Free Electron Gas \( T > 0 \)

For the free electron gas at \( T = 0 \) we saw that the energy per unit volume is:

\[
E = \int_0^{E_F} E g(E) \, dE
\]

where:

\[
g(E) \, dE = \text{number of electron states (including spin) per unit volume with energy } E \rightarrow E + dE
\] - (1)

Previously we found that the density of energy states is:

\[
g(E) = \begin{cases} \frac{2m}{h^2 \pi^2} \sqrt{\frac{m}{2\hbar^2}} \sqrt{E} & \text{for } E \leq E_F \\ 0 & \text{for } E > E_F \end{cases}
\]

The density of states arises from the distribution of energy eigenstates for single electrons. We now rewrite this as:

\[
g(E) = \frac{2m}{h^2 \pi^2} \sqrt{\frac{m}{2\hbar^2}} \sqrt{E}
\] - (2)

for all values of \( E \). We then introduce the probability that a given state with energy \( E \) is occupied:

\[
f(E) = \text{probability that a given state with energy } E \text{ is occupied.}
\] - (3)
For the free-electron gas at T=0:

\[ f(E) = \begin{cases} 
1 & E \leq E_F \\
0 & E > E_F 
\end{cases} \]  

Thus:

\[ E = \int_0^\infty E \ g(E) \ f(E) \, dE \]  

Now suppose that the temperature is no longer $T=0$. We expect that there will be some fluctuations in which energy states are occupied. It may be possible that energy states beyond the Fermi surface are occupied while some within the Fermi surface are unoccupied. Such fluctuations will manifest themselves in the electron probability density $f(E)$.

We can apply Fermi-Dirac statistics to compute $f(E)$ at any temperature $T$. The results are:

\[ f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1} \]  

where $\mu$ is called the chemical potential. In a preliminary study of metals, $\mu \approx E_F$ and this to a good approximation:

\[ f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1} \]
Let's plot this for various temperatures. For $T=0$ we get:

\[
\begin{align*}
    f(E) & \rightarrow \begin{cases} 
    1 & E < E_F \\
    0 & E > E_F 
    \end{cases} \\
    & T=0
\end{align*}
\]

At $T \neq 0$ we always have:

\[
\begin{align*}
    f(E_F) &= \frac{1}{2} \\
    f(E) &\rightarrow 0 \quad \text{as } E \rightarrow \infty
\end{align*}
\]

Now consider a metal at room temperature $T=300K$. Then $E_F \approx 5eV$ and $E_F/k_B T = 5/8.6 \times 10^{-5} \times 300 \approx 20$ and we get:

\[
\begin{align*}
    f(E) &\approx \frac{1}{e^{E/k_B T} e^{-20} + 1} \\
    &\rightarrow 1 \quad \text{as } E \rightarrow 0
\end{align*}
\]

In fact when $E = E_F - k_B T$

we get:

\[
\begin{align*}
    f(E) &= \frac{1}{e^{-1} + 1} = \\
\end{align*}
\]

and when $E = E_F - k_B T$ we get:

\[
\begin{align*}
    f(E) &= \frac{1}{e^{-2} + 1} = \\
\end{align*}
\]
Plotting the curve gives:

Exercise: Determine when \( f(e) = 0.9 \)

\[
\begin{align*}
f(e) &= 0.9 \\
\Rightarrow \quad \frac{(0.9)}{e^{+(E-E_F)/k_BT+1}} &= 1 \\
\Rightarrow \quad e^{(E-E_F)/k_BT} &= \frac{1}{0.9} \\
\Rightarrow \quad (E-E_F)/k_BT &= \ln \left(\frac{1}{0.9}\right) \\
\Rightarrow \quad E-E_F &= -k_BT \ln 0.9 \\
\Rightarrow \quad E &= E_F - k_BT \ln 0.9.
\end{align*}
\]

\[
\begin{align*}
f(e) &= 0.1 \\
\Rightarrow \quad \frac{(E-E_F)/k_BT}{k_BT} &= \ln 0.9 \\
\Rightarrow \quad E &= E_F + k_BT \ln 0.9.
\end{align*}
\]

Thus, the significant fluctuations all take place within a range of a few multiples of \( k_BT \) from the Fermi energy.
Heat capacity.

The total energy of the metal is:

$$E = \int_{0}^{\infty} E_g(e) f(e) \, de.$$  

and, in principle, you could calculate this by substituting from (2) and (3). But the integral cannot be evaluated easily.

An approximate sense of the behavior with changes in temperature can be gained as follows:

- At the ground state \((T=0)\) double the energy by \(E_0\).
- At temperature \(T\) a portion \(\Delta E\) electrons with energies in the range \(E_F - k_B T \rightarrow E_F\) have been excited into \(E_F \rightarrow E_F - k_B T\). Each electron doing so gains energy about \(2k_B T\). The number so excited depends on the frequency range — it is proportional.

Thus \(\Delta E \sim (k_B T)^2\)

and \(\frac{\Delta E}{\Delta T} \sim k_B T\).

We see that the specific heat is linear in \(T\). A more precise calculation gives:

$$E = E_0 + \frac{\pi^2}{6} (k_B T)^2 g(E_F).$$
Thus: the heat capacity per volume is:

\[ C = \frac{\pi^2}{3} k_B^2 T \ g(E_F). \]

where \( E_F \).

**Exercise:** Show that the heat capacity per mole is

\[ C_V = \frac{\pi^2}{2} \left( \frac{k_B T}{E_F} \right) \cdot R. \]

**Answer:**

\[ g(E_F) = \frac{2m}{\hbar^2 \pi^2} \sqrt{\frac{m}{2\hbar^2}} \sqrt{E_F}. \]

\[ = \frac{\sqrt{2} m^{3/2}}{(\hbar^2)^{3/2} \pi^2} \frac{1}{E_F} \frac{E_F^{3/2}}{E_F} \]

\[ = \frac{\sqrt{2} m^{3/2}}{(\hbar^2)^{3/2} \pi^2} \frac{1}{E_F} \frac{(\hbar^2)^{3/2}}{E_F} \frac{(3\pi^2 \hbar^2)}{3}\]

\[ = \frac{3n}{2E_F} \]

for one mole

\[ \Rightarrow C_V = \frac{\pi^2}{3} k_B^2 T \frac{3n}{2E_F} \text{ V one mole} \]

\[ = \frac{\pi^2}{2} \left( \frac{k_B T}{E_F} \right) \cdot n \text{ k} \text{B V one mole} \]

\[ = \frac{\pi^2}{2} R \left( \frac{k_B T}{E_F} \right) \]