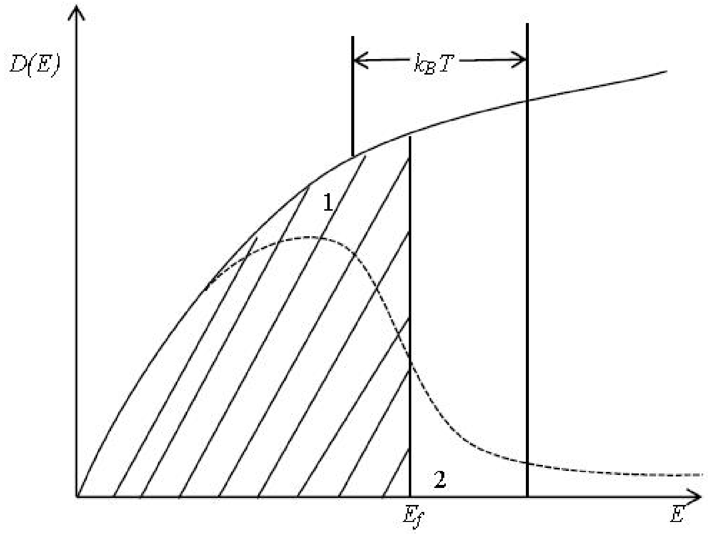
$\Rightarrow N = \frac{V}{3\pi^2}(\frac{2mE}{\hbar^2})^{\frac{3}{2}}$

$\frac{N}{E} = \frac{V}{3\pi^2}(\frac{2m}{\hbar^2})^{\frac{3}{2}}E^{\frac{1}{2}}$

$\frac{3N}{2E} = \frac{V}{2\pi^2}(\frac{2m}{\hbar^2})^{\frac{3}{2}}E^{\frac{1}{2}}$

$\frac{3N}{2E} = D(E)$

A graph of density of orbitals $D(E)$ against energy is of the form shown below:



The shaded area represents filled orbital at absolute zero (Fermi surface). A dashed curve represents density $f(E,T)D(E)$ of filled orbital at a finite temperature such that k_BT is small in comparison with E_f. The average energy is increased when the temperature is increased from 0 to T, for electrons thermally excited from region 1 to region 2.

FERMI DIRAC DISTRIBUTION FUNCTION

As seen earlier when electrons are filling the energy levels, two electrons occupy the lowest energy level, two or more the next level and the process continues until all the electrons in the metal have been accomodated. The distribution of electrons among the levels is best described by the distribution function $f(E)$ which is defined as the probability that the level E is occupied by an electron.

At T=0 K the distribution function takes the form

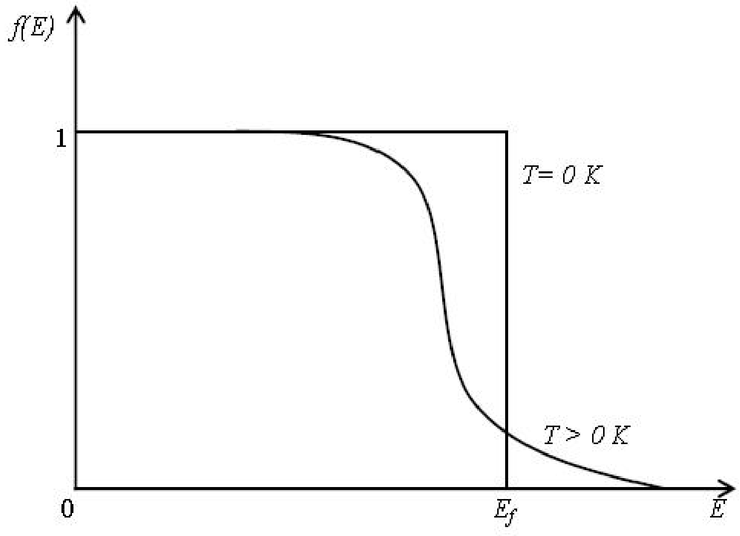
$$f(E) = \begin{cases} 1 \quad ; \ E < E_f, \\ \\ 0 \quad ; \ E_f < E, \end{cases}$$

The distribution means that all levels below E_f are completely filled and those above E_f are completely empty.

At $T \neq 0K$, $f(E)$ is given by $f(E) = \frac{1}{e^{\frac{E-\mu}{k_B T}}+1}$, where μ is a chemical potential usually a function of temperature. The function is known as the Fermi-Dirac distribution function.

At T=0 K; $\mu = E_f$ and $f(E) = 0$.

A graph of $f(E)$ against E is as shown;



Note: The distribution at $T \neq 0K$ is substantially the same as in T=0 K except very close to the fermi level where some of the electrons are excited from below E_f to above it. When the system is heated, thermal energy excites the electrons but this energy is not shared equally by all the electrons as would be the case in classical treatment. This is because the electrons lying below the fermi level E_f cannot absorb energy. If they did then they would move to higher level which would already be occupied, thus violating Pauli-exclusion principle. Thus only those electrons close to the fermi level can be excited because the levels above E_f are empty and hence they would move to those levels without violating Pauli exclusion principle. The above statement means that the fermi surface is not affected appreciably by temperature because as seen when the temperature is increased only those electrons close to the fermi surface are excited from the inside to the outside of the fermi sphere. Since they are few, they have very little effect over all. Thus fermi surface has an independent permanent identity and should be regarded as a real physical characteristic of the metal.

ELECTRONIC HEAT CAPACITY

In statistical mechanics the free particle has a heat capacity of $\frac{3}{2}k_B$. For N atoms, then heat capacity is equal to $\frac{3}{2}Nk_B$.

However the observed electronic contributions at room temperature is usually less than 0.01 of this value. To account for this discrepancy we shall use Fermi's finding which recognise that the specific heat varnishes at absolute zero and that at low temperatures it is proportional to absolute temperature.

When a specimen is heated from absolute zero, not every electrons gain energy $\approx k_BT$ as expected but only those electrons in orbitals within the energy range k_BT of the fermi level are thermally excited.

For a system of N electrons heated from 0 K to a temperature T, for $k_B << E_f$, then the increase in internal energy is given by

$\Delta U = \int_{E_f}^{\infty}(E - E_f)f(E)D(E)dE + \int_0^{E_f}(E_f - E)[1 - f(E)]D(E)dE$=A+B, where A represents energy needed to take electrons from E_f to orbitals of energy $E > E_f$, B is the energy needed to bring the electron to E_f from orbitals below E_f.

$f(E)D(E)dE$ is the number of electrons elevated to orbitals in the energy range dE at an energy E.

$[1 - f(E)]$ is the probability that an electron has been removed from an orbital E.

From $\int_x^y = \int_x^0 + \int_0^y = \int_x^0 - \int_y^0 = \int_0^y - \int_0^x$

Thus $\Delta U = [\int_0^\infty - \int_0^{E_f}](E - E_f)f(E)\Delta(E)dE - \int_0^{E_f}(E - E_f)[1 - f(E)]\Delta(E)dE.$

$\Delta U = \int_0^\infty (E - E_f)f(E)\Delta(E)dE - \int_0^{E_f}(E - E_f)\Delta(E)dE.$

The electronic heat capacity is given by $C_{el} = \frac{dU}{dT}$,

$C_{el} = \frac{d}{dT}\int_0^\infty (E - E_f)f(E)\Delta(E)dE - \int_0^{E_f}(E - E_f)\Delta(E)dE.$

Since E_f is a constant and E and $\Delta(E)$ are temperature independent, the second term vanishes;

$C_{el} = \int_0^\infty (E - E_f)\Delta(E)\frac{df(E)}{dT}dE.$

Recall that $f(E) = \frac{1}{e^{\frac{E-\mu}{k_BT}}+1}.$

When $k_BT << E_f$, $\mu = E_f$ and $k_BT = \tau$.

$\Rightarrow f(E) = \frac{1}{e^{\frac{E-E_f}{\tau}}+1}.$

From $\tau = k_BT$, $\frac{d\tau}{dT} = k_B$.

But $\frac{df}{d\tau} = (\frac{E-E_f}{\tau^2}.\frac{e^{\frac{E-E_f}{\tau}}}{(e^{\frac{E-E_f}{\tau}}+1)^2}.$

From chain rule, $\frac{df}{dT} = \frac{df}{d\tau}.\frac{d\tau}{dT}.$

$\Rightarrow \frac{df}{dT} = k_B(\frac{E-E_f}{\tau^2})\frac{e^{\frac{E-E_f}{\tau}}}{(e^{\frac{E-E_f}{\tau}}+1)^2}.$

Let $x = \frac{E-E_f}{\tau}$

$dE = \tau dx = k_BT dx$

Changing the limits gives,

$C_{el} = \Delta(E)\int_{-\frac{E_f}{\tau}}^{\infty} k_B\frac{x^2e^x}{(e^x+1)^2}dE$

E	x
0	-$\frac{E_f}{\tau}$
∞	∞

$C_{el} = \Delta(E)\int_{-\frac{E_f}{\tau}}^{\infty} \frac{k_B x^2 e^x}{(e^x+1)^2} k_B T dx$

$C_{el} = k_B^2 T\Delta(E)\int_{-\frac{E_f}{\tau}}^{\infty} \frac{x^2 e^x}{(e^x+1)^2} dx$

For $k_B T << E_f$, $\tau = k_B T \to 0$ as $T \to 0$.

$\Rightarrow -\frac{E_f}{\tau} \to \infty$ and $E \approx E_f$.

$C_{el} = k_B^2 T\Delta(E_f)\int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x+1)^2} dx$

$C_{el} = 2k_B^2 T\Delta(E_f)\int_{0}^{\infty} \frac{x^2 e^x}{(e^x+1)^2} dx$

Using standard integrals, $\int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x+1)^2} dx = \frac{\pi^2}{3}$.

$\Rightarrow \int_{0}^{\infty} \frac{x^2 e^x}{(e^x+1)^2} dx = \frac{\pi^2}{6}$.

$C_{el} = k_B^2 T\Delta(E_f).\frac{\pi^2}{3}$.

$C_{el} = \frac{1}{3}k_B^2 T\pi^2\Delta(E_f)$.

But $\Delta(E_f) = \frac{dN}{dE_f}$.

where $N = \frac{V}{3\pi^2}(\frac{2mE_f}{\hbar^2})^{\frac{3}{2}} = \frac{V}{3\pi^2}(\frac{2m}{\hbar^2})^{\frac{3}{2}}E_f^{\frac{1}{2}}E_f$.

$\Rightarrow \frac{N}{E_f} = \frac{V}{3\pi^2}(\frac{2m}{\hbar^2})^{\frac{3}{2}}E_f^{\frac{1}{2}}$.

$\frac{dN}{dE_f} = D(E_f) = \frac{3}{2}\frac{V}{3\pi^2}(\frac{2m}{\hbar^2})^{\frac{3}{2}}E_f^{\frac{1}{2}}$.

$D(E_f) = \frac{3}{2}\frac{N}{E_f}$.

Hence $C_{el} = \frac{1}{3}\pi^2 k_B^2 T.\frac{3}{2}\frac{N}{E_f}$.

$C_{el} = \frac{1}{2}\pi^2 k_B^2 T(\frac{N}{E_f})$.

For a free electron system, $E_f = k_B T_f$;

T_f is the fermi temperature.

Thus $C_{el} = \frac{1}{2}\pi^2 k_B^2 T(\frac{N}{k_B T_f})$.