§6 – Free Electron Gas

6.1 Overview of Electronic Properties

The main species of solids are metals, semiconductors and insulators.

One way to group these is by their resistivity:

Metals – $\rho \sim 10^{-8} - 10^{-5} \, \Omega \, \text{m}$

Semiconductors – $\rho \sim 10^{-5} - 10 \, \Omega \, \text{m}$

Insulators – $\rho \sim 10 - \infty \, \Omega \, \text{m}$

There is a striking difference in the temperature dependence of the resistivity:

Metals – ρ **increases** with T (usually $\rho \propto T$)

Semiconductors – ρ **decreases** with T

Alloys have higher resistivity than its constituents; there is no law of mixing. This suggests some form of "impurity" mechanism

The different species also have different optical properties.

Metals – Opaque and lustrous (silvery)

Insulators – often transparent or coloured

The reasons for these differing properties can be explained by considering the density of electron states:

6.2 Free Electron (Fermi) Gas

The simplest model of a metal was proposed by Fermi.

This model transfers the ideas of electron orbitals in atoms into a macroscopic object. Thus, the fundamental behaviour of a metal comes from the Pauli exclusion principle.

For now, we will ignore the crystal lattice.

For this model, we make the following assumptions:

- The crystal comprises a fixed background of N identical positively charge nuclei and N electrons, which can move **freely** inside the crystal without seeing any of the nuclei (monovalent case);
- Coulomb interactions are negligible because the system is neutral overall

This model works relatively well for **alkali** metals (Group 1 elements), such as *Na*, *K*, *Rb* and *Cs*.

We would like to understand why electrons are only weakly scattered as they migrate through a metal.

Consider the "electron in a box" paradigm.

In 1-dimension, the time independent Schrödinger equation for a system with no potential energy is given by:

$$H\,\psi = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \epsilon\,\psi$$

(6.1)

Where: $\mathcal{H}$ is the Hamiltonian operator, ε is the total energy of the system.

For free electrons, there is no potential energy (inside the box), so we can use equation (6.1) to describe the system.

For this problem we let $V \to \infty$ at the walls of the box. As such, we can set $\psi(0)=\psi(L)=0$.

Let $\psi_n(x)=A\sin\left(\frac{2\pi}{\lambda_n}x\right)$ be the solutions to the wavefunctions of the energy level ϵ_n .

Where: $\frac{2\pi}{\lambda_n}=\frac{n\pi}{L}$. This gives the wavefunction as $\lambda_n=2\frac{L}{n}$, where *n* is a non-negative integer.

Substituting into equation (6.1) gives:

$$\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{2\pi}{\lambda_n}\right)^2 = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$$

(6.2)

Thus, the energy levels are quadratically spaced.

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6.3 Filling of Energy Levels

Unlike phonons, where all the modes are independently excited by thermal activation, electrons (since they are fermions) interact strongly via the Pauli exclusion principle. So, at present, we can consider all energy levels to have two-fold degeneracy.

To count the energy states, we are concerned with two quantum numbers:

1. ***Principle quantum number*** – determines the total energy of the system ($n \in \mathbb{Z} \, ; n > 0$);

2. ***Spin magnetic quantum number*** – determines the spin of the system (particle). For single electrons, the spin is either spin-up ($m_S = \frac{1}{2}$) or spin-down ($m_s = -\frac{1}{2}$).

Two-fold degeneracy occurs because the total energy in the absence of a magnetic field, as defined in equation (6.2) does not include particle spin as a parameter.

Because electrons must obey the Pauli exclusion principle, they cannot all occupy the ground state (which would be the most preferable state). Instead, if the system is not excited, each electron will occupy the lowest possible energy state, progressively filling the levels.

Thus, for a system of *N* electrons, there will be a topmost energy level for an unexcited system $n_F \equiv$ Fermi principle quantum number , such that $N = 2 n_F$.

From this, we can define the ***Fermi energy*** ϵ_F as:

$$\epsilon_F = \frac{\hbar^2}{2m} \left(\frac{n_F \pi}{L} \right)^2 = \frac{\hbar^2}{2m} \left(\frac{N \pi}{2 L} \right)^2$$

(6.3)

This is the highest filled energy level of a 1-dimensional, unexcited *N*-electron system.

We can see that $\epsilon_F \propto (n_L)^2 \equiv \left(\frac{N}{L} \right)^2$, where n_L is the linear electron density.

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6.4 Filling of Energy Levels in 3-Dimensions

Let us consider a 3-dimensional cubic potential well of volume $V = L^3$.

The wavefunction solutions have components from each of the three dimensions, which in Cartesian coordinates are given by:

$$\psi_n(\vec{r}) = A \sin\left(\frac{\pi}{L} n_x x\right) \sin\left(\frac{\pi}{L} n_y y\right) \sin\left(\frac{\pi}{L} n_z z\right)$$

(6.4)

Where: n_i are the principal quantum numbers in the *i*-direction.

As with phonons, it is convenient to use periodic boundary conditions:
$\psi(x, y, z) = \psi(x+L, y, z) = \psi(x, y+L, z) = \psi(x, y, z+L)$

Now, we can write the wavefunction in terms of the wavevector $\vec{k}$:

$$\psi_{\vec{k}}(\vec{r}) = A e^{i \vec{k} \cdot \vec{r}}$$

(6.5)

Where: $\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$.

The energy states can then be written as a function of *k* (magnitude of wavevector):

$$\epsilon_k = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

(6.6)

In quantum mechanics, the wavevector is related to the **momentum** of the electron.

The momentum operator is defined by: $\hat{p} = -i\hbar\nabla$, where $\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$.

We can use this to operate on the wavefunction as defined by equation (6.5):

$$\hat{p}\psi = -i\hbar\left(i\vec{k} A e^{i\vec{k}\cdot\vec{r}}\right) = \hbar\vec{k}\psi$$

(6.7)

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So, $\hbar \vec{k}$ is the eigenvalue of the momentum operator.

The filling of levels will be as the 1D case.

Since the energy is quadratically proportional to k, we can see the energy levels as being filled in shells from the origin, with the total filled energy levels producing a sphere in k-space of radius k_F.
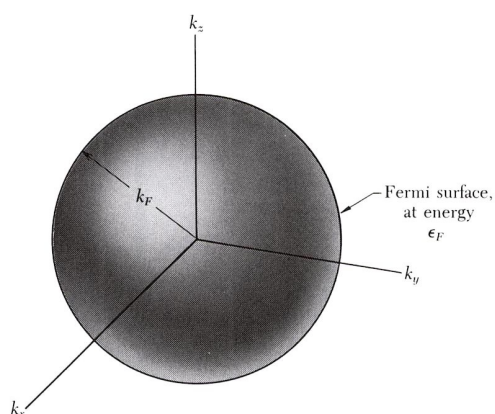

Figure 6.1: In the ground state of a system of N free electrons, the occupied orbitals of the system fill a sphere of radius k_F.

The volume of this sphere is given by:

$$V_{sphere} = \frac{4}{3} \pi k_F^3$$

(6.8)

The volume of a single state is given by:

$$V_{state} = \left(\frac{2\pi}{L}\right)^3$$

(6.9)

The number of electrons N is then given by:

$$N = 2 \frac{V_{sphere}}{V_{state}} = 2 \frac{\frac{4}{3}\pi k_F^3}{\left(\frac{2\pi}{L}\right)^3}$$

(6.10)

The factor of 2 comes from the two-fold degeneracy of the energy states (due to spin).

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Finally, expanding and cancelling factors, and letting $L^3 = V$ gives:

$$N = \frac{V}{3\pi^2} k_F^3 \qquad (6.11)$$

Alternatively, we may want to know the value of the **Fermi wavevector** k_F :

$$k_F = \left(3\pi^2 n_V\right)^{\frac{1}{3}} \qquad (6.12)$$

This is a favourable result, as it means that k_F depends **only** on the electron number density $n_V \equiv \dfrac{N}{V}$.

So, from first-principles, assuming that $m = m_e \equiv$ mass of electron , we have obtained electron states with:

1. Wavelength of the order of atomic spacing

2. Energy of the order of binding energy.

The density of electron states provides a big contribution to the binding energy in a metal. The electron kinetic energy increases with electron density due to Pauli repulsion.

6.5 Thermal Excitation

Thermal energy, 0.025eV at room temperature, cannot effect the deepest electrons (in terms of energy), only those in energy levels near ϵ_F .

The deepest states will be completely filled and inaccessible, just like the core electrons in atoms.

Electrons are fermions, so they must obey the statistical law of the Fermi-Dirac distribution, which gives the occupation number *f* of a particular energy level. If we assume non-degenerate energy levels (i.e. spin-up and spin-down have different energy levels for a given *n*), then we can write:

$$f(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1} \qquad (6.13)$$

Where: μ is the **chemical potential**. In thermodynamics, the chemical potential was defined as the partial derivative of the total internal energy (or other state function) with respect to the number of

molecules.

The electronic chemical potential can be seen as as normalisation parameters which sets the baseline energy. At absolute zero, it is identically equal to the Fermi energy.

Fermions, unlike Bosons are fundamental particles, which cannot be created or destroyed. Thus, there must be some reservoir at energy μ supplying the electrons.

At present, we do not have an exact definition of μ. Such a definition will need to be derived from the density of states, as with phonons.

6.6 Applications of FEG Model

The free electron gas model has several applications, some of which are highlighted below.

a) Field Emission

Field emission is a process in which electrons can tunnel through a barrier in the presence of a large electric field gradient. The effectiveness of this process depends on the **work function**, which is the minimum energy needed to remove an electron from the Fermi level to infinity (outside the surface): $W = \epsilon_{vacuum} - \mu$, where μ is the chemical potential ($\mu \approx \epsilon_F$) and W is the work function. Thus, metals such as tungsten are preferable, since they have very high work functions (i.e. very high Fermi energies).

There are numerous applications. One of the first was field emission microscopy, used to image the metal that comprises the tip. The liberated electrons are accelerated by a cathode-ray tube (CRT) and magnified on a fluorescent screen.

Field emission is used in more modern technology, such as flash memory (a type of erasable Read Only Memory commonly used in memory cards, digital cameras, mobile phones etc.) and field emission displays.

The latter similar to a CRT, but instead of using a single electron gun, it uses a large array of tips (preferably carbon nanotubes). These tips are individually placed behind phosphor dots, so when they undergo field emission, the liberated electrons can illuminate the screen in a similar way to a standard cathode-ray display.

b) Photoemission

The work function of a medium is also important in photoemission. Remember, in the photoelectric effect, photoemission occurs when a photon with an energy greater than the work function is incident on a metal. The work function in this case is defined as the minimum energy that must be given to an electron in order to liberate it from the surface of a metal. As the name suggests, the photoelectric effect is stimulated by the absorption of photons by the metal.
A small voltage can be applied to collect this current of photoelectrons, which can be used to analyse the energy distribution of the photoelectrons.

This is a quantum efficient process, since 1 photon cause the emission of (at most) 1 electrons. Thus, this process is commonly used in photodetectors.

It is also commonly used in photomultiplier tubes.

c) Contact Potential

When two metals are joined to make a thermocouple, electrons flow from one to the other until the Fermi levels are aligned. If they are dissimilar materials with different work functions, there will be a voltage offset. To make a circuit, a second opposite junction is required, which restores the voltage. Such a circuit, all at one temperature, does not give rise to a current. But if the two junctions are at different temperatures, the two band alignments are different and a net current flow is generated.

The potential difference, being dependent on the work functions of the two metals, increases with temperature difference. Thus, if the second thermocouple is held at reference temperature known to a high degree of accuracy (such as the triple point of water, freezing point of tungsten, triple point of argon), we can determine the temperature of the first thermocouple (in relation to the first). The choice of reference temperature depends on the temperature range required (e.g. triple point of neon for ultra-cold physics, or the freezing point of water).

6.7 Electron Heat Capacity

A major success of Fermi's consideration of electrons in metals is that it could explain the "excess" heat capacity in metals (beyond that given by the phonons).

The main elements of the free electron gas model are:

1. Fermi-Dirac distribution (temperature dependence on energy occupation number);

2. $\epsilon = \dfrac{\hbar^2}{2m} k^2$ energies of free electrons;

3. $N = (V/3\pi^2) k^3$ total number of electrons inside a sphere of radius k.

The total number of electrons inside a sphere of radius k is:

$$N = \left(\frac{V}{3\pi^2}\right) k^3 = \left(\frac{V}{3\pi^2}\right)\left(\frac{2m\epsilon}{\hbar^2}\right)^{\frac{3}{2}}$$

(6.14)

This gives the density of electron states:

(6.15)

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$$D(\epsilon) = \frac{dN}{d\epsilon} = \left(\frac{V}{3\pi^2}\right)\frac{3}{2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\epsilon^{\frac{1}{2}} = \frac{3N}{2\epsilon}$$

The density of electron states increases as $\epsilon^{\frac{1}{2}}$.

The total electron energy is given by the sum over all energies:

$$U = \int_0^\infty D(\epsilon) f(\epsilon) \epsilon \, d\epsilon \qquad\qquad (6.16)$$

For $T = 0$, the Fermi function becomes a step, so we can define ϵ_F implicitly as:

$$N = \int_0^\infty D(\epsilon) f(\epsilon) \, d\epsilon = \int_0^{\epsilon_F} D(\epsilon) \, d\epsilon \qquad\qquad (6.17)$$

We need a few approximations. In general, $T \ll \Theta_F$, where Θ_F is the **Fermi temperature**. In other words, $k_B T \ll \epsilon_F$.

In this case, $\mu \approx \epsilon_F$ we can approximate N as in equation (6.17).

This also allows us to approximate the occupation number as:

$$f(\epsilon) \approx \frac{1}{\exp(\epsilon - \epsilon_F)/k_B T + 1} \qquad\qquad (6.18)$$

Let $x = (\epsilon - \epsilon_F)/k_B T$. Then, $f(\epsilon) = \frac{1}{e^x + 1}$.

Multiplying equation (6.17) by ϵ_F and subtract from equation (6.16) gives:

$$U - N\epsilon_F = \int\limits_0^\infty (\epsilon - \epsilon_F) D(\epsilon) f(\epsilon) d\epsilon \qquad (6.19)$$

Taking the partial differential over equation (6.19) with respect to temperature, and noticing that N and ϵ_F are independent of temperature gives an expression for the heat capacity:

$$C_V = \frac{\partial U}{\partial T} = \int\limits_0^\infty (\epsilon - \epsilon_F) D(\epsilon) \frac{\partial f}{\partial T} d\epsilon \qquad (6.20)$$

Where: $\dfrac{\partial f}{\partial T} = \dfrac{e^x}{(e^x+1)^2} \dfrac{(\epsilon - \epsilon_F)}{k_B T^2}$.

This only becomes larger near $\epsilon = \epsilon_F$, corresponding to $-1 < x < 1$, so we can approximate $D(\epsilon) \approx D(\epsilon_F) = \text{const.}$

Thus, $C_V = D(\epsilon_F) \int\limits_0^\infty \dfrac{e^x}{(e^x+1)^2} \dfrac{(\epsilon - \epsilon_F)^2}{k_B T^2} d\epsilon$.

And using the definition of x: $dx = \dfrac{d\epsilon}{k_B T}$, gives:

$$C_V = k_B^2 T D(\epsilon_F) \int\limits_{-\frac{\epsilon_F}{k_B T}}^\infty \frac{e^x}{(e^x+1)^2} x^2 dx \qquad (6.21)$$

But, $\epsilon_F \gg k_B T \Rightarrow -\dfrac{\epsilon_F}{k_B T} \to -\infty$, so the integral becomes:

$\int\limits_{-\infty}^\infty \dfrac{x^2 e^x}{(e^x+1)^2} dx = \dfrac{\pi^2}{3}$ from a standard integral.

Thus, the specific heat becomes:

$$C_V = \frac{\pi^2}{3} k_B^2 T D(\epsilon_F) = \frac{\pi^2}{3} k_B^2 T \left(\frac{3N}{2\epsilon_F}\right) = \frac{\pi^3}{2} k_B^2 T \frac{N}{\epsilon_F} \qquad (6.22)$$

This is an important result, and tells us that $C_V \propto T$ for electrons.
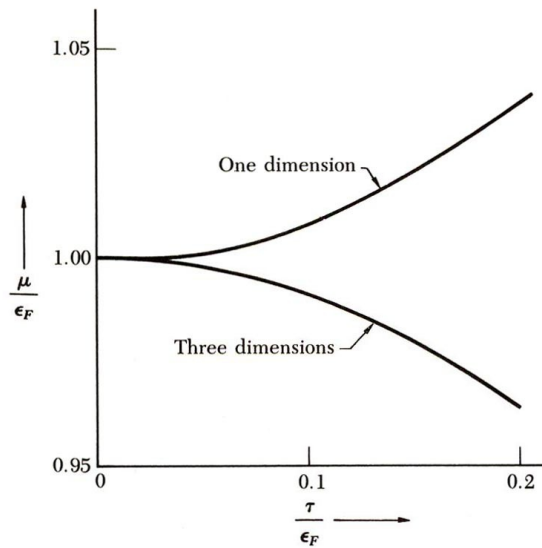
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Figure 6.2: Variation of the chemical potential with temperature for free electron Fermi gases in one and three dimensions.

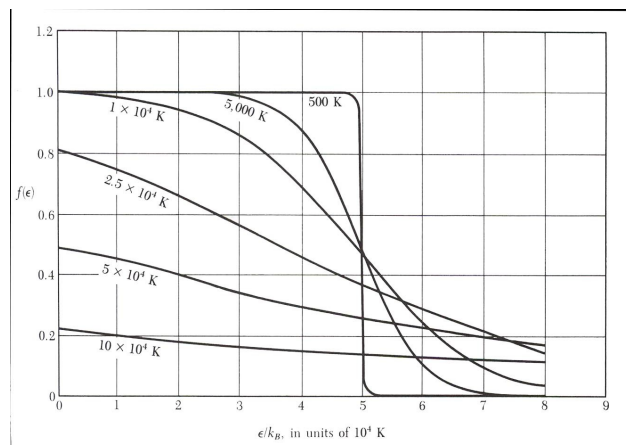## a) Qualitative Representation of Electron Specific Heat

Figure 6.3: Fermi-Dirac distribution for various temperatures, where $T_F \equiv \epsilon_F / k_B = 50,000\,\text{K}$. This result applies at a gas in three dimensions. The chemical potential at each temperature is the value at $f=0.5$.

At $T=0$, the Fermi-Dirac distribution function drops precisely at $\epsilon = \epsilon_F$. At low temperatures, the function remains roughly symmetric around $\epsilon = \epsilon_F$. The *number* of electrons promoted is proportional to the area between the T=0 and finite temperature curves, which is proportional to T.

The average increase of their energy is also proportional to T.

So the finite-T system has an excess energy proportional to T^2, giving $C_V \propto T$

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b) Experimental Result

We expect the total specific heat to be of the form:

$$C_V = \gamma T + A T^3$$

Dividing both sides by T gives:

$$\frac{C_V}{T} = \underbrace{\gamma}_{(C_V)_{\text{electrons}}} + \underbrace{A T^2}_{(C_V)_{\text{phonons}}}$$

(6.23)

Where the latter (phonon) term is from the Debye model

This has the form of a linear equation: $y = mx + c$. So if we plot $\dfrac{C_V}{T}$ as a function of T^2, the intercept gives γ, whilst the gradient gives A.

We can show that $\gamma \sim \dfrac{1}{\epsilon_F} \propto m_e$, where m_e is the rest mass of the electron.

We can define the ***thermal effective mass*** m_{th} as:

$$\frac{m_{\text{th}}}{m_e} = \frac{\gamma(\text{observed})}{\gamma(\text{FEG})}$$

(6.24)

Clearly, if the free electron gas model is accurate, then we would expect $\dfrac{m_{\text{th}}}{m_e} \approx 1$.

Clearly, the free electron gas model breaks down for electron-heavy metals.

6.8 Electrical Conduction

We know from electromagnetism that Lorentz force is the force exerted from a charged particle in an electromagnetic field and is given by:

$$\vec{F} = q(\vec{E} + \vec{v} \times \vec{B})$$

(6.25)

Where, for an electron, $q = -e$.

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For now, we will ignore the magnetic component of the Lorentz force.

We can also express the force using Newton's law:

$$\vec{F} = \frac{d\,\vec{p}}{d\,t} = m\frac{d\,\vec{v}}{d\,t} = \hbar\frac{d\,\vec{k}}{d\,t}$$

(6.26)

Equating equation (6.26) and equation (6.25) (assuming no magnetic field):

$$\hbar\frac{d\,\vec{k}}{d\,t} = -e\,\vec{E}$$

Rearranging, and integrating both sides for a time t gives:

$$\int_0^t d\,\vec{k} = \Delta\,\vec{k} = -\frac{e\,\vec{E}}{\hbar}\int_0^t dt$$

Thus, we have:

$$\Delta\,\vec{k} = -\frac{e\,\vec{E}}{\hbar}\,t$$

(6.27)

All electrons are affected in exactly the same way. For the free electron gas, the Fermi sphere shifts:

We have raised the energy of the system by depopulating on left and adding on right. This effect is reset by (inelastic) collisions that allow electrons to repopulate the lower-lying orbitals.

Electrons colliding with impurities, defects and phonons can cause the displaced sphere to be maintained in a steady state in an electric field.

Let τ be the *characteristic lifetime* of the displaced Fermi sphere (the average time of the displaced state). Then, the steady state displacement is given by setting $t = \tau$ in equation (6.27).

If in a constant electric field $\vec{E}$, there are *n* electrons per unit volume with an average velocity $\langle\vec{v}\rangle$, then the current density is given by:

$$\vec{j} = nq\,\vec{v} = n(-e)\left(-\frac{e\,\vec{E}}{m}\tau\right) = \frac{ne^2\tau}{m}\vec{E}$$

(6.28)

This is **Ohm's law**.

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The *electrical conductivity* σ is defined by $\vec{j} = \sigma \vec{E}$, so we can write:

$$\sigma = \frac{n e^2 \tau}{m}$$

(6.29)

The *resistivity* is defined as the reciprocal of the conductivity, so that:

$$\rho = \frac{1}{\sigma} = \frac{m}{n e^2 \tau}$$

(6.30)

In most metals, the resistivity at room temperature is dominated by collisions of the conducting electrons with impurity atoms and mechanical imperfections (scattering by phonons).

To a good approximation, there are independent, so that if the electric field were switched off, the momentum distribution would return to its ground state with a net (average) *relaxation time τ* given by:

$$\frac{1}{\tau} = \frac{1}{\tau_i} + \frac{1}{\tau_p}$$

(6.31)

Where: τ_i and τ_p are the collision times for scattering via lattice imperfections and phonons respectively.

Thus, we can write the total resistivity as:

$$\rho = \frac{m}{n e^2} \frac{1}{\tau_i} + \frac{m}{n e^2} \frac{1}{\tau_p} = \rho_i + \rho_p$$

(6.32)

Where ρ_i is the resistivity caused by scattering by static defects and ρ_p is the resistivity causes by thermal phonons.

This is known as *Matthiesen's rule*.

Often, ρ_i is independent of temperature and ρ_p independent of the number of defects if the concentration is small.

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We can define the *resistivity ratio* as the ratio of the resistivity of a material at room temperature (300*K*) to its resistivity at absolute zero:

$$\frac{\rho(T=300\text{K})}{\rho(T=0\text{K})} = \frac{\rho_i + \rho_p}{\rho_i}$$

This is a convenient indicator of sample purity.

For pure sample, the ratio is of the order 10^3, whilst for certain alloys it can be less than 10. The resistivity ratio can be as high as 10^6. At this point, the size of the sample becomes important.

τ_p occurs due to electron-phonon interaction, which conserves momentum but not energy.

For a standard electron-phonon scattering $\vec{k}\,' = \vec{k} + \vec{q}$, where $\vec{q}$ is the *momentum transfer*. The rate of this process is proportional to temperature (according to Debye)

For umklapp scattering $\vec{k}\,' = \vec{k} + \vec{q} + \vec{G}$, where $\vec{G}$ is a reciprocal lattice vector. This has a much higher rate than standard electron-phonon scattering.

In practice, these are difficult to calculate, because we require a lattice and not a free electron gas.

6.9 Thermal Conductivity of Metals

The argument here is identical for phonons and electrons.

We know from thermodynamics, that the change in internal energy of a system due to a change in temperature (which does not result in a change in state) is given by:

$$\Delta U = mc\,\Delta T \qquad (6.33)$$

Where *m* is the mass off the system and *c* is the *specific heat capacity*. We can also write this in terms of the molar specific heat c_{mol} :

$$\Delta U = c_{\text{mol}}\,\Delta T \qquad (6.34)$$

Where $c_{\text{mol}} = \dfrac{C_V}{n}$ (n = number density). For compactness, we will write this simply as *c*.

We can write the change in temperature as:

$$\Delta T = \frac{dT}{dx} l_x = \frac{dT}{dx} v_x \tau$$

(6.35)

Where: l_x is the **mean free path** (between collisions) in the *x*-direction, v_x is the speed in the *x*-direction and τ is the collision time.

Note:

For **phonons** $v_x = v_s$, while for **electrons** $v_x = v_F$.

The heat flowing per unit area is given by:

$$j_V = \underbrace{n}_{\text{density}} \underbrace{c \Delta T}_{\text{heat}} \underbrace{\langle v_x \rangle}_{\text{speed}} = n c \langle v_x^2 \rangle \tau \frac{dT}{dx} = \kappa \frac{dT}{dx}$$

(6.36)

Where κ is the **thermal conductivity**.

This can be written in terms of the specific heat as:

$$\kappa = n c \langle v_x \rangle^2 \tau = \frac{1}{3} C_V v^2 \tau = \frac{1}{3} C_V v l$$

(6.37)

For electrons, we defined the specific heat due to electrons in equation (6.22) as:

$$C_V = \frac{\pi^2}{2} k_B^2 T \frac{n}{\epsilon_F} \quad , \text{ where } \quad \epsilon_F = \frac{\hbar^2}{2m} k_F^2 = \frac{(m v_F)^2}{2m} = \frac{1}{2} m v_F^2 \quad .$$

Substituting into equation (6.37), using $l = v_F \tau$ gives:

$$\kappa = \frac{1}{3} \left(\frac{\pi^2}{2} n k_B^2 T \frac{2}{m v_F^2} \right) v_F (v_F \tau)$$

Simplifying this equation gives:

$$\kappa = \frac{\pi^2}{3} \frac{n k_B^2 T \tau}{m}$$

(6.38)

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In metals, this is much larger than the contribution of the phonons, which can be neglected.

In general, $\kappa_{\text{metal}} \gg \kappa_{\text{insulator}}$.

The exception to this is disordered/amorphous metals, which behave more like insulators.

6.10 Wiedemann-Franz Law

Experimental observation shows that the ratio of ***thermal*** to ***electrical*** conductivity is proportional to temperature.

This follows from our theory, if we assume that:

1. The (only) carriers of heat and electricity in the metal are electrons;

2. The scattering rate τ in both descriptions is the same(i.e. $\dfrac{1}{\tau} = \dfrac{1}{\tau_i} + \dfrac{1}{\tau_p}$).

Thus, the ratio is given by:

$$\frac{\kappa}{\sigma} = \frac{\dfrac{\pi^2}{3} k_B^2 T \left(\dfrac{\tau n}{m}\right)}{e^2 \left(\dfrac{\tau n}{m}\right)} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T = L\,T \tag{6.39}$$

Where $L = 2.45 \times 10^{-8}\,\text{W}\,\Omega\,(°\text{C})^{-2} \equiv$ ***Lorentz number*** .

Experimental values of the Lorentz number include:

Ag – 2.31

Cu – 2.23

Mo – 2.61

Pb – 2.47

W – 3.04 (worst case)

The slight departure from the theoretical Lorentz number roughly follows the increase in work function. There is very little change of L with temperature (approx. 2% per 100K). This is empirical proof that there is a common origin of electrical and thermal conductivities of metals.

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