Thermodynamics: Classical to Statistical

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Lecture – 27

Ideal Fermi Gas

Therefore, the average number of particles in FD and BE is given by,

$$<N>_{\substack{FD\\BE}} = \sum_k \frac{\lambda e^{-\beta\varepsilon_k}}{1 \pm \lambda e^{-\beta\varepsilon_k}}$$

We know that,

$$<N> = \sum_k \overline{n_k}$$

where, $\overline{n_k}$ is the average number of particles in the kth quantum state. Hence, we can write,

$$(\overline{n_k})_{\substack{FD\\BE}} = \frac{\lambda e^{-\beta\varepsilon_k}}{1 \pm \lambda e^{-\beta\varepsilon_k}} \quad \textbf{(1)}$$

The average energy and $\overline{P}V$ can also be written as follows,

$$<E>_{\substack{FD\\BE}} = \sum_k \varepsilon_k \overline{n_k} = \sum_k \frac{\lambda \varepsilon_k e^{-\beta\varepsilon_k}}{1 \pm \lambda e^{-\beta\varepsilon_k}}$$

$$(\overline{P}V)_{\substack{FD\\BE}} = k_B T \ln \Xi_{\substack{FD\\BE}} = \pm k_B T \sum_k \ln(1 \pm \lambda e^{-\beta\varepsilon_k})$$

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

The following points should be noted:

- The molecular partition function 'q' is NOT a relevant quantity when we are dealing with quantum statistics (i.e., FD and BE statistics).
- There are no intermolecular forces in the calculation.
- The individual particles are NOT independent because of the symmetry requirements of the wave functions.
- Both FD and BE statistics go over into Boltzmann or classical statistics in the limit of high temperature or low density, where the number of available molecular quantum states is much greater than the average number of particles in any state is very small, since most states will be unoccupied and those states that are occupied will most likely contain only 1 particle.

This means $\overline{n_k} \to 0$ in equation 1, which is achieved by $\lambda \to 0$. Thermodynamically, this means the limit of $N/V \to 0$ for fixed temperature or $T \to \infty$ for fixed N/V.

Thus, when the value of λ is small, equation 1 becomes,

$$\overline{n_k} = \lambda e^{-\beta \varepsilon_k} \quad \textbf{(2)}$$

If the average number of particles is N, then we can write,

$$< N >= N = \sum_k \overline{n_k} = \lambda \sum_k e^{-\beta \varepsilon_k}$$

Hence λ becomes

$$\lambda = \frac{N}{\sum_k e^{-\beta \varepsilon_k}}$$

Now, substituting the value of λ in equation 2, we get the population of distribution, p_k

$$\frac{\overline{n_k}}{N} = p_k = \frac{e^{-\beta \varepsilon_k}}{\sum_k e^{-\beta \varepsilon_k}}$$

The equation resembles the formula for Boltzmann distribution.

Hence, it is seen that both FD and BE statistics go over Boltzmann (classical) statistics in the limit of high temperature and low density.

Ideal Fermi Gas

From FD statistics, we get,

$$\overline{n_k} = \frac{\lambda e^{-\beta \varepsilon_k}}{1 \pm \lambda e^{-\beta \varepsilon_k}}$$

Which can be also written as,

$$f_+(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}$$

where, f_+ is the Fermi function.

Considering the above equations, we can say Fermi function is equivalent to $\overline{n_k}$.

Now, the following two cases are considered,

- **Case 1**: $T \to 0$ or $\beta \to \infty$, then,

$$f_+ = 1 \text{ if } \varepsilon < \varepsilon_F$$

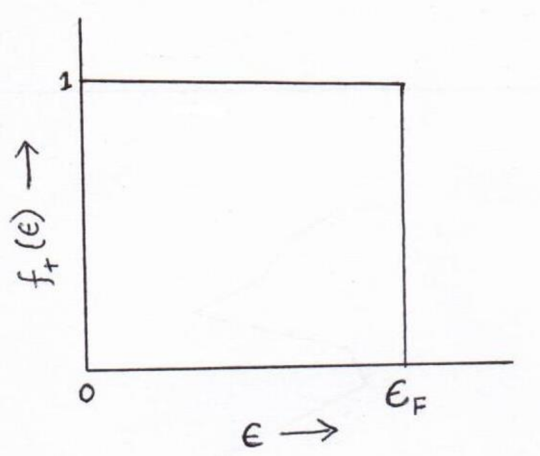
$$= 0 \text{ if } \varepsilon > \varepsilon_F$$

Using this condition, we can write,

$$\varepsilon_F = \lim_{T \to 0} \mu(T)$$

where μ is the chemical potential. Hence, Fermi energy is equal to the chemical potential when the limit of temperature tends to a very small value.

f_+ is a state function. The plot of f_+ versus ε_F, looks like,



From this plot, we can deduce that:

1. All states, up to ε_F are filled up with 1 particle.
2. All states above ε_F are empty.
3. This observation is very different from a classical gas where at zero temperature, all gas molecules would have zero energy.
4. It is a direct result of the exclusion principle which leads to an effective repulsion between fermions.

Calculation of Fermi energy (ε_F):

The total number of particles N is given by,

$$N = \sum_i f_+(\varepsilon_i) = \int_0^\infty d\varepsilon g(\varepsilon) f_+(\varepsilon)$$

where $g(\varepsilon)$ is the density of states,

$g(\varepsilon)d\varepsilon$ is number of states in energy range ε and $\varepsilon + d\varepsilon$.

For spinless particles in a box,

$$g(\varepsilon) = DV\varepsilon^{\frac{1}{2}}$$

where $D = \left(\frac{2m}{\hbar}\right)^{\frac{3}{2}} \frac{1}{4\pi^2}$ and m is the mass of fermion.

When we incorporate the idea of spin, each translational state (standing wave) corresponds to (2s+1) states since the particle has (2s+1) number of possible spin states. Thus, we can write

$$g(\varepsilon) = \widetilde{D}V\varepsilon^{\frac{1}{2}}$$

where, $\widetilde{D} = (2s+1)D$ and s is the spin of the particles. For electrons s is half.

Thus we can write average number of particles N is

$$N = \int_0^{\varepsilon_F} \widetilde{D}V\varepsilon^{\frac{1}{2}} d\varepsilon = \frac{2}{3}\widetilde{D}V\varepsilon_F^{\frac{3}{2}}$$

and from there we get,

$$\varepsilon_F = \left(\frac{3N}{2\widetilde{D}V}\right)^{\frac{2}{3}}$$

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 N}{(2s+1)V}\right)^{\frac{2}{3}}$$

where V is the volume.

This is the expression for Fermi energy.

Fermi energy depends on two quantities,

- mass of the fermion
- N/V or density of the system.

Similarly, we can also calculate the value of energy E, which is,

$$E(T=0) = \int_0^{\varepsilon_F} g(\varepsilon)\varepsilon d\varepsilon = \frac{3}{5}N\varepsilon_F$$

The conclusions that can be drawn from the above discussions are:

1. ε_F decreases with m, which is mass of the fermion.
2. ε_F increases with density N/V.
3. ε_F defines a characteristic temperature, T_F, which satisfies the equation, $\varepsilon_F = k_B T_F$
4. At zero temperature, there is a finite energy per particle, $\varepsilon = \frac{3}{5}\varepsilon_F$

$$\frac{E}{N} = \varepsilon = \frac{3}{5}\varepsilon_F$$

- **Case 2:**

The temperature limit is very low but finite. We know the Fermi function is

$$f_+(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)}+1}$$

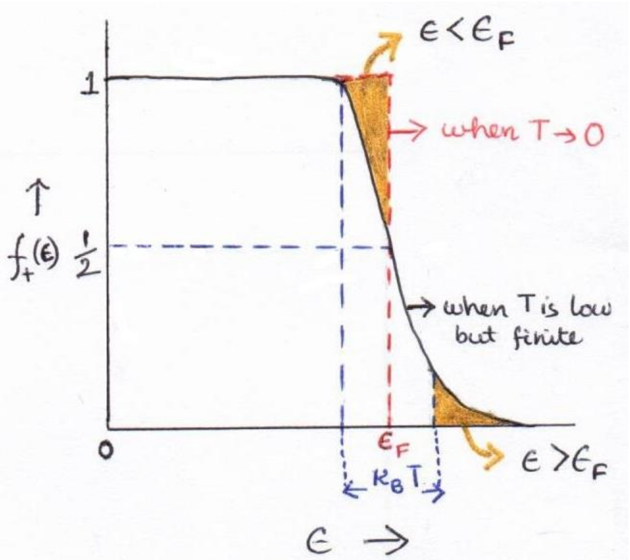
When T is low but finite we can write

$$f_+(\varepsilon) = 1 \text{ if } e^{\beta(\varepsilon-\mu)} << 1$$

$$= 0 \text{ if } e^{\beta(\varepsilon-\mu)} >> 1$$

$$= 1/2 \text{ if } \varepsilon=\mu << 1$$

The plot f plus versus epsilon, for this case, looks like this



This red line represents when $T \to 0$ and the black line represents when T is low but finite. If we concentrate on the upper yellow shaded region, we observe that in this region the value of $\varepsilon < \varepsilon_F$ but the states are unoccupied. Now, if we consider the lower yellow coloured region, we find here that the $\varepsilon > \varepsilon_F$, but the states are filled with finite probability. This is very different from the case of absolute temperature goes to 0.