Thermodynamics: Classical to Statistical

Prof. Sandip Paul
Department of Chemistry
Indian Institute of Technology Guwahati

Lecture –28

Ideal Bose gas; Introduction to Bose-Einstein condensation

Bose-Einstein condensation

The BE distribution is given by,

$$n_i = \frac{1}{Be^{\beta\varepsilon_i} - 1}$$

where B is $B = e^{-\beta\mu}$.

For degenerate states,

$$n_i = \frac{g_i}{Be^{\beta\varepsilon_i} - 1}$$

where g_i is the degeneracy of i-th quantum state.

Let us now consider the behaviour of the constant B that appears in the BE distribution.

This quantity corresponds to the partition function in the Boltzmann distribution or the chemical potential in the Fermi-Dirac distribution.

Calculation of the value of B:

We know,

$$N = \sum_i n_i \quad \textbf{(1)}$$

where N is the total number of particles. Now we will evaluate how does B depend on temperature.

The density of states for spinless particles moving in a box of volume V is,

$$g(\varepsilon) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar}\right)^{\frac{3}{2}} \varepsilon^{\frac{1}{2}} \quad \textbf{(2)}$$

Let us assume that we can replace the summation over discrete energy levels by an integration over a continuum of energy levels. Then the constraint of equation 1,

$$N = \sum_i n_i \approx \int_0^\infty n(\varepsilon) d\varepsilon \quad \textbf{(3)}$$

Using Bose-Einstein distribution and the density of states of equation 2, we obtain,

$$\frac{V}{4\pi^2}\left(\frac{2m}{\hbar}\right)^{\frac{3}{2}} \int_0^\infty \frac{\sqrt{\varepsilon}}{Be^{\beta\varepsilon} - 1} d\varepsilon = N \quad \textbf{(4)}$$

Now, we consider

$$y = \beta\varepsilon \quad \textbf{(5)}$$

Hence, when $\varepsilon \to 0,\ \mathrm{y} \to 0$

$\varepsilon \to \infty,\ \mathrm{y} \to \infty$

Substituting equation 5 in equation 4, we get,

$$\frac{V}{4\pi^2}\left(\frac{2m}{\hbar}\right)^{\frac{3}{2}} \int_0^\infty \frac{\sqrt{y}}{Be^{y} - 1} dy = N \quad \textbf{(6)}$$

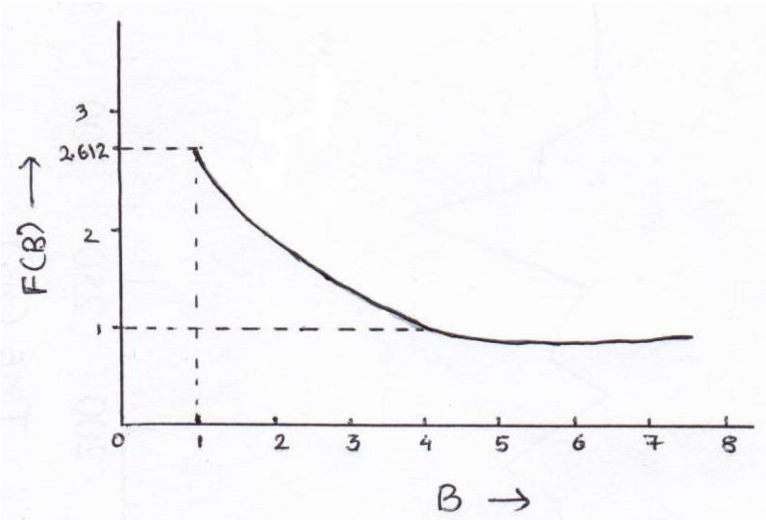
We consider another function, F, which is function of B,

$$F(B) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{y}}{Be^{y} - 1} dy \quad \textbf{(7)}$$

By substituting F(B) of equation 7 into equation 6, we get,

$$V\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{\frac{3}{2}} F(B) = N \quad \textbf{(8)}$$

The plot F(B) versus B is given below.



For large value of ‘B’ we can see, $F(B) \approx \dfrac{1}{B}$.

This is because for B >>1, we can write,

$$\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{\sqrt{y}}{Be^y - 1}dy \approx \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{\sqrt{y}}{Be^y}dy = \frac{1}{B} \quad \textbf{(9)}$$

Thus, from equation 8, for large ‘B’ value, we can write,

$$B \approx \frac{V}{N}\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{\frac{3}{2}} \quad \textbf{(10)}$$

But we find that the integral cannot be evaluated below B < 1.

This is because there is a singularity at B = 1.

This is important to note that the value of B cannot be less than 1 and there is a singularity at B equals to 1.

Thus, the Bose-Einstein distribution is

$$n_i = \frac{g_i}{Be^{\varepsilon_i / k_B T} - 1}$$

If B < 1, there is a possibility of an energy level ε_i where $n_i < 0$.

Clearly we cannot have a negative number of particles (occupation number) in any energy level, so, we expect $B \geq 1$. Next we see that F(B) takes a maximum value at B equals to 1.

The maximum value of F(B), when B equals to 1, is

$$F(1) = \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{\sqrt{y}}{e^y - 1}dy \approx \xi\left(\frac{3}{2}\right) \approx 2.612 \quad \textbf{(11)}$$

Where $\xi(x)$ is the Riemann zeta function defined by

$$\xi(x) = \sum_{n=1}^{\infty} \frac{1}{n^x} \quad \textbf{(12)}$$

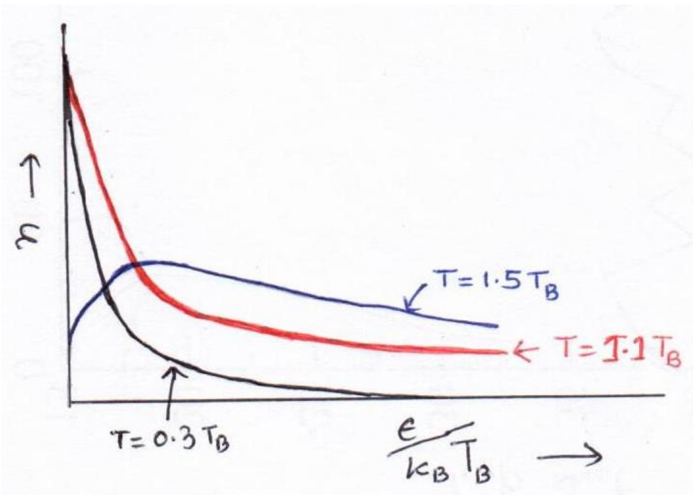
The fact that F(B) has a maximum value of 2.612 is somewhat disturbing.

If we consider equation 8, since 'N' is constant, as the temperature decreases, F(B) should increase. But, if F(B) has a finite maximum, then below some temperature T_B, which we define as Bose temperature, the number of particles we find by integrating the Bose-Einstein distribution over all energies is less than N (the number of particles in the system). Thus,

$$\frac{V}{4\pi^2}\left(\frac{2\pi m k_B T}{\hbar}\right)^{\frac{3}{2}} \int_0^{\infty} \frac{\sqrt{y}}{Be^y - 1} dy < 0$$

When $T < T_B$ and for all values of B.

The situation becomes clear if we plot the population density n(ε) as a function of energy ε for different temperatures.



For $T > T_B$, we see a smooth distribution curve, that for high temperatures, approaches the distribution expected for a Maxwell-Boltzmann gas. The area under the curves for $T > T_B$ are independent of temperature.

When $T < T_B$, strictly speaking, we cannot evaluate the population density, since we do not have a solution for the parameter B. At the best we can do is we set B = 1 for $T < T_B$ and we find a distribution that is sharply peaked at low energy. But, the peak is not high enough for the area under the curve to give the correct result for the number of particles in the system.

The temperature T_B is important because at this temperature the particles start to disappear, so,

$$V\left(\frac{m k_B T_B}{2\pi\hbar^2}\right)^{\frac{3}{2}} \xi\left(\frac{3}{2}\right) = N \quad \textbf{(13)}$$

Thus,

$$T_B = \frac{2\pi\hbar^2}{mk_B}\left(\frac{N}{\xi(3/2)V}\right)^{\frac{2}{3}} \quad \textbf{(14)}$$

Now, the question which arises is where are the missing particles for T < T_B?

The answer is in the ground state.

The problem, which we now need to rectify, is that when we replaced the summation over discrete energy levels by an integral over a continuum of energies in equation 3, we basically omitted the particles in the ground state. Since the lower limit of the integral is zero, we should assume (for consistency) that the ground state has zero energy.

But, the distribution function, $g(\varepsilon) \propto \sqrt{\varepsilon}$,

so at zero energy the density of states is zero and the population (in the small energy range 0 and dε) is 0. It means that the integral in equation 3 only estimates particles in the excited states omitting those in the ground state.

Remember we did similar exercise in FD distribution, but in the FD distribution in the ground state at the max we can have 2 particles or when there is no spin of the particle only 1 particle can be present in the ground state for FD statistics. For FD statistics, we can safely ignore the number of particles in the ground state because the total number of particles N is much much greater than 1, whereas in case of the BE statistics, since there is no restriction in the number of particles in the ground state, hence, we cannot neglect the number of particles in the ground state.

We made the same mistake when we considered the Fermi gas. But, in that case, there could be only two particles in the ground state (assuming degeneracy 2, for spin half particles). In other words, we omitted two particles out of a large number of particles 'N' and this did not affect our conclusions. But for a Bose gas or gas molecules, there is no limit in the number of particles that can be present in the ground state. So, if we ignore the ground state from the integration we can make a large error for BE distribution.