

PH20017/63 Condensed Matter Physics 1

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Lecture notes set 2 - Electrons in solids

These are only summary notes – you should annotate, expand and supplement.

Electrons in solids

Drude model

- Basic assumptions
- DC conductivity
- Heat capacity
- Hall effect
- Thermal conductivity

Sommerfeld theory

- Quantised free electrons
- Ground state properties
- Thermal properties
- Conduction and scattering

Electrons in periodic potentials

- Bloch's theorem
- Energy bands
- Equation of motion
- Effective masses
- Metals, semiconductors and insulators

Drude model

A simple theory of the metallic state introduced by P. Drude. [▶ Drude](#)

The Drude model provides a partial explanation for

- ▶ Electrical conductivity
- ▶ Hall effect
- ▶ Thermal conductivity

“The failures of the Drude model to account for some experiments, and the conceptual puzzles it raised, defined the problems with which the theory of metals was to grapple over the next quarter of a century. These found their resolution only in the rich and subtle structure of the quantum theory of solids.”

Ashcroft and Mermin

The Drude model provides the language of more correct theories.

Conduction electron density n

- Conduction is due to the loosely bound valence electrons.
- N atoms, volume V , valence Z : $n = Z(N/V)$. Typically
- n in metals is $\sim 1000 \times$ density of classical gas at S.T.P.

Element	Z	$n(10^{22}/\text{cm}^3)$	$r_s (\text{\AA})$	Element	Z	$n(10^{22}/\text{cm}^3)$	$r_s (\text{\AA})$
Li (78 K)	1	4.70	2.77	Nb	1	5.56	
Na (5K)	1	2.65		Fe	2	17.0	
K (5K)	1	1.40		Mn (α)	2	16.5	
Cu	1	8.47		Hg (78 K)	2	8.65	
Ag	1	5.86		Al	3	18.1	1.77
Au	1	5.90		Ga	3	15.4	
Be	2	24.7	1.59	In	3	11.5	
Mg	2	8.61		Tl	3	10.5	
Ca	2	4.61		Sn	4	14.8	
Sr	2	3.55		Pb	4	13.2	
Ba	2	3.15		Bi	5	14.1	


- Typical electron separation $r_s \sim (1/n)^{1/3}$ is 1 – 5 Å.

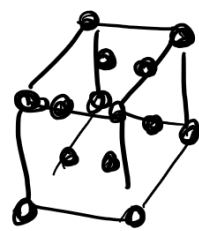
- Typical electron-electron interaction: $\frac{e^2}{4\pi\epsilon_0 r_s} \sim 1 \text{ eV}$ for $r_s \sim 1 \text{ Å}$ } not = 0V sharp e-e interaction even when not touching
 - If kinetic energy $\frac{1}{2}mv^2 = \frac{3}{2}k_B T$, typical K.E. $\sim 40 \text{ meV}$
- Even so, Drude boldly analysed the conduction electrons using a kinetic theory of neutral dilute gases.

Cu $z = 1$ fcc $a = 3.615 \text{ Å}$

Cond electron density

$$= \frac{n_0}{\text{vol}} = \frac{4 \times 1}{3.615^3 \text{ Å}^3} = 0.0897 \times 10^{24} \text{ cm}^{-3} = 8.97 \times 10^{22} \text{ cm}^{-3}$$

Vol 



Drude ignored this? we need for gas like behavior

electron densities $\sim \text{cm}^{-3}$

The 4 assumptions of the Drude model

$\chi \sim$

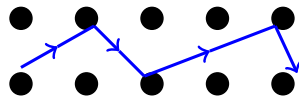
Between collisions, electron interactions with other electrons and the ions are neglected.

- Only external fields exert forces on electrons.
- Omitting electron-ion interactions is the *free-electron approximation* – see later. Omitting electron-electron interactions is the *independent electron approximation* – surprisingly good!

$\chi \sim$

Collisions are instantaneous, abruptly changing velocity.

- As in the kinetic theory of gases.
- Drude pictured collisions with the impenetrable ion cores, *not* other electrons which would be the classical gas analogue.



Naïve! But actual scattering mechanism is not as important as its effects.

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(

Electrons collide with probability $1/\tau$ per unit time.

- Probability of collision during interval dt is $\frac{dt}{\tau}$.
- The time τ is known as the **relaxation time**, the **collision time**, the **scattering time** or the **mean free time**. τ^{-1} is the relaxation rate, collision rate, etc.

Electrons are in thermal equilibrium with their surroundings.

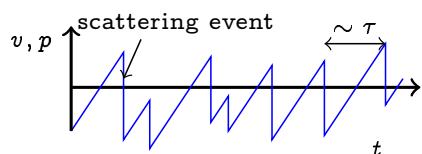
- Immediately after a collision an electron moves in random direction with a speed appropriate to the local temperature: $\frac{1}{2}m \langle v^2 \rangle_{\text{inst.}} = \frac{3}{2}k_B T_{\text{local}}$

Drude equation of motion (EOM)

In free space: $\frac{d\vec{p}}{dt} = \vec{F}$ $\left\{ \begin{array}{l} \vec{p} = \text{momentum} = m\vec{v}, \vec{v} = \text{velocity}, \\ \vec{F} = \text{external force.} \end{array} \right.$

In short interval δt , force \vec{F} causes velocity change $\delta\vec{v} = \frac{\vec{F}}{m}\delta t$.

In a solid: fraction $\frac{\delta t}{\tau}$ of the electrons scatter in time δt , after which their velocity is zero on average (random direction). Therefore the average velocity satisfies

$$\delta\vec{v} = \frac{\vec{F}}{m}\delta t - \vec{v}\frac{\delta t}{\tau} \quad \text{or} \quad \boxed{\frac{d\vec{p}}{dt} = \vec{F} - \frac{\vec{p}}{\tau}}$$


where $\vec{p} = m\vec{v}$ is now the average momentum of the electrons.

Collis introduce frictional damping into the eqn of mot.

Free spec $\frac{d\vec{p}}{dt} = \vec{F}$

Electrons in solid?

Given $\vec{p}(t)$, which is $\vec{p}(t+dt)$?

Put $\frac{dt}{\tau}$ of collisⁿ as $\vec{p}(t+dt) = 0$ \int
average
setting

$$\left(1 - \frac{dt}{\tau}\right) d\vec{p}(t+dt) = \vec{p}(t) + \vec{F}dt$$

$$\begin{aligned} \langle \vec{p}(t+dt) \rangle &= \frac{dt}{\tau} \cdot 0 + \left(1 - \frac{dt}{\tau}\right) (\langle \vec{p}(t) \rangle + \vec{F}dt) \\ &= \langle \vec{p}(t) \rangle + \vec{F}dt - \langle \vec{p}(t) \rangle \frac{dt}{\tau} - \vec{F} \frac{dt^2}{\tau} \end{aligned}$$

$$\frac{\langle \vec{p}(t+dt) \rangle - \langle \vec{p}(t) \rangle}{dt} = \vec{F} - \frac{\langle \vec{p}(t) \rangle}{\tau} - \vec{F} \frac{dt}{\tau}$$

$$\lim_{dt \rightarrow 0} \frac{d}{dt} \langle \vec{p}(t) \rangle = \vec{F} - \frac{\langle \vec{p}(t) \rangle}{\tau}$$

$$\vec{p} = \langle \vec{p} \rangle \quad \underline{\underline{\frac{d\vec{p}}{dt} = \vec{F} - \frac{\vec{p}}{\tau}}}$$

Drude theory of DC conductivity

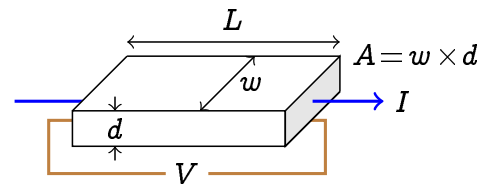
According to Ohm's Law, $V = IR$. The current flowing along a wire, I , is proportional to the potential drop V along its length. However, resistance R is not a material property, but also depends upon sample dimensions.

The intrinsic quantity is the **resistivity** ρ [units: $\Omega \text{ m}$]. This relates the electric field \mathcal{E} to the current density $\vec{j} = -ne\vec{v}_{av}$:

$$\mathcal{E} = \rho \cdot \vec{j} \quad \text{or} \quad \vec{j} = \sigma \cdot \mathcal{E}$$

σ is the **conductivity** [units: S/m].

For a wire, $V = \mathcal{E}L$, $j = I/A$, so $R = \rho L/A$.



The force on an electron in electric field \mathcal{E} is $\vec{F} = -e\mathcal{E}$.

From the Drude equation of motion, in steady state when $d/dt \rightarrow 0$

$$\frac{d\vec{p}}{dt} = \vec{F} - \frac{\vec{p}}{\tau} \Rightarrow 0 = -e\vec{\mathcal{E}} - \frac{\vec{p}}{\tau} \Rightarrow \vec{p} = -e\tau\vec{\mathcal{E}}$$

So on average the electrons move with a velocity $\vec{v}_d = \frac{\vec{p}}{m} = -\frac{e\tau}{m}\vec{\mathcal{E}}$

This is called the **drift velocity**, the average speed *with* collisions.

The corresponding current density is

$$\vec{j} = -ne\vec{v}_d = \frac{ne^2\tau}{m}\vec{\mathcal{E}}$$

Since $j \propto I$, & $\mathcal{E} \propto V$, the drude model predicts $V \propto I$ ✓

Resistivity, conductivity and the mean free path

From $\vec{j} = \sigma \mathcal{E}$, the Drude DC conductivity and resistivity are

$$\sigma = \frac{ne^2\tau}{m}$$

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

From experiments $R \xrightarrow{\text{gives}} \rho \xrightarrow{\text{gives}} \tau$. Find $\tau \sim 10^{-14} - 10^{-15} \text{ s}$ at $T = 300 \text{ K}$.

[See problems.]

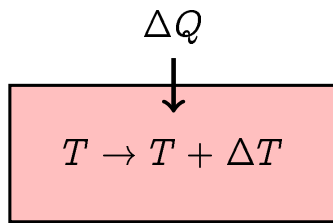
Then distance travelled between collisions $\ell = v\tau$ — the **mean free path**.

$$\text{Drude: } \frac{1}{2}m\langle v \rangle^2 = \frac{3}{2}k_B T \Rightarrow \left. \begin{array}{l} v \sim 10^7 \text{ cm/s} \\ \ell \sim 1 - 10 \text{ \AA} \end{array} \right\} \text{ at } 300 \text{ K}$$

— consistent with scattering from ions.

However, at low T and in very pure samples ρ is found to be much smaller, and we will see v is greater — then ℓ can be $\sim \text{cm}$ (10^8 \AA).

Drude theory of heat capacity



Heat ΔQ flows into solid, changing temperature from T to $T + \Delta T$.

$$C_V = \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta Q}{\Delta T} \right)_V = \left(\frac{dQ}{dT} \right)_V$$

From thermodynamics, $dQ = dU + pdV$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

Aside: theoretically C_V is more fundamental, but experimentally for a solid what is more normally determined is C_P , the heat capacity at constant pressure. C_V and C_P are related through material parameters (thermal expansion coefficient, bulk modulus).

In the Drude model, conduction electrons behave like classical gas particles. For these, each degree of freedom contributes an energy $\frac{1}{2}k_B T$.

Drude model prediction per mole:

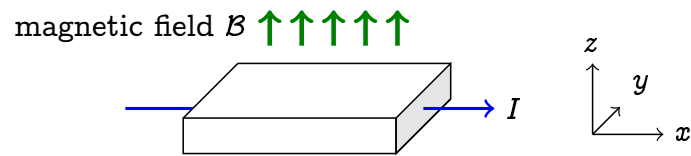
valence					energy, U	heat cap., C_V
$Z = 1$	$3 \times \frac{1}{2} N_A k_B T$	+	$6 \times \frac{1}{2} N_A k_B T$	=	$\frac{9}{2} N_A k_B T$	$\frac{9}{2} N_A k_B$
$Z = 2$	$6 \times \frac{1}{2} N_A k_B T$	+	$6 \times \frac{1}{2} N_A k_B T$	=	$6 N_A k_B T$	$6 N_A k_B$
$Z = 3$	$9 \times \frac{1}{2} N_A k_B T$	+	$6 \times \frac{1}{2} N_A k_B T$	=	$\frac{15}{2} N_A k_B T$	$\frac{15}{2} N_A k_B$
	electrons		ions			

(N_A : Avagadro's number; $N_A k_B = R$, gas constant.)

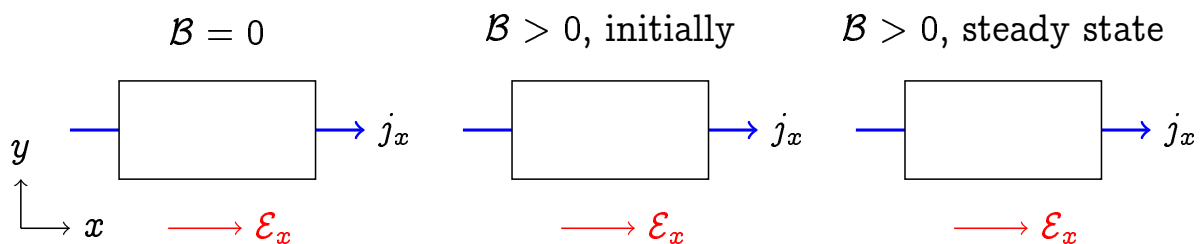
Experimentally, the heat capacity is actually found to be $\sim 3 N_A k_B$ at room temperature, independent of valence (law of Dulong and Petit).

Hall effect

Consider the following experiment: Apply a voltage to drive a current along a wire in the presence of perpendicular magnetic field.



Lorentz force acts on electrons: $\vec{F} = -e(\mathcal{E} + \vec{v} \times \mathcal{B})$.



Note: electrons move in opposite direction to classical current \vec{j} .

The Lorentz force bends the trajectories towards the lower edge. Electrons cannot pass through the edge, leading to a net accumulation of negative charge (and positive at upper edge). In steady state these charges generate a transverse electric field \mathcal{E}_y that exactly cancels the transverse Lorentz force.

In steady state, from the Drude equation of motion

$$\frac{d\vec{p}}{dt} = \vec{F} - \frac{\vec{p}}{\tau} \Rightarrow$$

But $\mathcal{E} = (\mathcal{E}_x, \mathcal{E}_y, 0)$, $\mathcal{B} = (0, 0, \mathcal{B})$, and $\vec{v}_d = (v_x, 0, 0)$

So in the y -direction,

$$(\vec{j} = -ne\vec{v}_d.)$$

- ▶ We define

R_H is independent of τ (scattering mechanism), and only depends upon n . We can measure R_H to find n .

- ▶ Longitudinal current $j_x = I/(wd)$, and the transverse or **Hall voltage** is $V_H = \mathcal{E}_y w$. Inserting,

- ▶ If N atoms in volume V , then



Some tabulated values:

Metal	Valence, Z	$-1/(R_H(N/V)e)$
Li	1	0.9
Na	1	0.9
Cu	1	1.3
Ag	1	1.5
Zn	2	-1.6
Cd	2	-1.1
Al	3	0.2
Bi	5	0.0001

In practice, values depend upon temperature and sample preparation (quality) – not predicted by Drude theory.

Even more surprising, some materials give negative values!

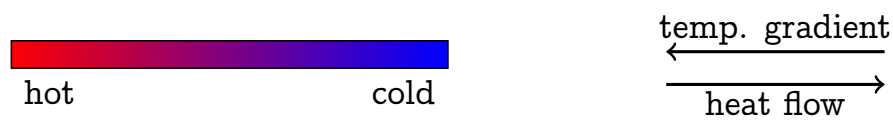
Cannot be explained in Drude picture.

► Nobel Prizes

$$R_H = -\frac{1}{ne}.$$

Thermal conductivity of metals

Metal rod: heat one end, then remove from heat source



Now continuously heat the hot end, and establish a steady state with both a temperature gradient and a uniform heat flow present.

Experimentally, find heat flow is proportional to temperature gradient:

$$j_x^Q = -\kappa \frac{dT}{dx}, \text{ or in 3D}$$

$$\vec{j}^Q = -\kappa \vec{\nabla} T \quad \text{Fourier's Law}$$

► Fourier

The material constant κ is the thermal conductivity.

Wiedemann-Franz Law – empirical, from expt.

Wiedemann-Franz: *Ratio of thermal and electrical conductivities is constant for different materials at a single temp.*

Lorenz: *Ratio proportional to temperature.*

$$\frac{\kappa}{\sigma} = \mathcal{L}T \quad \text{Wiedemann-Franz Law}$$

κ : Thermal conductivity σ : Electrical conductivity

T : Temperature \mathcal{L} : constant, Lorenz number

Element	273 K		373 K	
	κ (watt/cm-K)	$\kappa/\sigma T$ (watt-ohm/K ²)	κ (watt/cm-K)	$\kappa/\sigma T$ (watt-ohm/K ²)
Li	0.71	2.22×10^{-8}	0.73	2.43×10^{-8}
Cu	3.85	2.20	3.82	2.29
Ag	4.18	2.31	4.17	2.38
Au	3.1	2.32	3.1	2.36
Mg	1.5	2.14	1.5	2.25
Al	2.38	2.14	2.30	2.19
Pb	0.38	2.64	0.35	2.53
after Ashcroft & Mermin				

Drude model of thermal conductivity



arrow length \propto speed

Drude says: following collision, speed characteristic of the local temperature.

Electrons passing x from the hot side are moving faster than those from the cool side \Rightarrow net flow of thermal energy

Let $E[T]$ = energy of electron in thermal eq^m. at temp. $T = T(x)$.

Electrons passing x from the left on average had last collision at $x - v_x \tau$, and so have energy $E[T(x - v_x \tau)]$.

No. of electrons passing x per second is $\frac{1}{2} \times n \times v_x$.

Combining, heat flow/thermal current

For slowly varying T , use Taylor expansions:

$$T(x \pm v_x \tau) \simeq T(x) \pm v_x \tau \frac{dT}{dx},$$

$$\Rightarrow E \left[T(x) \pm v_x \tau \frac{dT}{dx} \right] \simeq E[T(x)] \pm \left(v_x \tau \frac{dT}{dx} \right) \frac{dE}{dT}$$

Substituting,

$$j^Q = -n v_x^2 \tau \frac{dE}{dT} \frac{dT}{dx}$$

Finally

$$\left. \begin{array}{l} \bullet \text{ In 3D } \langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle \\ \bullet n \frac{dE}{dT} = \frac{1}{V} \frac{d(N E)}{dT} = c_V, \text{ heat capacity} \end{array} \right\} \vec{j}^Q = -\frac{1}{3} \langle v^2 \rangle \tau c_V \vec{\nabla} T$$

Analysis

We can identify the thermal conductivity: $\kappa = \frac{1}{3}\langle v^2 \rangle \tau c_V$.

Previously: DC conductivity $\sigma = \frac{ne^2\tau}{m} \Rightarrow \text{ratio } \frac{\kappa}{\sigma} = \frac{\frac{1}{3}c_V m \langle v^2 \rangle}{ne^2}$

Drude used classical gas results: $c_V = \frac{3}{2}k_B n$, and $\frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}k_B T$.

$$\Rightarrow \quad \frac{\kappa}{\sigma} = \frac{3}{2} \left(\frac{k_B^2}{e^2} \right) T$$

$$\text{But } \frac{\kappa}{\sigma T} = \frac{3}{2} \left(\frac{k_B^2}{e^2} \right) =$$

Assessment of the Drude model

The Drude model is successful in accounting for some basic behaviour of electrons in metals – Ohm's Law, Wiedemann-Franz law, ... However, some serious problems exist

- ▶ mean free path in pure samples, at low T ; T -dep. of resistivity
- ▶ Heat capacity
- ▶ Sign of the Hall coefficient, and in some cases the magnitude
- ▶ Lorenz number/coefficient in Wiedemann-Franz law
- ▶ Effect of sample preparation & orientation on various quantities.
- ▶ Properties of alloys ▶ Alloy resistivity
- ▶ Optical properties
- ▶ Magnetism ▶ Magnetic susceptibility

Sommerfeld theory of quantum free electrons

Sommerfeld theory combines the Pauli exclusion principle and a quantum free electron gas.

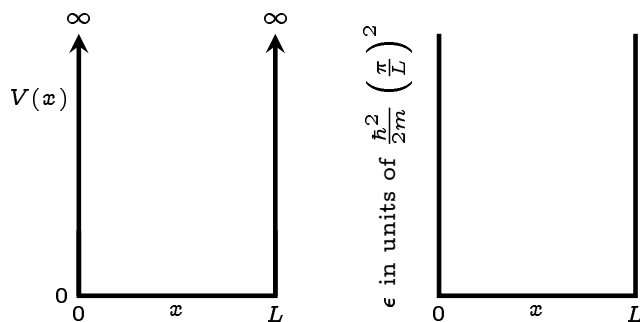
► Sommerfeld

Quantum mechanics tells us a single electron can be described by a wave function $\psi(\vec{r})$, and by specifying the electron spin as either \uparrow or \downarrow .

The electron wave function satisfies the time-independent Schrödinger equation.

► Schrödinger

A one dimensional model of a solid has the electrons confined to a region of length L :



$$\mathcal{H}\psi_n(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n(x) = \epsilon_n \psi_n(x)$$

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

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

Quantum statistics - revision

The Pauli exclusion principle prevents multiple occupancy of electron states with identical quantum numbers (here: n , spin)

At $T = 0$ K all states up to an energy called the **Fermi energy** ϵ_F are occupied; those above are unoccupied.

At a finite temperature the system become thermally excited: some levels empty at $T = 0$ become occupied, and some that were filled become vacant.

Thermal physics tells us the probability that a level with energy ϵ is occupied is given by the **Fermi-Dirac** distribution [▶ Fermi](#) [▶ Dirac](#)

$$f(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1}$$

– value of μ chosen to give N electrons

– at $T = 0$, $\mu = \epsilon_F$

– $f(\mu) = 1/2$ at all temperatures



If $\epsilon - \mu \gg k_B T$

$$f(\epsilon) \propto e^{-(\epsilon - \mu)/k_B T}$$

– Boltzmann distribution

Free electron states in 3D

In three dimensions, free particles satisfy the Schrödinger equation

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_{\mathbf{n}}(\mathbf{r}) = \epsilon_{\mathbf{n}} \psi_{\mathbf{n}}(\mathbf{r})$$

The surfaces of a material should not affect its bulk properties. Therefore, we ought to be free to choose the boundary conditions for convenience. If we choose our solid to be a cube of size $L \times L \times L = V$. Then

$$\psi_{\mathbf{n}}(\vec{r}) = A \sin(n_x \pi x / L) \sin(n_y \pi y / L) \sin(n_z \pi z / L) \quad n_i = 1, 2, 3, \dots$$

This corresponds to a standing wave. However, travelling solutions are more appropriate for transport problems (electrical conduction, thermal conduction). We get these by using

- Solutions of the Schrödinger equation satisfying PBCs are

- The electron wave vector $\vec{k} = (k_x, k_y, k_z)$ has quantised values

$$k_x = \frac{2\pi}{L}n_x, \quad k_y = \frac{2\pi}{L}n_y, \quad k_z = \frac{2\pi}{L}n_z \quad \text{where} \quad n_x, n_y, n_z = 0, \pm 1, \pm 2, \dots$$

$\vec{k} \longleftrightarrow n_x, n_y, n_z$: therefore we label the states with \vec{k} not n_x, n_y, n_z .

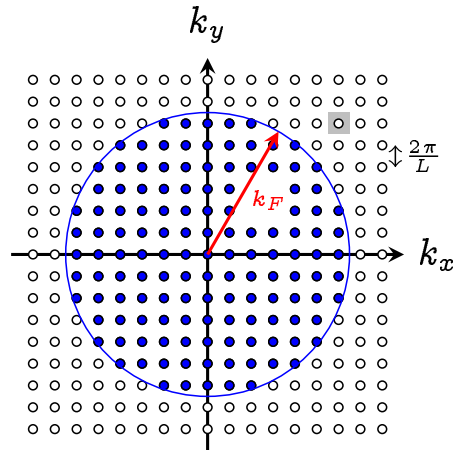
- The electron momentum (from $\hat{p}\psi = -i\hbar\vec{\nabla}\psi$) is

- The electron energy (from the Schr. eqⁿ) is

- Writing $\vec{p} = m\vec{v}$ we see

The Fermi sphere

The allowed \vec{k} points form a simple cubic lattice in 3D.
Neighbouring points are separated by
The volume per point is



2D representation of 3D space

The ground state of the electron gas is constructed by filling the lowest energy states with N electrons.

Since $\epsilon \propto k^2$, the lowest energy states are those closest the origin, and lie within a sphere, called

The radius of this sphere is the

Size of the Fermi sphere

The volume of the Fermi sphere is $\Omega = \frac{4\pi}{3} k_F^3$. The number of points within the sphere is

Each k -point corresponds to an energy level, for which we can have two electrons with different spin states (\uparrow, \downarrow). To accommodate N electrons then

Recall $n \sim 1 - 20 \times 10^{22} / \text{cm}^3$: therefore

The electron wavelength is $\lambda_F = 2\pi/k_F$ – electrons at the Fermi energy have wavelengths comparable to the spacing of crystal planes. *[From previous lectures, we should therefore expect they will undergo diffraction. They do – see later.]*

Typical values

We have:

$$k_F = (3\pi^2 n)^{1/3}$$

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

$$T_F = \frac{\epsilon_F}{k_B}$$

$$v_F = \frac{\hbar k_F}{m}$$

Element	n $10^{22}/\text{cm}^3$	ϵ_F eV	T_F 10^4 K	k_F \AA^{-1}	v_F 10^6 m/sec
Li	4.70	4.74	5.51	1.12	1.29
Na	2.65	3.24	3.77	0.92	1.07
K	1.40	2.12	2.46	0.75	0.86
Cu					
Ag	5.86	5.49	6.38	1.20	1.39
Au	5.90	5.53	6.42	1.21	1.40
Be	24.7	14.3	16.6	1.94	2.25
Mg	8.61	7.08	8.23	1.36	1.58
Ca					
Al					
Pb	13.2	9.47	11.0	1.58	1.83

after Ashcroft & Mermin

(gaps to be filled in via
problem sheet questions)

Density of states

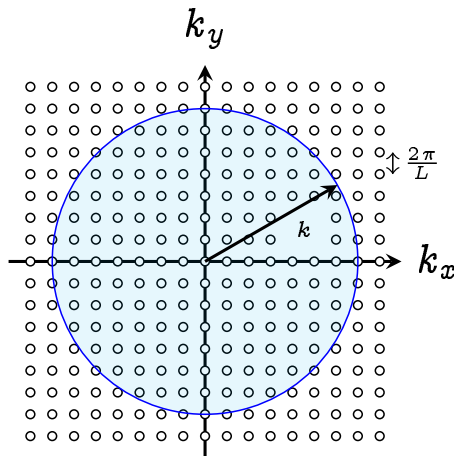
In calculating the electronic properties of solids, one often needs to sum over the electron states. Since there are typically $\sim 10^{23}$ states, it is useful instead to use the **density of states** to replace summations with integrals.

$\sum_{\text{occupied } \vec{k}} h_{\vec{k}} \rightarrow \int h(\epsilon)g(\epsilon)f(\epsilon)d\epsilon$	$h_{\vec{k}}$	quantity dependent upon \vec{k}
	$h(\epsilon)$	same quantity as fn of $\epsilon = \frac{\hbar^2 k^2}{2m}$
	$g(\epsilon)$	density of states
	$f(\epsilon)$	Fermi-Dirac distribution

Density of states $g(\epsilon)$:

- ▶ $g(\epsilon)$ is the number of electron states per unit energy at energy ϵ .
- ▶ The number of electronic states with energies between ϵ and $\epsilon + d\epsilon$ is $g(\epsilon)d\epsilon$.

Free electron density of states



2D representation of 3D space

Using k -space, the number of free electron states with energies up to $\epsilon = \frac{\hbar^2 k^2}{2m}$ is twice (spin $= \uparrow, \downarrow$) the number of k -points in a sphere of radius k :

$$N(\epsilon) = 2 \frac{\text{vol. of sphere}}{\text{vol. per point}} = \dots = \frac{V}{3\pi^2} \left(\frac{2m\epsilon}{\hbar^2} \right)^{\frac{3}{2}}$$

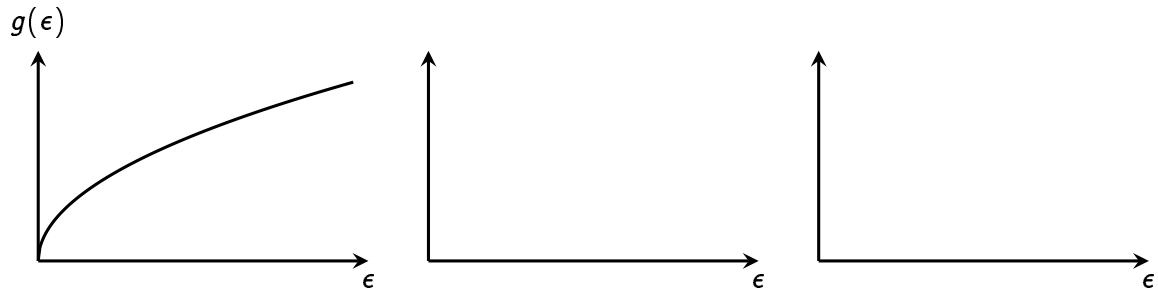
So

$$\begin{aligned} g(\epsilon)d\epsilon &= N(\epsilon + d\epsilon) - N(\epsilon) = \frac{dN(\epsilon)}{d\epsilon} d\epsilon \\ &= \dots = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \epsilon^{1/2} d\epsilon \end{aligned}$$

[Problem sheet question.]

So the density of states of a 3D free electron gas $g(\epsilon) = \alpha\epsilon^{1/2}$.

$g(\epsilon)f(\epsilon)$ gives the density of **occupied** electron states at energy ϵ .



Calculating properties with $g(\epsilon)$: Fermi energy

At $T = 0$

From before/problems $\alpha = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}}$. Therefore

Calculating properties with $g(\epsilon)$: Total energy

Total energy of the electron gas at $T = 0$ is

Since $N = \frac{2}{3} \alpha \epsilon_F^{3/2}$ (last slide),

This energy is kinetic energy.

Average kinetic energy = kinetic energy per electron

Electron speeds: classical vs. quantum

In the **classical** Drude theory, $\frac{1}{2}m \langle v^2 \rangle = \frac{3}{2}k_B T$.

Numbers: At $T = 0$ K: $v_{\text{av}} = 0$.

At $T = 300$ K: $v_{\text{av}} \sim 10^7$ cm/s.

In comparison, the **quantum** free electron gas at $T = 0$ has

$$\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3}{5} \times \frac{1}{2} m v_F^2 \quad \Rightarrow \quad v_{\text{av}} = \sqrt{\frac{3}{5}} v_F \simeq 0.77 v_F.$$

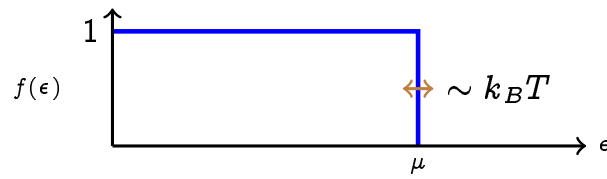
From our earlier table, we know $v_F \sim 10^8$ cm/s.

Quantum theory of the electronic heat capacity

Argument number 1: thinking like a physicist

Recall the Fermi-Dirac distribution, describing the occupation of the energy states with energy ϵ

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1}$$



Heating a solid from 0 K to temperature T , we expect individual electrons to gain an amount of energy of order $k_B T$

However, only electrons in states **within** $k_B T$ of the Fermi level can become thermally excited:

- electrons in states much lower in energy cannot be excited because states above them in energy by $\sim k_B T$ are already filled, and the exclusion principle forbids multiple occupancy
- states much higher in energy are unoccupied, so do not contain electrons that can be raised in energy

At $T = 0$, $\mu = E_F = k_B T_F$ — so only a **fraction** $\sim \frac{T}{T_F}$ will be excited.

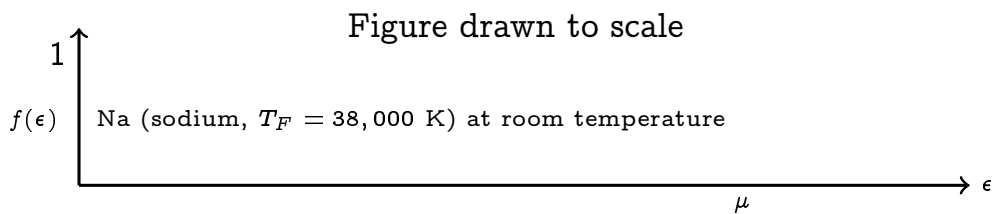
So

Then electronic heat capacity per mole ($N_A = \text{Avagadro's number}$)

$$C_V = \left(\frac{\partial U(T)}{\partial T} \right)_V$$

The quantum result is smaller than classical result ($\frac{3}{2} N_A k_B$) by factor

$T/T_F \sim 1\%$ in a metal at room temperature, so quantum magnitude agrees with experiment. Linear temperature dependance also agrees with experiment (see later in course).



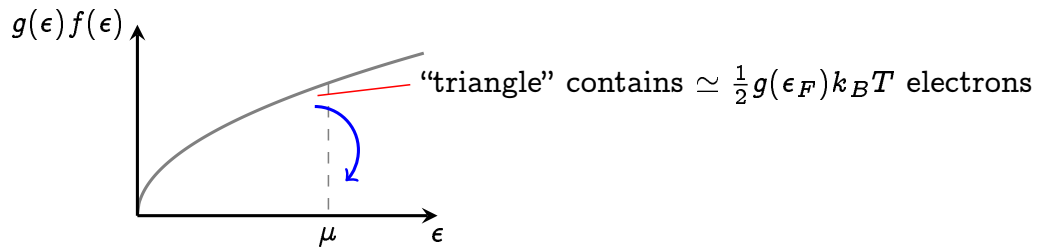
Quantum theory of the electronic heat capacity 2

Argument number 2: slightly more careful [not examinable]

Our previous argument neglects the density of states – there are proportionately more electrons with greater energies.

$$\frac{\partial f(\epsilon)}{\partial \epsilon} = \frac{\partial}{\partial \epsilon} \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1} = -\frac{1}{k_B T} \frac{e^{(\epsilon-\mu)/k_B T}}{(e^{(\epsilon-\mu)/k_B T} + 1)^2} \quad \Rightarrow \quad \left. \frac{\partial f(\epsilon)}{\partial \epsilon} \right|_{\epsilon=\mu} = -\frac{1}{4k_B T}$$

The slope of the Fermi-Dirac distribution at μ means $f(\epsilon)$ drops from 1 to zero over a range $\simeq 4k_B T$. Therefore approximately (see figure) $\frac{1}{2} \times 2k_B T \times \frac{1}{2} g(\epsilon_F) = \frac{1}{2} g(\epsilon_F) k_B T$ states go from below ϵ_F to above.



If a number $\frac{1}{2}g(\epsilon_F)k_B T$ electrons are thermally excited by $\simeq 2k_B T$

$$E(T) - E(0) \simeq \frac{1}{2}g(\epsilon_F)k_B T \times 2k_B T = g(\epsilon_F)k_B^2 T^2$$

Therefore $C_V = \left(\frac{\partial E}{\partial T} \right)_V \simeq 2g(\epsilon_F)k_B^2 T$ note density of states
at ϵ_F enters C_V

We saw in the previous lecture that $g(\epsilon) = \alpha \epsilon^{1/2}$ and $N = \frac{2}{3} \alpha \epsilon_F^{3/2}$, so

free electron gas: $g(\epsilon_F) = \frac{3N}{2\epsilon_F} = \frac{3N}{2k_B T_F}.$

Therefore for one mole (i.e. $N = N_A$, Avagadro's number)

$$C_V \simeq 3N_A k_B \left(\frac{T}{T_F} \right).$$

Note: a more exact calculation gives $C_V = (\pi^2/3)g(\epsilon_F)k_B^2 T$.
Kittel presents a derivation with flaws. Ashcroft & Mermin better.

Reminder: Thermal conductivity

Recall: Heat flow proportional to temperature gradient:

$$\vec{j}^q = -\kappa \vec{\nabla} T \quad \text{Fourier's Law}$$

Wiedemann-Franz: *Ratio of thermal and electrical conductivities is constant for different materials at a single temperature.*

Lorenz: *Ratio proportional to temperature.*

$$\frac{\kappa}{\sigma} = \mathcal{L} T \quad \text{Wiedemann-Franz Law}$$

κ :	Thermal conductivity	σ :	Electrical conductivity
T :	Temperature	\mathcal{L} :	constant, Lorenz number

Drude model gave:

$$\vec{j}^q = -\frac{1}{3} v^2 \tau c_V \vec{\nabla} T \quad \Rightarrow \quad \kappa = \frac{1}{3} v^2 \tau c_V$$

In quantum case, still use $\kappa = \frac{1}{3} v^2 \tau c_V$ ($\epsilon = \frac{\hbar^2 k^2}{2m} = \frac{1}{2} m v^2$) but:

The Drude value is seen to be fortuitously good, due to cancellation of large errors.

Using $c_V = \frac{1}{V} C_V = \frac{1}{V} \frac{\pi^2}{3} g(\epsilon_F) k_B^2 T$ gives [problems]

$$\text{Lorenz number } \mathcal{L} = \frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.4 \times 10^{-8} \text{ watt-ohm/K}^2$$

Compare with tabulated values given previously (Drude section)

Electrical conduction and scattering

We now consider electrical conduction in the Fermi sphere picture.

The momentum of a free electron state, wave vector \vec{k} , is $m\vec{v} = \hbar\vec{k}$.

In electric field \mathcal{E} force acts on electron: equation of motion

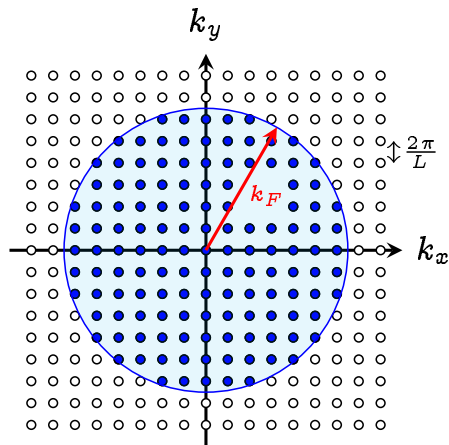
$$\vec{F} = m \frac{d\vec{v}}{dt} = \hbar \frac{d\vec{k}}{dt} = -e\mathcal{E}.$$

For a constant electric field \mathcal{E} , solving for $\vec{k}(t)$ gives

All wave vectors increase at a uniform rate – a uniform electric field rigidly displaces the Fermi sphere. The origin of the Fermi sphere is shifted by

Effect of electric field on Fermi sphere

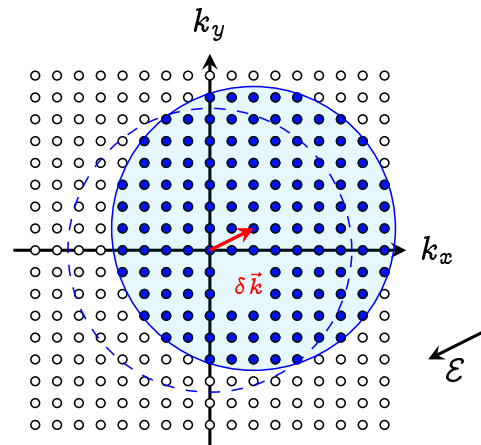
No field, $\mathcal{E} = 0$



2D representation of 3D space

average $\langle \vec{k} \rangle = 0$, no current

Field present, $\mathcal{E} \neq 0$



2D representation of 3D space

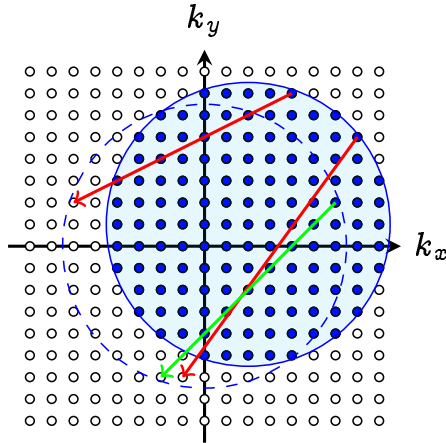
average $\langle \vec{k} \rangle \neq 0$, current flows

But current will keep increasing!!

Steady state

In steady state drift caused by applied field is balanced by **scattering** off impurities, defects and lattice vibrations [see later in course], which on their own would relax the distribution to that for no field.

In electrical conduction, the scattering mainly corresponds to $|\delta \vec{k}| \simeq 2k_F$.



inelastic - $\delta \epsilon \neq 0$

elastic - $\delta \epsilon = 0$

Maximum current densities normally used, $j \sim 10^7 \text{ A m}^{-2}$, correspond to

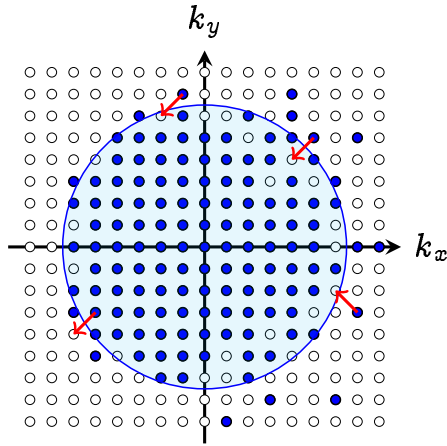
$$v_d = \frac{j}{ne} \sim \frac{10^7}{10^{28} \times 10^{-19}} \sim 1 \text{ cm/s}$$

This is a miniscule fraction of the Fermi velocity $v_F \sim 10^8 \text{ cm/s}$.

Hence figure is **greatly** exaggerated.
Difference between original and shifted spheres in reality very small!!!

Thermally excited Fermi sphere

The Fermi sphere for a metal sample where the left is hotter than the right shows more thermally excited states with positive k_x (i.e. travelling to the right) than with negative k_x (i.e. travelling to the left).

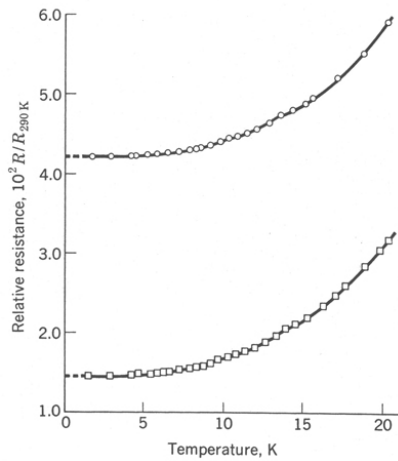


The different types of scattering in electrical and thermal conduction processes is one cause for departures from the ideal Wiedemann-Franz Law.

The figure is exaggerated again. At 300 K thermal fluctuations “smear” the Fermi surface by only $\frac{T}{T_F} \sim 1\%$.

Resistivity

If there are different scattering processes, we should expect there to be different scattering *rates* τ^{-1} . Recall in Drude model resistivity $\rho \propto 1/\tau$.



Left: Low temperature (< 20 K) resistivity of K (potassium) measured for two different samples [from Kittel].

$$\rho = \rho_i + \rho_{\text{ph}}(T)$$

or

$$\frac{1}{\tau} = \frac{1}{\tau_i} + \frac{1}{\tau_{\text{ph}}}$$

i: impurity; sample dependent

ph: phonon (lattice vibration); sample indep.

In general $\frac{1}{\tau_{\text{total}}} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \frac{1}{\tau_3} + \dots$ — this is Mathiessen's Rule.

Assessment of the quantum free electron model

- ▶ mean free path in pure samples, at low T ; T -dep. of resistivity ✓, ✗
- ▶ Heat capacity ✓
- ▶ Sign of the Hall coefficient, and in cases the magnitude ✗
- ▶ Lorenz number/coefficient in Wiedemann-Franz law (also deviation at intermediate T) ✓
- ▶ Effect of sample preparation, orientation on various quantities. ✓, ✗
- ▶ Properties of alloys ✗
- ▶ Optical properties ✗
- ▶ Paramagnetism ✓ (similar argument to heat capacity)

Some problems with Drude theory now fixed; but some remain.

Re-introducing the ions

Diffraction by a periodic crystal of a wave with wavevector \vec{k} results in additional waves with wavevectors $\vec{k} + \vec{G}$, where \vec{G} satisfies the Laue conditions.

In 1D, we have $\vec{G} \cdot \vec{a} = 2\pi h \Rightarrow G = \frac{2\pi}{a} \times \text{integer}$.

If $V = 0$, $\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\text{Vol}}} e^{i\vec{k} \cdot \vec{r}}$. In 1D this can be written $\psi_k(x) = C_k e^{ikx}$

If $V \neq 0$, diffraction means $\psi_k(x) = \sum_G C_{k+G} e^{i(k+G)x}$.

Factorising the exponential, $\psi_k(x) = e^{ikx} \left(\sum_{k+G} C_{k+G} e^{iGx} \right)$.

Since $e^{iG(x+a)} = e^{iGx} e^{iGa} = e^{iGx} e^{i \times 2\pi \times \text{integer}} = e^{iGx}$, we see that $\psi_k(x) = e^{ikx} u_k(x)$, where u_k is a periodic function.

Bloch's Theorem for electrons in lattices

Electron wave function in periodic crystals satisfy:

Bloch's theorem

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}}(\vec{r}) \quad \text{where} \quad u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})$$

↑

plane wave

← Bloch

↑

lattice periodic function

Bloch state or Bloch wave

Note that

$$\begin{aligned} \psi_{k+G'}(x) &= \sum_G C_{k+G'+G} e^{i(k+G'+G)x} \\ &= \sum_{G''} C_{k+G''} e^{i(k+G'')x} = \psi_k(x) \quad \text{where } G'' = G + G'. \end{aligned}$$

So – the wavefunction is a periodic function of \vec{k} .

All unique wavefunctions have a in the Brillouin zone.

Energy-wave vector relationship

$\epsilon_{\vec{k}}$ is the energy of electron with wavefunction $\psi_{\vec{k}}$: $\mathcal{H}\psi_{\vec{k}} = \epsilon_{\vec{k}}\psi_{\vec{k}}$.

Then $\mathcal{H}\psi_{\vec{k}+\vec{G}} = \epsilon_{\vec{k}+\vec{G}}\psi_{\vec{k}+\vec{G}}$. But $\psi_{\vec{k}+\vec{G}} = \psi_{\vec{k}}$ so $\mathcal{H}\psi_{\vec{k}} = \epsilon_{\vec{k}+\vec{G}}\psi_{\vec{k}}$.

Comparing,

The energy eigenvalues $\epsilon_{\vec{k}}$ are periodic functions of the quantum numbers \vec{k} , the wave vectors of the Bloch waves.

(Note: \vec{k} is quantised, but can normally be treated as a continuous variable.

E.g. in 1D, $k_n = \frac{2\pi}{L}n$, $n = 0, \pm 1, \dots$, so $\Delta k = \frac{2\pi}{L}$.

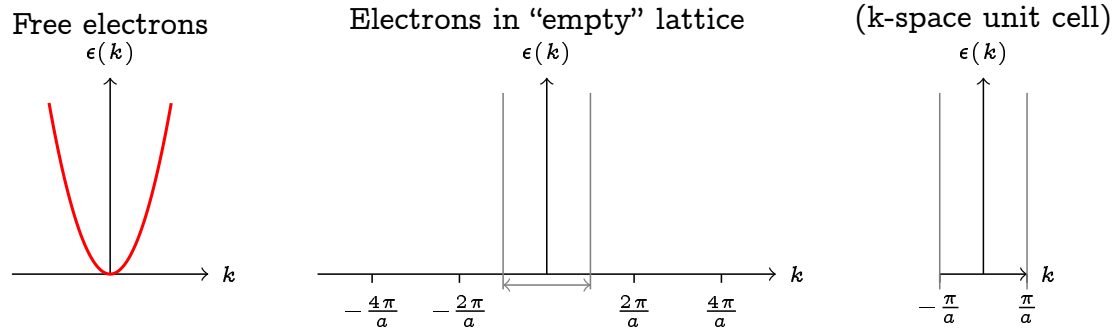
The Brillouin zone extends from $-\frac{\pi}{a}$ to $+\frac{\pi}{a} \Rightarrow$ width $\frac{2\pi}{a}$. Using $L \sim 1$ cm, $a \sim 1$ Å, there are $\frac{L}{a} \sim 10^8$ k values between $-\frac{\pi}{a}$ and $+\frac{\pi}{a}$.)

Very weak potential (“empty lattice”)

For free electrons, $\epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$.

If the periodic potential in a crystal differs from zero by an amount so small we cannot measure it, what are the electron energies?

Even a weak potential creates a lattice. So $\epsilon(\vec{k}) = \epsilon(\vec{k} + \vec{G})$, and the free electron parabola must be repeated every reciprocal lattice vector.



Increasing the potential

At $k = \pi/a$, the parabolas $\epsilon(k)$ and $\epsilon(k - G)$ for $G = \frac{2\pi}{a}$ intersect.

The corresponding free electron wave functions are $\begin{cases} \psi_k(x) = e^{i\pi x/a} \\ \psi_{k-G}(x) = e^{-i\pi x/a} \end{cases}$

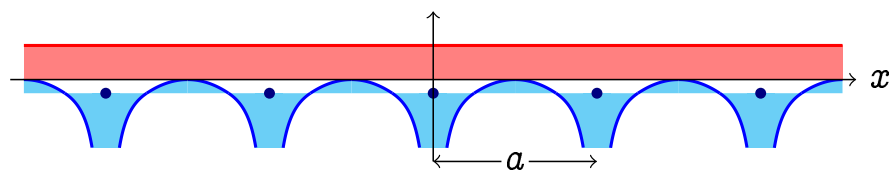
$k = \pi/a$ is at the edge of the Brillouin zone, and these two waves are a forward travelling wave, and a diffracted backward travelling wave.

Adding/subtracting we get standing waves

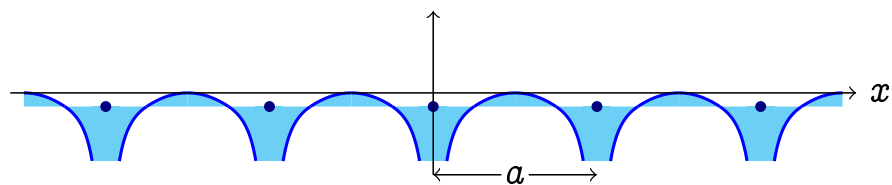
The corresponding probability densities are

These have the same energy when $V = 0$. But not when $V(x) \neq 0$.

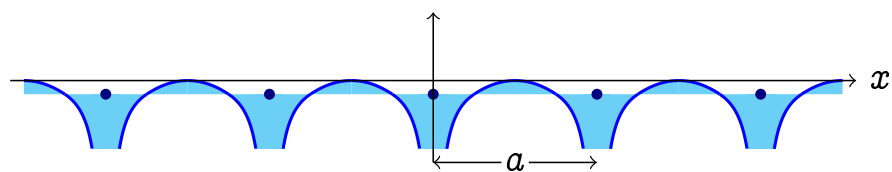
probability density, $|\psi|^2$, free electron state



$|\psi_+|^2$, probability density

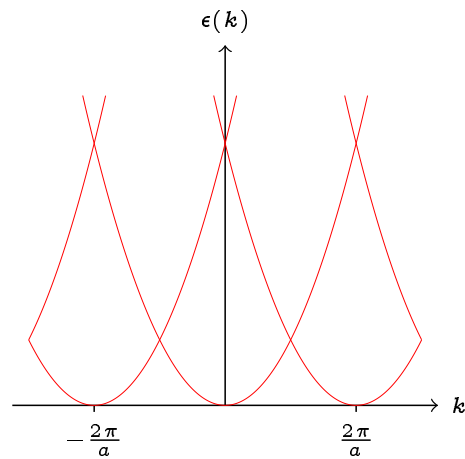


$|\psi_-|^2$, probability density



Nearly free electron energy bands

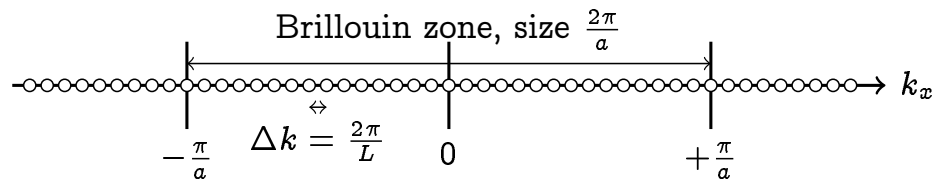
Electrons in nearly free electron potential



By raising/lowering energies, mostly near the edges of the Brillouin Zone, a weak potential creates **gaps** in the allowed energies, ranges of energies for which there are no electronic states within the crystal. The electron energies form **bands** that are periodic in \vec{k} -space.

Number of states in a band

In one dimension, each band extends from $-\frac{\pi}{a}$ to $+\frac{\pi}{a}$ – the Brillouin zone.



The number of \vec{k} -points within the interval is

Each state can accommodate 2 electrons, with spin \uparrow and spin \downarrow :

This is a general result, also valid for 3D crystals.

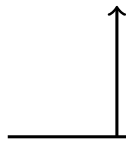
Semiclassical theory of conduction

The Bloch states are infinitely extended throughout the crystal.

To describe the motion of localised crystal electrons, we first of all construct a **wave packet** from Bloch waves.

The spatial localisation implies a spread in momentum through the uncertainty principle.

$\Re\psi$ (solid) or $|\psi|$ (dashed)



$$\psi(x) = \sum_{k-\delta k}^{k+\delta k} c_k \psi_k(x)$$

If the wave packet extends over several unit cells, the spread in momentum will be a small fraction of the Brillouin zone.

Electron velocity

The time dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi_{\vec{k}} = \mathcal{H} \psi_{\vec{k}} = \epsilon(\vec{k}) \psi_{\vec{k}}$$

tells us the Bloch states vary in time as

$$\psi_{\vec{k}} \sim e^{-i(\epsilon(\vec{k})/\hbar)t}$$

– like classical waves with frequency $\omega = \epsilon(\vec{k})/\hbar$.

Therefore, the **group velocity** of the Bloch wave packet, the velocity of the electron, will be

$$\left\{ \begin{array}{lcl} v & = & \frac{d\omega}{dk} = \\ \vec{v} & = & \vec{\nabla}_{\vec{k}} \omega = \end{array} \right.$$

Equation of motion (1D for clarity)

Electron in electric field \mathcal{E} feels force $= -e\mathcal{E}$.

If the electron moves a distance δx , the work done is

$$\text{work done} = \text{force} \times \text{distance} = -e\mathcal{E}\delta x.$$

So the electron energy increases by $\delta\epsilon = -e\mathcal{E}\delta x$.

If this happens in time δt , the rate of increase in energy is

$$\frac{\delta\epsilon}{\delta t} = -e\mathcal{E}\frac{\delta x}{\delta t} \quad \Rightarrow \quad \frac{d\epsilon}{dt} = -e\mathcal{E}v = -\frac{e\mathcal{E}}{\hbar} \frac{d\epsilon}{dk}$$

The change in energy will be accompanied by a change in wave vector:

$$\delta k = \left(\frac{dk}{d\epsilon}\right) \delta\epsilon \quad \Rightarrow \quad \frac{\delta k}{\delta t} = \left(\frac{dk}{d\epsilon}\right) \frac{\delta\epsilon}{\delta t} \quad \Rightarrow \quad \frac{dk}{dt} = \left(\frac{dk}{d\epsilon}\right) \times -\frac{e\mathcal{E}}{\hbar} \frac{d\epsilon}{dk}$$

or

The last term is the applied force. We see $\hbar\vec{k}$ acts like a momentum, and is called the

[Aside: In fact, from $\hat{\mathbf{p}}\psi_{\vec{k}} \neq \hbar\vec{k}\psi_{\vec{k}}$ we can show $\hbar\vec{k}$ is not the true momentum of a Bloch electron, which feels the force of external fields and the periodic force due to the lattice of ions (problem sheet). The rate of change of $\hbar\vec{k}$ gives the change due to the external field.]

Generalising, in 3D and including a possible magnetic field, the equation of motion for electrons in bands is

where

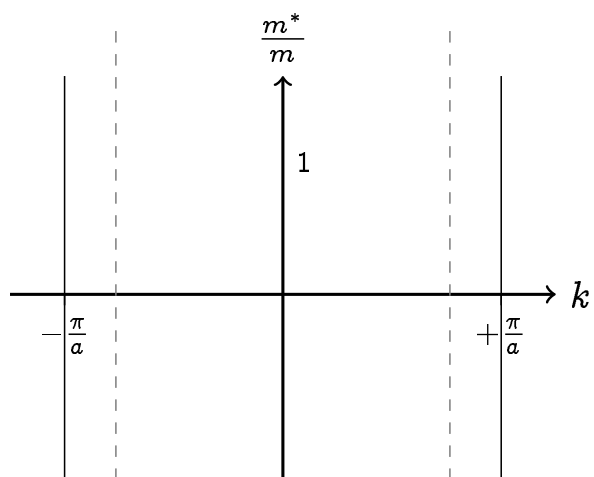
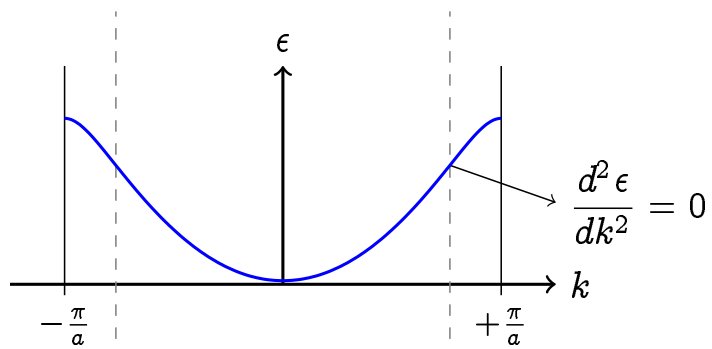
Effective mass

We now consider the acceleration of the electrons.

$$\frac{dv}{dt} = \frac{d}{dt} \left(\frac{1}{\hbar} \frac{d\epsilon}{dk} \right) = \frac{1}{\hbar} \frac{d^2\epsilon}{dk^2} \frac{dk}{dt} = \frac{1}{\hbar} \frac{d^2\epsilon}{dk^2} \times \frac{-e\mathcal{E}}{\hbar}$$

Rewriting,

Since force=mass \times acceleration, we identify the “**effective**” mass of the electrons as



Negative effective masses?

We have seen electron states in the presence of a periodic potential are made up of a set of waves with different wave vectors.

$$\psi_k(x) = \sum_G C_{k+G} e^{i(k+G)x}$$

As we increase k , we change the relative contributions of the different waves, some of which are waves traveling in the opposite direction.

The negative mass means the momentum transfer with the lattice (diffraction) is greater than the momentum picked up from the applied electric field, giving an overall decrease in the forward momentum of the electron.

Filled bands are inert

A band in which every state is occupied is called **filled**.

For every state occupied by an electron with wave vector $+\vec{k}$, there is another state occupied by an electron with wave vector $-\vec{k}$.

The average velocity of the electrons is zero — there is no contribution to the electrical conduction properties of the solid.

An applied field cannot continuously change the electron wave vectors — these states are already filled.



The conduction electron density in the Drude theory must represent the number of electrons in *partially* filled bands.

In some materials, an energy gap separates occupied and unoccupied bands. For these materials, at $T = 0$ there can be no conduction. At room temperature, if the gap is small thermal excitation may excite electrons across the gap — the material is then a . If the gap is large, it will remain an

Suggested further reading

For alternative descriptions and explanations, often at a different level, plus further problems, see

Drude/Sommerfeld theory

Hook and Hall (2nd Ed.)	Ch 3; p76–99
Myers	Ch 6; p154–198
Kittel (5th ed.)	Ch 6; p155–181
Ibach & Lüth (3rd Ed.)	Ch. 6–6.4; p137–152
Ashcroft & Mermin	Chs 1,2 & 3; p1–62

Electrons in periodic potentials

Hook and Hall (2nd Ed.)	Ch 4; p100–109, 116–121, 124–130
Myers*	Ch 7; p199–237
Kittel (5th ed.)	Ch 7; p183–204
Ibach & Lüth (3rd Ed.)	Ch 7; p161–169
Ashcroft & Mermin	Chs 8 & 12; p131–141, 214–239