

The Drude model description of the thermal conductivity of metals

The most important success of Drude's model was its explanation of the experimental Wiedemann-Franz law. The WF law states that the ratio between the thermal (κ) and electrical (σ) conductivities is proportional to the temperature with an almost identical coefficient of proportionality for many metals.

The ratio $\frac{\kappa}{\sigma T}$ is called Lorenz number.

The basic assumption of Drude is:

- The conduction electrons (the electron gas) are the main heat conductors (the heat conductivity of the ions may be neglected).
- This assumption was justified by the fact that metals are better heat conductors than insulators.

The Drude model description of the thermal conductivity of metals



The diagram shows a horizontal rod represented by a green rectangle. To the left of the rod is the label T_L and to the right is the label T_R .

$$T_L \quad \text{---} \quad T_R$$

Consider the rod illustrated above:

If $T_L > T_R$ the thermal energy will flow from the left to the right until the bar has a uniform temperature (thermal energy). If the ends are connected to thermal baths with different temperatures a steady state flow of thermal energy will be achieved (from hot to cold).

The thermal current density, \vec{j}^q , is defined to be a vector parallel to the direction of the thermal energy flow, whose magnitude is equal to the amount of thermal energy per unit area per unit time crossing a plane perpendicular to the direction of the flow.

For small temperature gradients Fourier's law states that:

$$\vec{j}^q = -\kappa \nabla T$$

Note the similarity to the charge current density.

The Drude model description of the thermal conductivity of metals

Consider the oversimplified picture of a 1D model where the electrons can only move along the x-axis. In the absence of electric field the average velocity of the electrons at each location is zero (because it is the thermal velocity).

At a location x , the electrons coming from the right have a negative velocity and their average thermal energy is $\varepsilon(T(x + v\tau))$ and those coming from the left have an average thermal energy $\varepsilon(T(x - v\tau))$.

Because the motion is thermal half the electrons arrive from the left and half from the right such that the average thermal energy current density is:

$$\vec{j}^q(x) = \frac{nv}{2} (\varepsilon(T(x - v\tau)) - \varepsilon(T(x + v\tau)))$$

The Drude model description of the thermal conductivity of metals

Assuming that the variation of the temperature over the mean free path is very small we may write it as

$$\vec{j}^q(x) = -n v^2 \tau \left(\frac{d\varepsilon}{dT} \frac{dT}{dx} \right)$$

When considering the 3D picture the generalization is straightforward, we replace the derivative with respect to x by the gradient and the velocity along any direction is just $1/3$ of the squared velocity because we assume that the scattering is isotropic.

Considering also the fact that $n = N/V$ and $\frac{dE}{dT} \frac{1}{V} = c_v$ the heat capacity of the electron gas we find

$$\vec{j}^q(\vec{r}) = -\frac{1}{3} v^2 \tau c_v \nabla T = -\kappa \nabla T \quad \text{where} \quad \kappa = \frac{1}{3} v^2 \tau c_v$$

The Drude model description of the thermal conductivity of metals

Problems with the assumptions

The above assumptions lead to the Lorenz number

$$\frac{\kappa}{\sigma T} = \frac{\frac{1}{3} v^2 \tau c_v}{\frac{ne^2 \tau}{m_e} T} = \frac{\frac{1}{3} m_e v^2 c_v}{ne^2 T} = \frac{\frac{1}{3} 3k_B T \frac{3}{2} nk_B}{ne^2 T} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2$$
$$\approx 1.11 \cdot 10^{-8} \text{ watt} \cdot \text{ohm} / \text{K}^2$$

where we used the ideal gas properties $c_v = \frac{3}{2} nk_B$ and $\frac{1}{2} m_e v^2 = \frac{3}{2} k_B T$. This value is about $\frac{1}{2}$ the typical value but due to Drude's mistake by a factor of two he got an answer that is in good agreement with experiments.

The Drude model description of the thermal conductivity of metals

Problems with the assumptions

- Note that in the derivation we assumed that the average thermal energy depends on the position but we neglected the velocity dependence on the position.
- In fact, the average speed of an electron is higher in regimes with higher average thermal energies and this leads to the accumulation of charge which yields an electric field that eventually stops the current.

The Drude model description of the thermoelectric effect

The electric field due to thermal gradient is known as the thermoelectric field. It is usually written as

$$\vec{E} = Q\nabla T$$

Q is the thermopower, a coefficient setting the proportion between the temperature gradient and the electric field resulting from that gradient.

Consider a 1D bar with temperature gradient.


$$T_L \quad \text{[Bar]} \quad T_R$$

The electric field is expected to balance the effect of the temperature gradient at steady state.

The average velocity due to the temperature gradient is:

$$\vec{v}_Q = \frac{1}{2} [v(x - v\tau) - v(x + v\tau)] = -v\tau \frac{dv}{dx} = -\frac{1}{2} \tau \frac{dv^2}{dx}$$

The Drude model description of the thermoelectric effect

The generalization to three dimensions is done by considering that

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

$$\vec{v}_Q(\vec{r}) = -\frac{1}{6} \tau \nabla T \frac{dv^2}{dT}$$

The mean velocity due to the electric field is

$$\vec{v}_E(\vec{r}) = -\frac{e\tau}{m_e} \vec{E}$$

As we mentioned earlier, in steady state the effects balance each other and we have

$$\vec{v}_Q + \vec{v}_E = 0 \rightarrow \frac{1}{6} \tau \nabla T \frac{dv^2}{dT} = -\frac{e\tau}{m_e} \vec{E} = -\frac{e\tau}{m_e} Q \nabla T \rightarrow Q = -\frac{m_e}{6e} \frac{dv^2}{dT}$$

The Drude model description of the thermoelectric effect

We rewrite the thermopower as:

$$Q = -\frac{m_e}{6e} \frac{dv^2}{dT} = -\frac{V}{3eNV} \frac{1}{d(N \frac{1}{2} m_e v^2)} = -\frac{c_v}{3ne}$$

Using the classical expression for the heat capacity

$$c_v = \frac{3nk_B}{2}, \text{ leads to}$$

$$Q = -\frac{\frac{3nk_B}{2}}{3ne} = -\frac{k_B}{2e} \approx -0.43 \cdot 10^{-4} \text{ volt/K}$$

About 100 times larger than observed

The Drude model description of the thermal properties of metals

- In the derivation of the thermopower there was no cancellation of the errors (in the thermal and electric conductivities) and, therefore, it is not in agreement with measurements.
- The sign of the thermopower is different for different metals, a behavior that cannot be explained by Drude's theory.
- A similar issue also exist in the Hall coefficient.
- These issues demonstrate that we cannot proceed much further using the classical electron gas picture and one has to consider the quantum nature of the electrons.

Quantum theory of free electron gas

- As we showed, Drude's model considered the electrons as classical particles.
- In particular, it assumed that the equilibrium distribution of the electron velocities is the Boltzmann distribution.
- This leads to a probability density function of the velocity which is given by:

$$f_B(\vec{v}) = n \left(\frac{m_e}{2\pi k_B T} \right)^{3/2} e^{-\frac{m_e v^2}{2k_B T}}$$

Quantum theory of free electron gas

- Note that the normalization is set such that the integral over the PDF yields the electron density, $n = N/V$.

$$\begin{aligned} & \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} n \left(\frac{m_e}{2\pi k_B T} \right)^{3/2} e^{-\frac{m_e v^2}{2k_B T}} dv_x dv_y dv_z \\ &= \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} v^2 \sin\theta n \left(\frac{m_e}{2\pi k_B T} \right)^{3/2} e^{-\frac{m_e v^2}{2k_B T}} dv d\theta d\phi \\ &= n 2\pi \left(\frac{m_e}{2\pi k_B T} \right)^{3/2} \int_0^{\pi} \int_0^{\infty} v^2 \sin\theta e^{-\frac{m_e v^2}{2k_B T}} dv d\theta \\ &= n 4\pi \left(\frac{m_e}{2\pi k_B T} \right)^{3/2} \int_0^{\infty} v^2 e^{-\frac{m_e v^2}{2k_B T}} dv = n \end{aligned}$$

Quantum theory of free electron gas

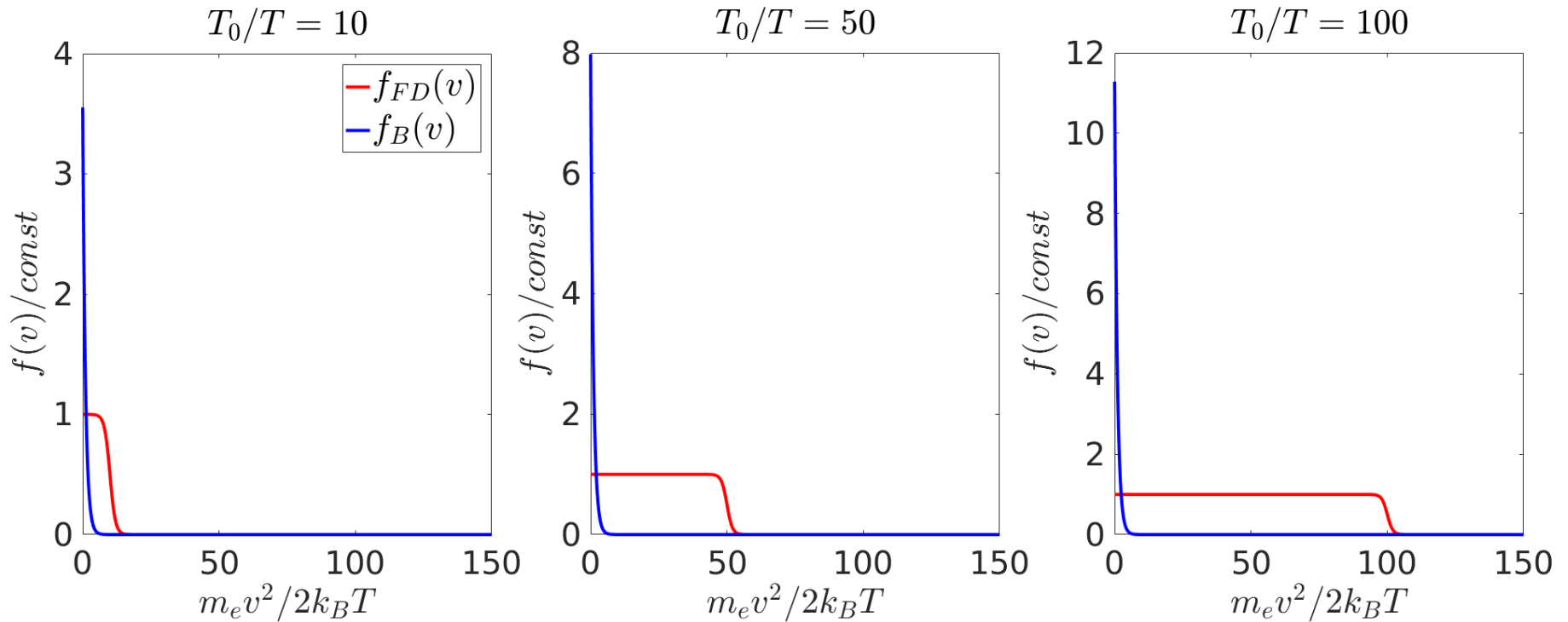
- The most important quantity which is ignored in the classical treatment is the fact that the electrons are fermions and, therefore, Pauli's exclusion principle applies to their distribution. Only one fermion may occupy a given state.
- This results in a distribution of energies (velocities) which deviates considerably from the Boltzmann distribution.

$$f_{FD}(\vec{v}) = \frac{(m_e/\hbar)^3}{4\pi^3} \frac{1}{1 + \exp((\frac{1}{2} m_e v^2 - k_B T_0)/k_B T)}$$

T_0 is determined by the normalization condition (the integral over the PDF is equal to the density, n) and is typically of the order of thousands of degrees Kelvin.

Quantum theory of free electron gas

- An illustration of the difference between the Boltzmann and Fermi-Dirac



Quantum theory of free electron gas

- In what follows we will try to explain the origin of the FD distribution and consider the Sommerfeld's model, which in most cases involves a single modification of Drude's model – Replacing the Boltzmann distribution by the FD distribution.
- In many cases, $T_0 \gg T$, therefore, we start our exploration of the quantum electron gas by considering its properties at $T = 0$.

Quantum Theory of the Free Electron Gas

The starting point is actually just the solution of the Schrödinger equation for a particle with no interactions – the electron gas approximation.

1D metal → 1D Schrödinger Equation:

$$-\frac{\hbar^2}{2m_e} \frac{\partial^2 \psi(x)}{\partial x^2} = E\psi(x)$$

The solution to this equation takes the form

$$\psi(x) = Ae^{ikx}$$

With corresponding energy

$$E(k) = \frac{\hbar^2 k^2}{2m_e}$$

Quantum Theory of the Free Electron Gas

The equation has to be supplemented by boundary conditions. Since we are interested in the bulk properties the boundaries are expected to have a negligible effect and we have the freedom to choose the most convenient boundary conditions.

We will use periodic boundary conditions where we require

$$\psi(x + L) = \psi(x)$$

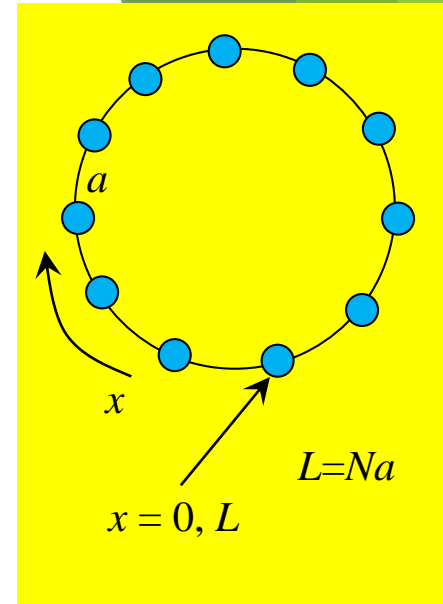
In 1D this choice corresponds to a ring of length L .

$$Ae^{ikx} = Ae^{ik(x+L)} \Rightarrow e^{ikL} = 1 \Rightarrow kL = 2n\pi \Rightarrow k = \frac{2n\pi}{L}$$

Where $n \in \text{Integers}$, and k_n can be positive or negative because the waves can travel in either direction.

The energies are:

$$E_n = \frac{\hbar^2}{2m_e} \left(\frac{2n\pi}{L} \right)^2$$



Quantum Theory of the Free Electron Gas

In 3D the generalization is trivial.

The second derivative in the Schrödinger equation is replaced by the Laplacian

$$-\frac{\hbar^2}{2m_e} \nabla^2 \psi(x, y, z) = E\psi(x, y, z)$$

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

With solution $\psi(x, y, z) = Ae^{i\vec{k}\cdot\vec{r}}$; $\vec{k} = (k_x, k_y, k_z)$ and $\vec{r} = (x, y, z)$ and the boundary conditions take the form:

$$\psi(x + L_x, y, z) = \psi(x, y, z)$$

$$\psi(x, y + L_y, z) = \psi(x, y, z)$$

$$\psi(x, y, z + L_z) = \psi(x, y, z)$$

Quantum Theory of the Free Electron Gas

We consider a cube of dimensions $L_x = L_y = L_z = L = V^{\frac{1}{3}}$.

The periodic boundary conditions imply that

$$k_x = \frac{2\pi n_x}{L_x}; k_y = \frac{2\pi n_y}{L_y}; k_z = \frac{2\pi n_z}{L_z}$$

And the energies are given by

$$E_{\vec{n}} = \frac{\hbar^2 (2\pi)^2}{2m_e V^{\frac{2}{3}}} (n_x^2 + n_y^2 + n_z^2)$$

The most important aspect of the quantization is that one can count the number of allowed states within a given volume of the k space, Ω . We are mostly interested in volumes that include $\sim 10^{22}$ states and so the boundary conditions can be neglected and $N_k(\Omega) = \frac{\Omega}{\left(\frac{2\pi}{L}\right)^3} = \frac{\Omega V}{8\pi^3}$ leading to the density of k levels

$$\frac{N_k(\Omega)}{\Omega} = \frac{V}{8\pi^3}$$

Quantum Theory of the Free Electron Gas

- The electrons are fermions and as such Pauli's principle states that no two electrons can be at the same state.
- The electrons have the spin degree of freedom which can take two values and, therefore, the maximal number of electrons at each \vec{k} state is 2.
- At zero temperature, the case we consider now, the electrons are assigned to the momentum levels starting from the lowest energy states and filling up until all N electrons are "placed" in the k space.
- For a large number of states/electrons, the volume occupied in k -space is indistinguishable from a sphere. This sphere is known as Fermi sphere and its radius, k_F , is the Fermi radius such that the occupied k space volume is:

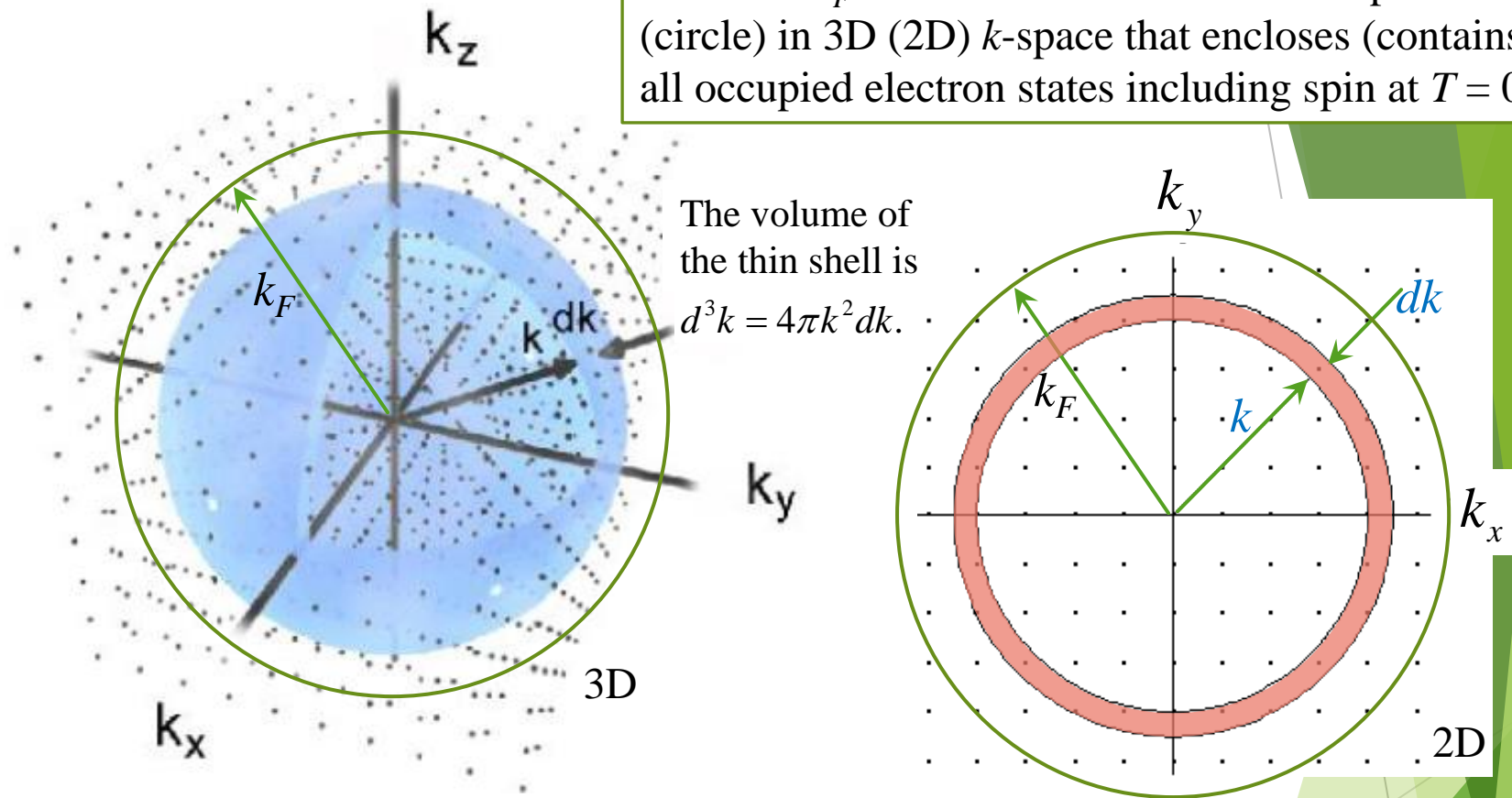
$$\Omega_F = \frac{4\pi k_F^3}{3} \Rightarrow N_k(\Omega_F) = \frac{4\pi k_F^3}{3} / \frac{8\pi^3}{V} = \frac{k_F^3 V}{6\pi^2} \Rightarrow N_e(\Omega_F) = \frac{k_F^3 V}{3\pi^2}$$

$N_k(\Omega_F)$ is the number of k states within the Fermi sphere

$N_e(\Omega_F)$ is the number of electron states within the Fermi sphere

The discrete values of \vec{k} in k -space as shown for 3D and 2D lattices

Note that k_F is the radius of the smallest sphere (circle) in 3D (2D) k -space that encloses (contains) all occupied electron states including spin at $T = 0$.



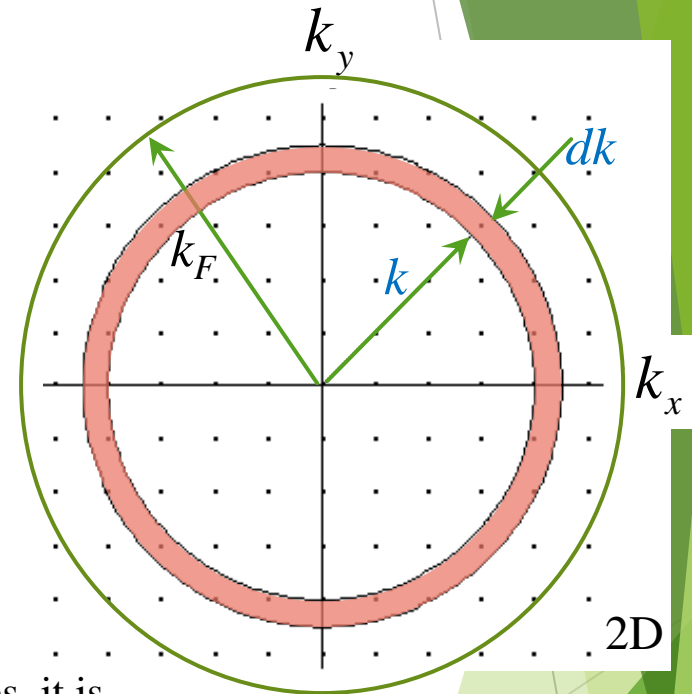
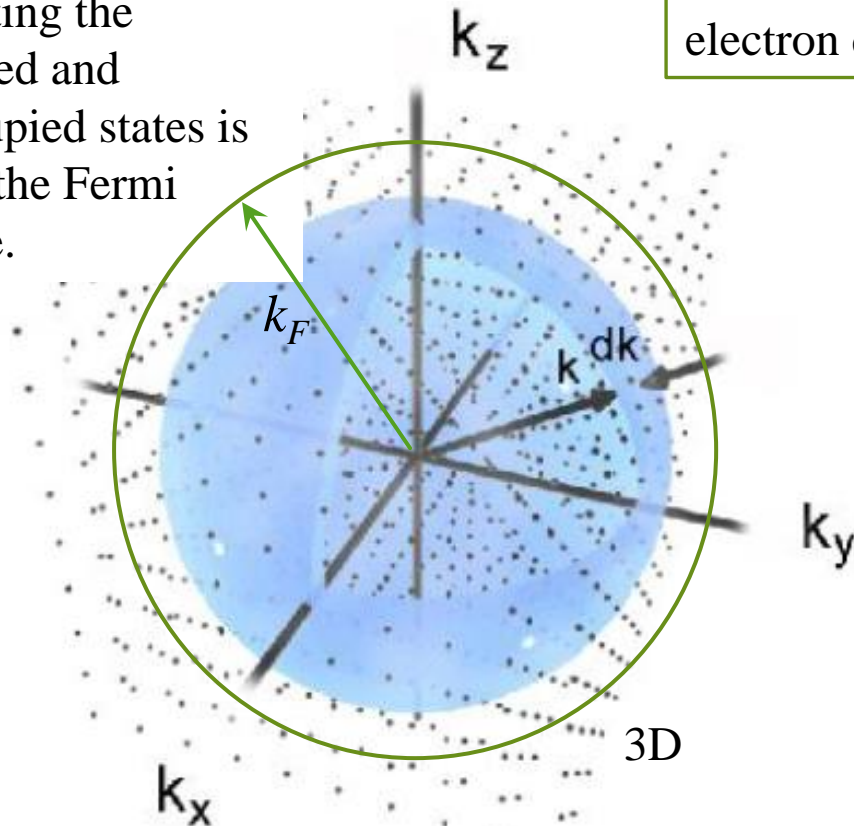
Note that the minimum spacing (distance between dots) in k -space depends on the size of the volume that we choose in real space (the dimension of the cube that we used for the quantization).

The area of the thin annulus (shaded red region) is $d^2k = 2\pi k dk$.

The discrete values of \vec{k} in k -space

The surface separating the occupied and unoccupied states is called the Fermi surface.

The relation between the Fermi radius and the electron density is $n = k_F^3/3\pi^2$.



In order to get an estimate of the magnitude of these quantities, it is

convenient to use the relation we found earlier, $r_s = \left(\frac{3}{4\pi n}\right)^{\frac{1}{3}}$

$$k_F = \frac{3.63}{r_s/r_0} \text{ \AA}^{-1} \text{ and } v_F = \frac{\hbar k_F}{m_e} = \frac{4.2}{r_s/r_0} 10^8 \text{ cm/s}; \text{ note that this}$$

velocity is about 1% of the speed of light in vacuum.

The momentum of the electron on the highest occupied level is called Fermi momentum.

Fermi energy and the ground state energy

- The Fermi energy can be written as

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m_e} = \left(\frac{e^2}{2r_0} \right) (k_F r_0)^2 = \frac{50.1}{(r_s/r_0)^2} \text{ eV}$$

Rydberg energy – Ground state binding energy of the Hydrogen atom 13.6eV

Enables estimation of the range of Fermi energies because r_s/r_0 is within a limited range for most metals 2-3 and at most 10.

- The total energy of the ground state can be calculated by summing the energies of all the electrons up to the Fermi level.

$$E = 2 \sum_{k < k_F} \frac{\hbar^2 k^2}{2m_e}$$

In order to calculate the sum, we will approximate it as an integral.

Fermi energy and the ground state energy

- The sum over any function of \vec{k} may be written as

$$\sum_{\vec{k}} F(\vec{k}) = \frac{V}{8\pi^3} \sum_{\vec{k}} F(\vec{k}) \Delta\vec{k}$$

The volume in k -space of each state

- In the limit $\Delta\vec{k} \rightarrow 0$ (which is equivalent to $V \rightarrow \infty$) the sum approaches the integral

$$\lim_{V \rightarrow \infty} \frac{1}{V} \sum_{\vec{k}} F(\vec{k}) = \int \frac{1}{8\pi^3} F(\vec{k}) d\vec{k}$$

- Applying this relation to the energy of the ground state we find

$$\frac{E}{V} = \frac{2}{V} \sum_{k < k_F} \frac{\hbar^2 k^2}{2m_e} = \int_0^{k_F} \frac{1}{4\pi^3} \frac{\hbar^2 k^2}{2m_e} 4\pi k^2 dk = \frac{k_F^5}{10} \frac{1}{\pi^2} \frac{\hbar^2}{m_e}$$

Fermi energy and the ground state energy

- The energy per electron in the ground state is

$$\frac{E}{N} = \frac{E}{V} \cdot \frac{V}{N} = \frac{k_F^5}{10\pi^2} \frac{1}{m_e} \frac{\hbar^2}{k_F^3} \cdot \frac{3\pi^2}{k_F^3} = \frac{3}{5} \frac{\hbar^2 k_F^2}{2m_e} = \frac{3}{5} \mathcal{E}_F$$

- It is common to write this energy per electron as:

$$\frac{E}{N} = \frac{3}{5} k_B T_f$$

Which defines the Fermi temperature.

$$T_f = \frac{\mathcal{E}_F}{k_B} = \frac{58.2}{(r_s/r_0)^2} \cdot 10^4 K.$$

Note that the energy per electron in the classical electron gas is $\frac{3}{2} k_B T$ which

vanishes for $T \rightarrow 0$. The value found above is only achieved for $T = \frac{2}{5} T_f$

$\approx 10^4 K$.

The Fermi Dirac distribution

- In the previous slides we discussed the state of the system for $T = 0$. When the temperature is not zero we have to account for the distribution of the energies/momenta of the system.
- In thermal equilibrium the Boltzmann distribution characterizes the system

$$p_N(E) = \frac{e^{-\frac{E}{k_B T}}}{\sum_{E_{\alpha,N}} e^{-\frac{E_{\alpha,N}}{k_B T}}}$$

$E_{\alpha,N}$ is the energy of a system of N electron in a system state α . The sum is over all the possible states of the N electron system.

- The denominator is known as the partition function (often denoted as Z). It is related to the Helmholtz free energy, $F = U - TS$ where U is the internal

energy and S is the entropy, through $\sum_{E_{\alpha,N}} e^{-\frac{E_{\alpha,N}}{k_B T}} = e^{-\frac{F_N}{k_B T}}$

The Fermi Dirac distribution

- Using the definition of the Helmholtz free energy we can rewrite the Boltzmann distribution as

$$p_N(E) = e^{-\frac{(E-F_N)}{k_B T}}$$

- The electrons are subject to Pauli's exclusion principle and, therefore, we need to specify the probability that a state is occupied.

$$f_{i,N} = \sum p_N(E_{\alpha,N}) \quad \left\{ \begin{array}{l} \text{Summing over all states, } \alpha, \text{ of the } N \text{ electron system} \\ \text{in which the single electron state, } i, \text{ is occupied} \end{array} \right.$$

Note that

$$f_{i,N} = 1 - \sum p_N(E_{\gamma,N}) \quad \left\{ \begin{array}{l} \text{Summing over all states, } \gamma, \text{ of the } N \text{ electron system} \\ \text{in which the single electron state, } i, \text{ is NOT occupied} \end{array} \right.$$

The Fermi Dirac distribution

- Any N electrons state in which the i^{th} state **is not** occupied can be constructed from an N+1 electrons state in which the i^{th} state **is** occupied by removing the electron in the i^{th} state.
- The set of N electron states in which i^{th} state **is not** occupied is equal to the set of N+1 states in which the i^{th} state **is** occupied. The energy of each pair of corresponding states in these two states differ in their energies by an amount ε_i , the energy of an electron in the the i^{th} state.

The Fermi Dirac distribution

➤ Therefore,

$$f_{i,N} = 1 - \sum p_N(E_{\alpha,N+1} - \varepsilon_i) \quad \left\{ \begin{array}{l} \text{Summing over all states, } \alpha, \text{ of the } N + 1 \text{ electron system} \\ \text{in which the single electron state, } i, \text{ is occupied} \end{array} \right.$$

$$\begin{aligned} \text{➤ } p_N(E) &= e^{-\frac{(E-F_N)}{k_B T}} \Rightarrow p_N(E_{\alpha,N+1} - \varepsilon_i) = e^{-\frac{(E_{\alpha,N+1} - F_N + F_{N+1} - F_{N+1} - \varepsilon_i)}{k_B T}} \\ &= e^{-\frac{(E_{\alpha,N+1} - F_{N+1})}{k_B T}} e^{-\frac{(\varepsilon_i - (F_{N+1} - F_N))}{k_B T}} = p_{N+1}(E_{\alpha,N+1}) e^{-\frac{(\varepsilon_i - \mu)}{k_B T}} \end{aligned}$$

➤ $\mu = F_{N+1} - F_N$ is the chemical potential

The Fermi Dirac distribution

- Using the definition of the chemical potential and the relation we found we rewrite the probability of state i being occupied as

$$f_{i,N} = 1 - e^{\frac{\varepsilon_i - \mu}{k_B T}} \sum p_{N+1}(E_{\alpha, N+1}) \left\{ \begin{array}{l} \text{Summing over all states, } \alpha, \text{ of the } N + 1 \text{ electron} \\ \text{system in which the single electron state, } i, \text{ is occupied} \end{array} \right.$$

- Earlier we wrote

$$f_{i,N} = \sum p_N(E_{\alpha, N}) \left\{ \begin{array}{l} \text{Summing over all states, } \alpha, \text{ of the } N \text{ electron system} \\ \text{in which the single electron state, } i, \text{ is occupied} \end{array} \right.$$

Which for $N+1$ becomes

$$f_{i,N+1} = \sum p_{N+1}(E_{\alpha, N+1}) \left\{ \begin{array}{l} \text{Summing over all states, } \alpha, \text{ of the } N \text{ electron system} \\ \text{in which the single electron state, } i, \text{ is occupied} \end{array} \right.$$

- Combining the two equation we find

$$f_{i,N} = 1 - e^{\frac{\varepsilon_i - \mu}{k_B T}} f_{i,N+1}$$

The Fermi Dirac distribution

- In the limit of large N , and we are usually interested in N of the order of 10^{22} , $f_{i,N} \sim f_{i,N+1}$.
- Therefore,

$$f_{i,N} = \frac{1}{1 + e^{\frac{\epsilon_i - \mu}{k_B T}}}$$

- The number, N , can be dropped because it is given by the sum over the average occupation of the single electron states

$$N = \sum f_i = \sum \frac{1}{1 + e^{\frac{\epsilon_i - \mu}{k_B T}}}$$

In many cases the chemical potential is not given but rather determined from the known density and temperature.

Note that f_i is simply the Fermi Dirac distribution.

The Fermi Dirac distribution

- Note that the chemical potential, μ , depends on the temperature because the free energy required to add a particle depends on the temperature.
- For $\varepsilon = \mu$, the Fermi Dirac probability density is equal $\frac{1}{2}$.
- In the limit $\varepsilon - \mu \gg k_B T$ the Fermi Dirac distribution approaches the Boltzmann distribution

$$\frac{1}{1 + e^{\frac{\varepsilon - \mu}{k_B T}}} \approx \frac{1}{e^{\frac{\varepsilon - \mu}{k_B T}}} = e^{\frac{\mu}{k_B T}} e^{-\frac{\varepsilon}{k_B T}}$$

The Fermi Dirac distribution

➤ The density of independent electrons may be written as:

$$n = \frac{N}{V} = \sum_{\vec{k}} \frac{1/V}{1 + e^{\frac{\varepsilon(\vec{k}) - \mu}{k_B T}}} = \int \frac{d\vec{k}}{4\pi^3} \frac{1}{1 + e^{\frac{\varepsilon(\vec{k}) - \mu}{k_B T}}} = \int \frac{d\vec{k}}{4\pi^3} f_{FD}(\varepsilon(\vec{k}))$$

It is convenient (and useful) to write the integral in terms of the energy rather than the wavevector when the energy is only a function of $k = |\vec{k}|$

$$n = \int \frac{d\vec{k}}{4\pi^3} f_{FD}(\varepsilon(\vec{k})) = \int \frac{k^2 dk}{\pi^2} f_{FD}(\varepsilon(k)) = \int d\varepsilon g(\varepsilon) f_{FD}(\varepsilon)$$

By definition, $g(\varepsilon) \equiv (k^2/\pi^2)dk/d\varepsilon$, is the density of states:

$$g(\varepsilon) = \frac{1}{V} \times \text{Number of one electron levels in the interval } [\varepsilon, \varepsilon + d\varepsilon]$$

The Fermi Dirac distribution at $T=0$

- For free electron gas, in which the states are specified by the momentum \vec{k} and the spin state, σ , the energies are independent of the spin (in the absence of magnetic field) and are given by $\varepsilon(\vec{k}) = \hbar^2 k^2 / 2m_e$.
- At $T=0$ the energies below the fermi energy are occupied and those above it are not,

$$f_{\vec{k},\sigma} = \begin{cases} 1 & \varepsilon(\vec{k}) < \varepsilon_F \\ 0 & \varepsilon(\vec{k}) > \varepsilon_F \end{cases}$$

- For the Fermi Dirac distribution as we wrote it

$$f_{\vec{k},\sigma} = \begin{cases} 1 & \varepsilon(\vec{k}) < \mu \\ 0 & \varepsilon(\vec{k}) > \mu \end{cases}$$

Therefore, consistency requires that $\lim_{T \rightarrow 0} \mu = \varepsilon_F$

The constant volume heat capacity

- The constant volume heat capacity is defined as

$$c_v = \left(\frac{\partial u}{\partial T} \right)_V \quad \text{where } u = \frac{U}{V} \quad \text{and } U \text{ is the internal energy}$$

In the independent electron approximation, the internal energy is simply the sum of the energies of the occupied states

$$U = 2 \sum_{\vec{k}} \varepsilon(\vec{k}) f_{FD}(\varepsilon(\vec{k})) \quad \text{and} \quad f_{FD}(\varepsilon(\vec{k})) = \frac{1}{1 + e^{\frac{\varepsilon(\vec{k}) - \mu}{k_B T}}}$$

Dividing both sides by the volume allows us to write it as

$$u = \frac{U}{V} = \int \frac{d\vec{k}}{4\pi^3} \varepsilon(\vec{k}) f_{FD}(\varepsilon(\vec{k})) = \int_0^\infty \frac{k^2 dk}{\pi^2} \varepsilon(k) f_{FD}(\varepsilon(k)) = \int_{-\infty}^\infty \varepsilon g(\varepsilon) f_{FD}(\varepsilon) d\varepsilon$$

The constant volume heat capacity

Where

$$g(\varepsilon) = \begin{cases} \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2m\varepsilon}{\hbar^2}} & \varepsilon > 0 \\ 0 & \varepsilon < 0 \end{cases}$$

Because $\varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m} \rightarrow \frac{d\varepsilon}{dk} = \frac{\hbar^2 k}{m} = \frac{\hbar^2}{m} \sqrt{\frac{2m\varepsilon}{\hbar^2}}$ and $k^2 = 2m\varepsilon/\hbar^2$.

The density of states is often written using the definition of the fermi energy as

$$g(\varepsilon) = \begin{cases} \frac{3}{2} \frac{n}{\varepsilon_F} \sqrt{\frac{\varepsilon}{\varepsilon_F}} & \varepsilon > 0 \\ 0 & \varepsilon < 0 \end{cases}$$

Where we used n
 $= k_F^3/3\pi^2$ and ε_F
 $= \hbar^2 k_F^2/2m$

The constant volume heat capacity

Note that

$$g(\varepsilon_F) = \frac{3 n}{2 \varepsilon_F} = \frac{3 k_F^3/3\pi^2}{2 \hbar^2 k_F^2/2m} = \frac{m_e k_F}{\hbar^2 \pi^2}$$

Where we used $n = k_F^3/3\pi^2$ and $\varepsilon_F = \hbar^2 k_F^2/2m_e$

The constant volume heat capacity

Integrals of the form we found for u are complicated. However, a very good approximation can be found using several properties of the Fermi Dirac distribution.

$$u = \int_{-\infty}^{\infty} \varepsilon g(\varepsilon) f_{FD}(\varepsilon) d\varepsilon$$

For n we have a similar integral and for many quantities of interest we may write the result in the form of

$$\int_{-\infty}^{\infty} Z(\varepsilon) f_{FD}(\varepsilon) d\varepsilon$$

For $T = 0$ the Fermi Dirac distribution is simply a step function (with the step being at $\varepsilon = \varepsilon_F = \mu$). For finite temperatures the distribution deviates from the step function only in a small range of a few $k_B T$ around the Fermi energy.

By expanding the function $Z(\varepsilon)$ in a Taylor series around $\varepsilon = \mu$ we can derive an excellent approximation for the integral.

$$Z(\varepsilon) = \sum_{n=0}^{\infty} \left. \frac{d^n Z(\varepsilon)}{d\varepsilon^n} \right|_{\varepsilon=\mu} \frac{(\varepsilon - \mu)^n}{n!}$$

And the integral is

$$\int_{-\infty}^{\infty} Z(\varepsilon) f_{FD}(\varepsilon) d\varepsilon = \int_{-\infty}^{\mu} Z(\varepsilon) d\varepsilon + \sum_{n=1}^{\infty} (k_B T)^{2n} a_n \left. \frac{d^{2n-1} Z(\varepsilon)}{d\varepsilon^{2n-1}} \right|_{\varepsilon=\mu}$$

This expansion is known as the Sommerfeld expansion.

- The a_n 's are dimensionless constants of order 1
- Typically, $\left. \frac{d^{2n-1} Z(\varepsilon)}{d\varepsilon^{2n-1}} \right|_{\varepsilon=\mu} \sim \frac{Z(\mu)}{\mu^n}$ and successive terms in the expansion are smaller

by $O\left(\left(\frac{k_B T}{\mu}\right)^2\right)$ which is usually 10^{-4} at room temperature.

Consequently, only the first and occasionally the second terms are retained and the explicit form for the integral is:

$$\int_{-\infty}^{\infty} Z(\varepsilon) f_{FD}(\varepsilon) d\varepsilon$$

$$= \int_{-\infty}^{\mu} Z(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 \left. \frac{dZ(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=\mu} + \frac{7\pi^4}{360} (k_B T)^4 \left. \frac{d^3 Z(\varepsilon)}{d\varepsilon^3} \right|_{\varepsilon=\mu} + O\left(\left(\frac{k_B T}{\mu}\right)^6\right)$$

In order to calculate the specific heat of metals, at temperatures considerably smaller than T_F , we apply this formula to the energy density and the number density.

$$u = \int_{-\infty}^{\infty} \varepsilon g(\varepsilon) f_{FD}(\varepsilon) d\varepsilon = \int_{-\infty}^{\mu} \varepsilon g(\varepsilon) f_{FD}(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 (\mu g'(\mu) + g(\mu)) + O\left(\left(\frac{k_B T}{\mu}\right)^4\right)$$

$$n = \int_{-\infty}^{\infty} g(\varepsilon) f_{FD}(\varepsilon) d\varepsilon = \int_{-\infty}^{\mu} g(\varepsilon) f_{FD}(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 g'(\mu) + O\left(\left(\frac{k_B T}{\mu}\right)^4\right)$$

The expression for the density shows that μ deviates from its $T = 0$ value, ε_F by terms of order T^2 . Therefore, we can write:

$$\int_0^\mu Z(\varepsilon)d\varepsilon = \int_0^{\varepsilon_F} Z(\varepsilon)d\varepsilon + (\mu - \varepsilon_F)Z(\varepsilon_F) + O(T^2)$$

Applying this relation and replacing μ by ε_F in terms that are already of order T^2 in the expressions for the energy and number densities (neglecting terms of order T^4) we find

$$u = \int_{-\infty}^{\varepsilon_F} \varepsilon g(\varepsilon)d\varepsilon + \varepsilon_F \left((\mu - \varepsilon_F)g(\varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F) \right) + \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F)$$

$$n = \int_{-\infty}^{\varepsilon_F} g(\varepsilon)d\varepsilon + (\mu - \varepsilon_F)g(\varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F)$$

Since we are interested in constant volume and density (same as for $T = 0$) it implies:

$$(\mu - \varepsilon_F)g(\varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F) = 0 \rightarrow \mu = \varepsilon_F - \frac{\pi^2}{6} (k_B T)^2 \frac{g'(\varepsilon_F)}{g(\varepsilon_F)}$$

Consistent with our initial assumption that $\mu - \varepsilon_F \sim O(T^2)$

The constant volume heat capacity

For free electrons $g(\varepsilon) = \frac{3n}{2\varepsilon_F} \sqrt{\frac{\varepsilon}{\varepsilon_F}}$, therefore,

$$\mu = \varepsilon_F \left(1 - \frac{\pi^2}{3} \left(\frac{k_B T}{2\varepsilon_F} \right)^2 \right)$$

A small deviation from the zero temperature value proportional to $\left(\frac{k_B T}{\varepsilon_F} \right)^2$.

The condition of constant (independent of temperature) density simplifies the expression for the energy density

$$u = \int_{-\infty}^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon + \cancel{\varepsilon_F \left((\mu - \varepsilon_F) g(\varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F) \right)} + \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F)$$

$$u = \int_{-\infty}^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F) \rightarrow c_v = \left(\frac{\partial u}{\partial T} \right)_v = \frac{\pi^2}{3} k_B^2 T g(\varepsilon_F)$$

The constant volume heat capacity for quantum electron gas

$$c_v = \left(\frac{\partial u}{\partial T} \right)_V = \frac{\pi^2}{3} k_B^2 T g(\varepsilon_F) = \frac{\pi^2}{3} k_B^2 T \frac{3}{2} \frac{n}{\varepsilon_F} \sqrt{\frac{\varepsilon_F}{\varepsilon_F}} = \frac{\pi^2}{2} \frac{k_B T}{\varepsilon_F} n k_B$$

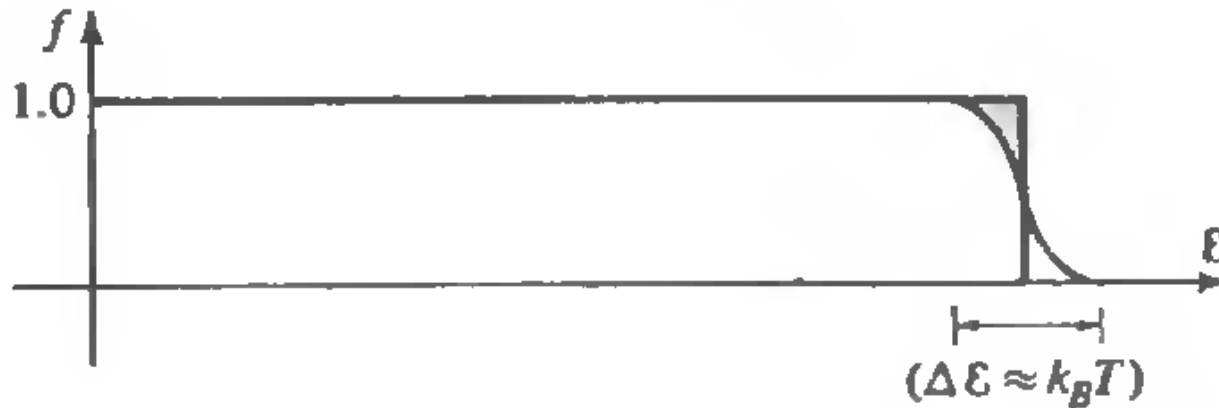
The classical expression we derived from Drude's model is:

$$c_v^{classical} = \frac{3}{2} n k_B$$

The corrections are a numerical factor and most importantly a factor of $\frac{k_B T}{\varepsilon_F}$ which is of order 0.01 at room temperature. This explains the fact that it was not observed experimentally at Drude's time.

The constant volume heat capacity

The explanation to this correction (not the numerical factors) is the fact that the FD distribution implies that only a small fraction of the electrons of order $k_B T g(\epsilon_F)$ are excited to states with energy higher by $k_B T$ when the temperature increases. So the total change in the energy density is $k_B^2 T^2 g(\epsilon_F)$ which results in a specific heat capacity smaller by $\pi^2/6$ than the one derived earlier.



The constant volume heat capacity

- The prediction of a linear dependence of the specific heat on the temperature is one of the most important results of the Sommerfeld model.
- It makes it possible to measure it if the contribution of other degrees of freedom are negligible compared with the electronic contribution.
- At high temperatures the ionic degrees of freedom completely dominate the specific heat but at low temperatures their contribution becomes smaller than the electronic one.
- The general form of the specific heat is

$$c_v = \gamma T + AT^3$$

And therefore it is common to look at

$$\frac{c_v}{T} = \gamma + AT^2$$

Sommerfeld conductivity

- In order to find the response of the electrons to electric field one has to calculate their velocity.
- The Fermi Dirac distribution can be written in terms of the velocity as:

$$f_{FD}(\vec{v}) = \frac{(m/\hbar)^3}{4\pi^3} \frac{1}{1 + e^{(\frac{1}{2}mv^2 - \mu)/k_B T}}$$

- Sommerfeld described the dynamics using classical equation only replacing the Boltzmann distribution by the Fermi Dirac one.
- In order to justify this treatment, there are several conditions and assumptions that have to be made.

Sommerfeld conductivity

- The typical momentum of an electron is $\hbar k_F$ and in order to allow for a classical description the uncertainty in its momentum must be much smaller than the typical momentum, i.e., $\Delta p \ll \hbar k_F$.
- The uncertainty in the position is $\Delta x \sim \frac{\hbar}{\Delta p} \gg 1/k_F$.
- Earlier we showed that $k_F = \frac{3.63}{r_s/r_0} \text{Å}^{-1}$ so the uncertainty in the position is of the order the interatomic distance.
- Therefore, the classical description is only valid for distances much larger than the inter atomic distances, which luckily, are the relevant distances for conducting electrons in metals.

Sommerfeld conductivity

- The classical description requires the knowledge of the position for two reasons:
1. Varying EM field or temperature gradient. In most cases the variation is considerable only over larger scales, for instance the EM field of visible light varies over the scale of its wavelength which is of the order of 10^3 \AA . For the effect of X-ray on the electrons we would need a QM description of the dynamics.
 2. The mean free path, the typical distance the electron travels between successive scatterings should be much larger than tens of \AA .

Sommerfeld conductivity

- The use of the Fermi Dirac distribution only affects quantities requiring knowledge of the velocity probability distribution. If we assume that the scattering time (the time between successive scattering events), τ , is independent of the electron velocity, then only the mean free path, thermal conductivity and thermopower are affected.
- Mean free path:

$$l = v_F \tau \sim 10^{-14} \text{ s} \cdot \frac{4.2}{\left(\frac{r_s}{r_0}\right)} 10^8 \frac{\text{cm}}{\text{s}} \sim O(100 \text{ \AA})$$

- Thermal conductivity:

$$\kappa = \frac{1}{3} v_F^2 \tau c_v$$

We replaced the thermal velocity by Fermi velocity and use the correct c_v to get the Weidman-Franz relation

Sommerfeld conductivity

➤ Thermal and electric conductivities:

$$\sigma = ne^2\tau/m_e$$

$$v_F^2 = \frac{2\varepsilon_F}{m_e}$$

$$c_v = \frac{\pi^2 k_B T}{2 \varepsilon_F} nk_B$$

$$\kappa = \frac{1}{3} v_F^2 \tau c_v = \frac{1}{3} \frac{2\varepsilon_F}{m_e} \tau \frac{\pi^2 k_B T}{2 \varepsilon_F} nk_B = \frac{\pi^2}{3} \frac{1}{m_e} \tau k_B^2 T n$$

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.44 \cdot 10^{-8} \text{ watt} \cdot \text{ohm}/K^2$$

Very close to Drude's result (except for the factor of 2) in which two errors cancelled in the calculation of the ratio.

Sommerfeld conductivity

- Thermopower:

$$Q = -\frac{c_v}{3ne} = -\frac{\frac{\pi^2}{2} \frac{k_B T}{\varepsilon_F} nk_B}{3ne} = -\frac{\pi^2}{6} \frac{k_B}{e} \frac{k_B T}{\varepsilon_F} = -1.42 \cdot 10^{-4} \left(\frac{k_B T}{\varepsilon_F} \right) \text{ Volt/K}$$

Which is smaller than Drude's estimate by a factor of ~ 0.01 at room temperatures.

- The electric AC and DC conductivities are unchanged because the dynamics of the electrons is considered classically and the velocity distribution has no role if one assumes scattering which is energy independent.
- One may consider the fact that since the ions are fixed, faster electrons have a shorter scattering time (Lorentz). However, this correction has a little effect in the Sommerfeld model because the replacement of the scattering time by the scattering time of electrons with Fermi energy dominates the response.

Failures of the “free electron” theory

The free electron theory, especially the Sommerfeld model, accounts for many properties of metals but there are several phenomena that cannot be explained using the Drude or Sommerfeld models.

- Hall coefficient: The Hall coefficient predicted by the free electron models is independent of the temperature and the strength of the magnetic field. Experiments show that in certain cases the dependence is quite strong and even the sign can be different for very strong magnetic field. $R_H = -1/nec$.
- Magnetoresistance: The observed magnetoresistance depends on the field and the free electron models do not explain it. $\sigma_0 E_x = j_x$.
- Thermoelectric effect: The sign of the thermoelectric field is not always what predicted by the models $Q = -\frac{c_v}{3ne}$.
- Wiedemann-Franz law: Only valid at high and low temperatures but fails at intermediate temperatures ($\kappa/\sigma T$ depends on the temperature).

Failures of the “free electron” theory

- Conductivity: The dependence of the DC conductivity on the temperature and its anisotropy are not explained. The measured frequency dependence of the conductivity is very different from the predicted dependence.
- Specific heat: The magnitude of the term linear in T is very different from the predicted one in some metals and the theory does not explain the T^3 term.

In order to overcome these failures the following assumptions have to be modified:

- Free electrons: The models do not account for the interaction of the electrons with the ions except for scattering.
- Independent electrons: The models do not account for the electron interactions with each other.
- Relaxation time: The models assumed that the relaxation time is independent of the electronic configuration.