# The Drude model description of electron dynamics under the influence of a time dependent force

Therefore,

$$\vec{p}(t+dt) = \vec{p}(t) - \frac{dt}{\tau}\vec{p}(t) + \vec{f}(t)dt + O\left(dt^2\right)$$

Taking the limit $dt \rightarrow 0$

$$\lim_{dt\rightarrow 0} \frac{\vec{p}(t+dt) - \vec{p}(t)}{dt} = \frac{d}{dt}\,\vec{p}(t) = -\frac{1}{\tau}\vec{p}(t) + \vec{f}(t)$$

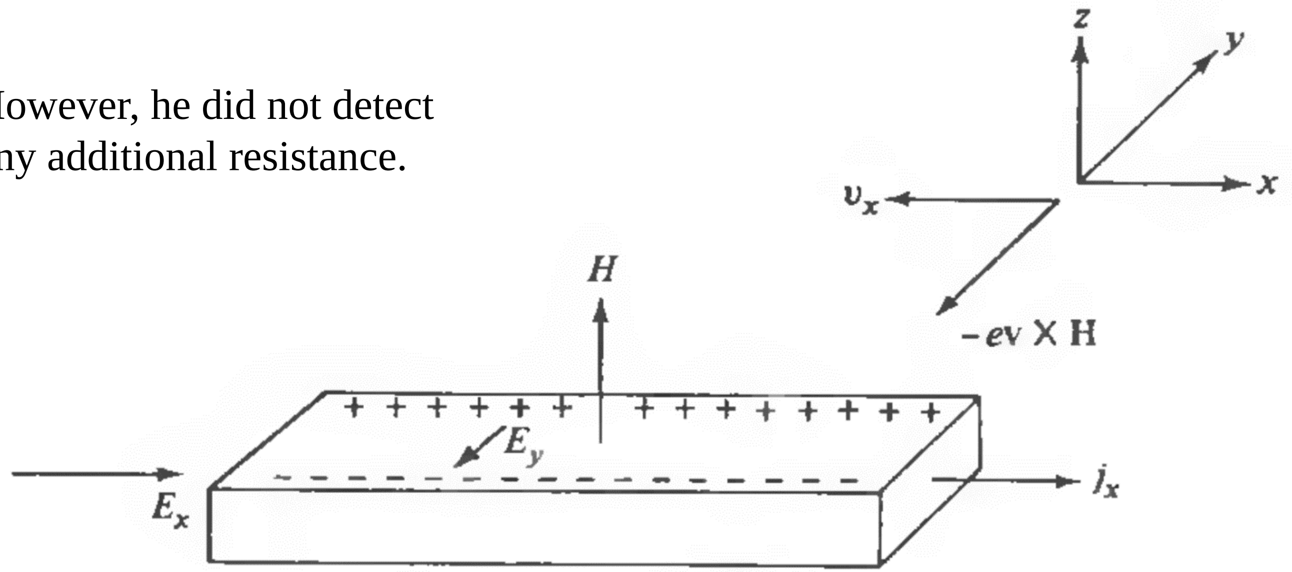
The formal solution is:

$$\vec{p}(t) = \vec{p}(0)e^{-\frac{t}{\tau}} + \int_0^t \vec{f}(t')e^{-\frac{t-t'}{\tau}}dt'$$

# The Drude model description of electron dynamics in the presence of magnetic field

In 1879 E. H. Hall tried to determine whether the force experienced by a current carrying wire in a magnetic field was exerted on the whole wire or only upon (what we would now call) the moving electrons in the wire. He suspected it was the latter, and his experiment was based on the argument that "if the current of electricity in a fixed conductor is itself attracted by a magnet, the current should be drawn to one side of the wire, and therefore the resistance experienced should be increased."

However, he did not detect any additional resistance.




Schematic view of Hall's experiment.

# The Drude model description of electron dynamics in the presence of magnetic field

The force experienced by an electron in magnetic field, the Lorentz force, is:

$$\vec{F} = -\frac{e}{c}\,\vec{v} \times \vec{H}$$

$\vec{v}$ is the velocity of the electron, $\vec{H}$ is the external magnetic field and c is the speed of light.

In the setup we consider, the magnetic field is in the positive $z$ direction. The electric field is in the positive $x$ direction which implies that the velocity of the electrons is in the negative $x$ direction.

$$\vec{F} = -\frac{e}{c}\,(-v_x)\,\hat{x} \times H\,\hat{z} = -\frac{e}{c} v_x H\,\hat{y}$$

# The Drude model description of electron dynamics in the presence of magnetic field

The force in the negative *y*-direction causes the accumulation of electrons on that side of the wire. This accumulation results in electric field which, in the steady state, balances the magnetic force (the electrons cannot leave the wire).

Two quantities of interest are the magnetoresistance:

$$\rho(H) = \frac{E_x}{j_x}$$

Which Hall found to be field-independent.

# The Drude model description of electron dynamics in the presence of magnetic field

The other quantity is the magnitude of the electric field in the y direction, which is expected to be proportional to both the magnetic field and the current density in the x direction (because in steady state it balances the Lorentz force). The Hall coefficient is defined as

$$R_H = \frac{E_y}{j_x H}$$

# The Drude model description of electron dynamics in the presence of magnetic field

- As we mentioned earlier, the electric field that balances the Lorentz force is in the negative *y* direction, therefore $E_y$ is negative.
- The magnetic field is in the positive *z* direction and is, therefore, positive.
- The current density in the *x* direction is positive (the electrons, that have negative charge, move in the negative direction).
- So $R_H = \frac{E_y}{j_x H}$ is expected to be negative for negative charge carriers.

# The Drude model description of electron dynamics in the presence of magnetic field

What if the current was due to positive charge carriers?

- The sign of the Lorentz force ($\vec{F} = -\frac{e}{c} v_x H\, \hat{y}$) would remain the same (the charge and the velocity change sign), so the sign of $E_y$ would be the opposite (in order to balance the Lorentz force for positive charges the field would be in the positive y direction).
- The magnetic field remains in the same direction and so is the sign of $H$.
- The current density remains in the same direction because both the charge and the velocity change sign.
- Therefore, the Hall coefficient would be positive for positive charge carriers.

This enables to verify that the charge carriers are indeed the electrons (negatively charged).

# The Drude model description of electron dynamics in the presence of magnetic field

- Hall's original data agreed with the sign of the electron charge (which was later verified by Thomson).
- However, several metals showed positive Hall coefficients which Drude's model cannot explain.

In order to calculate the magnetoresistance and the Hall coefficient we go back to the equation of motion

$$\frac{d}{dt}\,\vec{p}(t) = -\frac{1}{\tau}\vec{p}(t) - e\left(\vec{E} + \frac{1}{c}\frac{\vec{p}(t)}{m_e} \times \vec{H}\right)$$

# The Drude model description of electron dynamics in the presence of magnetic field

In the steady state the current (and the momenta) components are independent of time and, therefore,

$$\frac{dp_x}{dt} = 0 = -\frac{p_x}{\tau} - eE_x - \frac{eH}{m_e c} p_y$$

$$\frac{dp_y}{dt} = 0 = -\frac{p_y}{\tau} - eE_y + \frac{eH}{m_e c} p_x$$

It is convenient to define the cyclotron frequency $\omega_c = eH/m_e c$, which is the frequency with which an electron rotates in the plane perpendicular to a uniform magnetic field.

We multiply the equations by $-ne\tau/m_e$

$$\sigma_0 E_x = j_x + j_y \tau \omega_c$$

$$\sigma_0 E_y = j_y - j_x \tau \omega_c$$

$$\sigma_0 = \frac{ne^2\tau}{m_e}$$

# The Drude model description of electron dynamics in the presence of magnetic field

- In steady state, the current in the *y* direction should be zero:

$$\sigma_0 E_x = j_x + \cancel{j_y \tau \omega_c} \Rightarrow \sigma_0 E_x = j_x$$

$$\sigma_0 E_y = \cancel{j_y} - j_x \tau \omega_c \Rightarrow E_y = -\frac{j_x \tau \omega_c}{\sigma_0} = -\frac{H}{nec} j_x$$

$$\frac{\omega_c}{\sigma_0} = \frac{\frac{eH}{m_e c}}{\frac{ne^2\tau}{m_e}}$$

So the Hall coefficient is:

$$R_H = \frac{E_y}{j_x H} = -\frac{1}{nec}$$

- Interestingly, the result is independent of the field, temperature (in Drude's picture) and other factors and it only depends on the density of the atoms in the metal!
- Note that the magnetoresistance is simply the regular resistance. In agreement with Hall's original results.

*the units of the Hall coefficient are: $cm^2 s/C$

# The Drude model description of electron dynamics in the presence of magnetic field

However, Drude's model cannot explain:

- The positive Hall coefficient observed for some metals.
- The later observed dependence of the Hall coefficient on the temperature, magnetic field and the care by which the conducting sample was prepared.
- The additional magnetoresistance that was observed in later experiments.

Note that $\frac{E_y}{E_x} = -\tau\omega_c$ while the current density is in the x direction.

Therefore the angle between the current density and the electric field is given by $\rightarrow \tan(\phi) = \tau\omega_c$

# The Drude model description of electron dynamics in AC field

In order to evaluate the response to AC field we start by considering the Fourier transform of the equation of motion

$$\frac{d}{dt}\vec{p}(t) = -\frac{1}{\tau}\vec{p}(t) - e\vec{E}(t) \rightarrow -i\omega\,\tilde{\vec{p}}(\omega) = -\frac{\tilde{\vec{p}}(\omega)}{\tau} - e\tilde{\vec{E}}(\omega)$$

$$\rightarrow \tilde{\vec{p}}(\omega) = -\frac{e\tilde{\vec{E}}(\omega)}{\left(\frac{1}{\tau} - i\omega\right)}$$

The current density is related to the momentum through

$$\vec{j} = -ne\frac{\vec{p}}{m_e} \rightarrow \tilde{\vec{j}}(\omega) = \frac{\sigma_0}{(1 - i\omega\tau)}\tilde{\vec{E}}(\omega) = \sigma(\omega)\tilde{\vec{E}}(\omega)$$

$$\sigma_0 = \frac{ne^2\tau}{m_e}$$

Note that in the DC limit one gets the correct limit.

Can we use this result to describe the propagation of radiation (EM field) in a metal?

# The Drude model description of electron dynamics in AC field

We made two assumption:

*i*) We neglected the magnetic field. However, the neglected Lorentz force has a factor of $v/c$ compared with the electric field force. The drift velocity of electrons in a metal, even for relatively strong current densities, is of the order of *cm/s* so it's orders of magnitude smaller than the force due to the electric field.

# The Drude model description of electron dynamics in AC field

*ii*) We assumed that the force acting on each electron is the same. However, the field spatially varies within the metal (because it's a wave).

This suggests that our treatment would be relevant for radiation with wavelengths that are much larger than the typical mean free path of the electrons (thereby varying only slightly during the motion between collisions) and we may write

$$\tilde{\vec{j}}(\omega,\vec{r}) = \sigma(\omega)\tilde{\vec{E}}(\omega,\vec{r})$$

Note that for visible light, whose wavelength is $400 - 700nm$ $(4000 - 7000\text{Å})$, the condition is usually satisfied.

# The Drude model description of electron dynamics in AC field

Assuming that the description above is valid, we write the Maxwell equations in the presence of a current density $\vec{j}$ as

$$\nabla \cdot \vec{E} = 0; \nabla \cdot \vec{H} = 0;$$

$$\nabla \times \vec{E} = -\frac{1}{c}\frac{\partial \vec{H}}{\partial t}; \nabla \times \vec{H} = \frac{4\pi}{c}\vec{j} + \frac{1}{c}\frac{\partial \vec{E}}{\partial t}$$

Considering the Fourier transform with respect to time we obtain for the latter equations

$$\nabla \times \tilde{\vec{E}} = i\frac{\omega}{c}\tilde{\vec{H}}; \nabla \times \tilde{\vec{H}} = \frac{4\pi}{c}\tilde{\vec{j}} - i\frac{\omega}{c}\tilde{\vec{E}}$$

Using the relation we found between the electric field and the current density we rewrite it as

$$\nabla \times \tilde{\vec{E}}(\omega) = i\frac{\omega}{c}\tilde{\vec{H}}(\omega); \nabla \times \tilde{\vec{H}} = \left(\frac{4\pi}{c}\sigma(\omega) - i\frac{\omega}{c}\right)\tilde{\vec{E}}(\omega)$$

# The Drude model description of electron dynamics in AC field

Taking the curl of the first equation and substituting the second one, we find

$$\nabla \times \nabla \times \vec{\tilde{E}}(\omega) = -\nabla^2 \vec{\tilde{E}}(\omega) = i\frac{\omega}{c}\nabla \times \vec{\tilde{H}}(\omega) = i\frac{\omega}{c}\left(\frac{4\pi}{c}\sigma(\omega) - i\frac{\omega}{c}\right)\vec{\tilde{E}}(\omega)$$

$$-\nabla^2 \vec{\tilde{E}}(\omega) = i\frac{\omega}{c}\left(\frac{4\pi}{c}\sigma(\omega) - i\frac{\omega}{c}\right)\vec{\tilde{E}}(\omega) = \frac{\omega^2}{c^2}\left(1 + i\frac{4\pi}{\omega}\sigma(\omega)\right)\vec{\tilde{E}}(\omega)$$

$$\equiv \frac{\omega^2}{c^2}\epsilon(\omega)\,\vec{\tilde{E}}(\omega)$$

Where we used the identity $\nabla \times \nabla \times \vec{E} = \nabla\left(\nabla \cdot \vec{E}\right) - \nabla^2 \vec{E} = -\nabla^2 \vec{E}$.

We also defined the complex dielectric constant

$$\epsilon(\omega) = \left(1 + i\frac{4\pi}{\omega}\sigma(\omega)\right)$$

# The Drude model description of electron dynamics in AC field

Substituting explicitly the expression for $\sigma(\omega)$

$$\epsilon(\omega) = \left(1 + i\frac{4\pi}{\omega}\frac{\sigma_0}{(1 - i\omega\tau)}\right)$$

For $\omega\tau \gg 1$

$$\epsilon(\omega) = \left(1 - \frac{4\pi}{\omega^2}\frac{\sigma_0}{\tau}\right) = \left(1 - \frac{\omega_p^2}{\omega^2}\right)$$

Where $\omega_p^2 \equiv \frac{4\pi n e^2}{m_e}$ is called the plasma frequency.

# The Drude model description of electron dynamics in AC field

Considering the spatial Fourier transform to the wave equation we may write the dispersion relation as

$$k^2 = \frac{\omega^2}{c^2}\epsilon(\omega) \sim \frac{\omega^2}{c^2}\left(1 - \frac{\omega_p^2}{\omega^2}\right)$$

For $\omega < \omega_p$ the RHS is negative and, therefore, $k$ is imaginary which implies an exponential decay of the wave inside the metal.

However, for $\omega > \omega_p$, $k$ is real and the wave may propagate through the metal without decaying.

# The Drude model description of charge density oscillations

In our previous derivation we assumed that there is no charge density in the metal. However, under certain conditions there is a possibility for charge oscillations in the metal.

$$\nabla \cdot \vec{E} = 4\pi\rho \quad Gauss's\ law$$

$$\nabla \cdot \vec{j} = -\frac{\partial \rho}{\partial t} \qquad continuity\ equation$$

Taking the Fourier transform with respect to time we write the equations as

$$\nabla \cdot \tilde{\vec{E}}(\omega) = 4\pi\tilde{\rho}(\omega) \quad Gauss's\ law$$

$$\nabla \cdot \tilde{\vec{j}} = i\omega\tilde{\rho}(\omega) \qquad continuity\ equation$$

Using $\tilde{j}(\omega) = \sigma(\omega)\tilde{\vec{E}}(\omega)$ we rewrite the continuity equation as

$$\nabla \cdot \tilde{\vec{E}}(\omega) = \frac{i\omega\tilde{\rho}(\omega)}{\sigma(\omega)} \qquad continuity\ equation$$

# The Drude model description of charge density oscillations

Combining the two equations we find

$$4\pi\tilde{\rho}(\omega) = \frac{i\omega\tilde{\rho}(\omega)}{\sigma(\omega)}$$

Which has a solution with non-zero charge density only for

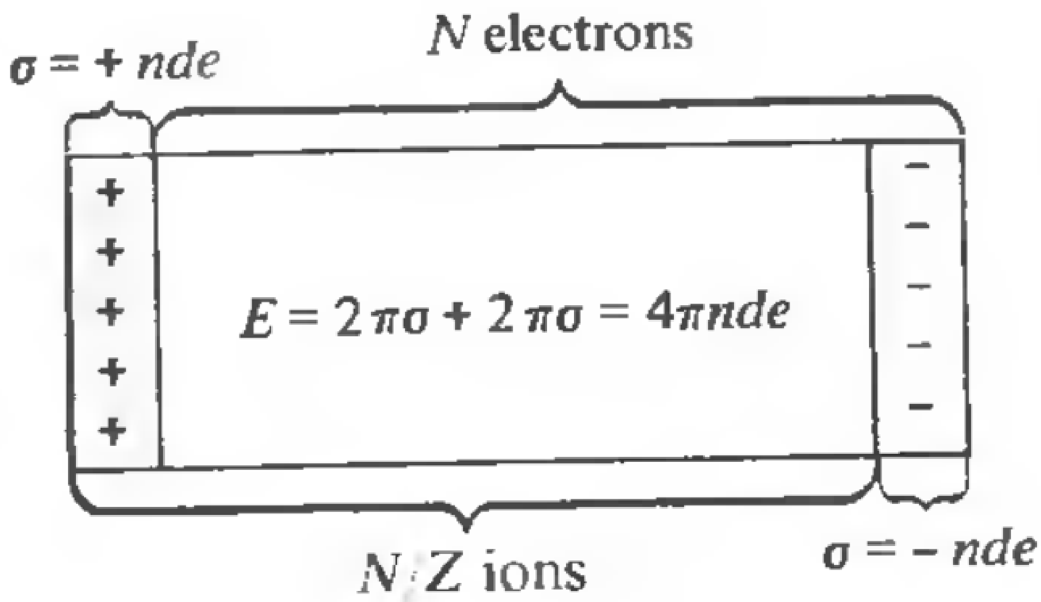
$$1 + i\frac{4\pi\sigma(\omega)}{\omega} = 0$$

This is exactly the case for which $\epsilon(\omega) = \left(1 + i\frac{4\pi}{\omega}\sigma(\omega)\right) = 0$

(for positive $\epsilon(\omega)$ EM waves can propagate in the metal -- k is real) .

If the condition is satisfied by the frequency then a charge density can propagates through the metal. This is known as plasma oscillations or Plasmon.

# The Drude model description of charge density oscillations




If we have an initial displacement of the electron gas with respect to the background of ions by a distance d, the charge at the edges will result in an electric field $4\pi\rho_{edge}$ where $\rho_{edge} = nde$ is the charge density at either end. The electron gas dynamics in this case may be described by

$$Nm_e\ddot{d} = -Ne(4\pi ned) \rightarrow \ddot{d} = -\omega_p^2 d$$

Namely the charge density would oscillate with the plasma frequency.

## 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 ($\kappa$) and electrical ($\sigma$) conductivities is proportional to the temperature with an almost identical coefficient of proportionality for many metals.

The ratio $\frac{\kappa}{\sigma \mathrm{T}}$ 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

$T_L$  $T_R$

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:

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

# 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

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

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

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

# The Drude model description of the thermal conductivity of metals Problems with the assumptions

The above assumptions lead to the Lorenz number

$$\frac{\kappa}{\sigma T} = \frac{\frac{1}{3}v^2\tau c_v}{\frac{ne^2\tau}{m_e}T} = \frac{\frac{1}{3}m_e v^2 c_v}{ne^2T} = \frac{\frac{1}{3}3k_BT\frac{3}{2}nk_B}{ne^2T} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2$$

$$\approx 1.11 \cdot 10^{-8} watt \cdot ohm/K^2$$

where we used the ideal gas properties $c_v = \frac{3}{2}nk_B$ and $\frac{1}{2}m_e v^2 = \frac{3}{2}k_BT$. This value is about ½ 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.


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:

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

Using the classical expression for the heat capacity

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

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

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 exists 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, $n = N/V$.

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} n\left(\frac{m_e}{2\pi k_B T}\right)^{3/2} e^{-\frac{m_e v^2}{2k_B T}} dv_x dv_y dv_z$$

$$= \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} v^2 sin\theta n\left(\frac{m_e}{2\pi k_B T}\right)^{3/2} e^{-\frac{m_e v^2}{2k_B T}} dv d\theta d\phi$$

$$= n2\pi\left(\frac{m_e}{2\pi k_B T}\right)^{3/2}\int_0^{\pi}\int_0^{\infty} v^2 sin\theta e^{-\frac{m_e v^2}{2k_B T}} dv d\theta$$

$$= n4\pi\left(\frac{m_e}{2\pi k_B T}\right)^{3/2}\int_0^{\infty} v^2 e^{-\frac{m_e v^2}{2k_B T}} dv = n$$

# Quantum theory of free electron gas

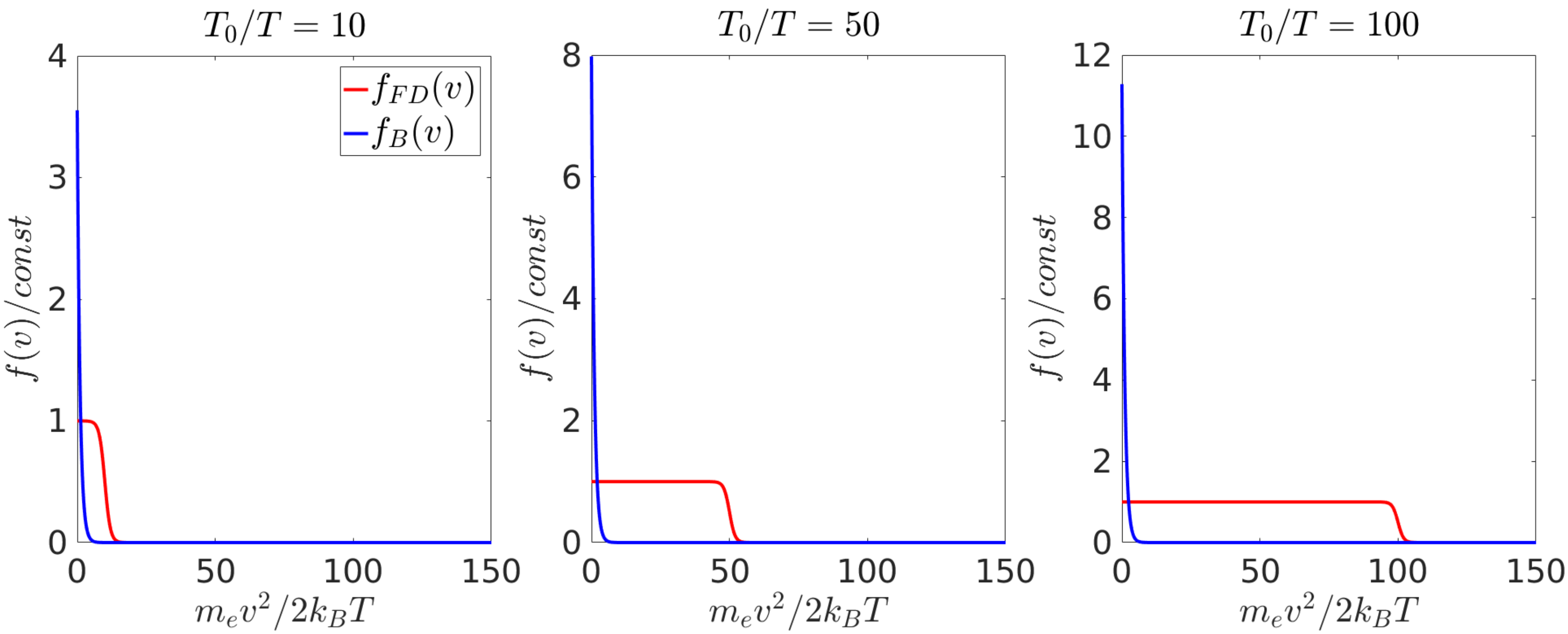
- The most important quantity which is ignored in the classical treatment is the fact that the electrons are fermions and, therefore, Pauli's exclusion principle applies to their distribution. Only one fermion may occupy a given state.
- This results in a distribution of energies (velocities) which deviates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

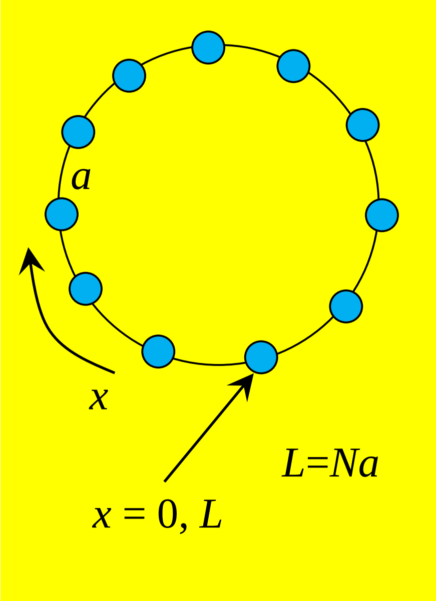
$$\psi(x) = Ae^{ikx}$$

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 chose 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 $n \in Integers$, 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

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

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:

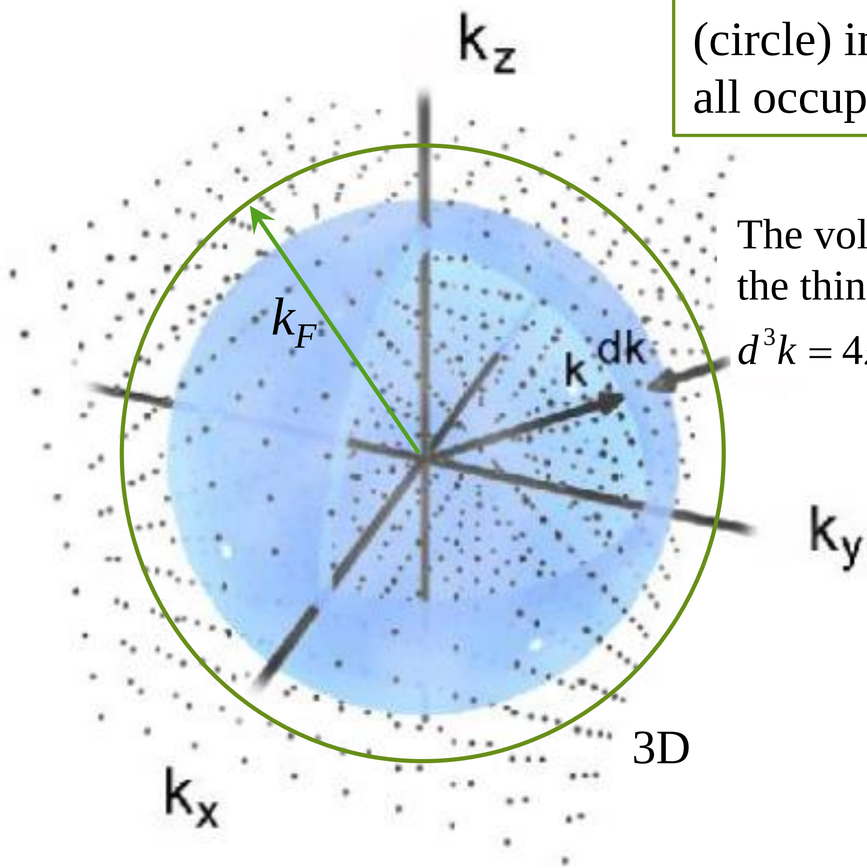
$$\Omega_F = \frac{4\pi k_F^3}{3} \Rightarrow N_k(\Omega_\mathrm{F}) = \frac{4\pi k_F^3}{3} / \frac{8\pi^3}{V} = \frac{k_F^3 V}{6\pi^2} \Rightarrow N_e(\Omega_F) = \frac{k_F^3 V}{3\pi^2}$$

$N_k(\Omega_\mathrm{F})$ is the number of k states within the Fermi sphere

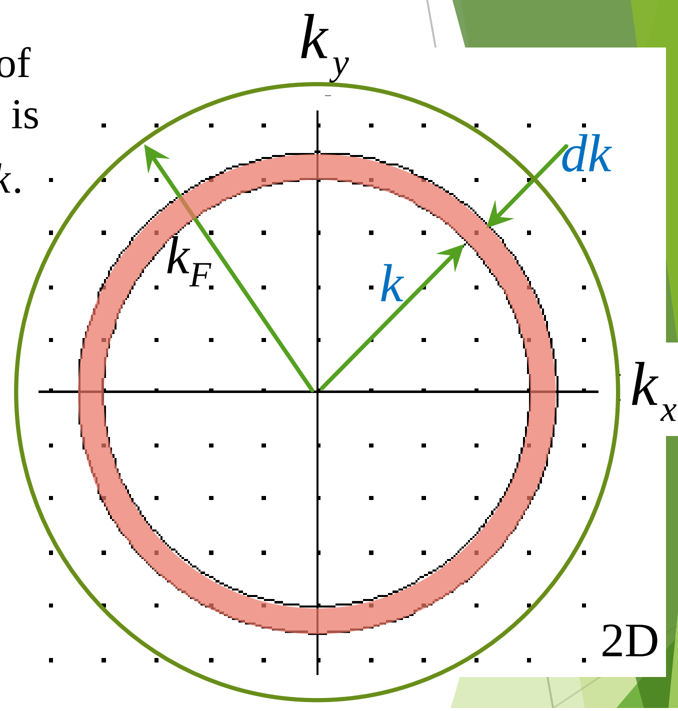
$N_e(\Omega_\mathrm{F})$ is the number of electron states within the Fermi sphere

# 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 $T = 0$.




The volume of the thin shell is $d^3k = 4\pi k^2 dk$.



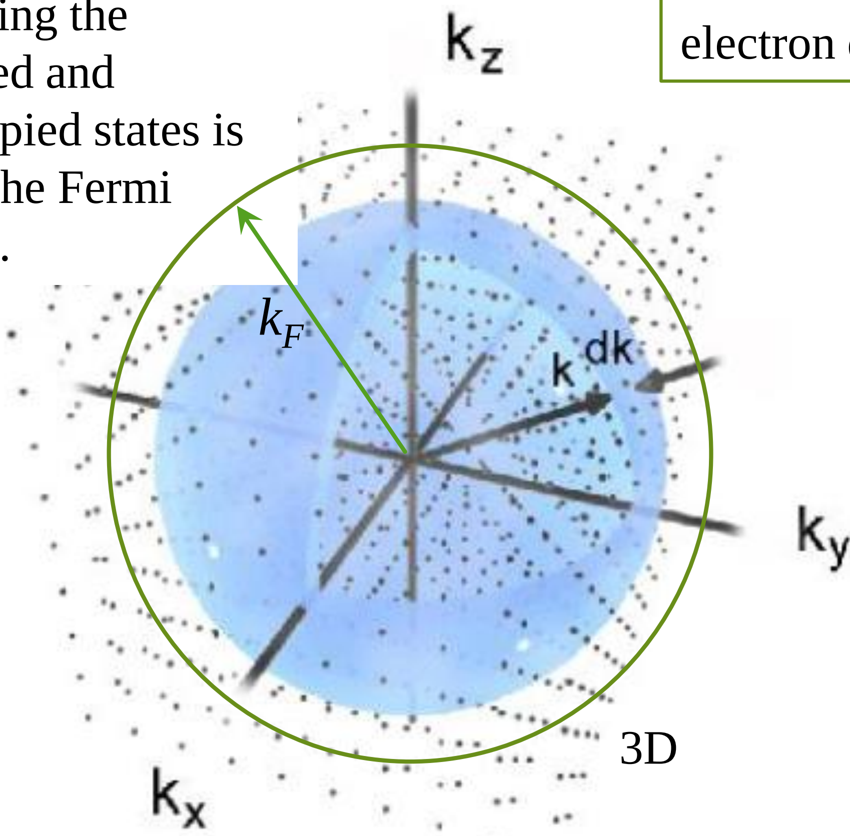

The area of the thin annulus (shaded red region) is $d^2k = 2\pi k dk$.

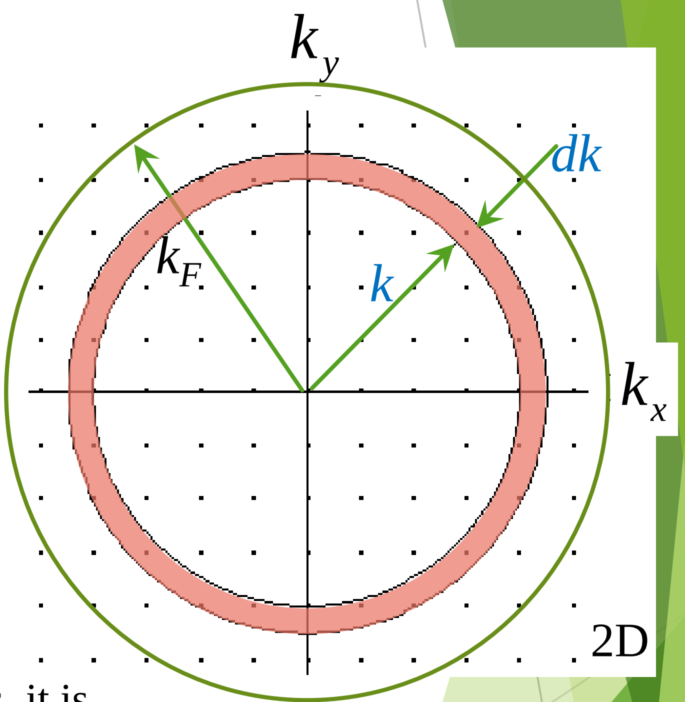
Note that the minimum spacing (distance between dots) in $k$-space depends on the size of the volume that we choose in real space (the dimension of the cube that we used for the quantization.

## The 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 $\boldsymbol{n = k_F^3/3\pi^2}$.




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

In order to get an estimate of the magnitude of these quantities, it is convenient to use the relation we found earlier, $r_s = \left(\frac{3}{4\pi n}\right)^{\frac{1}{3}}$

$k_F = \frac{3.63}{r_s/r_0} \text{Å}^{-1}$ and $v_F = \frac{\hbar k_F}{m_e} = \frac{4.2}{r_s/r_0} 10^8 cm/s$; note that this velocity is about 1% of the speed of light in vacuum.

# Fermi energy and the ground state energy

- The Fermi energy can be written as

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

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

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

- 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

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

- 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.

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

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 $T = \frac{2}{5} T_f$

$\approx 10^4 K$.