Thermodynamics: Classical to Statistical

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Lecture - 29

Bose-Einstein Condensation

Hence, at temperature $T > T_B$, all particles are in excited states and the ground state is essentially unoccupied. But, when $T < T_B$, particles gradually occupy the ground state, which essentially, in the limit T tends to 0 kelvin contains all the particles in the system.

The particles in the ground state for $T < T_B$ constitute a Bose Einstein Condensation and the temperature T_B is known as Bose temperature.

Below a critical temperature T_B, in a system of indistinguishable bosons, the population of the ground state in a series of quantized states becomes very large, and discontinuous with the population of the excited states. This "extra" population of the ground state is the Bose-Einstein Condensation. The existence of the Bose-Einstein Condensation leads to a dramatic effect in systems of bosons at temperature below T_B.

The population density in the excited state (not ground state), in a Bose-Einstein gas is,

$$n_{ex}(\varepsilon) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar}\right)^{\frac{3}{2}} \frac{\sqrt{\varepsilon}}{Be^{\varepsilon/k_BT} - 1} \quad \textbf{(15)}$$

The function B(T) plays the role for the Bose-Einstein Distribution that the chemical potential does for the Fermi-Dirac distribution.

For a Bose Einstein gas,

$$B(T) = \begin{cases} 1 & \Rightarrow \mathrm{T} \le T_B \\ F^{-1}\left[\xi\left(\frac{3}{2}\right)\left(\frac{T_B}{T}\right)^{\frac{3}{2}}\right] & \Rightarrow \mathrm{T} \ge T_B \end{cases} \quad \textbf{(16)}$$

The function F^{-1} is the inverse function of F(B), defined in equation 7.

The total population in the excited state, when $T < T_B$,

$$N_{ex} = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar}\right)^{\frac{3}{2}} \int_0^\infty \frac{\sqrt{\varepsilon}\,d\varepsilon}{e^{\varepsilon/k_BT} - 1} \quad \textbf{(17)}$$

$$N_{ex} = \frac{V}{4\pi^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{\sqrt{y}}{e^y - 1}dy \quad \textbf{(18)}$$

$$N_{ex} = V\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{\frac{3}{2}} \xi\left(\frac{3}{2}\right) \quad \textbf{(19)}$$

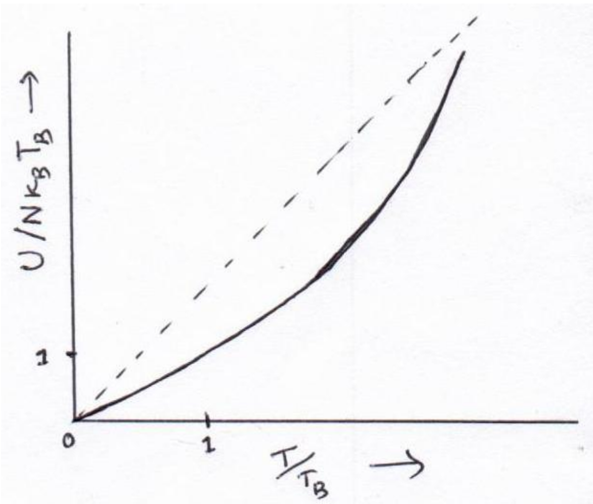
$$N_{ex} = N\left(\frac{T_B}{T}\right)^{\frac{3}{2}} \quad \textbf{(20)}$$

This is the population in the excited state.

Similarly, the population in the ground state is,

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

The plot N_0, which is function of T, versus T/T_B looks like,



The Bose-Einstein gas: Total energy

If we assume that the ground state is a state of zero energy, then particles in the Bose-Einstein Condensation make no contribution to the total energy of the Bose-Einstein gas. The contribution in the total energy will come mainly from the particles present in the excite state.

Thus, the total energy, U, can be written using equation 15 for the density of particles in the excited state.

$$U = \int_0^\infty \varepsilon n_{ex}(\varepsilon) d\varepsilon = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar}\right)^{\frac{3}{2}} \int_0^\infty \frac{\varepsilon^{\frac{3}{2}} d\varepsilon}{Be^{\varepsilon/k_B T} - 1}$$

By changing the variable of integration, the total energy can be written as,

$$U = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar}\right)^{\frac{3}{2}} (k_B T)^{\frac{5}{2}} \int_0^\infty \frac{y^{\frac{3}{2}}}{Be^y - 1} dy$$

Now, by using the expression for Bose-temperature (equation 14), we obtain,

$$U = \frac{2}{\sqrt{\pi}\xi(3/2)} Nk_B T \left(\frac{T}{T_B}\right)^{\frac{3}{2}} \int_0^\infty \frac{y^{\frac{3}{2}}}{Be^y - 1} dy$$

Now, we consider two different cases.

- **Case 1**:
  At low temperature, we consider B = 1 and the total energy becomes

$$U = \frac{2}{\sqrt{\pi}\xi(3/2)} Nk_B T \left(\frac{T}{T_B}\right)^{\frac{3}{2}} \int_0^\infty \frac{y^{\frac{3}{2}}}{e^y - 1} dy$$

$$U = \frac{3\xi(5/2)}{2\xi(3/2)} Nk_B T \left(\frac{T}{T_B}\right)^{\frac{3}{2}}$$

$$U \approx 0.77 Nk_B T \left(\frac{T}{T_B}\right)^{\frac{3}{2}}$$

  Therefore, for $T < T_B$, $U \propto T^{\frac{5}{2}}$

- **Case 2**:
  At high temperature, $T \geq T_B$, then B >> 1. Then,

$$Be^y - 1 \approx Be^y$$

  Thus, the total energy is

$$U \approx \frac{2}{\sqrt{\pi}\xi(3/2)} Nk_B T \left(\frac{T}{T_B}\right)^{\frac{3}{2}} \frac{1}{B} \int_0^\infty \frac{y^{\frac{3}{2}}}{e^y} dy$$

$$U \approx \frac{3}{2\xi(3/2)} Nk_B T \left(\frac{T}{T_B}\right)^{\frac{3}{2}} \frac{1}{B}$$

  Substituting, the value of B from equation 17, average energy becomes,

$$U \approx \frac{3}{2} Nk_B T$$

From the above expression, we can note that this is the same result as for the Maxwell-Boltzmann gas. This expression for average energy meets our expectation since one should go over to Boltzmann Distribution in the high temperature limit. The plot of the total energy versus temperature is shown below,

Problems

Problem 1:

The Fermi energy is given by $\varepsilon_F = \lim_{T\to 0} \mu(T)$ and for ideal Fermi gas, is

$$\varepsilon_F = (3N/8\pi V)^{2/3} h^2/2m$$

The molar volume of metallic sodium is 23.7 cc. Each atom of Na contributes its single 3s electron to the conduction electron gas. Determine

i. the number the number of electrons per unit volume
ii. Fermi energy ε_F.

Solution:

1 mole of Na has volume = 23.7 cc. = 23.7×10^{-6} m^3

Since, each atom contributes one 3s electron to the electron gas, such a volume contains Avogadro's number ($N_A = 6.023 \times 10^{23}$) electrons.

1 mole contains N_A number of atoms of Na and each Na atom contributes one 3s electrons.

So number of electrons = $N_A = 6.023 \times 10^{23}$

(i)Thus, number of electrons per unit volume, $N/V = 6.023/23.7 \times 10^{26}$ m^{-3}

(ii) $\varepsilon_F = (3N/8\pi V)^{2/3} h^2/2m$

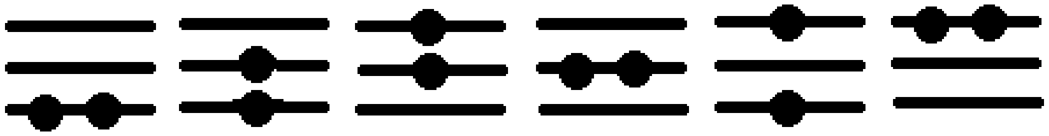
Substituting all the values we get, $\varepsilon_F = 5.06\times 10^{-19}$ J

Problem 2:

Consider a very simple gas made up of two identical particles. Suppose that each particle can be in one of the three possible quantum states. Show that ξ(BE) > ξ(MB) > ξ(FD). The terms BE, MB and FD have their own meanings and ξ is probability that the two particles are found in the same state by probability that the two particles are found in different states.

Solution:

For BE, statistics, we have two identical particles and three different quantum states. The particles can be distributed in the following arrangements,



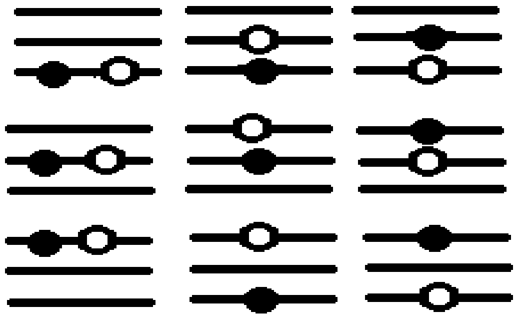
Now, there are six distributions, out of which, there are three distributions where both the particles in the same state and three distributions, where the two particles are present in two different states.

So, the probability of having both the particles present in the same state is 3 /6.

The probability of having the particles present in two different states is 3/6.

$$\text{So, } \xi(BE) = \frac{3/6}{3/6} = 1$$

For MB statistics, where the particles are distinguishable, the possible distributions are shown.



So, we get 9 distribution here. Out of 9 distributions,

the probability having both particles present in the same state is 3/9.

And the probability having the particles present in different states is 6/9.

$$\text{So, } \xi(MB) = \frac{3/9}{6/9} = \frac{1}{2}$$

For FD statistics, since, no two particles can be present in the same quantum state, the probability of having both the particles present in the same quantum state = zero.

$$\text{So, } \xi(FD) = 0 \,.$$

Thus, ξ(BE) > ξ(MB) > ξ(FD). This problem based on distinguishability indistinguishability concept.