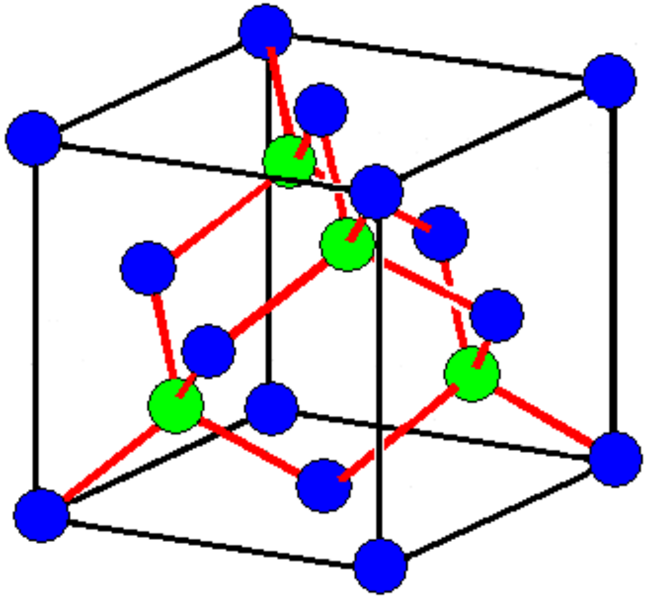

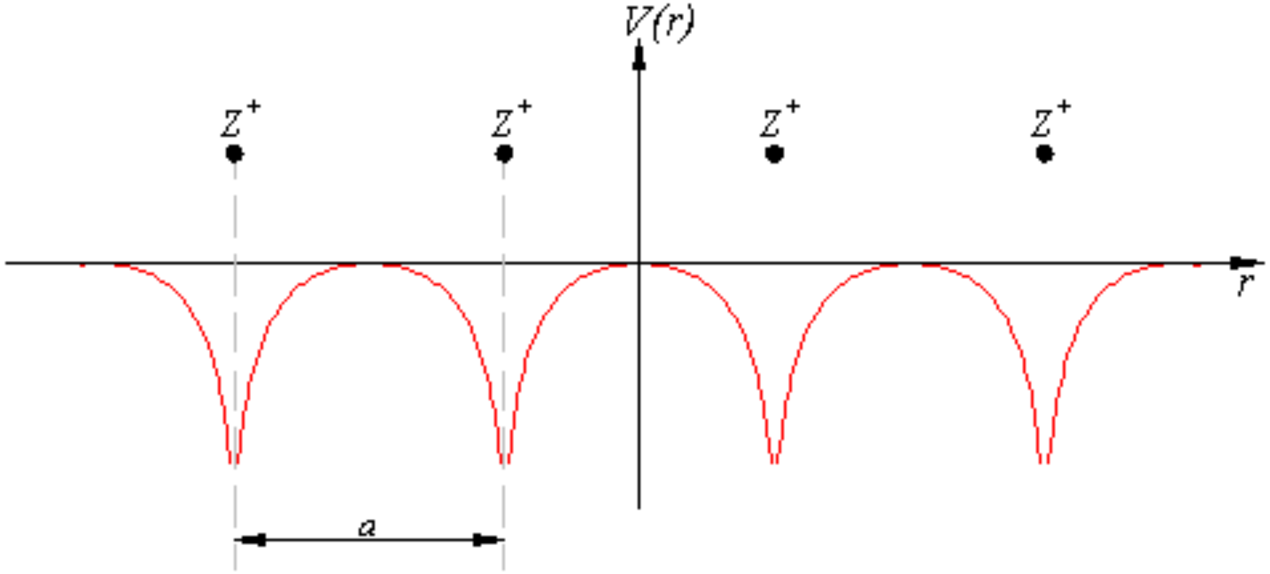

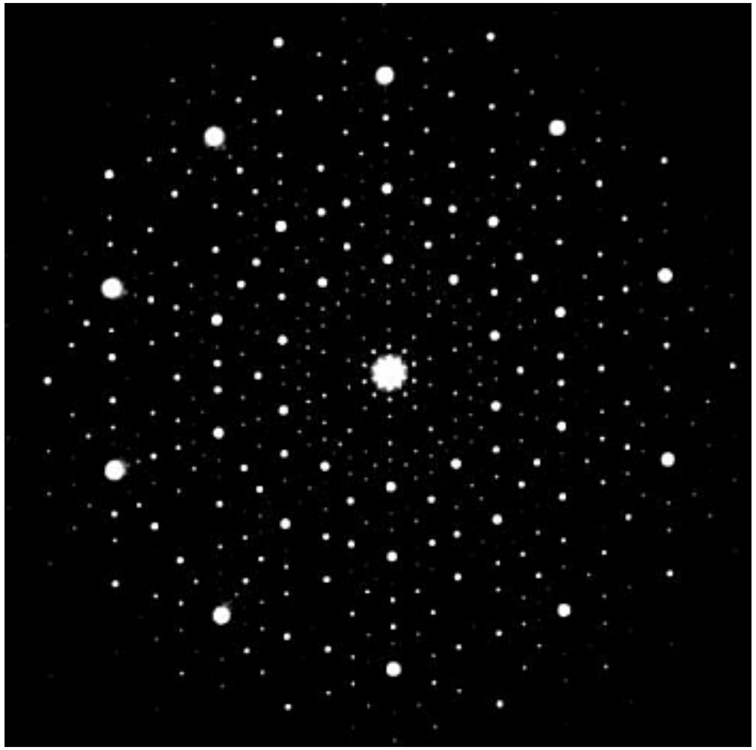

KYA322

Solid State Physics

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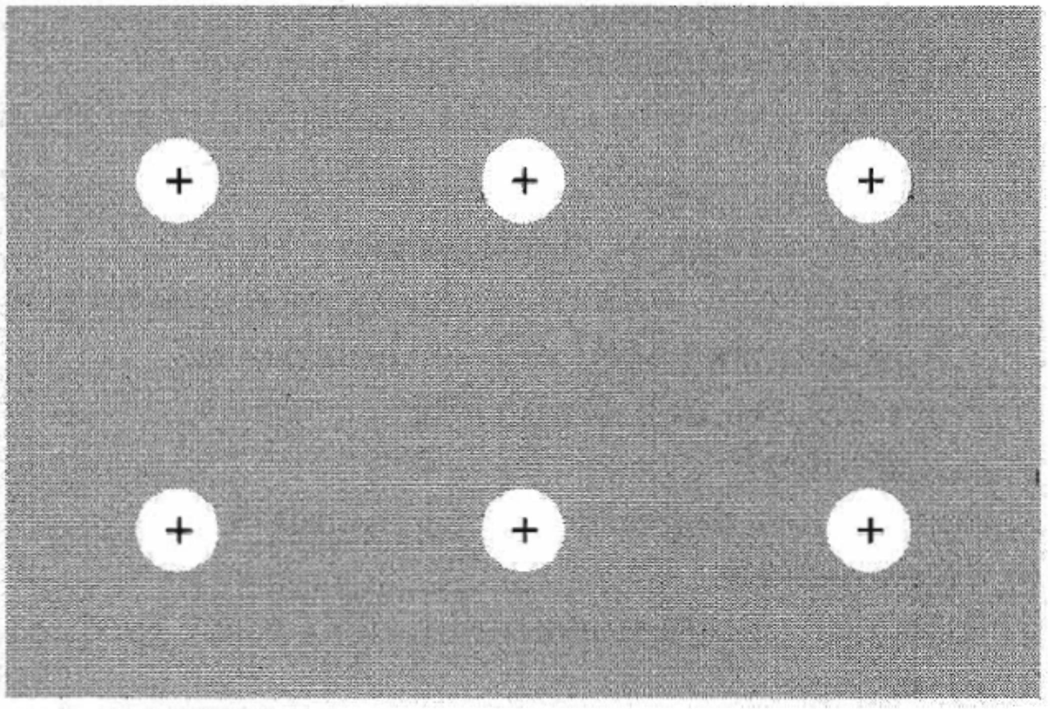
Electrons in Solids

For many properties of metals it is useful to treat the solid using the *free electron model*. The ion cores are embedded in a sea of conduction electrons, which are contributed by the valence electrons of the free atoms.

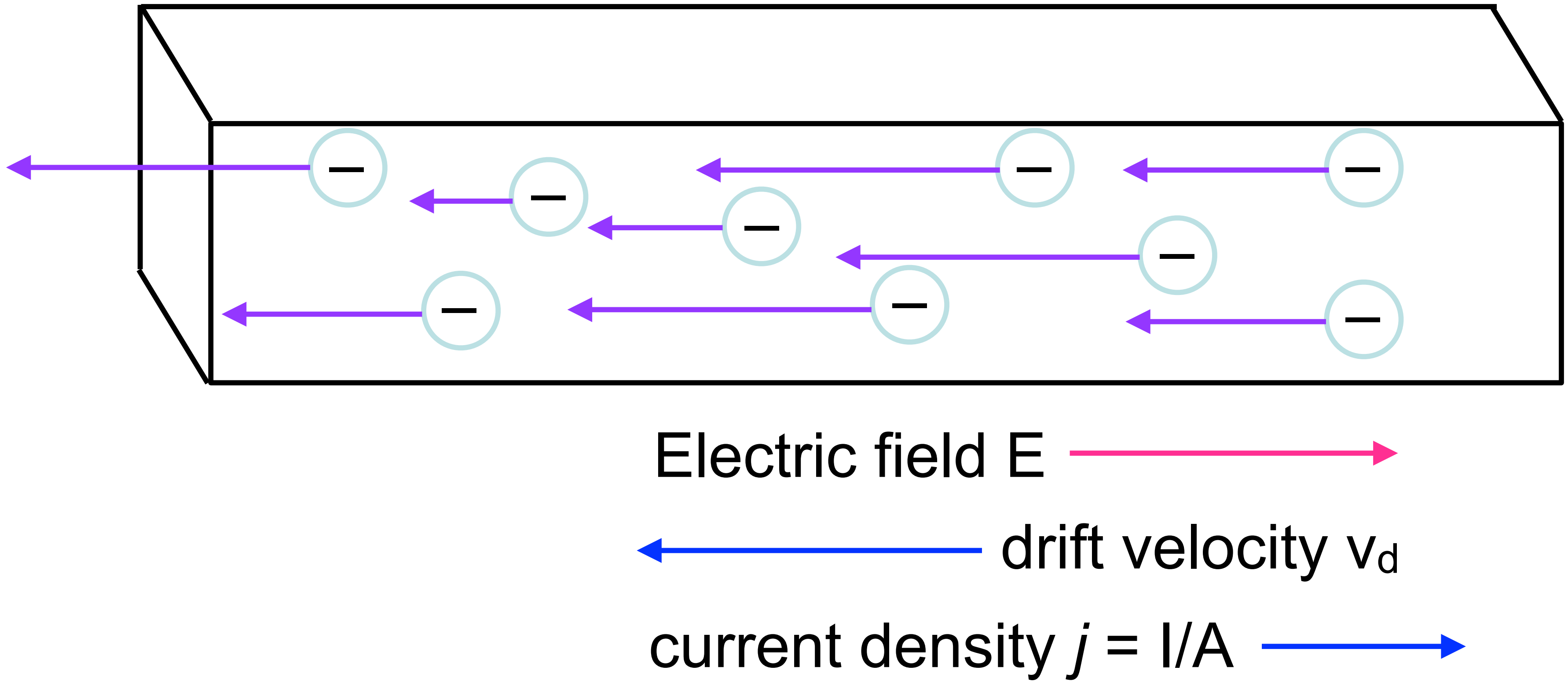


In alkali metals the ion cores may occupy only 10-20% of the crystal volume, while in noble metals the cores may be in “contact” with each other. Common crystal structures are bcc or fcc.

The Classical Free Electron Model

This model explains properties that depend primarily on kinetic properties of the conduction electrons, and not on interactions with the ion lattice.

E.g., the form of Ohm's law and some aspects of the relationship between thermal and electrical conductivity.



Electric field E

drift velocity v_d

current density j = I/A

Classical Free Electron Model

- Due to charge screening, the valence electrons have so little potential energy with respect to the ion cores that we can treat the electrons as free to stream in response to any applied electric field (but see below).

- The electrons are classical particles (the model predates quantum).

- The valence electrons do not interact with each other; they may be taken to act independently (this is the assumption that real materials most significantly violate, because the electron gas is actually extremely dense).

- Defects in the crystal lattice act as perturbations to the free flow of electrons. They scatter off of these defects and the collisions are what limits real materials to finite conductivity.

- Calculations made under these assumptions can be useful approximations, which are known as ***the relaxation time approximation.***

Ohm's Law and Electron Drift

Write Ohm's Law in a way that removes the impact of sample size/shape:

resistivity $\rho = RA/L$

conductivity $\sigma = 1/\rho$

$V = IR$

$V/L = IR/L$

$E = jA\,(\rho L/A)\,/\,L = j\rho$

$$j = \sigma E$$

Electron Mobility

A similar concept to Ohm's Law is the idea that there is an equilibrium average drift velocity for the electrons. The drift velocity is finite because of crystal defects and scattering off of phonons. We can then define the *mobility* μ and write

$$v_d = \mu E$$

Mobility is closely related to conductivity and to the concentration of electrons in the free electron gas: $n = \left(\frac{dQ}{dVolume}\right)/e$

I ≡ dQ/dt. For a constant cross-section A, Volume = $dA\,dx$ and

j dA = $-ne(dx/dt)$ dA, which leads to $j = -nev_d$

$$\sigma E = -nev_d$$

$$\sigma = -ne\mu$$

Anisotropic Materials

The simplest form of conductivity is just a scalar, such that the current density and electric field are always proportional to each other and parallel.

Real materials can display anisotropic behaviour:

$$\begin{bmatrix} J_x \\ J_y \\ J_z \end{bmatrix} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

In this case, the flow of current may not be parallel to the electric field.

Classical Theory: the Drude model

Using the classical free electron model and a kinetic theory picture of drift velocity/conductivity, attempt to predict the relationship between E and *j* given material properties (density, crystal structure) and chemical properties (concentration of free electrons). This is the "pinball machine" view of conduction.

Key assumptions:

- Electrons accelerate due to the electric field, but are scattered by collisions, which occur on average every τ seconds.

- The thermal speed of electrons is high, so the collision frequency is high, so that they only acquire a small amount of momentum dp between collisions.

Classical Theory: the Drude model

From the definition of change in momentum and the assumption of isotropy, the *average* electron has its velocity completely randomized during each collision, so that the total average momentum of an arbitrary electron at time τ is $\langle p \rangle = qE\tau$.

Because $\langle p \rangle = m\langle v \rangle$ and $j = nqv_d$, we can substitute to predict

$$j = \left(\frac{nq^2\tau}{m} \right) E$$

There are more sophisticated analyses, but they give the same result for the conductivity, $\sigma = (nq^2\tau/m)$.

This is actually a successful model, because it does not depend on whether the electrons follow Maxwell-Boltzmann statistics or the (correct) Fermi-Dirac distribution.

Frequency Response

For DC resistance of many materials, and the AC resistance of metals for relatively low frequencies and near room temperature, the Drude model proved remarkably successful.

For magnetic effects, the model is less successful, but not totally inaccurate.

However, it totally fails to reproduce the heat capacity of solids. According to this model, conductors and insulators should have wildly different heat capacities, which they do not. The model ignores the role of phonons.

In the AC impedance of some metals, the relaxation time τ gives a characteristic frequency τ^{-1} in the infrared range, where it coincides with the optical branch of the phonon dispersion relation. When the frequency is much lower (e.g., in semiconductors), it accurately predicts the frequency dependence of conductivity.

Success & Failure

Classical free electron theory fails to explain why the electrons control the thermal and electrical conductivity of the metal, but do not contribute to the heat capacity at normal temperatures.

It also fails to explain why the mean free path for electrons can be on the order of centimetres, or ~10^8 times the lattice spacing.

A gas of free electrons subject to the Pauli exclusion principle is known as a *free electron Fermi gas*.

Electrons that are separated by a few ångstroms are not sufficiently far apart from each other to be considered a dilute classical gas. The failures come from failure to consider the quantum nature of the gas, not because the free electron picture is wrong.

Electron Energy Levels

Electron wave functions in atoms are not independent. The exact quantum description of N interacting electrons is an extremely complicated function that typically has to be solved numerically.

$$\psi_\alpha = \psi(x_1, x_2, x_3, ..., x_N)$$

$$\psi_\alpha \neq \psi_1(x_1)\psi_2(x_2)\psi_3(x_3)...\psi_N(x_N)$$

We typically use a simplified wave function for only one electron, known as an orbital. The approximate quantum state of the atom is given by assigning N different electrons to N different orbitals, each one of which is a valid solution of the wave equation for one electron.

$$\psi_\alpha \approx \phi_1(x_1)\phi_2(x_2)\phi_3(x_3)...\phi_N(x_N)$$

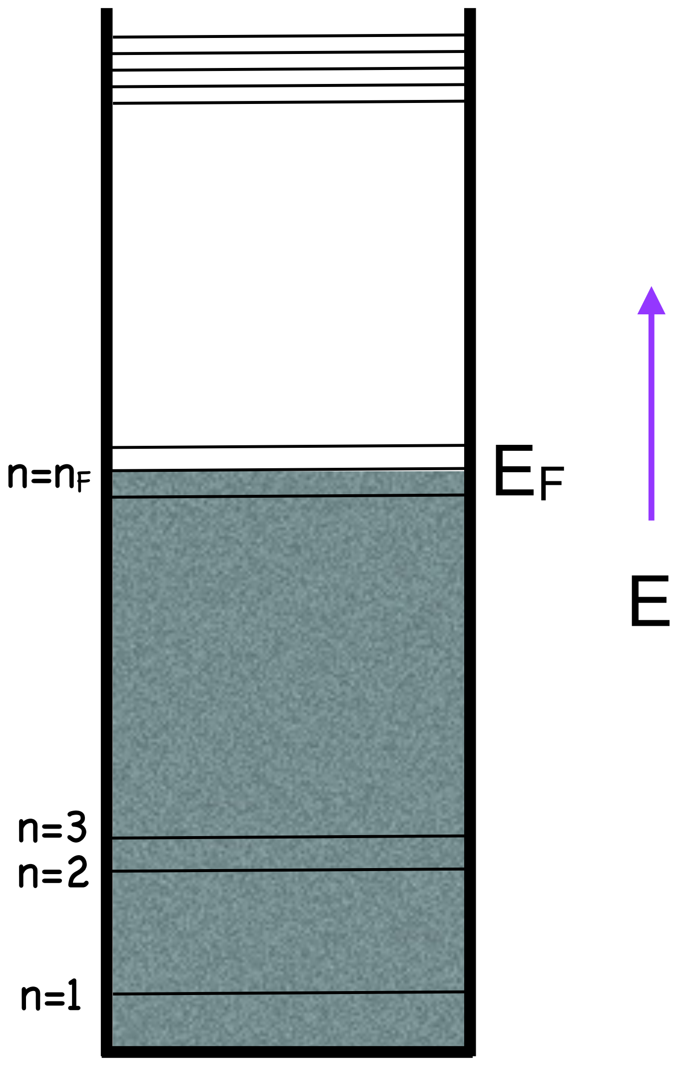
If there are no electron interactions, the orbital model is exact. **The orbital approximation is usually quite good for the conduction electrons.**

Label the atomic energy levels by an integer n, which runs from 1 to N. The number of electrons in an orbital is dictated by the Pauli exclusion principle. Each additional electron needs to have a distinct set of quantum numbers (to the extent that we can identify individual quantum numbers with a single electron in a highly correlated mess).

If we start filling the energy levels from the bottom (n=1), and always add electrons to the the orbital with the lowest energy available, we define the ground state of the system.

The topmost filled energy level is called the Fermi level, n_F.

The energy of this level is called the Fermi energy, E_F

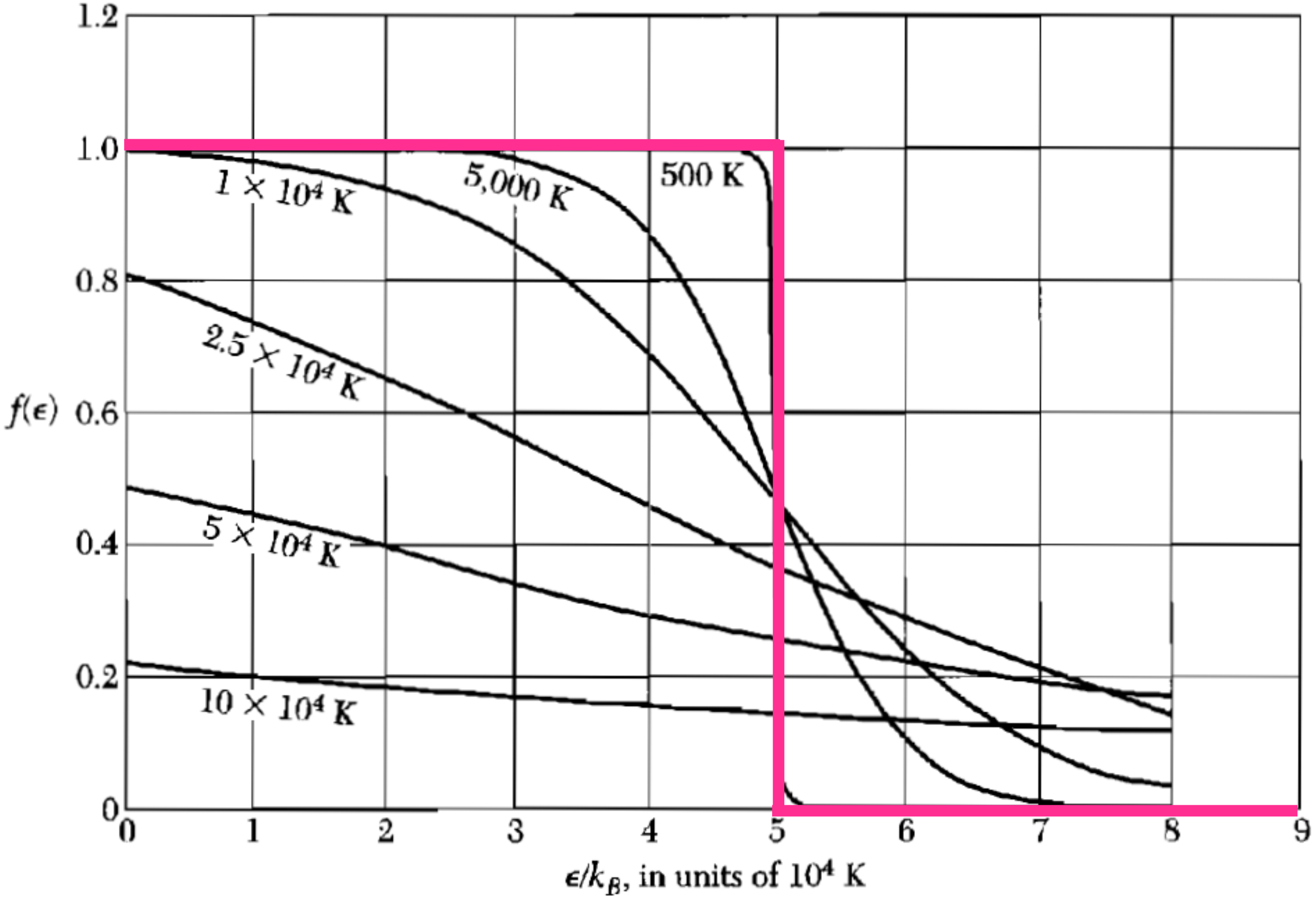


cartoon potential well

The ground state is the state of the system at absolute zero (pink line).

As the temperature is increased, the kinetic energy of the electron gas increases, and some energy levels are occupied that were vacant at absolute zero.

f(E) is the fraction of levels at energy E that are occupied by electrons. At T = 0, it is 1 for E < E_F and 0 for E > E_F.



The distribution is described by the Fermi-Dirac distribution:

$$f(\varepsilon) = \frac{1}{\exp[(\epsilon - \mu)/kT] + 1}$$

Fermi-Dirac Distribution

$$f(\varepsilon) = \frac{1}{\exp[(\epsilon - \mu)/kT] + 1}$$

μ is a function of temperature, determined so that the total number of particles in the system is equal to N.

μ is the *chemical potential*. At absolute zero, μ = ϵ_F, the Fermi energy. At other temperatures, μ is the energy at which f(ϵ) = 0.5.

If the energy of the energy level, $\epsilon \gg \mu + k\mathrm{T}$, the distribution asymptotically approaches the Maxwell-Boltzmann distribution.

Free Electron Gas in 3d

For a particle in three dimensions, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_k(r)=\epsilon_k\psi_k(r)$$

If the particles are confined to a cube of length L, this has the solution

$$\psi_k(r) = A\sin(\pi n_x x/K)\sin(\pi n_y y/L)\sin(\pi n_z z/L)$$

As for the phonons discussed earlier, we impose periodic boundary conditions, so that $\psi(x+L,y,z) = \psi(x,y,z)$.

Solutions with this form are travelling waves, with $\psi_k(r) = e^{ik\cdot r}$,
and the boundary conditions that $k_i = 0,\ \pm\frac{2\pi}{L},\ \pm\frac{4\pi}{L},\ \ldots$

The energy of the orbital with wavevector k is $\epsilon_k = \frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right)$

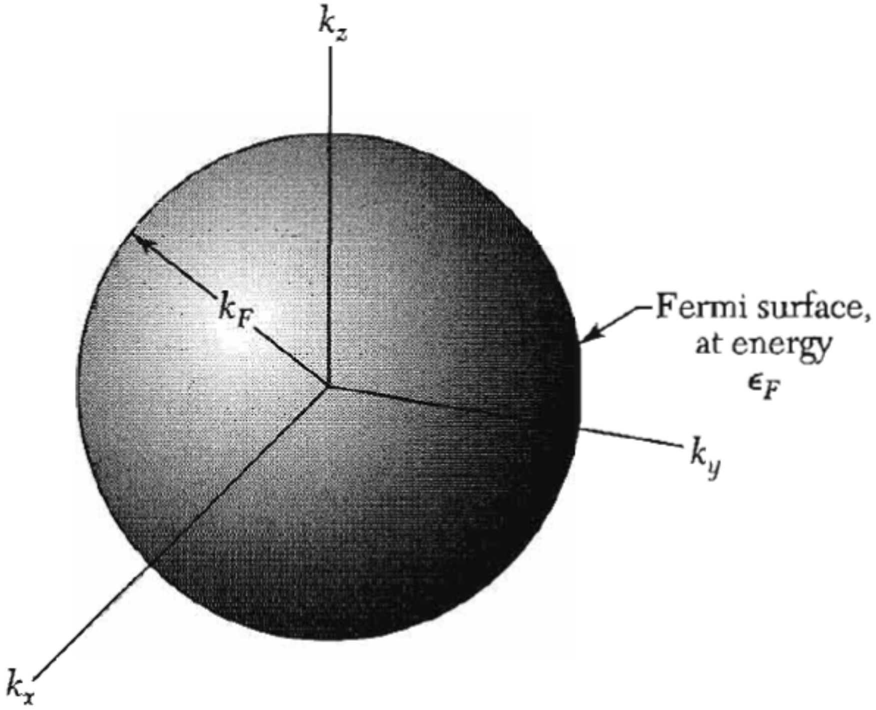
The plane wave ψ_k is an eigenfunction of momentum with $p = \hbar k$ and velocity $v = \hbar k/m$.

In a system of N free electrons, we can consider the occupied orbitals as points in k-space. In the ground state, these can be represented as points inside a sphere, where the energy at the surface is the Fermi energy, $\epsilon_F = \frac{\hbar^2}{2m} k_F^2$.

Each wave vector takes up volume $8\pi^3/L$, and the total volume is $4\pi k_F^3/3$, so the total number of orbitals is

$$N = 2\frac{4\pi k_F^3/3}{8\pi^3 V} = \frac{V}{3\pi^2} k_F^3$$

So that $k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$



Fermi Energy & Density of States

Once the Fermi surface is determined in k-space, $\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$

Note that the Fermi energy only depends on the electron concentration.

The number of electron orbitals per unit energy is known as the density of states $D(\epsilon) = \frac{dN}{d\epsilon} = \frac{3N}{2\epsilon}$.

The density of orbitals is, within a factor of order unity, the number of conduction electrons divided by the Fermi energy.

The number of occupied states per unit volume at a given energy (in thermal equilibrium) will be equal to the product of the density of states times the probability distribution function (the Fermi-Dirac function, for electrons).

Heat Capacity of the Electron Gas

Classical physics predicts that N free electrons should have a heat capacity of (3/2)Nk, just as for any other monatomic gas. The observed heat capacities of metals are often ~100 times less than this.

Why? Not every electron gains ~kT of energy as the system is heated, because all the orbitals up to the Fermi level are all filled. For most electrons, there are no empty orbitals available within kT of the ground state energy.

Only the electrons near the Fermi level can be excited thermally. Very roughly speaking, the fraction of electron that are close enough to the Fermi level is T/T$_F$. (Defining the Fermi temperature T$_F$ = ϵ_k/T

The total internal energy of these electrons is $U \approx N(T/T_F)kT$.

Differentiating, $C \approx Nk(T/T_F)$ - this linear component can be important for metals at low temperature.
A more accurate calculation gives $C = \dfrac{\pi^2}{2}Nk(T/T_F)$

Experimental Heat Capacity of Metals

For temperatures far below both the Debye temperature and the Fermi temperature, $C = \gamma T + AT^3$. γ and A are constants characteristic of the material. The linear term from the free electrons dominates at temperatures close to absolute zero.

Actual values for these parameters don't usually agree well with theoretical calculations, because the electrons aren't 100% free. The electrons must be treated as if they were more massive than they actually are, for three reasons (from most to least important):

1. Interaction with the periodic potential of the crystal lattice.
2. Interaction with phonons. Electrons tend to polarise the lattice nearby, which changes the phonon spectrum.
3. Interaction of electrons with each other.

Some materials have been discovered (e.g., $CeAl_3$) in which the thermal effective mass is ~1000 m_e, possibly due to interactions between *f*-subshell electrons.

Conductivity & Ohm's Law

Conductivity in a solid is related to the motion of conduction electrons through the lattice. The electrons have some typical speed and mean free path that dictate how quickly they can respond to an applied electric field.

The electromagnetic force on an electron is $\frac{dp}{dt} = -e\left(\vec{E} + \frac{1}{c}\vec{v} \times \vec{B}\right)$.

For a free electron, $p = \hbar k$.

If we set B = 0 and consider the applied E field only, substitution gives $\delta k = -e\mathrm{E}t/\hbar$.

If the force is applied at time $t = 0$ to an electron gas that fills a sphere in k-space up to the Fermi level, then at later time the sphere will be displaced to a new centre at δk.

In the absence of lattice imperfections, phonons and electron interactions, all the electrons would accelerate as a whole and δk would just continuously increase.

Conductivity & Ohm's Law

In a real crystal, δk can reach a steady state constant value even in the presence of an applied electric field.

If the time taken to come into equilibrium at the steady state electron speed is $\boldsymbol{\tau}$, then the mean change in wavevector between collisions is $\langle \delta k \rangle = -eE\tau/\hbar$ and during this time the electrons gain average velocity $\langle v \rangle = -eE\tau/m$.

The current density $j = nqv = ne^2\tau E/m$, which we can write as $j = \sigma E$.

The conductivity $\sigma = 1/\rho$ is related to the resistance ($R = \rho L/A$), and this is therefore the microscopic formulation of Ohm's law for DC conductivity.

The charge transported is proportional to the charge density (*ne*), and the acceleration is proportional to (e/m).

Since we know the momentum at the Fermi level, we can also write the conductivity in terms of the drift speed and lattice spacing: $\sigma = ne^2 d/(mv_F)$

Experimental Resistivity

At room temperature the resistivity is mostly due to collisions of the electrons with lattice phonons. At temperatures of a few K, the resistivity is dominated by collisions with mechanical imperfections in the lattice or impurities.

The net resistivity is approximately given by $\rho = \rho_{\mathrm{th}} + \rho_{\mathrm{i}}$ (*Matthiessen's rule*), where ρ_{th} is the resistivity due to thermal phonons (~independent of the number of lattice defects), and ρ_{i} is the resistivity caused by static imperfections (~independent of temperature).

ρ_{th} goes to zero as $T \rightarrow 0$. ρ_{i} can be determined by measuring ρ as a function of temperature, and extrapolating down to 0 K. It is found that ρ_{th} is very similar for many metals. At $T = 0$, the extrapolated value is called the *residual resistivity*.

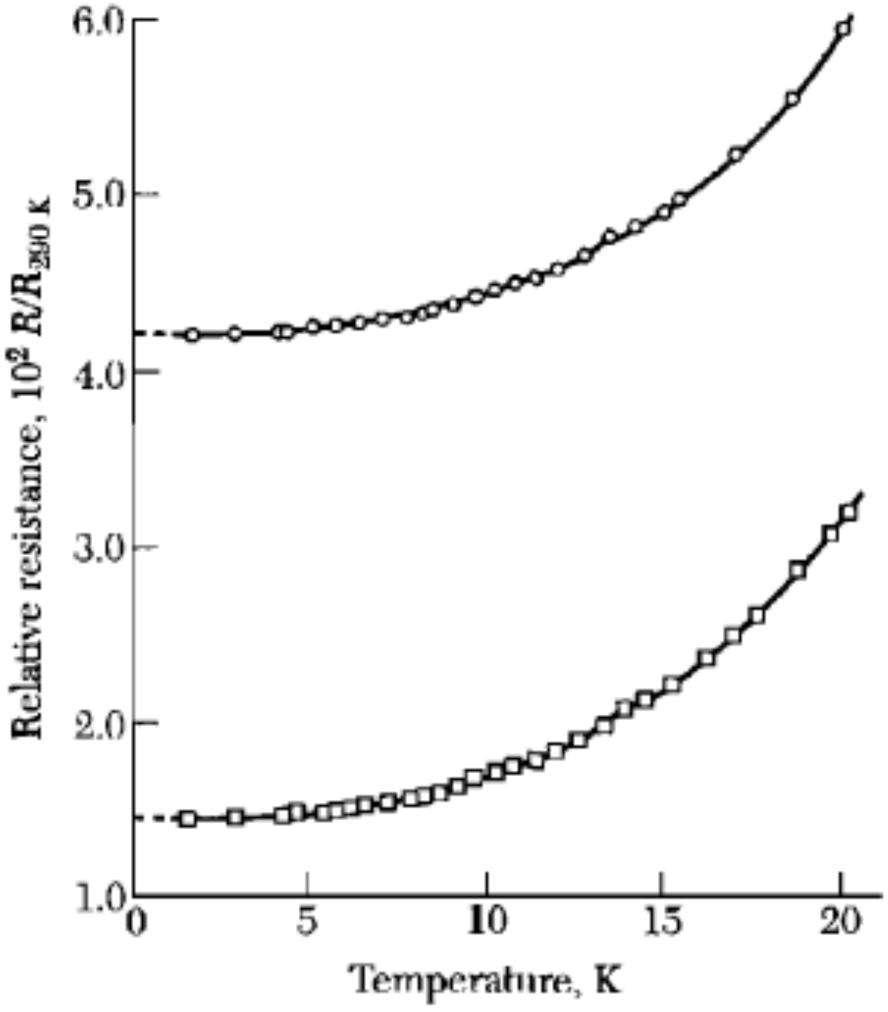
An approximate indicator of crystal purity is the *resistivity ratio*, the ratio of the resistivity at room temperature to the residual resistivity. In many cases a residual resistivity of 1 $\mu\Omega$-cm results per 1% impurity

Residual Resistivity

For example, impurities in copper in the range of ~20 ppm may produce a residual resistivity of ~2 n*Ω*-cm, for a resistivity ratio of around 10^3.

The purer the crystal, the higher the resistivity and the lower the residual resistance. Electron mean free paths as long as ~10 cm have been observed at temperatures below 4 K.

The plot shows two different measurements of residual resistivity in potassium. Differences arise because of different concentrations of impurities and lattice imperfections.



Ohm's Law Example: Copper

Copper in its metallic state has 1 electron in the $4s$ orbital. From this we can calculate the electron density n:

$$n = \left(\frac{1 \text{ electron}}{\text{atom}}\right)\left(\frac{1 \text{ atom}}{63.546\,u}\right)\left(\frac{8.96 \times 10^3 \text{ kg}}{\text{m}^3}\right) = 8.49 \times 10^{28} e^- / \text{m}^3$$

The Fermi energy for copper is around 7 eV, which can be translated to a velocity scale using $v_f = \sqrt{E_F/2m}$, $= 1.57\times10^6$ m/s.

If the conductivity is known from experiment to be $\sigma = 5.9\times10^7$ $(\Omega\text{m})^{-1}$, the mean free path of electrons in copper can be worked out from the appropriate formula, $d = \sigma m v_F(ne^2)$, which works out to 3.9×10^{-8} m = 390 Å.

If we put a potential of 10 mV across a 1 metre length of copper wire, the current density $j = \sigma E = 5.9\times10^5$ A/m^2. For a wire cross-section of 10^{-5} m^2, the current is 5.9 A, and the drift velocity of electrons works out to 43 microns/second.

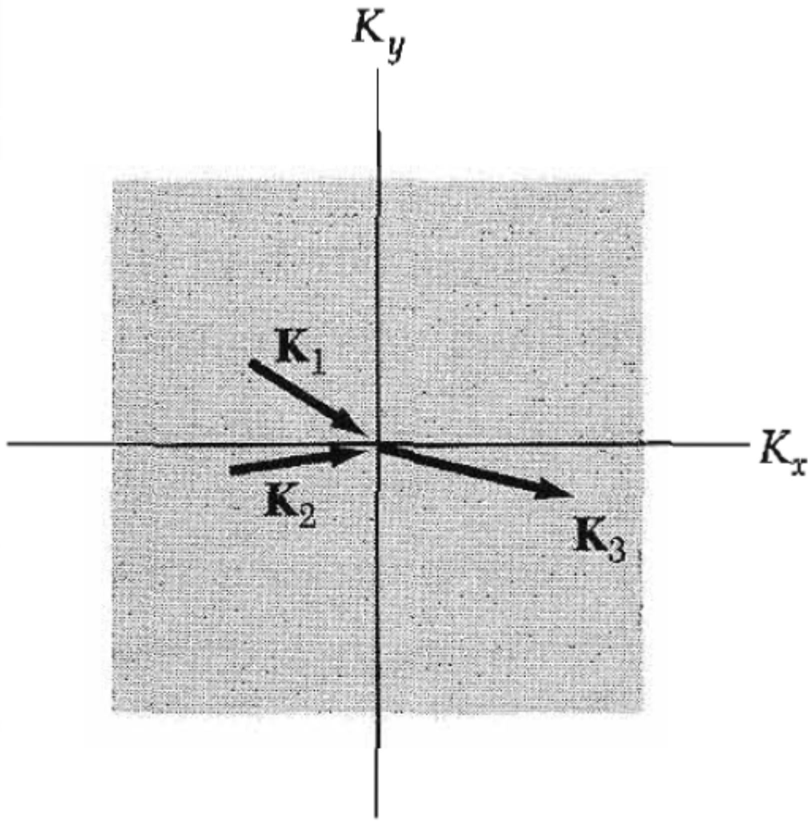
Umklapp Scattering

At low temperatures, electron-phonon scattering accounts for most of the resistivity of metals. Momentum must be conserved in all phonon scattering events, but in the "umklapp" processes, some momentum is exchanged between phonons and electrons, contributing to electrical resistance.

This figure shows a "normal", or N-scattering event. The grey square represents the first Brillouin zone of a crystal in *k*-space.

Two waves, K_1 and K_2, interact and a new wave K_3 is created, with $K_1 + K_2 = K_3$.

In "N" scattering, all the wavevectors lie within the first Brillouin zone.



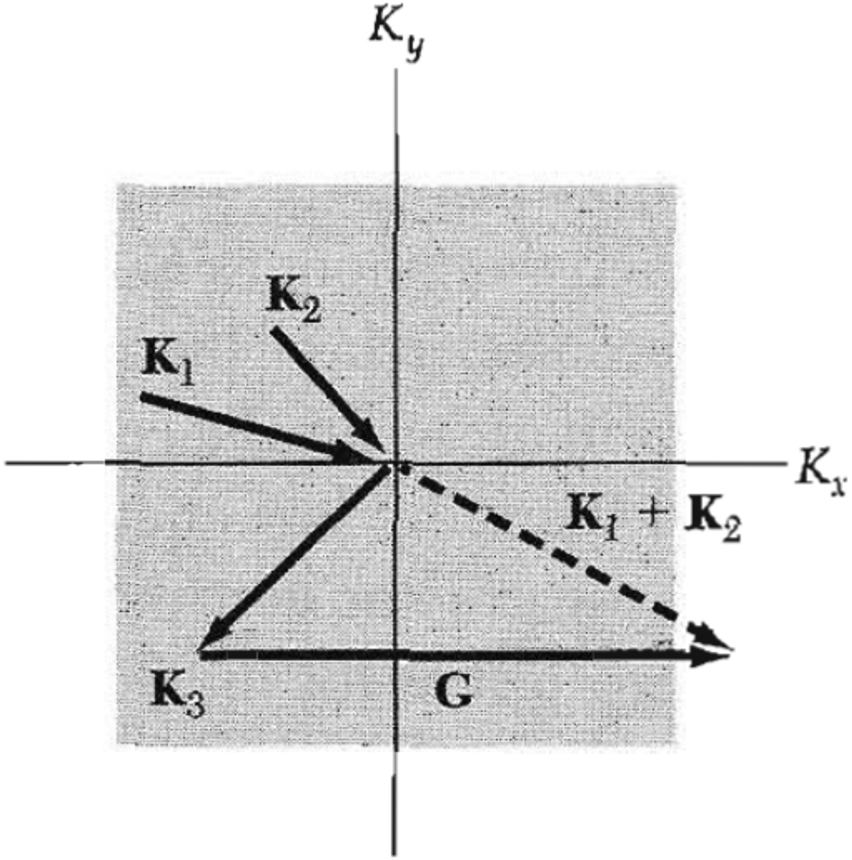
Umklapp Scattering

"umklapp" comes from the German word for "flipping over", because the scattered wave changes direction due to momentum transfer to the lattice. The conservation of momentum equation is $K_1 + K_2 = K_3 + G$, where G is a vector in the reciprocal lattice.

This figure shows an "umklapp", or U-scattering event. The grey square represents the first Brillouin zone of a crystal in *k*-space.

In "U" scattering, the new wavevector may lie far outside the first Brillouin zone, which means it is not independent from an equivalent vector inside the zone (K_3).

In this way large amounts of momentum may be transferred to an electron, with the excess/deficit going to/from the lattice.



Magnetic Fields

For a Fermi sphere of particles acted on by a force F and with time between collisions equal to $\boldsymbol{\tau}$, the equation of motion is $\hbar\left(\frac{d}{dt}+\frac{1}{\tau}\right)\delta k = F$.

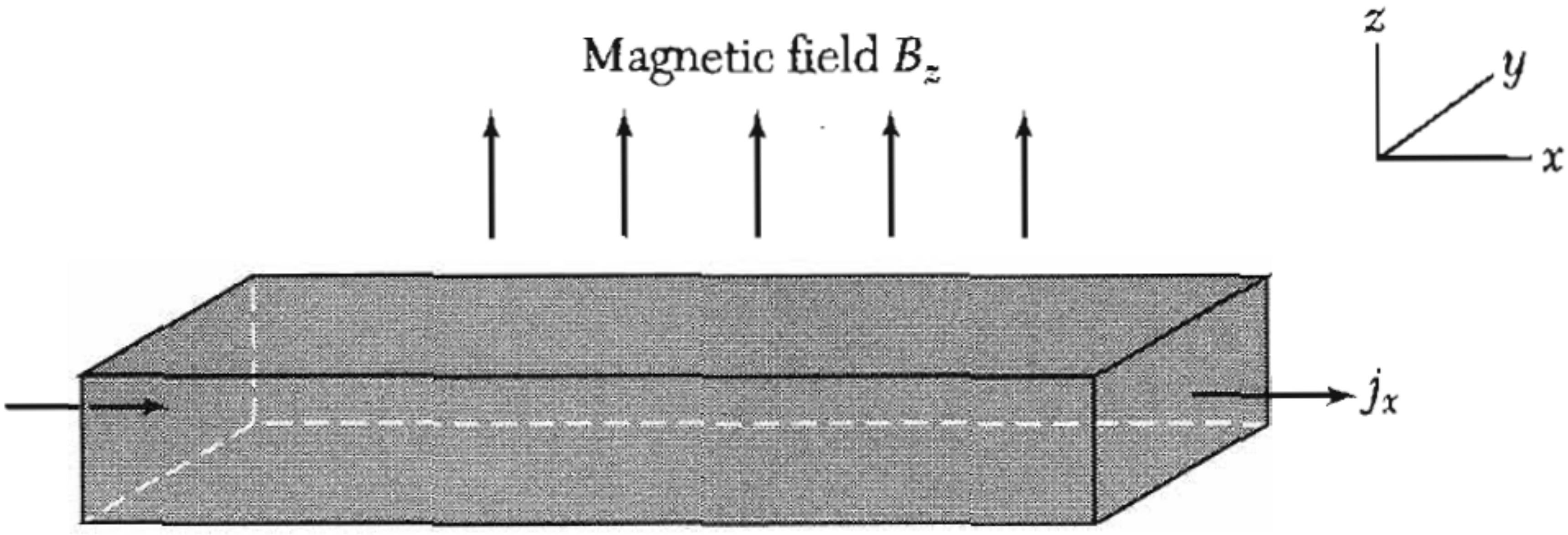
In the presence of a magnetic field, this becomes $\hbar\left(\frac{d}{dt}+\frac{1}{\tau}\right)\delta k = -e\left(\vec{E}+\frac{1}{c}\vec{c}\times\vec{B}\right)$

If there is a steady state in a constant field, the drift velocities now have a helical form instead of following the E field. For the B field directed along the *z* axis, the drift velocities are:

$$v_x = -\frac{e\tau}{m}E_x - \omega_c\tau v_y \qquad v_y = -\frac{e\tau}{m}E_y + \omega_c\tau v_x \qquad v_z = -\frac{e\tau}{m}E_z$$

where $\omega_c = eB/mc$ is the cyclotron frequency and cgs units are used.

The Hall Effect

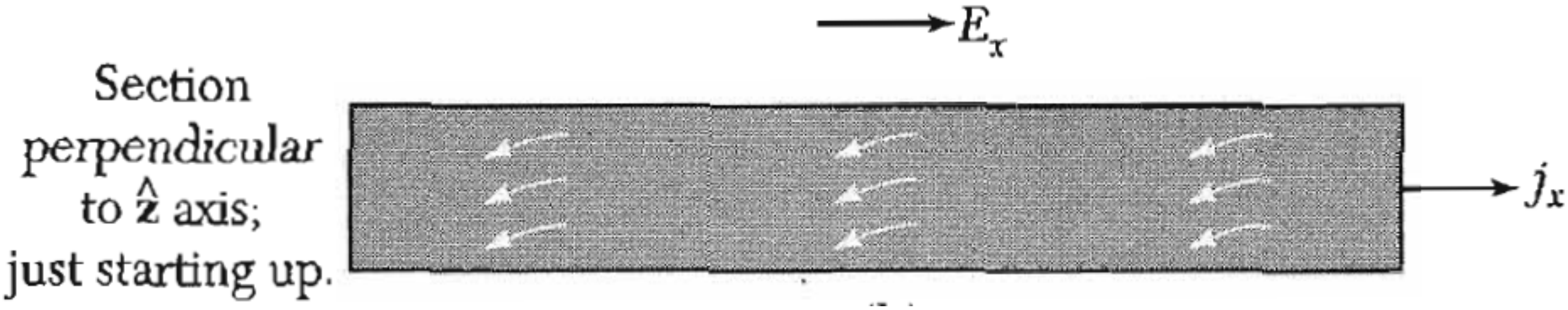


When a current flows across a magnetic field B, an electric field develops across conductor with direction given by *j*×B.

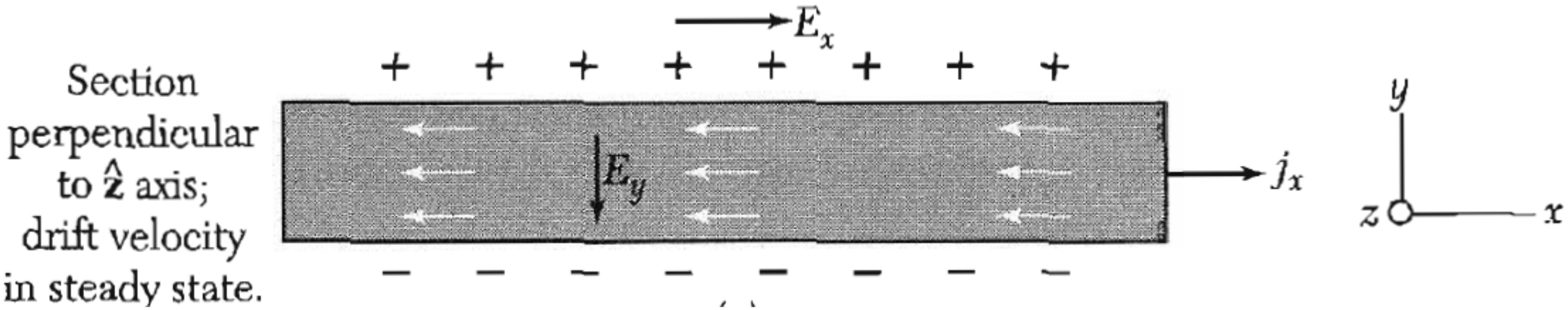
If current cannot flow out of the conductor in the *y* direction, then the drift velocity in *y* must be zero.

This can only happen if there is an electric field $E_y = -\omega_c \tau E_x = -\dfrac{eB\tau}{mc} E_x$

The Hall Effect



When the current is turned on at $t = 0$, the electrons respond to the B field by beginning to drift in the -y direction.



Because current cannot leave the conductor through the y direction, charge builds up on the opposite surfaces, establishing the Hall effect voltage.

Hall Effect

The strength of the Hall effect in a metal is given by $R_H = E_y/j_xB$.

From the simple equation of motion, $R_H = -1/ne$. This is negative for electrons. Historically the Hall effect was taken as evidence that the charge carriers are negative, due to the direction of the voltage appearing.

The size of R_H can be used to infer the number of conduction electrons per atom and as a test of the free electron theory for solids.

Experimental measures of R_H are typically around several 10^{-24} in cgs units, and in reasonable agreement with theory for many metals.

In some metals (e.g., aluminium, indium, arsenic) the sign of R_H is positive, indicating that the material behaves as though the unoccupied orbitals ("holes" in the electron distribution) are mobile, behaving as pseudo-particle carrying the charge. This is a failure of the free electron model and requires (quantum) band theory to explain.

The Weidemann-Franz Law

The Weidemann-Franz law is an empirical relationship stating that for metals at a moderate temperature, the ratio of thermal to electrical conductivity is directly proportional the temperature, with proportionality constant independent of the type of metal.

This was interpreted as strong evidence in favour of the free electron gas model for metallic solids.

The electrical conductivity is predicted to be $\sigma = \dfrac{ne^2\tau}{m}$.

The thermal conductivity from basic kinetic theory is $K \approx \dfrac{1}{3}Cv\ell$.

C and v are known for a Fermi gas, with $C = \dfrac{1}{2}\pi^2 Nk(T/T_F)$ and $v = v_{\mathrm{F}}$, and the mean free path $\ell = v_F\tau$.

Electron contribution to the thermal conductivity of metals is $K_{\mathrm{el}} = \dfrac{\pi^2 nk^2 T\tau}{3m}$

The Weidemann-Franz Law

With the two predictions based on the Fermi gas model, it is predicted that:

$$\frac{K}{\sigma} = \frac{\pi^2}{3}\left(\frac{k}{e}\right)^2 T$$

This result involves neither the electron mass nor concentration. Under the assumption that the relaxation time $\boldsymbol{\tau}$ is identical for thermal and electrical processes, it does not involve the collision rate between electrons.

The Lorenz number is $L \equiv K/(\sigma T)$ and it is predicted to be $L = 24.5\ \mathrm{nW} \cdot \Omega/\mathrm{deg}^2$. For a wide range of metals at 0° and 100° C this is a reasonable approximation.

The classical result from kinetic theory has no temperature dependence.

At very low temperatures the value of L is observed to decrease, e.g., for copper at 15 K the observed value is a factor of 10 less than at room temperature. This is because thermal and electrical relaxation times are no longer roughly equal.

The Fermi Liquid

A Fermi gas is a system of noninteracting identical particles subject to the Pauli exclusion principle. If the same system is extended to include interactions between the particles, it is described as a Fermi liquid.

Strictly speaking, the conduction electrons in a metal are a Fermi liquid. This causes the small deviations from the predictions of the Fermi gas model that become more obvious at low temperature. Non-nearest-neighbour interactions cannot be ignored in the liquid.

The theory of the Fermi liquid was developed by Landau and discusses the system in the language of “quasiparticles”. A quasiparticle is an excitation in a system of interacting electrons, analogous to a photon or a phonon. A single quasiparticle can be thought of as an electron plus an oscillating distortion to the nearby electron gas.

The main effect at reasonable temperatures is to increase the effective mass of the electron (e.g., by up to ~25% in alkali metals).

Energy Bands

The free electron model did a reasonable job of calculating some properties of metals, but it doesn't do a great job of explaining the differences between conductors and insulators, or the existence of semiconductors.

E.g., a conductor can have resistivity as low as $10^{-10}\ \Omega \cdot \mathrm{cm}$, but an insulator can be as high as $10^{22}\ \Omega \cdot \mathrm{cm}$. This is an enormously high range that the free electron model doesn't account for.

The most general treatment uses the Schrödinger equation for electrons in the presence of a strictly periodic lattice of atomic potentials.

Model the electrons as moving independently of each other in an average field that is determined by the symmetries of the crystal structure.

There are a few different approximate analytical techniques, and computational techniques based on them that add complexity.