Fermi-Dirac statistics

Fermi-Dirac distribution

Matter particles that are elementary mostly have a type of angular momentum called *spin*. These particles are known to have a magnetic moment which is attributed to spin. Particles that have half odd-integral values of spin ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$) are called *fermions*[1]. Electron, proton, neutron, neutrino etc are all fermions. A system with two fermions, labelled A and B, located at $\mathbf{x}_1$ and $\mathbf{x}_2$ have a wavefunction that is antisymmetric under the exchange of particles.

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \left(\psi^A(\mathbf{x}_1)\psi^B(\mathbf{x}_2) - \psi^B(\mathbf{x}_2)\psi^A(\mathbf{x}_1) \right) = -\psi(\mathbf{x}_2, \mathbf{x}_1)$$

It is clear from the above that if we interchange the locations of the two fermions, the wavefunction only changes by a sign. $|\psi(\mathbf{x}_1, \mathbf{x}_2)|^2$ does not change and thus the probability densities do not change under this interchange. The two fermions are said to be *indistinguishable*.

One important consequence of the above wavefunction is that it vanishes if we put $\mathbf{x}_1 = \mathbf{x}_2$. This means that two identical (indistinguishable) fermions cannot be found in the same position. More generally, it is true that two identical fermions cannot be found in same state. This fact is called *Pauli's exclusion principle*. This property makes it interesting to find the distribution of fermions collected inside a box held at some temperature.

We will consider a box of N fermions. Each fermion is allowed to have one of the m different values of energy $E_1, E_2, \ldots, E_m$. Let $g_1, g_2, \ldots, g_m$ be the number of ways of occupying each of these energy levels. If $n_1, n_2, \ldots, n_m$ be the number of particles in each of these energy levels the total energy E, we have

$$N = n_1 + n_2 + \ldots + n_m = \sum_{i=1}^{m} n_i \tag{1}$$

$$E = n_1 E_1 + n_2 E_2 + \ldots + n_m E_m = \sum_{i=1}^{m} n_i E_i \tag{2}$$

We will now derive a formula for the *occupation number* - the number of particles n_i in the i^{th} energy level as a function of the energy E_i of that level. With this objective we will count the number of ways N fermions can be distributed in the manner described above. Starting with the first energy level E_1, the n_1 particles that occupy this level has g_1 ways to do it. These can be thought of as g_1 cells, all corresponding to energy E_1. We need to fill these cells by requiring Pauli's exclusion principle to hold. This means that we can put at most one fermion per cell. Thus at most one particle can go into one cell. Clearly this requires $g_1 \gg n_1$.

We will first find the number of ways n_1 fermions can be distributed into g_1 cells. Taking the first fermion, it has all the g_1 cells open to it. After the first one is provided a cell, the second fermion has $g_1 - 1$ cells to choose from. There are $g_1(g_1 - 1)$ of filling the first two

[1]Those that have integral values of spin $(0, 1, 2, \ldots)$ are *bosons*.

fermions. Continuing this, we can see that there are $g_1(g_1-1)\dots(g_1-n_1+1)$ ways of filling n_1 fermions into g_1 cells. We can write this count as

$$g_1(g_1-1)\dots(g_1-n_1+1)=\frac{g_1!}{(g_1-n_1)!}$$

These n_1 fermions are identical and any of their permutations must be indistinguishable. Thus the number of distinct ways in which n_1 fermions can be filled in g_1 cells is

$$\frac{g_1!}{n_1!(g_1-n_1)!} \tag{3}$$

Similarly the number of distinct ways to fill n_2 fermions in g_2 cells is

$$\frac{g_2!}{n_2!(g_2-n_2)!}$$

The number of distinct ways to fill n_1 fermions in g_1 cells, n_2 fermions in g_2 cells,..., n_m fermions in g_m cells gives us the thermodynamic probability

$$W(E)=\frac{g_1!}{n_1!(g_1-n_1)!}\ \frac{g_2!}{n_2!(g_2-n_2)!}\cdots\frac{g_m!}{n_m!(g_m-n_m)!} \tag{4}$$

Taking a logarithm of this we get

$$\ln W(E)=\ln\frac{g_1!}{n_1!(g_1-n_1)!}+\ln\frac{g_2!}{n_2!(g_2-n_2)!}+\ldots+\ln\frac{g_m!}{n_m!(g_m-n_m)!}=\sum_{i=1}^{m}\ln\frac{g_i!}{n_i!(g_i-n_i)!} \tag{5}$$

For $g_i \gg 1$, $n_i \gg 1$, we can use the Stirling's approximation to simplify eqn(**??**) to obtain

$$\begin{aligned}\ln W(E) &= \sum_{i=1}^{m}\left[g_i\ln g_i-g_i-n_i\ln n_i+n_i-(g_i-n_i)\ln(g_i-n_i)+g_i-n_i\right]\\ &= \sum_{i=1}^{m}\left[g_i\ln g_i-n_i\ln n_i-(g_i-n_i)\ln(g_i-n_i)\right]\end{aligned} \tag{6}$$

We put this box in contact with a heat bath and let it reach equilibrium. After it reaches equilibrium if we observe this box for a short enough period of time we see no change in energy, ie. E remains constant[2]. This requires

$$\Delta E=0 \implies \sum_{i=1}^{m}E_i\Delta n_i=0 \tag{7}$$

At equilibrium, the amount of energy supplied or taken by the heat bath is not sufficient to affect energy values E_i or allowed for the individual particles nor their degeneracies g_i. Therefore neither the E_i nor g_i varies at equilibrium.

[2]Even if we observe for long enough times, we will see fluctuations of energy ΔE that are too small compared to the energy E. Thus the system can be considered to be at equilibrium for all times

Note that the total number of particles N always remain the same despite the variation in the occupation numbers n_i. Thus

$$\Delta N = 0 \;\Rightarrow \sum_{i=1}^{m} \Delta n_i = 0 \tag{8}$$

Further the thermodynamic probability $W(E)$ will be maximum at equilibrium, which requires $\Delta W(E)$ to vanish at the equilibrium value of energy. $\Delta \ln W(E)$ also vanishes at the same values of energy at which $\Delta W(E)$ vanishes.

$$\Delta \ln W(E) = \frac{\Delta W(E)}{W(E)} = 0 \tag{9}$$

Using the form of $W(E)$ obtained in eqn(6), we can write the condition in eqn(8) as

$$\begin{aligned}
& \Delta \ln W(E) = 0 \\
\Rightarrow \quad & \sum_{i=1}^{m} \left[-\Delta n_i \ln n_i - n_i \frac{\Delta n_i}{n_i} + \Delta n_i \ln(g_i - n_i) + (g_i - n_i)\frac{\Delta n_i}{g_i - n_i} \right] = 0 \\
\Rightarrow \quad & \sum_{i=1}^{m} \left(\ln \frac{g_i - n_i}{n_i} \right) \Delta n_i = 0 \qquad (10)
\end{aligned}$$

We must require the condition in eqn(10) to hold along with the conditions in eqn(7) and eqn(8). It is obvious that if we multiply an arbitrary constant γ' (that is independent of n_i) to the left hand side of eqn(10) it must still vanish.

$$\gamma' \sum_{i=1}^{m} \left(\ln \frac{g_i - n_i}{n_i} \right) \Delta n_i = 0 \tag{11}$$

Similarly, multiplying eqn(7) and eqn(8) with arbitrary constants β' and α'

$$\beta' \sum_{i=1}^{m} E_i \Delta n_i = 0 \tag{12}$$

$$\alpha' \sum_{i=1}^{m} \Delta n_i = 0 \tag{13}$$

Clearly if sum the left hand sides of eqns(11,12, 13) it must vanish too.

$$\sum_{i=1}^{m} \left(\gamma' \ln \frac{g_i - n_i}{n_i} + \beta' E_i + \alpha' \right) \Delta n_i = 0 \tag{14}$$

Now, the only way eqn(14) can be satisfied for arbitrary variations Δn_i is if its coefficient vanishes for each Δn_i.

$$\gamma' \ln \frac{g_i - n_i}{n_i} + \beta' E_i + \alpha' = 0 \tag{15}$$

Dividing through out by γ' and defining new arbitrary constants $\alpha = \frac{\alpha'}{\gamma'}$ and $\beta = \frac{\beta'}{\gamma'}$, we can rewrite eqn(15) as

$$\begin{aligned}
& \ln \frac{g_i - n_i}{n_i} + \beta'' E_i + \alpha'' = 0 \\
\Rightarrow & \ln \frac{g_i - n_i}{n_i} = -\beta'' E_i - \alpha'' \qquad (16)
\end{aligned}$$

Exponentiating this eqn(16) and writing n_i in terms of the rest of the quantities

$$n_i = \frac{g_i}{e^{-\alpha''}e^{-\beta''' E_i} + 1} \tag{17}$$

In order to evaluate the arbitrary constant β'' we will supply a small amount of energy to this box of fermions at a fixed volume and find out by how much the entropy changes. The rate of change of entropy with energy at constant volume is the inverse of the temperature of the system in absolute scale (Kelvins).

$$\frac{1}{T} = \frac{\Delta S}{\Delta E}\bigg|_V \tag{18}$$

When a small amount of energy ΔE is supplied it leads to a change in the number of fermions n_i in different energy levels $\Delta E = \sum_{i=1}^{m} \Delta n_i E_i$. The amount of energy supplied will be insufficient to change the nature of the energy levels E_i of individual fermions or their degeneracies g_i and hence these remain constant.

$$\Delta E_i = 0; \qquad \Delta g_i = 0$$

The entropy of the system is found using eqn(6) to be

$$S = k_B \ln W(E) \simeq k_B \sum_{i=1}^{m} \left[g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln(g_i - n_i)\right] \tag{19}$$

We have used Stirling's approximation to get the final expression in eqn(19).
The change in entropy due to an excess energy ΔE is obtained from eqn(19) as

$$\begin{aligned}
\Delta S &= k_B \sum_{i=1}^{m} \left[-n_i \frac{\Delta n_i}{n_i} - \Delta n_i \ln(n_i) + \Delta n_i \ln(g_i - n_i) + (g_i - n_i)\frac{\Delta n_i}{g_i - n_i}\right] \\
&= k_B \sum_{i=1}^{m} \left[\Delta n_i \ln \frac{g_i - n_i}{n_i}\right] \qquad (20)
\end{aligned}$$

Substituting the expression for $\frac{g_i}{n_i}$ from eqn(17) into eqn(20)

$$\begin{aligned}
\Delta S &= k_B \sum_{i=1}^{m} \Delta n_i \left(\ln e^{-\alpha'' - \beta'' E_i}\right) = k_B \sum_{i=1}^{m} \Delta n_i (-\alpha'' - \beta'' E_i) \\
&= -k_B \alpha'' \sum_{i=1}^{m} \Delta n_i - k_B \beta'' \sum_{i=1}^{m} \Delta n_i E_i \qquad (21) \\
&= -\beta'' k_B \Delta E \qquad (22)
\end{aligned}$$

In eqn(21), the first sum is zero as the total number of particle remain unchanged (as in eqn(8) and the second sum gives us the quantity in eqn(22).
Using the result of eqn(22) in eqn(18) we get

$$\begin{aligned}
\frac{\Delta S}{\Delta E} &= -\beta'' k_B = \frac{1}{T} \\
\beta'' &= -\frac{1}{k_B T} \qquad (23)
\end{aligned}$$

This fixes the arbitrary constant β. Substituting this into eqn(17) we get the *Fermi-Dirac distribution* for the occupation number as

$$n_i = \frac{g_i}{e^{-\alpha''} e^{\frac{E_i}{k_B T}} + 1} \tag{24}$$

Now consider the box of N fermions at $T = 0K$. At absolute zero all the particles tend to sit at the lowest possible energy level available to them. But fermions obey Pauli's exclusion principle and only one at a time can occupy any quantum state. If the total number of fermions N is much greater than the degeneracy g_1 of the lowest energy level E_1, the remaining fermions will have to occupy the remaining lower energy levels. Thus, even at $T = 0K$ there could be fermions up to a certain energy level E_F. This energy level is called the *Fermi level* of the system. At $T = 0K$, or energy levels with $E_i \leq E_F$, will have all the g_i cells will be filled up by one fermion each. The number of fermions in such energy levels will be thus equal to the number cells, $n_i = g_i$. For energy levels with $E_i > E_F$ we find no fermions $n_i = 0$. Thus the ratio

$$\frac{n_i}{g_i} = \begin{cases} 1 & \text{for } E \leq E_F; \\ 0 & \text{for } E > E_F \end{cases}$$

From Fermi-Dirac probability distribution in eqn(24) we see that this ratio is

$$\frac{n_i}{g_i} = \frac{1}{e^{-\alpha''} e^{\frac{E_i}{k_B T}} + 1} \tag{25}$$

The expression in eqn(25) on the right hand side has the desired behaviour if $\alpha'' = \frac{E_F}{k_B T}$ as explained below.
At $T = 0K$ for $E_i < E_F$, the quantity $\frac{E_i - E_F}{k_B T}$ becomes $-\infty$. Then the expression on the RHS of eqn(25) becomes

$$\frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = 1$$

This matches with the expected value of $n_i = g_i$.
At $T = 0K$ for $E_i > E_F$, the quantity $\frac{E_i - E_F}{k_B T}$ becomes ∞. Then the expression on the RHS of eqn(25) becomes

$$\frac{1}{e^{\infty} + 1} = \frac{1}{\infty + 1} = 0$$

Again the expected value $n_i = 0$ is reproduced correctly.
Thus having fixed both the arbitrary constants we can write down the Fermi-Dirac distribution as

$$n_i = \frac{g_i}{e^{\frac{E_i - E_F}{k_B T}} + 1} \tag{26}$$

At $T = 0K$, this distribution is, strictly speaking, not valid for $E = E_F$. Mathematically this is because the ratio $\frac{E_i - E_F}{k_B T}$ is undetermined in this case. Physically, this indicates an ambiguity for the number of fermions n_F at this energy level as all the g_F cells corresponding to this energy value need not be filled up. However at any finite temperature $T \neq 0K$, Fermi level is the energy value at which the ratio $\frac{n_i}{g_i} = \frac{n_F}{g_F} = \frac{1}{2}$.
Next we will use Fermi-Dirac distribution to obtain the energy distribution of electrons in metals.