
Now consider the thermal properties of the conduction electrons. Again we shall calculate the average energy of an entire gas consisting of $N$ electrons. We shall use this to determine the specific heat capacity of the electron gas.

The statistical mechanics treatment requires us to:

1) describe the states of one electron

2) determine the probability that any electron is in one of these states.

The state of one electron is described by its position and momentum, $\mathbf{x}$ and $\mathbf{p}$. In general we divide the position and momentum co-ordinates into discrete blocks. For example, the possible position values can be divided into rectangles of dimensions $dx, dy, dz$.

\[ \int_{dx} \int_{dy} \]

A similar decomposition can be done for the $\mathbf{p}$ values. Thus we divide the possible $\mathbf{x}$ and $\mathbf{p}$ values into ranges:

\[
\begin{align*}
    & x \rightarrow x + dx & p_x \rightarrow p_x + dp_x \\
    & y \rightarrow y + dy & p_y \rightarrow p_y + dp_y \\
    & z \rightarrow z + dz & p_z \rightarrow p_z + dp_z
\end{align*}
\]
Thus specifying a state consists of specifying one of these blocks. The probability with which an electron is in this state is:

\[
\text{Prob (electron in } \mathbf{x} \to \mathbf{x} + d^3x \text{ and } \mathbf{p} \to \mathbf{p} + d^3\mathbf{p}) = \frac{e^{-E(\mathbf{x},\mathbf{p})/k_B T} d^3x \, d^3\mathbf{p}}{\int d^3\mathbf{p} \int d^3x \, e^{-E(\mathbf{x},\mathbf{p})/k_B T}}
\]

\[-(1)\]

Where \( E \) is the energy in of an electron with position \( \mathbf{x} \) and momentum \( \mathbf{p} \). For non-interacting electrons:

\[
E = \frac{1}{2m_e} \mathbf{p}^2.
\]

\[-(2)\]

and we note that the distribution of states does not depend on \( \mathbf{x} \). It follows that:

The state of an electron is completely specified in terms of \( \mathbf{p} \).

Thus we need to compute:

\[
\text{Prob (electron in state } \mathbf{p} \to \mathbf{p} + d\mathbf{p}) = \int \text{Prob (electron in } \mathbf{x} + \mathbf{d}x \text{ and } \mathbf{p} \to \mathbf{p} + d\mathbf{p}) \, d^3x.
\]

\[-(3)\]

Now consider substituting from (1) into (3). First evaluate the denominator of (1).
Then:

\[ \int d^3\vec{p} \int d^3\vec{x} \ e^{-\frac{\vec{p}^2}{2mk_BT}}. \]

\[ = \int_{-\infty}^{\infty} dp_x \ e^{-\frac{P_x^2}{2mk_BT}} \int_{-\infty}^{\infty} dp_y \ e^{-\frac{P_y^2}{2mk_BT}} \int_{-\infty}^{\infty} dp_z \ e^{-\frac{P_z^2}{2mk_BT}} \int d^3\vec{x} \]

Each of these is a Gaussian integral giving

\[ \sqrt{\frac{1}{2\pi mk_BT}} \]

Thus the denominator gives:

\[ V \left( 2\pi mk_BT \right)^{3/2} \]

Now substituting into (3) gives:

\[ \text{Prob} (\vec{p} \rightarrow \vec{p} + d\vec{p}) = \frac{1}{V \left( 2\pi mk_BT \right)^{3/2}} V e^{-\frac{\vec{p}^2}{2mk_BT}} d^3\vec{p}. \]

and thus for a single electron:

\[ \text{Prob} (\vec{p} \rightarrow \vec{p} + d\vec{p}) = \frac{1}{(2\pi mk_BT)^{3/2}} e^{-\frac{\vec{p}^2}{2mk_BT}} d^3\vec{p}. \] - (4)
Exercise: Show that if there are $N$ electrons in volume $V$ then, the average number of electrons per unit volume with momentum in region $\vec{p} \rightarrow \vec{p} + d^3\vec{p}$ is:

\[
N \frac{1}{(2\pi mk_bT)^{3/2}} e^{-\frac{\vec{p}^2}{2mk_bT}} d^3\vec{p}
\]  \quad -(5)

where $n = N/V$.

Exercise: Show that

\[
\int f_{ce}(\vec{p}) \, d^3\vec{p} = n
\]

where

\[
f_{ce}(\vec{p}) = n \frac{1}{(2\pi mk_bT)^{3/2}} e^{-\frac{\vec{p}^2}{2mk_bT}}.
\]

Average energy + heat capacity

If there are $n$ atoms per unit volume, then the average energy is:

\[
E = \int d^3\vec{p} \frac{\vec{p}^2}{2m} \frac{1}{n} f_{ce}(\vec{p})
\]

\[
= \frac{1}{2m} \frac{1}{(2\pi mk_bT)^{3/2}} \int \vec{p}^2 e^{-\frac{\vec{p}^2}{2mk_bT}} d^3\vec{p}
\]

and converting from $(p_x, p_y, p_z) \rightarrow (p, \theta, \phi)$ gives

\[
E = \frac{1}{2m} \frac{1}{(2\pi mk_bT)^{3/2}} 4\pi \int_0^\infty p^4 e^{-\frac{p^2}{2mk_bT}} dp
\]
which implies that

\[ E = \frac{3m k_b T}{2m} = \frac{3}{2} k_b T. \]

Thus for one mole of such a gas:

\[ E = \frac{3}{2} N k_b T. \]

The specific heat is just \( \frac{\partial E}{\partial T} \) and this gives:

\[ C_v = \frac{3}{2} R. \tag{7} \]

Implications for heat capacity of solids.

The heat capacity for solids will contain contributions from both the lattice and the conduction electrons. Thus

\[ C = C_e + C_{ph} \]

\[ \text{conduction electrons} \quad \text{and lattice phonons} \]

At high temperatures:

\[ C = \frac{3}{2} R + 3R \]

However, we only observe \( 3R \)!
Heat Capacity: Quantum Treatment

We now consider a quantum mechanical treatment of the heat capacity. To do so we need to:

1) Describe the conduction electrons in terms of quantum states and wavefunctions.

2) Take the fact that electrons are Fermions into account.

Quantum States

We shall imagine a cubic solid of sides $L$. The electrons are confined to the cube but inside it are free.

This amounts to a particle in a three-dimensional box. The potential is:

$$V(x,y,z) = \begin{cases} 0 & 0 \leq x, y, z \leq L \\ \infty & \text{otherwise} \end{cases}$$

The energy eigenstates satisfy:

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x,y,z) + V(x,y,z) \psi(x,y,z) = E \psi(x,y,z)$$

- (8)
Boundary conditions:

In ordinary quantum mechanics we require the following **fixed boundary conditions**:

\[
\begin{align*}
\Psi(0, y, z) &= \Psi(L, y, z) = 0 \\
\Psi(x, 0, z) &= \Psi(x, L, z) = 0 \\
\Psi(x, y, 0) &= \Psi(x, y, L) = 0
\end{align*}
\]  

- (9)

So that in one dimension possible wavefunctions are:

\[\text{etc., etc.} \]

Another possibility is to require **periodic boundary conditions**: Physically this means that we identify each face of the cube with its opposite face. This is easy to illustrate in one dimension:

Mathematically we require that the wavefunction take the same values at \(x = 0\) and \(x = L\). In fact we require:

\[\Psi(x, y, z) = \Psi(x + L, y, z)\]

for any \(x, y, z\).
The periodic boundary conditions are:

\[
\psi(x, y, z) = \psi(x + L, y, z)
\]
\[
\psi(x, y, z) = \psi(x, y + L, z)
\]
\[
\psi(x, y, z) = \psi(x, y, z + L)
\]  \( - (10) \)

Generally there is a greater symmetry with these and they are mathematically easier to deal with. For periodic boundary conditions some possible one dimensional wavefunctions are:

\[
\begin{array}{c}
\includegraphics[width=0.3\textwidth]{wavefunction1.png} \\
\includegraphics[width=0.3\textwidth]{wavefunction2.png}
\end{array}
\]

\[
\text{etc}...
\]

We shall work with periodic boundary conditions. In this case possible solutions to the Schrödinger equation are:

\[
\psi(x, y, z) = Ae^{i(k_x x + k_y y + k_z z)} = Ae^{i(\hat{k} \cdot \vec{x})}  \quad (11)
\]

where \( A \) is a normalization constant. Substituting \((11)\) into \((8)\) gives:

\[
\frac{h^2}{2m} (k_x^2 + k_y^2 + k_z^2) = E
\]

or

\[
\frac{h^2}{2m} \hat{k}^2 = E  \quad - (12)
\]
Now we can apply the boundary conditions to determine possible values for $k$.

**Exercise:** Show that the periodic boundary conditions are only satisfied if

$$
\begin{align*}
    k_x &= \frac{2\pi}{L} n_x \\
    k_y &= \frac{2\pi}{L} n_y \\
    k_z &= \frac{2\pi}{L} n_z
\end{align*}
$$

where $n_x, n_y, n_z$ are any integers.

Note that solutions for $k$ and $-k$ correspond to distinct quantum states. That with $k$ describes a particle moving along the $+k$ direction. That with $-k$ a particle moving along the $-k$ direction and since these are opposite the states are distinct.

**Napping the states $-k$-space diagrams.**

We can display the possible states using orthogonal axes to represent $k_x, k_y,$ and $k_z$ in two dimensions.

![Diagram](image)
Ground state energy at \( T=0 \) for \( N \) electrons.

Suppose that there are \( N \) electrons in the solid. What will the total energy of the electrons be? Each electron will be in one state corresponding to a particular value of \( \mathbf{k} \). The energy of this electron will be

\[ E = \frac{\mathbf{k}^2}{2m} \]

If \( T>0 \), fluctuations will allow electrons to occupy higher energy states than they otherwise might do.

Thus we consider the energy at \( T=0 \). Statistical mechanics informs you that the total energy of the electrons will be as low as it can possibly get. This is the ground state. Now the energy \( E \) of an electron depends on \( \mathbf{k}^2 \) and in terms of the \( \mathbf{k} \)-space diagram, the distance from the origin. You might expect that the lowest state will have all electrons at \( \mathbf{k}=0 \).

However, electrons are Fermions and no two electrons can occupy the same state. As electrons can have one of two spin values, thus means that only two electrons can occupy one \( \mathbf{k} \) state. Immediately, you can conclude that for the ground state \( E_{\text{total}} > 0 \).

We now have a scheme for determining the ground state:

- Fill out energy levels in order of increasing distance from the origin in \( \mathbf{k} \)-space. Ensure that only two electrons occupy each state.
For a small number of electrons, the diagram, on a usual scale will look discrete.

Example: Two dimensions and $N=26$

![Diagram of two-dimensional electron distribution]

Shaded circles indicate filled levels.

However, for larger numbers, viewed at the same scale, the diagram will appear more and more "continuous." For example, with $N=122$ in two dimensions.

![Diagram of high-density electron distribution]

The filled region starts to appear spherical.
For typical values of $N$ you barely notice the discrete structure of the lattice. Instead, one finds a region, inside which the shells are filled.

Inside this region, every energy level contains two electrons. Outside the region, every energy level contains no electrons. The boundary between the regions is called the Fermi surface. The main purpose of the Fermi surface is to demarcate filled and unfilled energy levels.

At $T=0$, within the Fermi surface every state is occupied by two electrons. Beyond the Fermi surface every state contains no electrons.

For a free electron gas, the Fermi surface is a spherical shell. The region it encloses is called the Fermi sphere. The radius of the Fermi sphere is called the Fermi wavenumber, $k_F$. The energy associated with the states on the Fermi surface is called the Fermi energy, $E_F$.

Thus

$$E_F = \frac{\hbar^2}{2m} k_F^2$$

- (14)