Thermodynamics: Classical to Statistical

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Lecture 26

Fermi - Dirac and Bose-Einstein statistics

We will start now quantum statistic. We will discuss Fermi Dirac and Bose Einstein statistics. So far we have discussed classical statistics or Maxwell Boltzmann statistics. Since, all the known particles are either fermions or bosons, so Fermi Dirac and Bose Einstein these two statistics are exact statistics and in special condition they will reduce to Maxwell Boltzman statistics.

Coming back to Fermi Dirac and Bose Einstein statistics, we consider a system of 'N' identical particles, described by a wave function $\Psi(1, 2, 3\ldots. N)$ where '1' denotes the coordinates of particle '1', '2' denotes the coordinates of particle 2 and so on. Now, if we interchange the positions of any of the two particles, the wave function must either remain the same or changes sign.

If we operate an operator $\widehat{P_{12}}$ on the wave functions $\Psi(1, 2, 3\ldots. N)$ and this operator exchanges the coordinates of particles 1 and 2.

$$\widehat{P_{12}}\,\Psi(1, 2, 3\ldots. N) = \Psi(1, 2, 3\ldots. N)$$

$$= +\Psi(1, 2, 3\ldots. N)$$

$$= -\Psi(1, 2, 3\ldots. N)$$

So it turns out that whether the wave function remains the same or changes its sign is a function of the nature of the two identical particles that are exchanged.

For particles with integral spin (such as nucleus of He-4, photon etc), the wave function remains the same. In this case the wave function is called a symmetric wave function, such particles are known as bosons. So bosons have integral spins.

On the other hand, for particles with half integrals spin (such as electron, proton, etc), the wave function is called antisymmetric wave function and such particles are known as fermions. Basically for half integral spin particles we get $-\Psi(1, 2, 3 \ldots. N)$ after operating the exchange operator. Since all known particles are either fermions or bosons, so these two statistics are only exact statistics.

Since all known particles are either fermions or bosons, which are indistinguishable particles these two statistics that is Fermi Dirac (FD) and Bose-Einstein statistics (BE) are the exact distributions.

However, in the case of high-temperature and/or low density both these distributions (that is FD and BE) go over into the Boltzmann or classical distribution.

Let $E_j(N, V)$= the energy states available to a system containing ‘N’ particles.

$\in_k$= molecular quantum states,

$n_k = n_k(E_j)$ = the number of molecules in the k-th molecular state when the system itself in the j-th state with energy E_j.

So, the energy of the system in the j-th state

$$E_j(N, V) = \sum_k n_k \in_k$$

And $N = \sum_k n_k$

We know, $Q\,(N,V,T) = \sum_j e^{-\beta E_j}$……………….(1)

$$= \sum_{\{n_k\}}{}^{*}\, e^{-\beta \sum_i \epsilon_i n_i} \ldots\ldots\ldots(2)$$

summing over the states of the system is equivalent to summing over the occupation numbers of each molecular level subjected to the condition $N = \sum_k n_k$

we also know $\Theta\ (V,T,\mu) = \sum_{N=0}^{\infty} e^{\beta\mu N}\ Q\ (N,V,T)$

$$\Rightarrow\ \Theta\ (V,T,\mu) = \sum_{N=0}^{\infty} \lambda^{N}\ \sum_{\{n_k\}^*} e^{-\beta\sum_i \epsilon_i n_i}$$

$$\Rightarrow\ \Theta\ (V,T,\mu) = \sum_{N=0}^{\infty} \sum_{\{n_k\}^*} \lambda^{\sum_i n_i}\ e^{-\beta\sum_i \epsilon_i n_i}$$

Where $\lambda = e^{\beta\mu}$

$$\Rightarrow\ \Theta\ (V,T,\mu) = \sum_{N=0}^{\infty} \sum_{\{n_k\}^*} \prod_k (\lambda\ e^{-\beta\epsilon_k})^{n_k} \ \ldots\ldots\ldots..(3)$$

here k varies from 1, 2, 3.

Since, we are summing over all values of N, each n_k ranges over all possible values. So, equation (3) can be written as

$$\Theta\ (V,T,\mu) = \sum_{n_1=0}^{n_1^{max}} \sum_{n_2=0}^{n_2^{max}} \prod_k (\lambda\ e^{-\beta\epsilon_k})^{n_k}$$

$$\Rightarrow\ \Theta\ (V,T,\mu) = \sum_{n_1=0}^{n_1^{max}} (\lambda\ e^{-\beta\epsilon_1})^{n_1} \sum_{n_2=0}^{n_2^{max}} (\lambda\ e^{-\beta\epsilon_2})^{n_2}$$

$$\Rightarrow\ \Theta\ (V,T,\mu) = \prod_k \sum_{n_k=0}^{n_k^{max}} (\lambda\ e^{-\beta\epsilon_k})^{n_k} \ \ldots\ldots\ldots..(4)$$

For Fermi-Dirac statistics since no two particles can be in the same quantum state because of Pauli's exclusion principle, the maximum possible values of

$n_1^{max} = 1, n_2^{max} = 1$, and so on

Thus equation (4) becomes

$$\Theta_{FD} = \prod_k (1 + e^{-\beta\epsilon_k})^{+1} \ldots\ldots\ldots..(5)$$

$$\Theta = \prod_k \sum_{n_k=0}^{n_k^{max}} (\lambda\ e^{-\beta\epsilon_k})^{n_k}$$

For FD – statistics,

$$\Theta_{FD} = \sum_{n_1=0}^{1}(\lambda\, e^{-\beta\epsilon_1})^{n_1} \sum_{n_2=0}^{1}(\lambda\, e^{-\beta\epsilon_2})^{n_2}$$

$$= (1+\lambda e^{-\beta\epsilon_1})\,(1+\lambda e^{-\beta\epsilon_2})$$

$$= \prod_k (1+\lambda e^{-\beta\epsilon_k})^{n_k}$$

In Bose-Einstein statistics, on the other hand n_k can be 0, 1, 2, etc. since, there is no restriction on the occupancy of each state. Therefore, $n_1^{max} = \infty, n_2^{max} = \infty,$ and so on

Thus equation (4) becomes

$$\Theta_{BE} = \prod_k (1-\lambda e^{-\beta\epsilon_k})^{n_k} \ldots\ldots\ldots\ldots\ldots(6)$$

From Equation 4 we have the actual derivation I am showing now.

$$\Theta = \prod_k \sum_{n_k=0}^{n_k^{max}}(\lambda\, e^{-\beta\epsilon_k})^{n_k}$$

$$\Rightarrow \quad \Theta = \{\sum_{n_1=0}^{n_1^{max}}(\lambda\, e^{-\beta\epsilon_1})^{n_1}\}\{\sum_{n_2=0}^{n_2^{max}}(\lambda\, e^{-\beta\epsilon_2})^{n_2}\}\{\sum_{n_3=0}^{n_3^{max}}(\lambda\, e^{-\beta\epsilon_3})^{n_3}\}$$

$$\Rightarrow \quad \Theta = \{1+\lambda\, e^{-\beta\epsilon_1}+(\lambda\, e^{-\beta\epsilon_1})^2+\ldots\ldots\}\times\{1+\lambda\, e^{-\beta\epsilon_2}+(\lambda\, e^{-\beta\epsilon_2})^2+\ldots\ldots\}$$

$$\times\{1+\lambda\, e^{-\beta\epsilon_3}+(\lambda\, e^{-\beta\epsilon_3})^2+\ldots\ldots\}\times\ldots\ldots\ldots\ldots\ldots\ldots$$

Like $1+x+x^2\ldots\ldots\ldots\ldots$

So $\Theta_{BE} = \prod_k (1-\lambda e^{-\beta\epsilon_k})^{n_k}$, here we consider $e^{-\beta\epsilon_k} < 1$

So in general we can write

$$\Theta_{FD,BE} = \prod_k (1 \pm e^{-\beta\epsilon_k})^{\pm 1}$$

Where plus sign is for FD statistics and minus sign is for BE statistics.

Next we will calculate average number of particles

$$< N >= N = \sum_k n_k.$$

$$= k_B T \left(\frac{\partial \ln \Theta}{\partial \mu}\right)_{V,T}$$

Now, $\lambda = e^{\beta\mu}$

$$\Rightarrow \quad d\lambda = \beta e^{\beta\mu}\, d\mu = \beta\lambda\, d\mu$$

$$\Rightarrow \quad d\mu = \frac{1}{\beta\lambda}\, d\lambda$$

$$< N >= \; k_B T \left(\frac{\partial \ln \Theta}{\partial \lambda}\right)_{V,T} \times \frac{1}{\frac{1}{\beta\lambda}} = \lambda\left(\frac{\partial \ln \Theta}{\partial \lambda}\right)_{V,T}$$

For FD statistics,

$$\ln \Theta_{FD} = \sum_k \ln(1 + \lambda\, e^{-\beta\epsilon_k})$$

$$= \ln(1+\lambda e^{-\beta\epsilon_1}) + \ln(1 + \lambda e^{-\beta\epsilon_2}) + \ldots\ldots\ldots$$

$$\left(\frac{\partial \ln \Theta_{FD}}{\partial \lambda}\right)_{V,T} = \frac{1}{1 + \lambda e^{-\beta\epsilon_1}} \times e^{-\beta\epsilon_1} + \frac{1}{1 + \lambda e^{-\beta\epsilon_2}} \times e^{-\beta\epsilon_2}$$

$$\Rightarrow \quad \left(\frac{\partial \ln \Theta_{FD}}{\partial \lambda}\right)_{V,T} = \sum_k \frac{e^{-\beta\epsilon_k}}{1+\lambda e^{-\beta\epsilon_k}}$$

So average number of particles for FD statistics is

$$< N >_{FD} = \sum_k \frac{e^{-\beta\epsilon_k}}{1+\lambda e^{-\beta\epsilon_k}}$$

Similarly for BE statistics,

$$< N >_{BE} = \sum_k \frac{e^{-\beta\epsilon_k}}{1-\lambda e^{-\beta\epsilon_k}}$$

In general , $< N >_{FD,BE} = \sum_k \frac{e^{-\beta\epsilon_k}}{1\pm\lambda e^{-\beta\epsilon_k}}$

'+' sign is for FD statistics and '$-$' sign is for BE statistics.