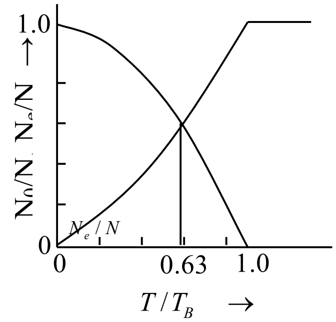
the excited states can occupy the number of particles given by equation and therefore, rest (N_0) of them would be in the ground state $(E = 0)$. Hence, as long as

$$N \le 2.612V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$

all the particles in the gas are in the excited states $(E \ne 0)$. From equations $N_e = 2.612V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$ we get the number of particles in the excited states

$$N_e = N\left(\frac{T}{T_B}\right)^{3/2}$$ and the number of particles in the ground state

$$N_0 = N - N_e = N\left[1 - \left(\frac{T}{T_B}\right)^{3/2}\right]$$



Variation of N_e / N and N_0 / N vs T

Showing that a large number of particles accumulate in the ground state when $T < T_B$. This famous phenomenon is known as **Bose-Einstein condensation**. At T = 0, all the particles occupy the ground state, and at $T = T_B$, all the particles occupy the excited state. For $T > T_B$ the particles occupy higher excited states only.

Thermodynamic quantities at $T < T_B$:

At $T < T_B$, we have A = 1

- Energy $\frac{U}{N_e} = \frac{(3/2)k_B T (gV/\lambda^3) g_{5/2}(1)}{(gV/\lambda^3) g_{3/2}(1)}$,

$$U = \frac{3}{2}\frac{g_{5/2}(1)}{g_{3/2}(1)} N_e k_B T = \frac{3}{2}\frac{g_{5/2}(1)}{g_{3/2}(1)} N k_B T \left(\frac{T}{T_B}\right)^{3/2}$$

At $T = T_B$ $\quad U(T_B) = \frac{3}{2}\frac{g_{5/2}(1)}{g_{3/2}(1)} N k_B T_B$

- Specific heat at constant volume C_V is

$$C_V = \left[\frac{\partial U}{\partial T}\right]_V = \frac{15}{4}\frac{g_{5/2}(1)}{g_{3/2}(1)} N k_B \left(\frac{T}{T_B}\right)^{3/2} = 1.926 N k_B \left(\frac{T}{T_B}\right)^{3/2}$$

- Helmholtz free energy F is

$$F = U - ST = U - \frac{5}{3}\frac{U}{T}T = -\frac{2}{3}U$$

- Pressure P is

$$P = \frac{2}{3}\frac{U}{V}, \quad P = \frac{g_{5/2}(1)}{g_{3/2}(1)}\frac{N k_B T}{V}\left(\frac{T}{T_B}\right)^{3/2}$$

At T = T_B $\quad P(T_B) = \frac{g_{5/2}(1)}{g_{3/2}(1)}\frac{N k_B T_B}{V}$

Examples: (a) Write down distribution function of photon at temperature T, if average energy in each state is given by $\varepsilon = h\nu$.

(b) What is density of state of photon gas between frequency ν to $\nu + d\nu$

(c) Write down expression of no of particle for photon gas at temperature T .

(d) Write down expression of average energy for photon gas at temperature T .

Solution: (a) the Bose Einstein distribution is given by $f(E) = \frac{1}{e^{(\alpha+\beta E)} - 1} = \frac{1}{Ae^{\beta E} - 1}$

where $A = e^{\alpha} = e^{-\mu/k_B T} = \frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$, for boson $\mu = 0$

so $f\left(E\right)=\frac{1}{e^{\beta E}-1}$ for if average energy in each state is given by $\varepsilon=h\nu$ then $f\left(E\right)=\frac{1}{e^{\frac{h\nu}{k_BT}}-1}$

(b) If j is quantum number associate with frequency ν then total no of frequency between ν to $\nu+d\nu$ is same as the number of points between j to $j+dj$. The volume of spherical shell of radius j and thickness dj is $4\pi j^2 dj$.

Hence all three component of j is positive (same as particle in box) and there are two direction of polarization so degeneracy $g=2$.

So number of standing wave $g(j)dj=(2)\left(\frac{1}{8}\right)4\pi j^2 dj=\pi j^2 dj$

It is given $j=\frac{2L}{\lambda}=\frac{2L\nu}{c}$ and $dj=\frac{2Ld\nu}{c}$ $\quad g(\nu)d\nu=\frac{8\pi L^3\nu^2}{c^3}d\nu$

So density of standing wave in cavity is given by $g(\nu)d\nu=\frac{g(\nu)}{L^3}d\nu$

$$g(\nu)d\nu=\frac{8\pi\nu^2}{c^3}d\nu$$

(c) $N=\int_0^\infty f\left(E\right)g\left(E\right)dE \Rightarrow \int_0^\infty f\left(\nu\right)g\left(\nu\right)d\nu$

$$N=\frac{8\pi V}{c^3}\int_0^\infty \frac{\nu^2 d\nu}{e^{\frac{h\nu}{k_BT}}-1} \quad \text{put } x=\frac{h\nu}{k_BT} \quad N=\frac{8\pi V}{c^3}\left(\frac{k_BT}{hc}\right)^3\int_0^\infty \frac{x^2dx}{e^x-1}$$

The integral have value, $N=19.2V\left(\frac{k_BT}{hc}\right)^3$

(d) $U=\int_0^\infty Ef\left(E\right)g\left(E\right)dE \Rightarrow \int_0^\infty h\nu f\left(\nu\right)g\left(\nu\right)d\nu$

$$\mathrm{U}=\frac{8\pi Vh}{c^3}\int_0^\infty \frac{\nu^3 d\nu}{e^{\frac{h\nu}{k_BT}}-1} \quad \text{put } x=\frac{h\nu}{k_BT}, \quad \mathrm{U}=8\pi Vc\left(\frac{k_BT}{hc}\right)^4\int_0^\infty \frac{x^3dx}{e^x-1} \quad U=\frac{8\pi^5Vk^4{}_BT^4}{15c^3h^3}.$$

Example: A system consisting of two boson particles each of which can be any one of three quantum state of respective energies $o,\varepsilon,3\varepsilon$ is in equilibrium at temperature T.write the expression of partition function.

Two boson can be distributed in three given state with their respective energy level shown in table

	Energy 0	Energy ε	Energy 3ε	Total energy
1	A A	0	0	0
2	0	AA	0	2ε
3	0	0	AA	6ε
4	A	A	0	ε
5	A	0	A	3ε
6	0	A	A	4ε

$$Z = 1 + \exp(-\beta\varepsilon) + \exp(-2\beta\varepsilon) + \exp(-3\beta\varepsilon) + \exp(-4\beta\varepsilon) + \exp(-6\beta\varepsilon)$$

Example: Calculate the ratio of the number of molecules in the lowest two rotational states in a gas of H_2 at $50\,K$ (take inter atomic distance $= 1.05\,\overset{0}{\mathrm{A}}$)

Solution: Probability for the rotational state to be found with quantum number J is given by the Boltzmann's law.

$$P(E) \propto (2J+1)\exp\left[-J(J+1)\hbar^2 / 2I_0 kT\right]$$

where I_0 is the moment of inertia of the molecules, k is Boltzmann's constant, and T the Kelvin temperature. The two lowest states have $J = 0$ and $J = 1$

$I_0 = M(r/2)^2 + M(r/2)^2 = \frac{1}{2}Mr^2$, where $M = 938 MeV/c^2$

$$2I_0 = Mr^2 = 938 \times \left(1.05 \times 10^{-10}\right)^2 / c^2$$

$$\hbar c = 197.3\, MeV - 10^{-15}\, m$$

$$kT = 1.38 \times 10^{-23} \times \frac{50}{1.6 \times 10^{-13}} = 43.125 \times 10^{-10}$$

$$\frac{\hbar^2}{2I_0 kT} = \frac{\hbar^2 c^2}{Mc^2 r^2 kT} = \frac{(197.3)^2 \times 10^{-30}}{938 \times \left(1.05 \times 10^{-10}\right)^2 \times 43.125 \times 10^{-10}} = 0.8728$$

For $J = 1, \frac{J(J+1)\hbar^2}{2kT} = 1 \times (1+1) \times 0.8728 = 1.7457$

For $J = 0, P(E_0) \propto 1.0$

For $J = 1, P(E_0) \propto (2 \times 1 + 1)\exp(-1.7457) = 0.52$ $\therefore P(E_0) : P(E_1) :: 1 : 0.52$

Example: Consider a photon gas in equilibrium contained in a cubical box of volume $V = a^3$. Calculate the number of allowed normal modes of frequency ω in the interval $d\omega$.

Solution: For stationary waves, in the x - direction

$k_x a = n_x \pi$

or $n_x = k_x a / \pi$

$dn_x = (a/\pi) dk_x$

Similar expressions are obtained for y and z directions.

$dn = dn_x dn_y dn_z = (a/\pi)^3 d^3k$

However, only the first octant of number space is physically meaningful.

Therefore,

$$dn = (1/8)(a/\pi)^3 d^3k$$

Taking into account the two possible polarizations

$$dn = \frac{2V}{(2\pi)^3} d^3k = \frac{2V}{8\pi^3} \cdot 4\pi k^2 dk$$

But $k - \frac{\omega}{c}; dk - d\omega / c$ $\quad\quad \therefore dn = \frac{V\omega^2 d\omega}{\pi^2 c^2}$

Example: Assuming that the moment of inertia of the H_2 molecule is $4.64 \times 10^{-48} kg\text{-}m^2$, find the relative population of the $J = 0,1,2$ and 3 rotational states at $400\,K$.

Solution: $p(E_J) = (2j+1) e^{\frac{-J(J+1)\hbar^2}{2I_0 kT}}$

The factor $\frac{\hbar^2}{2I_0 k} = \frac{(1.055 \times 10^{-34})^2}{2 \times 4.64 \times 10^{-48} \times 1.38 \times 10^{-23} J} = 86.9$

$p(E_0) = 1$

$p(E_1) = 3e^{-2\times 86.9/400} = 1.942$

$p(E_2) = 5e^{-6\times 86.9/400} = 1.358$

$p(E_3) = 7e^{-12\times 86.9/400} = 0.516$

Example: Calculate the relative numbers of hydrogen atoms in the chromospheres with the principal quantum numbers *n* = 1, 2, 3 and 4 at temperature 6,000 K.

Solution: For Boltzmann statistics $p(E) \propto e^{-E/kT}$, therefore, $\frac{p(E_n)}{p(E_1)} = e^{-(E_n - E_1)/kT}$

In hydrogen atom, if the ground state energy $E_1 = 0$, then $E_2 = 10.2,\ E_3 = 12.09$ and

$E_4 = 12.75\, eV$

The factor $kT = 8.625 \times 10^{-5} \times 6000 = 0.5175$

$$P(E_2)/P(E_1) = e^{-10.2/0.5175} = 2.75 \times 10^{-9}$$

$$P(E_3)/P(E_1) = e^{-12.09/0.5175} = 1.4 \times 10^{-10}$$

$$P(E_4)/P(E_1) = e^{-12.75/0.5175} = 1.99 \times 10^{-11}$$

$$P(E_1) : P(E_2) : P(E_3) :: 1 : 2.8 \times 10^{-9} : 1.4 \times 10^{-10} : 2.0 \times 10^{-11}$$

Example: Calculate the probability that an allowed state is occupied if it lies above the Fermi level by $k_B T$, by $5k_B T$, by $10k_B T$.

Solution: $p(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$

$$E - E_F = kT,\ p(E) = \frac{1}{e+1} = 0.269$$

$$E - E_F = 5kT,\ p(E) = \frac{1}{e^5 + 1} = 6.69 \times 10^{-3}$$

$$E - E_F = 10\,kT,\ p(E) = \frac{1}{e^{10} + 1} = 4.54 \times 10^{-5}$$

Example: The probability for occupying the Fermi level $P_F = 1/2$. If the probability for occupying a level ΔE above E_F is P_+ and that for a level ΔE below E_F is P_-, then show that for $\frac{\Delta E}{k_B T} < 1$, P_F is the mean of P_+ and P_-

Solution: $P_+ = \frac{1}{e^{(E-E_F)/kT} + 1} = \frac{1}{e^{\Delta/kT} + 1} \approx \frac{1}{2 + \Delta/kT} = \frac{1}{2}(1 - \Delta/2kT)$

$$P_- = \frac{1}{2}(1 + \Delta/2kT)$$

$$\therefore \frac{P_+ + P_-}{2} = \frac{1}{2} = P_F$$

Example: Find the number of ways in which two particles can be distributed in six states if

(a) the particles are distinguishable

(b) the particles are indistinguishable and obey Bose-Einstein statistics

(c) the particles are indistinguishable and only one particle can occupy any one state

Solution: (a) For n states, the number of ways is $N = n^2$. Therefore, for $n = 6$ states $N = 36$

(b) For n states, the number of ways is $N = n^2 - (n-1)$ or $n^2 - n + 1$. Therefore, for $n = 6,\ N = 31$

(c) For n states, $N = n^2 - n + 1 - n$ or $n^2 - 2n + 1$. Therefore, for $n = 6,\ N = 25$

Example: From observations on the intensities of lines in the optical spectrum of nitrogen in a flame the population of various vibrationally excited molecules relative to the ground state is found as follows:

v	0	1	2	3
N_v / N_0	1.000	0.210	0.043	0.009

Show that the gas is a thermodynamic equilibrium in the flame and calculate the temperature of the gas $(\theta_v = 3350\,K)$

Solution: If the gas is in equilibrium, the number of particles in a vibrational state is

$$N_v = N_0 \exp\left(-\frac{hv}{kT}\right) = N_0 \exp\left(-\frac{\theta}{T}\right)$$

The ratios, $\frac{N_0}{N_1} = 4.7619, \frac{N_1}{N_2} = 4.8837, \frac{N_2}{N_3} = 4.7778$ are seen to be constant at 4.8078. Thus, the ratio $\frac{N_v}{N_{v+1}}$ is constant equal to 4.81, showing the gas to be in equilibrium at a temperature

$$T = 3350/(\ln 4.81) \approx 2130\,K$$

Example: A system has non-degenerate energy levels with energy $E=\left(n+\frac{1}{2}\right)\hbar\omega$, where $\hbar\omega=8.625\times10^{-5}eV$ and $n=0,1,2,3,.....$ Calculate the probability that the system is in the $n=10$ state if it is in contact with a heat bath at room temperature $(T=300K)$. What will be the probability for the limiting cases of very low temperature and very high temperature?

Solution: $P(n,T)=\dfrac{e^{-\frac{\left(n+\frac{1}{2}\right)\hbar\omega}{kT}}}{\sum_{n=0}^{\infty}e^{-\frac{\left(n+\frac{1}{2}\right)\hbar\omega}{kT}}}=\dfrac{e^{-\left(n+\frac{1}{2}\right)\hbar\omega/kT}}{e^{-\frac{1}{2}\hbar\omega/kT}\sum_{n=1}^{\infty}e^{n\hbar\omega/kT}}$

$$=\frac{e^{-n\hbar\omega/kT}}{\frac{e^{-\hbar\omega/kT}}{1-e^{-\hbar\omega/kT}}}=\frac{e^{-n\hbar\omega/kT}}{\frac{1}{e^{\hbar\omega/kT}-1}}=e^{-n\hbar\omega/kT}\left(e^{\hbar\omega/kT}-1\right)$$

Substitute $n=10,\dfrac{\hbar\omega}{k}=\dfrac{8.625\times10^{-5}}{\left(1.38\times10^{-23}/1.6\times10^{-19}\right)}=1.0$

$P(10,300)=3.2\times10^{-3}$

In the limit $T\to0$, the state $n=0$ alone is populated so that $n=10$ state is unpopulated.

In the limit $T\to\infty$, probability for $n=10$ again goes to zero, as higher states which are numerous, are likely to be populated.