# Physics A - Condensed Matter Physics

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# 1 Periodic structure

### Bravais Lattice

Definition: the Bravais lattice is an infinite array of discrete points, represented mathematically as an array of delta functions. All the lattice points are equivalent and atoms do not necessarily lie at these points. There are 14 lattice types.

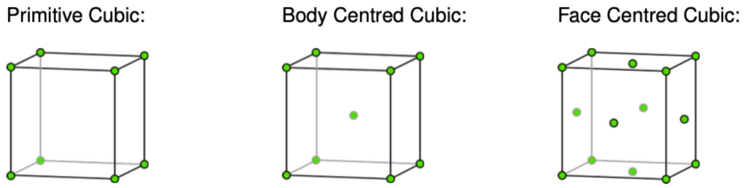
### Basis/motif

The repeat unit that exist at each lattice point.

$$\boxed{\text{crystal} \longrightarrow \text{convolution of lattice and basis}}$$

## 1.1 Cubic unit cells

1. Primitive cubic (contains only 1 lattice point) [p]
2. Body centered cubic [I]
3. Face centered cubic [F]



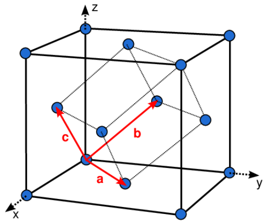
## 1.2 Wigner-Seitz unit cell

A construction that forms a unique primitive unit cell. Used in reciprocal space.
Method:

1. Select any lattice point as the origin
2. Draw vectors from origin to all neighbouring points. Those vectors are **primitive translation vectors**.

3. Construct planes normal to each vector, intersecting each vector at its midpoint
4. Wigner-Seitz unit cell is region enclosed by the planes

Example: primitive FCC unit cell:



Primitive translation vectors for FCC lattice:

$$\frac{a}{2}[110], \ \ \frac{a}{2}[101], \ \ \frac{a}{2}[011]$$

*Each structure can be represented by a set of primitive translation vectors.

## 1.3 Directions and planes in crystals

Direction: take the edge of unit cells as basis vectors

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

written as [u v w] with ū indicating negative. Can be integers or fractional.
*Example*: set of symmetrically-related directions in cubic lattice is

$$\langle 1\ 0\ 0 \rangle = \{[1\ 0\ 0], [0\ 1\ 0], [0\ 0\ 1], [\bar{1}\ 0\ 0], [0\ \bar{1}\ 0], [0\ 0\ \bar{1}]\}$$

Planes: intercept with **a**, **b**, **c** axis, take reciprocal, to get Miller index planes:

$$\text{Planes pass through } \left(\frac{\mathbf{a}}{h}, \frac{\mathbf{b}}{k}, \frac{\mathbf{c}}{l}\right) \Rightarrow (h\ k\ l)$$

Set of symmetrically related planes is written as: $\{h\ k\ l\}$.

## 1.4 Reciprocal lattice/reciprocal space/k-space

Definition: reciprocal lattice is a mathematical construct used to describe the periodicity of a crystal lattice by performing Fourier transform of the real lattice.

The diffraction pattern is the Fourier Transform of the lattice

$$\text{FT(lattice)} \ = \sum_{h,k,l=-\infty}^{\infty} C_{hkl}\, e^{i(\mathbf{G}_{hkl}\cdot\mathbf{r})} = \sum_{h,k,l=-\infty}^{\infty} C_{hkl}\, e^{i(k_h x + k_k y + k_l z)}$$

where $k_h = 2\pi h/a$, $k_k = 2\pi k/b$ and $k_l = 2\pi l/c$.

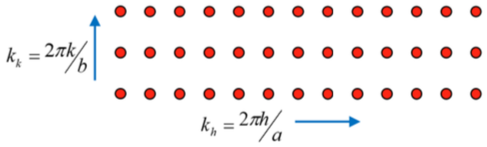


Figure 1: Example: 2D reciprocal lattice

Reciprocal lattice vector are referred to as G-vectors. We use $\mathbf{G}_{hkl}$.

Reciprocal lattice vectors:

$$\mathbf{G}_{hkl} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C}$$

where

$$\mathbf{A} = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \quad \mathbf{B} = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{[\mathbf{a}, \mathbf{b}, \mathbf{c}]} \quad \mathbf{C} = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{[\mathbf{a}, \mathbf{b}, \mathbf{c}]}$$

and the following are the behaviour of the reciprocal lattice vector:

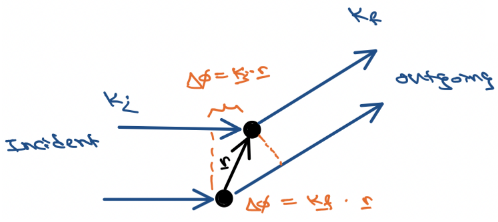
$$\mathbf{A} \cdot \mathbf{a} = 2\pi \quad \mathbf{A} \cdot \mathbf{b} = 0 \quad \mathbf{A} \cdot \mathbf{c} = 0 ...$$

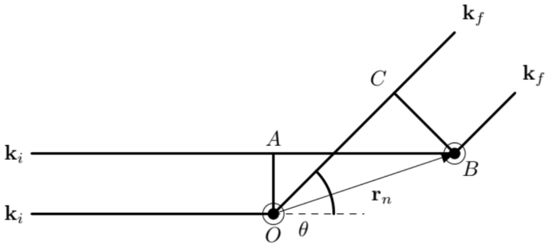
Allows us to generalise to 2D as long as these behaviours are obeyed.

Each point in k-space corresponds to a set of planes in real space i.e. $\mathbf{G}_{hkl}$ is perpendicular to planes (hkl), length is inversely proportional to plane spacing.

## 1.5 Diffraction

Assume elastic process so length must be the same.





$$\text{phase difference: } \Delta\phi = \mathbf{k}_f \cdot \mathbf{r} - \mathbf{k}_i \cdot \mathbf{r} = \mathbf{k}_s \cdot \mathbf{r}$$

where $\mathbf{k}_s = \mathbf{k}_f - \mathbf{k}_i$ is the scattering wavevector and $\mathbf{r}$ is a lattice vector.

So, if **$\mathbf{k}_s$ is a reciprocal lattice vector**, then the dot product is always an integer number of $2\pi$ and we get strongly diffracted beam:

$$\mathbf{k}_s \cdot \mathbf{r} = (h\mathbf{A} + k\mathbf{B} + l\mathbf{C}) \cdot (u\mathbf{a} + v\mathbf{b} + w\mathbf{c}) = 2\pi(uh + vk + wl)$$

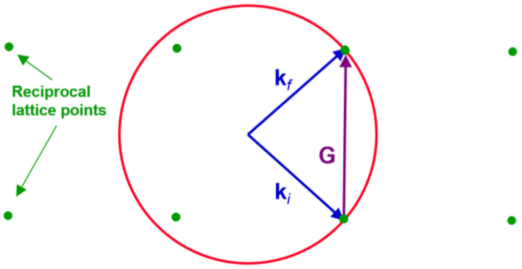
Hence, condition for diffraction: scattering vector is a reciprocal lattice vector,

$$\mathbf{k}_s = \mathbf{k}_f - \mathbf{k}_i = \mathbf{G}_{hkl}$$

### 1.5.1 Ewald sphere construction

Principle: conservation of energy

In reciprocal space, $\mathbf{k}_i$ and $\mathbf{k}_f$ must lie on the surface of a sphere, and be separated by a $\mathbf{G}$ vector.



If there is no $\mathbf{G}$ vector that links $\mathbf{k}_i$ to another point on the sphere, there is no diffraction from the lattice. Allow us to understand if diffraction can occur, and where we might see it.

## 1.6 Applications

1. Single crystal diffraction
   - Diffracted beams form 'spots', angles and strengths are recorded and analysed.
2. Powder diffraction (uses many small crystals in all possible orientations)
   - Diffracted beams form 'rings', used to identify phases or follow changes in a known structure.

Diffraction can be used to measure crystal parameters such as size of unit cell.

# 2 Lattice vibrations

In a solid, the motion of every atom is coupled with that of its neighbours, we use a normal modes approach to describe the system.

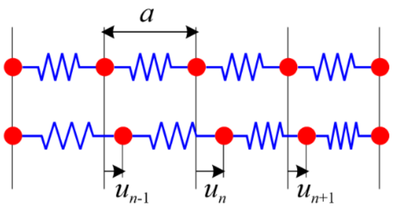
## 2.1 Phonons and normal modes

1. In each normal mode, all the coordinates oscillates at the **same frequency** and maintain **fixed ratios** to each other.
2. Overall motion is a sum of **independent normal modes**.

Description of phonon: a **phonon** is a collective harmonic excitation of the atoms with a well-defined frequency, with a fixed relative phase and amplitude between all of the atoms. They are normal modes of the systems.

## 2.2 Insight into phonons: 1D Harmonic Chain

Consider one dimensional chain of atoms, with identical mass, m, and connected by springs with spring constant, $\alpha$. Assume N atoms with cyclic boundary conditions.



There are N normal modes (one per degree of freedom).

Step 1: equation of motion for $n^{th}$ atom:

$$m\ddot{u}_n = \alpha(u_{n+1} - u_n) - \alpha(u_n - u_{n-1}) = \alpha(u_{n+1} + u_{n-1} - 2u_n)$$

Step 2: since all atoms are equivalent, symmetry ensues:
1. all atoms have same amplitude $u_0$ and same frequency $\omega$
2. constant phase shift, $\delta$, between adjacent atoms

$$\Rightarrow u_{n+1} = u_0 e^{i(\delta - \omega t)} \quad , \quad u_{n-1} = u_0 e^{i(-\delta - \omega t)}$$

Step 3: look for normal modes solution: assume $u_n = u_0 e^{-i\omega t}$ and substitute into equation of motion.

We obtain:

$$\omega(\delta) = \sqrt{\frac{4\alpha}{m}} \left| \sin\left(\frac{\delta}{2}\right) \right|$$

where $\delta \in [-\pi, \pi]$.

More generally, for the $n^{th}$ atom:

$$u_n = u_0 e^{i(n\delta - \omega t)}$$

writing $\delta = qa$, where q is phonon wavevector. q is the phase shift per unit distance at the lattice point.

$$u_n = u_0 e^{i(qna-\omega t)} = u_0 e^{i(qx-\omega t)}$$

where $x = na$ is the distance along the chain. Basically, phonons are **just waves travelling** along the chain.

**Dispersion relation** for the longitudinal waves that is allowed to run along the monoatomic chain of atom:

$$\boxed{\omega_L(q) = \sqrt{\frac{4\alpha}{m}}\left|\sin\left(\frac{qa}{2}\right)\right|}$$

where $-\frac{\pi}{a} \leq q \leq \frac{\pi}{a}$. Nearest neighbour interactions ⟶ sinusoidal dispersion.

Properties of phonon:

1. Energy stored in each mode:

$$E = \left(n + \frac{1}{2}\right)\hbar\omega$$

   Ground state energy of $\frac{1}{2}\hbar\omega$ plus n phonons, each of energy $\hbar\omega$

2. Momentum of phonon $= \hbar q$
3. Velocity of phonon $= \frac{d\omega}{dq}$ (group velocity)

### Dispersion curve

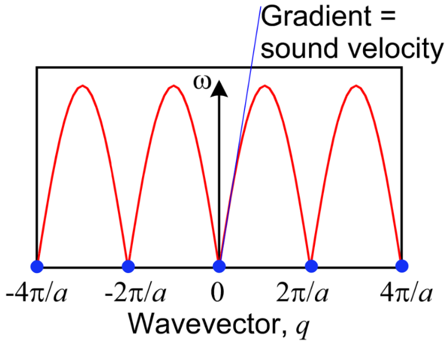


Figure 3: Blue dots are reciprocal lattice points!

$$q_1 = q_1 + nG$$

where $G = \frac{2\pi}{a}$. They are the same phonon. Also, $qa$ gives the phase shift in the wave between subsequent unit cells.

1. Long wavelength limit ($q \to 0$)

$$\omega(q) \approx \sqrt{\frac{4\alpha}{m}}\frac{qa}{2} = q\sqrt{\frac{\alpha a^2}{m}} = q\sqrt{\frac{\alpha a}{m/a}}$$

$$v_p = \frac{\omega}{q} = \sqrt{\frac{\alpha a}{m/a}} = \sqrt{\frac{Y}{\rho}}$$

   Dispersion curve tend to **continuum speed of sound**. Meaning on large length scales, the fact that matter are made of atoms/is lumpy does not matter. Measuring phonon speed: measure elastic properties of the material e.g. bulk modulus.

2. Short wavelength limit ($q = \pi/a$)
   Largest unique-wavevector when $q = \pi/a \Rightarrow \lambda = 2a$

$$\omega_{max} = \sqrt{\frac{4\alpha}{m}}$$

   Since $d\omega/dq = 0$, we have a **standing wave**. No propagation of energy through the system.

## 2.3 Real lattice

Sources of discrepancy/complexity:

1. **Interaction beyond nearest neighbour**. 1D model assumes interaction is only between nearest neighbours.

2. **Lattice anharmonicity**, adding additional anharmonic terms. 1D model assumes harmonic lattice, where the potential energy is a quadratic function of the displacement from equilibrium.

3. **Thermal vibrations**, causing deviation from perfect alignment. 1D model assumes perfect alignment of atoms in a linear chain.

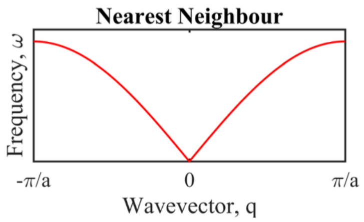
Linear system means we can superpose solutions.

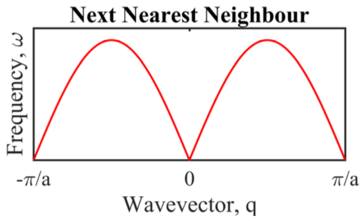
Example: nearest and next nearest neighbour

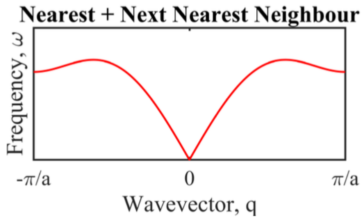
$$\omega^2 = \frac{4}{m}\left(k_1 \sin^2\left(\frac{qa}{2}\right) + k_2 \sin^2(qa)\right)$$

If $\frac{k_1}{k_2} > 2$, it justifies the approximation of considering only the nearest and next nearest neighbour, since the contribution from third neighbour onwards is insignificant.

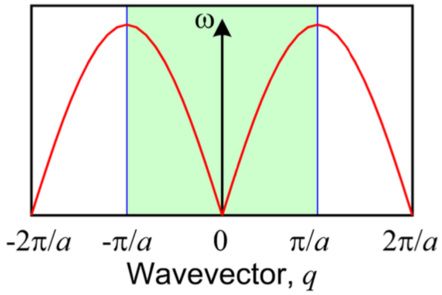
*Derived in example sheet Qn 3.*


Nearest Neighbour


Next Nearest Neighbour


Nearest + Next Nearest Neighbour

## First Brillouin Zone



$$\boxed{-\frac{\pi}{a} \leq q \leq \frac{\pi}{a}} \qquad \text{(2 atoms)}$$

Phonon modes for chain of N atoms:

1. Number of modes = number of atoms in the chain
2. For chain of N atoms, $q = \frac{2\pi}{Na}$
3. Each mode is a quantised SHO with $E = \left(n + \frac{1}{2}\right) \hbar\omega$
4. Phonons have particle character (quasiparticle) - they are bosons. Does not obey Pauli exclusion, each mode can have any number of phonons within it.

## 2.4 Interactions - Crystal momentum

$$\text{Momentum} = \hbar q$$

Consider a neutron scattering and generating a phonon, resulting in dynamics distortion to the lattice (creating compressions and rarefactions in the material), we end up with a lattice that is distorted on some larger periodic distance (phonon wavelength).

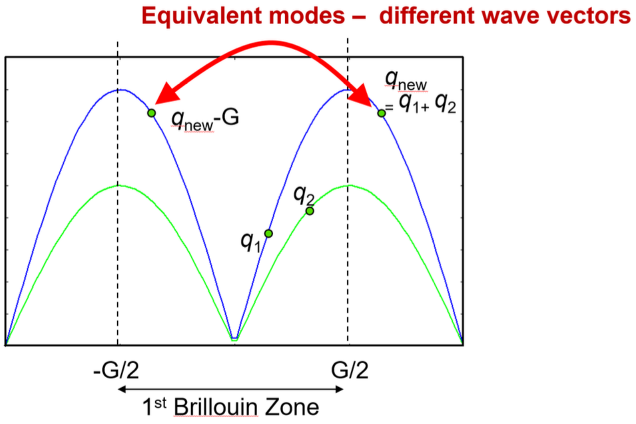
Neutron can diffract from the distorted lattice according to:

$$\mathbf{k}_f = \mathbf{k}_i + \mathbf{q}$$

Neutron can create a phonon and lose momentum ($\hbar\mathbf{q}$) and energy ($\hbar\omega$) to the phonon. Or neutron can absorb energy and gain momentum by annihilating a phonon (create phonon with wavevector -**q**)

### 2.4.1 Combining two phonons

They interact because of the small amount of anharmonicity in the system.



If **q** lies outside the 1st Brillouin zone, a **G** vector could be subtracted to represent it within the 1st BZ.

$$\boxed{\mathbf{k}_f = \mathbf{k}_i + \mathbf{q} + n\mathbf{G}}$$

So, a neutron scattering from a phonon can leave with its momentum changed by $\hbar\mathbf{q}$ plus any amount $\hbar\mathbf{G}$.

### 2.4.2 Measuring phonons

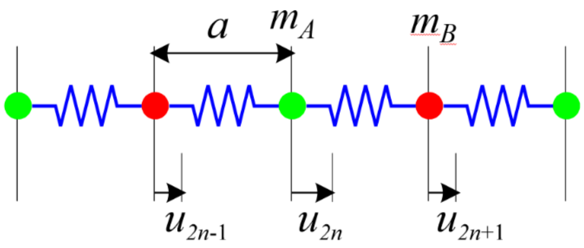
Measure phonon spectrum by **inelastic neutron scattering**.

$$\boxed{\begin{array}{c}\text{Energy conservation: } \hbar\omega = \dfrac{\hbar^2}{2m}(k_i^2 - k_f^2) \\ \text{Momentum conservation: } \mathbf{k}_i = \mathbf{k}_f \pm \mathbf{q} \pm \mathbf{G} \quad \text{(- annihilation, + creation)}\end{array}}$$

Probe particle $\xrightarrow{\text{send in}}$ interact $\longrightarrow$ measure energy and momentum afterwards to infer what the phonon must have been to cause these changes.
Process:

1. Send probe particle with comparable momentum and energy (~ 40 meV). E.g. neutrons for bulk phonons and He atoms for surface phonons. Sample illuminated with monochromatic beam of particles with wavevector, $\mathbf{k}_i$
2. Particles interact with the lattice and exchanges energy and momentum, creating or annihilating phonons
3. Select particles scattered into a particular outgoing direction, with wavevector $\mathbf{k}_f$
4. Energy analyse the scattered beam. Detected peaks correspond to single phonon creation/annihilation at that particular $\mathbf{k}_f$

## 2.5 1D Diatomic Lattice



Know the derivation.

### 2.5.1 Equations of motion

$$m_A\ddot{u}_{2n} = \alpha(u_{2n+1} + u_{2n-1} - 2u_{2n})$$
$$m_B\ddot{u}_{2n+1} = \alpha(u_{2n+2} + u_{2n} - 2u_{2n+1})$$

Trial solutions:

$$u_{2n} = U_1 e^{i(2nqa-\omega t)}$$
$$u_{2n+1} = U_2 e^{i((2n+1)qa-\omega t)}$$

Substituting back in:

$$-m_A\omega^2 U_1 = \alpha(U_2 e^{iqa} + U_2 e^{-iqa} - 2U_1)$$

$$-m_B\omega^2 U_2 = \alpha(U_1 e^{iqa} + U_1 e^{-iqa} - 2U_2)$$

Put in matrix form, set det $= 0$ and solve for $\omega^2$:

$$\left|\begin{pmatrix} 2\alpha - m_A\omega^2 & -2\alpha\cos qa \\ -2\alpha\cos qa & 2\alpha - m_B\omega^2 \end{pmatrix}\right| = 0$$

### 2.5.2 Dispersion relation

We get the dispersion relation:

$$\omega^2 = \frac{\alpha}{m_A m_B}\left[(m_A + m_B) \pm \sqrt{(m_A+m_B)^2 - 4m_A m_B \sin^2(qa)}\right]$$

Physical interpretation:
Two branches of solution: Negative root → acoustic mode. Positive root → optical mode.

### 2.5.3 Dispersion plot

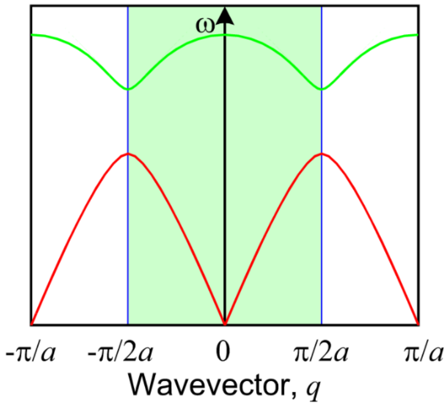
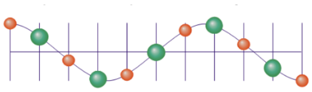


Figure 4: Unit cell is 2a in real space so in reciprocal space it is $^1/_{2a}$

**Acoustic mode (lower branch / lower energy mode)**

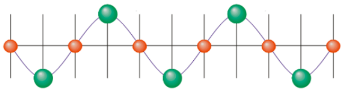
- Neighbouring atoms **in phase**.



- **Intersect origin**: $\omega \to 0$ as $q \to 0$.

- At zone boundaries ($q = \pm\frac{\pi}{2a}$), become standing wave where only the **heavier mass move**:

$$\omega = \frac{2\alpha}{m_A}$$



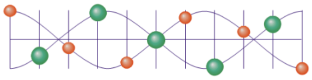
- As $q \to 0$, acoustic mode has angular frequency:

$$\omega \approx qa \underbrace{\sqrt{\frac{2\alpha}{m_A + m_B}}}_{\text{speed of sound}}$$

**Speed of sound** is given by $v = \frac{d\omega}{dq}$.

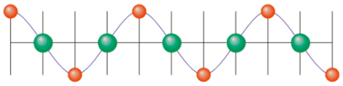
### Optical mode (upper branch / higher energy mode)

- Neighbouring atoms **out of phase**.



- **Floating**: $\omega \to$ finite value as $q \to 0$
- At zone boundaries, becomes standing wave where only the **lighter mass moves**:

$$\omega = \frac{2\alpha}{m_B}$$

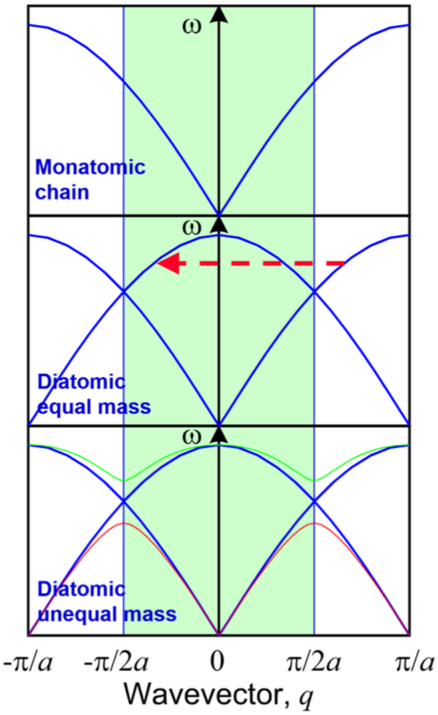


- As $q \to 0$, optical mode has angular frequency:

$$\omega = \sqrt{\frac{2\alpha}{\mu}} = \sqrt{\frac{2\alpha(m_A + m_B)}{m_A m_B}}$$

- Called the optical mode as it **interacts strongly with EM radiation**. It has strong optical absorption: photons annihilated and phonons created.

### 2.5.4 Backfolding*



Example procedure for 2 types of atoms:

1. Start with monatomic chain of period a. 1st BZ spans $-\pi/a \leq q \leq \pi/a$
2. Switch alternate atoms, assuming the masses are the same for now, to form a diatomic chain. Period becomes 2a. New 1st BZ is halved: $-\pi/2a \leq q \leq \pi/2a$
3. Modes with q outside the new 1st BZ must be **backfolded** into the zone, by adding $G = \pm\pi/a$, so forming two branches

   [think of snake game boundary / shift in]

4. If the atoms have different mass, the two modes **split**.
   Can be extended to N modes, which requires N foldings

## 2.6 3D phonons

Multiple modes:

- Longitudinal (L) modes, higher energy
- Transverse (T) modes, lower energy and often degenerate along high symmetry directions.

Higher frequency ⟶ more energy ⟶ stronger bonds.

# 3 Insulators

In insulating crystals, thermal energy is stored in the phonons.

## 3.1 Debye theory to model heat capacity

Assumption of dispersion relation:

$$\omega = v_s k$$

is true for all wavelengths; it essentially ignore the atomic nature of the material.

**Key experimental observations** that the model need to explain:

1. Near room temperature, $\boldsymbol{C \approx 3R}$ per mole/$3k_B$ per atom (Dulong-Petit Law)
2. At low temperatures, $\boldsymbol{C \propto T^3}$

### 3.1.1 Derivation

Approach:

1. **Find average energy in the $\boldsymbol{i^{th}}$ mode**
   Consider energy stored in each phonon mode:

   $$E_n = n\hbar\omega \quad \text{with probability} \;\; P_n = e^{-\frac{E_n}{k_B T}}$$

   where n is the number of phonons in the mode and $\omega$ is the angular frequency of the mode. The zero point energy $1/2\hbar\omega$ is ignored.

   The average energy in $i^{th}$ mode is:

   $$E_i = \frac{\sum_{n=0}^{\infty} n\hbar\omega_i e^{-\frac{n\hbar\omega_i}{k_B T}}}{\sum_{n=0}^{\infty} e^{-\frac{n\hbar\omega_i}{k_B T}}}$$

   Evaluating by spotting geometric series and $-\frac{\partial}{\partial\beta}$, we obtain:

   $$\boxed{E_i = \frac{\hbar\omega_i}{e^{\hbar\omega\beta} - 1}} \quad \text{(Planck's formula)}$$

2. **Internal energy is the sum of the contribution from all the modes**:

   $$\boxed{U = \int_0^{\infty} \frac{\hbar\omega_i}{e^{\frac{\hbar\omega_i}{k_B T}} - 1} g(\omega) d\omega}$$

   where $g(\omega) = \frac{dN}{d\omega}$ is the density of states. $g(\omega)d\omega$ gives the number of states with energies between $\hbar\omega$ and $\hbar(\omega + d\omega)$.

### 3.1.2 Density of states for phonons (reflecting B.C.)

Consider rectangular box of side lengths A, B and C and use **reflecting** boundary conditions to give **standing waves** in the box. Similar to solving particle-in-box, wavevector is:

$$\mathbf{k} = \left[\frac{n_x\pi}{A}, \frac{n_y\pi}{B}, \frac{n_z\pi}{C}\right]$$

These allowed states form a regular lattice of points in k-space, separated by ${}^{\pi}/_{A}$ in a x-direction, ${}^{\pi}/_{B}$ in a y-direction and ${}^{\pi}/_{C}$ in a z-direction.

$$\text{Volume of each state: } V_{\text{state}} = \frac{\pi^3}{ABC}$$

Consider number of states, $dN$ within shell of radius dk at radius k (in the positive octant):

$$dN = g(k)dk = \frac{3 \cdot \boldsymbol{\frac{4\pi k^2}{8}} \cdot dk}{V_{\text{state}}}$$

The factor of 3 is to allow for 2 transverse modes and 1 longitudinal mode.

$$\boxed{g(k) = \frac{3Vk^2}{2\pi^2}}$$

where $V = ABC$ is the volume of the box. The $k^2$ dependence comes from considering shells of states in k-space.
Also,

$$\boxed{g(\omega) = g(k)\frac{dk}{d\omega}}$$

If we know the phonon dispersion relationship $g(k)$, we can obtain energy density $g(\omega)$.

Now, substituting in the assumed dispersion relation:

$$\boxed{g(\omega) = \frac{3V\omega^2}{2\pi^2 v_s^3}}$$

### 3.1.3 Debye frequency/Debye temperature

In order to **integrate over the correct number of modes**, we choose a Debye frequency, $\omega_D$ such that:

$$\boldsymbol{3N} = \int_0^{\omega_D} g(\omega)d\omega = \int_0^{\omega_D} \frac{3V\omega^2}{2\pi^2 v_s^3}d\omega$$

$$\Rightarrow \boxed{\omega_D^2 = \frac{6\pi^2 v_s^3 N}{V}}$$

Internal energy integral:

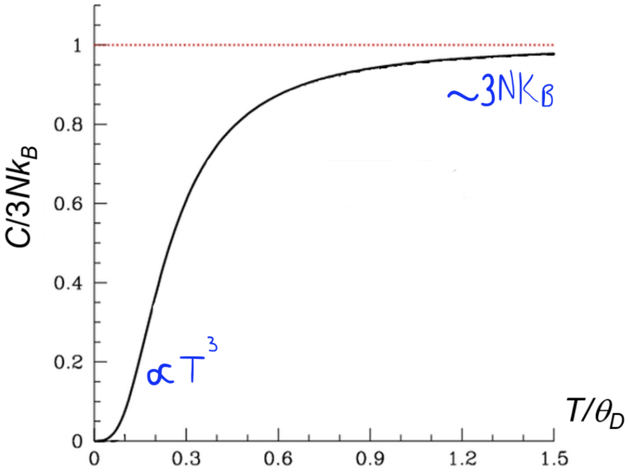
$$U = \int_0^{\omega_D} g(\omega) \cdot \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1}d\omega$$

where the mean speed of sound is given by $\frac{1}{v_s^3} = \frac{1}{3}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right)$.

### 3.1.4 Heat capacity

$$C = \frac{\partial U}{\partial T} = ... = \boxed{9Nk_B\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x-1)^2} dx}$$

where the Debye temperature $\theta_D$ is $\hbar\omega_D = k_B\theta_D$.



**High temperature limit** $(T \gg \theta_B) \longrightarrow$ Dulong-Petit Law.

$$\frac{e^x}{(e^x-1)^2} \approx \frac{1}{x^2} \quad \text{(Taylor expansion)}$$

$$\boxed{C = 3Nk_B}$$

At high T, $E_i = 2 \times \frac{1}{2}k_BT$. There are 3N possible phonon modes in a 3D crystal with N atoms. $U = 3Nk_BT$ and $C = {}^{\partial U}/_{\partial T} = 3Nk_B$. It agrees!

**Low temperature limit** $(T \to 0) \longrightarrow$ Debye $T^3$.

Higher frequency modes are not excited (only long wavelength acoustic modes are thermally excited), so contributions to the integral for large $\omega$ is not important, we can just integrate to $\infty$.

Of the allowed volume in k-space, the fraction occupied by excited mode is on the order of $\left(\frac{k_T}{k_D}\right)^3$ where $\hbar v k_T = k_BT$. Thus, the fraction occupied is $\propto \left(\frac{T}{\theta_D}\right)^3$ each having energy $k_BT$.

$$\boxed{U \sim 3N \cdot \left(\frac{T}{\theta_D}\right)^3 \cdot k_BT = 3Nk_B\frac{\boldsymbol{T^4}}{\theta_D^3}}$$

### 3.1.5 Density of states: Debye model v.s. Actual

Example: Aluminium.

1. At low $\omega$, Debye agrees with measurement. At low $q$, phonon dispersion curve tends to continuum speed of sound which agrees with the assumed dispersion relation.
2. Near zone boundary, largest deviations occur, as assumption that $\omega \propto q$ breaks down.
3. Measured $g(\omega)$ is more complex as:
   (i) the 3D 1st Brillouin zone has a more complicated shape.
   (ii) Both transverse and longitudinal modes have different dispersion curves.

## 3.2 Thermal conductivity

Heat is carried by phonons in insulators. We can use kinetic theory to establish phonon contribution to thermal conductivity.

Heat flux, H:

$$H = \int_0^\pi \int_0^\infty \underbrace{\left[ nf(v)dv \cdot \frac{1}{2}\sin\theta d\theta \right]}_{\substack{\text{number of phonons with} \\ \text{speed between } v \text{ and } v+dv \\ \text{travelling at angle } \theta \text{ to } \theta+d\theta}} \cdot \underbrace{[v\cos\theta]}_{\substack{\text{speed normal} \\ \text{to plane}}} \cdot \underbrace{\left[ -c_{ph}\frac{dT}{dz} l\cos\theta \right]}_{\substack{\text{excess heat} \\ \text{per mode}}}$$

1. Excess heat. Consider phonons crossing a plane at angle $\theta$,

   $$\Delta T = \frac{dT}{dz}\Delta z = -\frac{dT}{dz} l\cos\theta$$

   $$\text{heat } = c_{ph}\Delta T$$

   where $c_{ph}$ is the heat capacity of a phonon mode.

2. Distribution of phonons: $nf(c)\ dc$ is the number of phonons with speed c to $c+dc$. Fraction with angles $\theta$ to $\theta + d\theta$ is $\frac{1}{2}\sin\theta\ d\theta$

Integral over speed distribution:

$$\langle c \rangle = \int_0^\infty cf(c)dc$$

After evaluating the integral using substitution for the angular part, we obtain the result for thermal conductivity by recognising the coefficient of $\frac{dT}{dz}$ is $\kappa$:

$$\boxed{\kappa = \frac{1}{3} C_V \langle c \rangle l}$$

where $C_V$ is the **heat capacity per unit volume** and $l$ is the phonon mean free path.

### 3.2.1 Mean free path

Scattering processes reduce the mean free path and there are many different processes that can contribute.

Add the rate from each process to obtain the total scattering rate,

$$\Gamma = \frac{\langle c \rangle}{l} = \sum_i \frac{\langle c \rangle}{l_i}$$

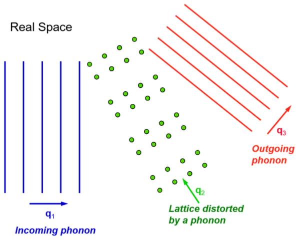
Mean free path add reciprocally.

$$\Rightarrow \boxed{\frac{1}{l} = \frac{1}{l_1} + \frac{1}{l_2} + ...}$$

Types of scattering:

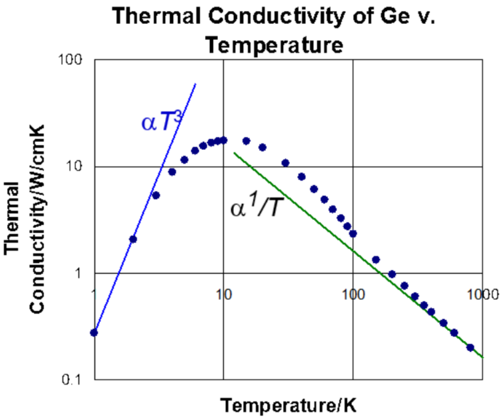
1. Geometric scattering
   - Independent of T.
   - From sample boundaries, impurities, gain boundaries.
2. Phonon-phonon scattering
   - Depends on T.
   - In an anharmonic (real) lattice, phonons can scatter because a phonon can distort the lattice and another phonon can diffract off the grating produced.

$$\text{Diffraction condition: } \mathbf{q}_3 = \mathbf{q}_1 + \mathbf{q}_2$$



   - 2 ways of phonon-phonon scattering:
     (a) Normal scattering (N-processes)
       – After phonons combine, resulting wavevector **stays within 1st BZ** → not much randomisation of phonon propagation → weak effect on thermal conductivity.
     (b) Umklapp scattering (U-processes)
       – Resultant phonon wavevector goes **outside 1st BZ** → folding back into 1st BZ gives negative group velocity → strong randomisation of phonons → limit mean free path → strong reduction of $\kappa$.
       – However, only dominant at **high temperature** to have enough high energy/momentum phonons.

### 3.2.2 Temperature dependence of $\kappa$ for insulators



**Low temperatures**:

- Few phonons, so phonon scattering is insignificant. Geometric scattering dominates.
- $l$ not dependent on temperature as geometric scattering is independent of temperature.
- $C \propto T^3$ so $\kappa \propto T^3$

**High temperatures**:

- Lots of phonons, so phonon-phonon scattering dominates. Umklapp processes fully active. 1/2 U-processes + 1/2 N-processes.
- C is constant at $3Nk_B$.
- Since number of phonons $\propto T$, $l \propto \frac{1}{T}$ so $\kappa \propto \frac{1}{T}$

**Intermediate temperature**:

- Umklapp processes gradually turn off and effect of phonon scattering on mean free path reduces greatly.
- $\kappa$ rise above $\frac{1}{T}$ asymptote as dependence of $l$ on $\frac{1}{T}$ weakens at lower temperatures. Gradient deviates away from -1.
- At the same time, low temperature $T^3$ dependence starts dominating and the gradient tends towards 3.

### 3.2.3 Validity of Debye model at different temperatures

Low T: dispersion is indeed linear so assumption holds
High T: Reproduce classical argument
Intermediate T: more complex dispersion relation that is not the same as assumption

# 4 Free electron model

## 4.1 Principles and approximations:

1. Valence electrons are free to move through the lattice
2. Ignore electron-electron repulsion
3. Positive ions treated as continuous background
4. Ignore lattice periodicity

**Key predictions FEM is able to make:**
1. Electronic heat capacity. 2. Electron Fermi pressure. 3. Electronic conductivity

## 4.2 Density of states for electrons (cyclic B.C.)

$g(\epsilon)\, d\epsilon$ tells you the total number of states with energy between $\epsilon$ and $\epsilon + d\epsilon$.

Consider states in the box and use **cyclic boundary conditions** to give **travelling** wave states:

$$\text{Box volume} = ABC$$

$$\text{Wavevector} = \left[\pm n_x \frac{2\pi}{A}, \pm n_y \frac{2\pi}{B}, \pm n_z \frac{2\pi}{C}\right]$$

$$\text{Volume of each state} = \frac{(2\pi)^3}{V}$$

$$\text{Volume of full shell of thickness dk at radius k } = 4\pi \boldsymbol{k^2} dk$$

So,

$$dN = g(k)dk = 2 \cdot \frac{4\pi k^2 dk}{8\pi^3/V}$$

$$\Rightarrow g(k) = \frac{Vk^2}{\pi^2}$$

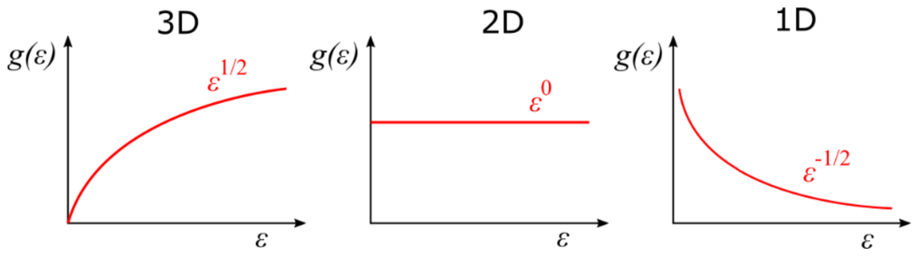
where factor of 2 allows for spin-degeneracy of electron.

$$g(\epsilon) = g(k)\frac{dk}{d\epsilon} \quad \text{and} \quad \epsilon = \frac{\hbar^2 k^2}{2m}$$

Obtain:

$$\boxed{g(\epsilon) \propto \epsilon^{1/2}}$$

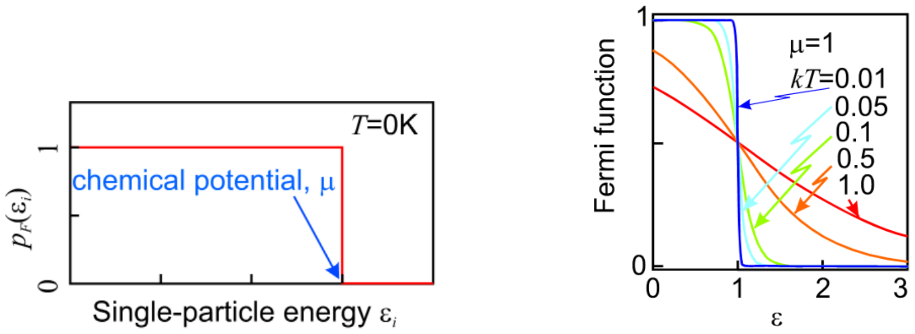
Can also do it for 1D or 2D case. Each state occupy area (2D) or length (1D) in k-space. Consider either circle (annulus) or line (both sides), instead of shell.



## 4.3 Fermi-Dirac Distribution

Fermi-Dirac distribution tells you the probability that the states with energy $\epsilon$ is occupied at temperature $T$.

$$p_F(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_BT}+1}$$



Note: distribution is symmetric about the chemical potential

At $T = 0$, there is no thermal excitation, so energy states are completely filled from ground level until the Fermi energy ($\epsilon_F$). All higher states are unoccupied. (Step function)

As $T$ increase, sharp step is progressively more **smeared out** by thermal excitation ($k_BT$) around $\epsilon_F$.

**Chemical potential v.s. Fermi energy**
At all T, chemical potential, $\mu$, is the energy when $p_F = 0.5$. At $T = 0$, $\mu$ is the Fermi energy, $\epsilon_F$.

We can prove/assume that $\mu$ varies weakly with temperature i.e. $\mu(T) \approx \epsilon_F$. At room temperature the chemical potential for metals is virtually the same as the Fermi energy – typically the difference is only of the order of 0.01. Not surprisingly, the chemical potential for metals at room temperature is often taken to be the Fermi energy.

**Derivation - Fermi energy (counting the correct number of states)**

At T = 0, in k-space, states are filled up to the Fermi energy and all lie inside a sphere of radius $k_F$, the Fermi wavevector.

$$\mathbf{N} = 2 \cdot \frac{\frac{4}{3}\pi k_f^3}{\frac{8\pi^3}{V}} \Rightarrow \boxed{k_f^3 = 3\pi^2 n}$$

where $n = N/V$.

Then, use dispersion relation to find Fermi energy,

$$\boxed{\epsilon_F = \frac{\hbar^2 k_f^2}{2m_e} = \frac{\hbar^2}{2m_e}(3\pi^2 n)^{2/3}}$$

**Derivation of Fermi-Dirac distribution**

Start with First Law of Thermodynamics:

$$dU = TdS - pdV + \mu dN$$

$$dS = \frac{dU}{T} - \frac{\mu dN}{T} \quad \text{(for constant V)}$$

In ground state, entropy of reservoir is $S_0 = k_B \ln \Omega_0$. To excite the system we need to transfer 1 particle and $\epsilon$ of energy from reservoir to system. New reservoir entropy is:

$$S_0 + dS = S_0 - \frac{\epsilon}{T} + \frac{\mu}{T} = k_B \ln \Omega$$

We have:

$$\ln \Omega_0 = \frac{S_0}{k_B} \quad \text{and} \quad \ln \Omega = \frac{S_0}{k_B} - \frac{(\epsilon - \mu)}{k_B T}$$

$$\ln \Omega - \ln \Omega_0 = -\frac{(\epsilon - \mu)}{k_B T} \quad \Rightarrow \quad \Omega = \Omega_0 e^{-(\epsilon-\mu)/k_B T}$$

Normalise to obtain probability of state being occupied:

$$p_F(\epsilon) = \frac{0 \cdot 1 + 1 \cdot e^{-(\epsilon-\mu)/k_B T}}{1 + e^{-(\epsilon-\mu)/k_B T}} = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1}$$

The number of **occupied** electron states is:

$$dN = p_F(\epsilon) \times g(\epsilon) d\epsilon$$

$$N = \int_0^\infty p_F(\epsilon) \times g(\epsilon) d\epsilon = \int_0^{\epsilon_F} g(\epsilon) d\epsilon$$

## 4.4 Electronic Heat Capacity of Metals (successes of FEM)

1. Find total thermal energy $U_{el}$. 2. Differentiate it w.r.t. T.

$$U_{el} = \int_0^\infty \epsilon \cdot g(\epsilon) \cdot p_F(\epsilon)\, d\epsilon = \int_0^\infty \frac{\epsilon g(\epsilon)}{e^{(\epsilon-\mu)/k_B T}+1} d\epsilon$$

Then,

$$\boxed{C_{el} = \frac{\partial U_{el}}{\partial T} \approx \frac{\boldsymbol{\pi^2}}{2} N k_B \frac{T}{T_F} \boldsymbol{\propto T}}$$

where $T_F$ is the Fermi temperature, given by $T_F = \frac{\epsilon_F}{k_B}$.

---

**Easier way**

Instead of evaluating the difficult integral, we can obtain similar result by assuming only electrons within $k_B T$ of $\epsilon_F$ is thermally active and they can treated classically so they each have $\frac{3}{2} k_B T$ of energy.

$$U_{el} = n_{ex} \cdot \frac{3}{2} k_B T = g(\epsilon_F) k_B T \cdot \frac{3}{2} k_B T$$

Find $g(\epsilon_F)$ by first noting,

$$g(\epsilon_F) \propto \epsilon_F^{1/2}$$

$$N = \int_0^{\epsilon_F} 1 \times A \epsilon^{1/2} d\epsilon = \frac{2}{3} \epsilon_F \cdot g(\epsilon_F)$$

So,

$$g(\epsilon_F) = \frac{3N}{2\epsilon_F} = \frac{3N}{2 k_B T}$$

Putting in expression of $g(\epsilon_F)$ into $U_{el}$ and differentiating with respect to T:

$$\boxed{C_{el} \approx \frac{\mathbf{9}}{2} N k_B \frac{T}{T_F} \propto T}$$

Approximate expression and actual expression only differ by $\pi^2$ v.s. 9.

${}^{T}/_{T_F}$ is typically 0.01 for typical metals at room temperature.

### 4.4.1 Total heat capacity of metals

In metals electrons provide an additional contribution to the thermal conductivity, which can therefore be much greater than in non–metals in which only phonons contribute.

Both phonons and electrons contribute to heat capacity.

At low temperatures, $C_{ph} \propto T^3$ and $C_{el} \propto T$,

$$\boxed{C_{tot} = \gamma T + \beta T^3}$$

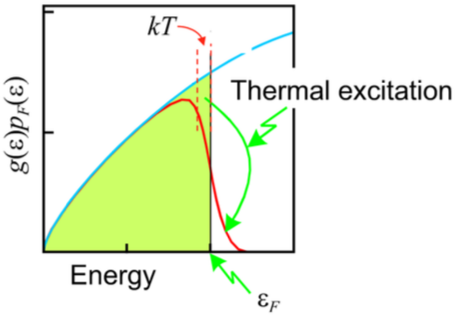
### 4.4.2 Fudge factor: effective mass $m^*$

A parameter to tune the heat capacity expression to match experimental values.

$$C_{el} \propto NTm^*n^{-2/3}$$

Discrepancy arise from electron-phonon coupling: ions pushed around by moving electron ⟶ other electrons avoid first electron, leading to extra contribution to KE ⟶ increase $m^*$.

## 4.5 Most important graph



## 4.6 Electron pressure (successes of FEM)

When the box is compressed ⟶ wavelength shortens ⟶ the KE of the states increase ⟶ since the number of states occupied remains the same, the total energy increase ⟶ there must be an outward pressure from the free electron gas.

$$\boxed{P = -\frac{\partial U}{\partial V}}$$

Find **average energy $\langle U \rangle$ per electron** by integrating over filled electron states:

$$\langle U \rangle = \frac{\int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon}{\int_0^{\epsilon_F} g(\epsilon) d\epsilon} = \frac{\int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon}{\int_0^{\epsilon_F} \epsilon^{1/2} d\epsilon} = \frac{3}{5}\epsilon_F \text{ per electron}$$

Noting that $\epsilon_F \propto \left(\frac{N}{V}\right)^{2/3}$, electron pressure for N electrons is:

$$P = -\frac{\partial U}{\partial V} = -\frac{\partial U}{\partial \epsilon_F}\frac{\partial \epsilon_F}{\partial V} = \boxed{\frac{2}{5} n \epsilon_F}$$

### 4.6.1 Property 1: bulk modulus

Pressure from electron gas has significant contribution to mechanical properties of metals. From the definition in Classical Dynamics:

$$\Delta P = -B\frac{\Delta V}{V}$$

Isothermal bulk modulus: $\boxed{k_B = -V\left(\frac{\partial P}{\partial V}\right)_T = \frac{2}{3}nE_F}$

## 4.7 Motion of electrons (successes of FEM)

### 4.7.1 Ingredient 1: Scattering

Electron can collide with **phonons and defects** in mean time $\tau$. We **add rates** to obtain total rate:

$$\boxed{\frac{1}{\tau} = \frac{1}{\tau_{\text{phonon}}} + \frac{1}{\tau_{\text{geometric}}}}$$

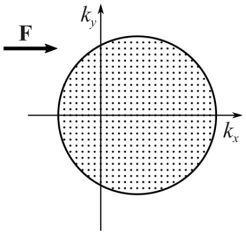
After time t, the probability that an electron has not collided is $e^{-t/\tau}$. After collision, the average velocity is zero.

$$\langle v\rangle = v\cdot e^{-t/\tau} + 0\cdot(1-e^{-t/\tau}) = \boxed{v\cdot e^{-t/\tau}}$$

$$F_{\text{scattering}} = \frac{d\langle v\rangle}{dt} = -\frac{\langle v\rangle}{\tau} \longrightarrow \begin{matrix}\text{goes into}\\ \text{equation}\\ \text{of motion}\end{matrix}$$

**Scattering in k-space**

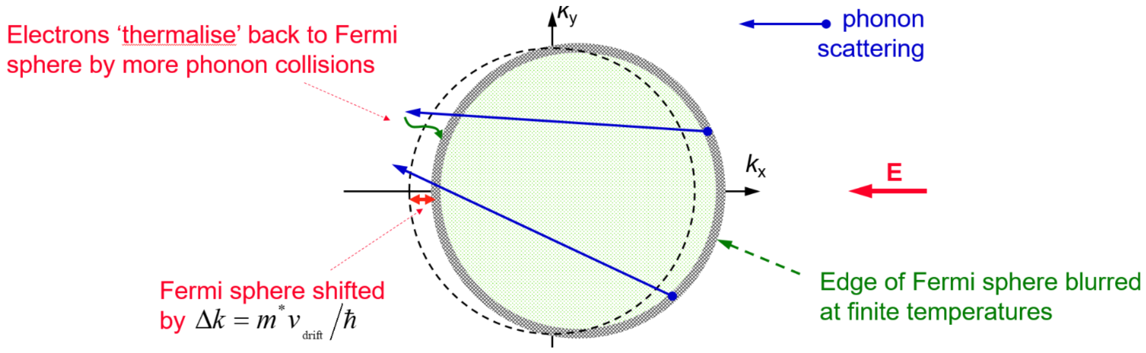
E-field ⟶ displacement of Fermi sphere.
Scattering ⟶ limit displacement of Fermi sphere.



$\frac{d\mathbf{k}}{dt} = -\frac{\hbar}{e}\mathbf{E}$

Both phonon and defect scattering **strongly change direction** of $\mathbf{k}$, but only **slightly change the magnitude**, $|\mathbf{k}|$ (weak changes in energy).

Electrons can only scatter into unfilled states with similar energy (so cannot scatter inwards into sphere). So, **only electrons states near the Fermi surface can be scattered**.



E-field to the left⟶ sphere shift right.
+
Majority of electrons that are scattered are at the 'front' of the Fermi sphere. They scatter to the back.

Result: sphere reach equilibrium displacement in k-space, which corresponds to **drift velocity**.

$$\boxed{\Delta k = \frac{m^* v_{\text{drift}}}{\hbar}}$$

### 4.7.2 Ingredient 2: Influence of E and B fields

Total force on electron is Lorentz force + velocity dependent drag term due to scattering.

**Equation of motion**:

$$\boxed{m^* \left( \frac{d\mathbf{v}}{dt} + \frac{\mathbf{v}}{\tau} \right) = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) = -e\mathbf{E}}$$

First term: rate of loss of momentum due to collisions with the lattice.

Second term: assumed that in every collision an electron of expected momentum $m^* v$ loses all of its momentum, and this happens at a rate of one collision per $\tau$.

### 4.7.3 Property 2: electrical conductivity

For steady state, $\frac{d\mathbf{v}}{dt} = 0$,

1. Find drift velocity:

$$\text{Drift velocity: } m^* \frac{v_{\text{drift}}}{\tau} = -eE$$

$$\text{So, } \boxed{v_{\text{drift}} = \frac{e\tau}{m^*} E = \mu E}$$

where $\mu = \frac{v_{\text{drift}}}{E} = \frac{e\tau}{m^*}$ is electron mobility.

2. Link to current density (using $J = nvq = \sigma E$):

$$J = nev_{\text{drift}} = \underbrace{ne\mu}_{\sigma} E$$

$$\boxed{\therefore \sigma = ne\mu = \frac{ne^2\tau}{m^*}}$$

For the same material under the same conditions, the ratio of electrical conductivity is just the ratio of number density.

### 4.7.4 Property 3: optical reflectivity

Optical reflectivity is related to **inertia of free electrons** when they are driven by the high frequency electric field in light.

At optical frequency, $\omega \gg {}^1/_\tau$, so ignore scattering. Apply E field: $E = E_0 e^{-i\omega t}$ giving response $x = x_0 e^{-i\omega t}$,

$$m^* \omega^2 x = eE$$

$$\Rightarrow x_0 = \frac{eE_0}{m^* \omega^2}$$

Dipole moment for one electron: $p = -ex_0$ and $P = \epsilon_0 \chi E$,

$$P = -nex_0 = -\frac{ne^2}{m^*\omega^2} E_0 = \epsilon_0 \left( -\frac{ne^2}{\epsilon_0 m^* \omega^2} \right) E_0$$

$$\text{Dielectric: } \epsilon = \chi + 1 = 1 - \frac{ne^2}{\epsilon_0 m^* \omega^2} = \boxed{1 - \frac{\omega_p^2}{\omega^2}}$$

where $\omega_p^2 = \frac{ne^2}{\epsilon_0 m^*}$ is the plasma frequency. Things are coming back yeah. Then, refractive index is just:

$$n = \sqrt{\epsilon}$$

Below the plasma frequency, n is imaginary, giving high reflectivity. At high frequency, n is real and the metal is transparent.

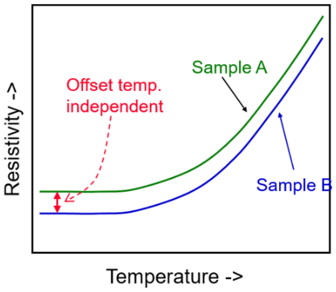
### 4.7.5 Property 4: electrical resistivity

**High temperatures**:

- Many phonons, phonon scattering dominant.
- Number of density of phonon is proportional to temperature.
- Hence, $\boldsymbol{\rho \propto n \propto T}$

**Low temperatures**

- Few phonons, defect scattering dominant.
- Different sample have different defect density.
- Hence, there is **T independent offset** (Matthiessen's rule).



### 4.7.6 Property 5: Thermal conductivity of metals

Contribution to thermal conductivity by phonons is small as $\langle c\rangle_{el}$ (speed of light) $\gg$ $\langle c\rangle_{ph}$ (speed of sound). Use:

$$\kappa = \frac{1}{3}C_{el}\langle c\rangle l$$

Since electrons only near the Fermi level are excited, $\langle c\rangle = v_F$ and $l = v_F\tau$, we have:

$$\kappa_{el} = \frac{1}{3}\cdot\left(\frac{\pi^2}{2}nk_B\frac{T}{T_F}\right)\cdot v_F\cdot v_F\tau$$

$$k_{el} = \frac{1}{3}\cdot\left(\frac{\pi^2}{2}nk_B\frac{T}{\frac{1}{2}m^*v_F^2/k_B}\right)\cdot v_F^2\tau$$

$$\boxed{\therefore k_{el} = \frac{\pi^2 nk_B^2T\tau}{3m^*}}$$

At room temperature, electron thermal conductivity swamps phonon conductivity.
At high temperatures, phonons dominate scattering. Since $1/\tau_{ph} \propto n \propto T$, so thermal conductivity is roughly constant with temperature.

Pure metal (e.g. Cu) v.s. Alloy (e.g. stainless steel):

1. $C_{el} \propto T$
2. $\langle c \rangle$ independent of T
3. Cu: pure copper atoms, large distance between impurity. Small contribution from geometric scattering. Phonon scattering dominates:

$$l \approx l_{ph} \propto \frac{1}{T}$$

So, $\kappa$ nearly constant.

Stainless steel: 10% Nickel, short distances to nearest impurity. Geometric scattering dominate.

$$l \approx l_g \propto T^0$$

So, $\kappa \propto T$.

### 4.7.7 Validity test 1: Wiedemann-Franz Law (support)

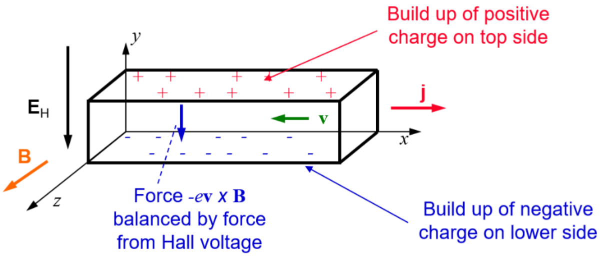
Experimental law: for metals at not too low temperatures, the ratio of the thermal to electrical conductivities is directly proportional to temperature, with the same constant of proportionality for all metals.

$$\boxed{\frac{\text{thermal conductivity}}{\text{electrical conductivity}} = \frac{\kappa}{\sigma} = LT} \quad \text{where} \quad L = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 \quad \textbf{(Lorenz number)}$$

Theoretical $\boxed{L = 2.45 \times 10^{-8}\, W\Omega K^{-2}}$

It has very good agreement with experimental values, giving strong support to the validity of the free electron model.

### 4.7.8 Validity test 2: Hall effect (model breaking down)



If a steady current flows in a conductor under the influence of a magnetic field, then there would be a transverse force acting on the charge carriers due to Lorentz force, $q\mathbf{v} \times \mathbf{B}$. This causes the electrons to be pushed sideways and they 'pile up' on opposite faces creating an electric field $E_H$. The electric force on electron by $E_H$ balances with the magnetic force:

$$qE = qvB \quad \text{and} \quad I = nAvq$$

$$E_H = v_{\text{drift}}B = B\left(\frac{J}{nq}\right) = R_H B J$$

where $\boxed{R_H = \frac{1}{nq} = \frac{E_H}{BJ}}$ is the **Hall coefficient**.

We can deduce the **number density** of the charge carriers.

Look at ratio:

$$\frac{n}{n_{\text{atom}}} = -\frac{1}{n_{\text{atom}} e R_H}$$

Found that values for Be and Cd is negative! Make no sense.

## 4.8 Comment on validity of free electron model

The free electron model works remarkably well given its simplicity - especially for alkali metals (Li, Na, K, ...) and some noble metals (Cu, Ag, Au).

However, the Hall effect demonstrates that we need to go beyond free electrons. Interaction with the lattice will be included using the ‘nearly free electron model.

## 4.9 Q & A

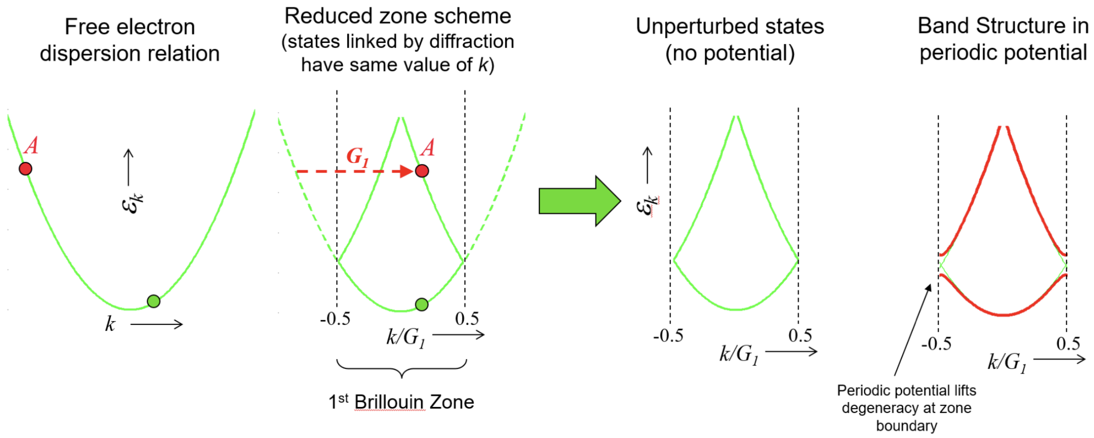
Q1: Explain the hall effect, and show how, by measuring the Hall coefficient, one can deduce the average number of free electrons per atom.

A1: When a steady current flows in a wire, subject to a steady magnetic field perpendicular to the direction of current flow, the charges cannot have any net force on them. Since there is a force of magnitude *Bqv* (where B is the magnetic flux density, v the mean speed of the charge carriers, and q their charge), this must be opposed by a static potential difference due to a concentration gradient of charge carriers, perpendicular to both the current and the magnetic field.

# 5 Nearly Free Electron Model

## 5.1 Result of accounting for lattice periodicity

Introducing **periodicity results in back-folding** of electron dispersion curve and a **finite potential splits** the dispersion into separate **bands!**. Bands, bands, bands.



Basic approach:

1. Define the potential
    - **Periodic** potential to represent a NFE with the lattice. Choose a **weak** potential to simplify calculation. Expand as Fourier series in terms of **G-vectors**.
2. Establish a generalised electron wavefunction
    - Use **Bloch's theorem** to find form of electron wavefunction and write the basis states as Fourier series in terms of G-vectors.
3. Satisfy the Schrodinger Equation
    - Solve using **matrix**

## 5.2 Step 1: Periodic Potential

Weak potential (nearly free): only a few electron basis states need to be included. A free electron is describe by a single plane-wave.

All electron-electron interactions/correlations/exchange is ignored.

$$\boxed{V(x) = \sum_{p=-\infty}^{\infty} V_p \cos(pG_1 x)} \quad \text{where} \quad G_1 = \frac{2\pi}{a}$$

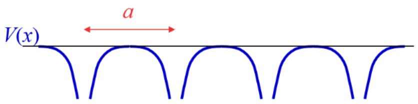


Figure 6: 1D potential

## 5.3 Step 2: Bloch's Theorem

Bloch's theorem states that the electron probability density must have the same translational symmetry as the lattice, $|\Psi(x+a)|^2 = |\Psi(x)|^2$. The wavefunction can only change by a phase factor, $\delta = ka$, between unit cell.

$$\Psi_k(r) = u_k(r)e^{i\mathbf{k}\cdot\mathbf{r}}$$

where $\boldsymbol{u_k}$ has the **periodicity** of the potential and $e^{i\mathbf{k}\cdot\mathbf{r}}$ is a phase factor. Hence, we can expand $u_k(r)$ (as it is periodic function) as a Fourier series:

$$u_k(x) = \sum_{n=-\infty}^{\infty} C_{k,n}\frac{1}{\sqrt{A}}e^{inG_1x}$$

We have:

$$\boxed{\Psi(x) = \sum_{n=-\infty}^{\infty} C_{k,n}\,|\phi_{k,n}\rangle \quad \text{where} \quad |\phi_{k,n}\rangle = \frac{1}{\sqrt{A}}e^{i(k+nG_1)x}}$$

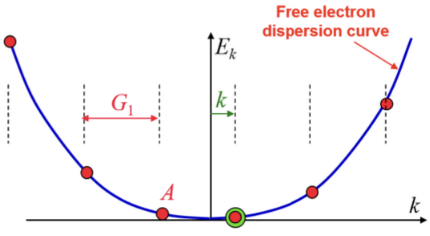


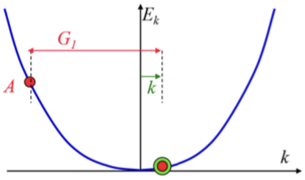
Figure 7: 1D potential in k-space

Small red dots: basis states $|\phi_{k,n}\rangle$ lie on the free electron dispersion curve and are separated by $G_1$ along the k-axis.

Large green dot: **weighted linear combination** of the basis states give the overall wavefunction, $\psi_k(x)$

**For small k values** (lowest energy states),
There is significant difference in energy between neighbouring basis-states, so any additional basis state other than the one next to it has little contribution to the overall wavefunction, according to Boltzmann distribution. So,

$$\Psi_k(x) \sim |\phi_{k,0}\rangle$$



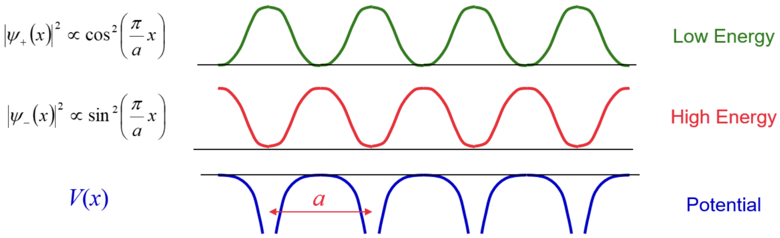
The energy is close to free particle energy.

**For larger k**,
Both basis-states have comparable energy, and give significant contribution to $\Psi_k(x)$.

At **zone boundary**, $\boldsymbol{k = {}^{G_1}\!/_2}$, both basis-states contribute equally and travel in opposite directions, superposing them forms standing waves in two ways (sum or difference):

$$\Psi_+(x) = \frac{1}{2}[|\phi_{G_1/2}\rangle + |\phi_{-G_1/2}\rangle] \propto \cos\left(\frac{\pi x}{a}\right)$$

$$\Psi_-(x) = \frac{1}{2}[|\phi_{G_1/2}\rangle - |\phi_{-G_1/2}\rangle] \propto \sin\left(\frac{\pi x}{a}\right)$$



**Origin of splitting**: the two new states, $\Psi_+$ and $\Psi_-$ have different energies so the degeneracy in the dispersion relationship is lifted; the two branches split apart in energy.

## 5.4 Step 3: Matrix

Starting with the Hamiltonian,

$$\hat{H}\Psi(x) = \epsilon\Psi(x) \quad \text{where} \quad \hat{H} = -\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x^2} + V(x)$$

$$\hat{H}\sum_m C_{k,m}|\phi_{k,m}\rangle = \epsilon\sum_p C_{k,p}|\phi_{k,p}\rangle$$

$$\sum_m C_{k,m}\underbrace{\langle\phi_{k,n}|\hat{H}|\phi_{k,m}\rangle}_{H_{nm}} = \epsilon\sum_m C_{k,p}\langle\phi_{k,n}|\phi_{k,p}\rangle$$

Note: Can find $H_{nm}$ by writing the operator in integral form and doing the integral.

Hence, the equation reduces to an **eigenvalue problem**:

$$\sum_m H_{nm} C_{k,m} = \epsilon C_{k,n} \Rightarrow \underline{\underline{H}}\vec{\mathbf{C}} = \epsilon \vec{\mathbf{C}}$$

$$\boxed{\left(\underline{\underline{H}} - \epsilon \underline{\underline{I}}\right) \vec{\mathbf{C}} = 0}$$

where $H_{nm}$ are the matrix elements of $\underline{\underline{H}}$ and $\vec{C}$ are the coefficients of the basis-states.

$$\boxed{\text{The eigenvectors of } \underline{\underline{H}} \text{ gives the coefficients } C_{k,n}}$$

In the two state approximation, where $\Psi_k(x) = C_{k,0}\left|\phi_{k,0}\right\rangle + C_{k,-1}\left|\phi_{k,-1}\right\rangle$, only the matrix elements $H_{0,0}$, $H_{\bar{1},0}$, $H_{0,\bar{1}}$, $H_{\bar{1},\bar{1}}$ are needed.

Now,

$$\underbrace{\left[\begin{pmatrix} H_{\bar{1},\bar{1}} & H_{\bar{1},0} \\ H_{0,\bar{1}} & H_{0,0} \end{pmatrix} - \epsilon_k \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right]}_{det=0} \begin{pmatrix} C_{k,-1} \\ C_{k,0} \end{pmatrix} = \mathbf{0}$$

Diagonal terms of $H$:

$$H_{00} = E_{k,0} = \frac{\hbar^2 k^2}{2m} \quad \text{(free electron dispersion)}$$

$$H_{\bar{1},\bar{1}} = E_{k,-1} = \frac{\hbar^2}{2m}(k - G_1)^2 \quad \text{( free dispersion shifted by } G_1\text{)}$$

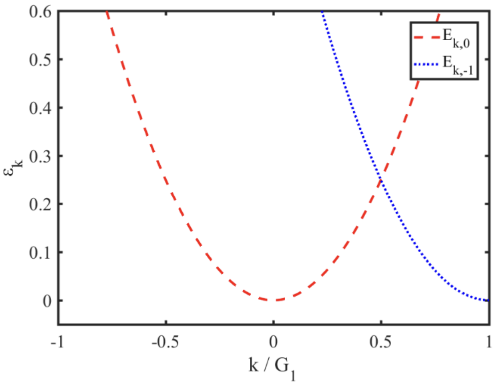
Off-diagonal terms: $\frac{V_1}{2}$.

Solving the characteristic determinant equation gives you energy eigenvalues, $\epsilon_k$.

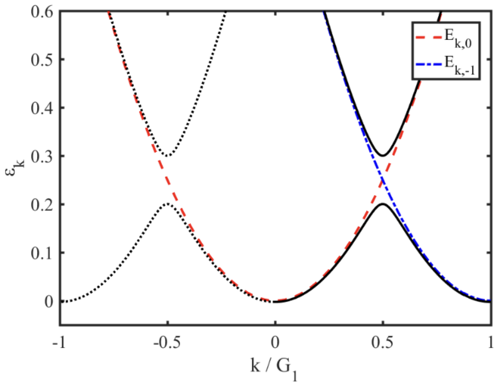
In general,

$$\boxed{E_{k,n} \text{ of } \left|\phi_{k,n}\right\rangle = \frac{\hbar^2 (k + nG)^2}{2m}}$$

They are quadratic curves offset by $G$.



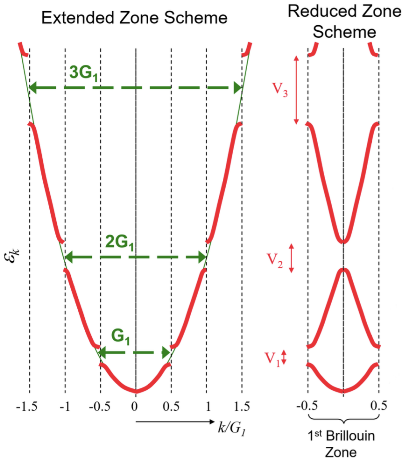
(a) Basis states



(b) Electron wavefunction

With a more general potential:

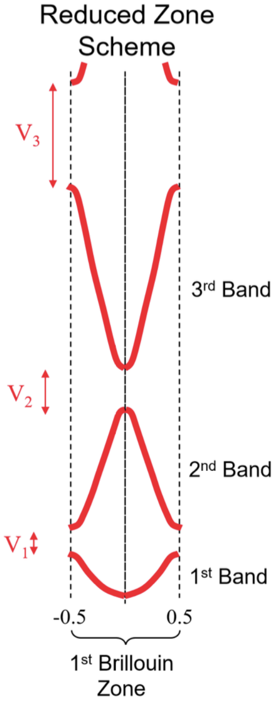
$$V(x) = \sum_n V_n \cos(nG_1 x)$$



1. Energy gaps of $V_n$ at $k = nG_1/2$
2. Periodicity folds back k-space into the first BZ.

## 5.5 Band structure

Available electron states form a **band structure**.

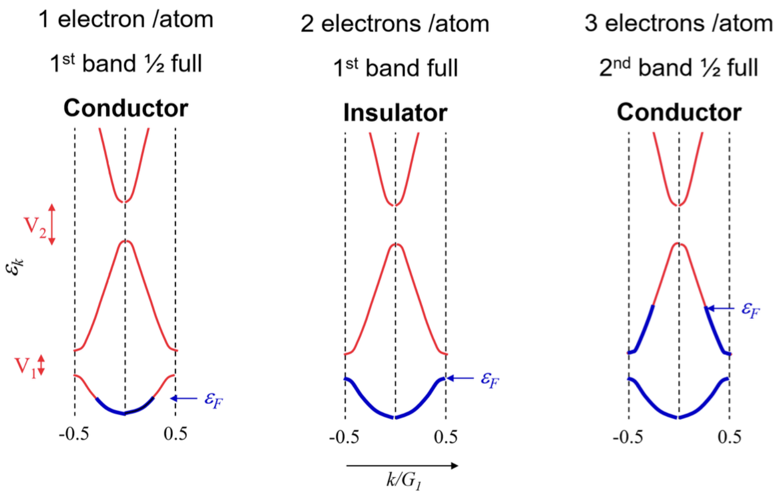


- **Bands**: allowed electron states states lie in certain energy ranges.
- **Gap**: between bands are gaps.
- **Fermi energy** determine how far up the band structure fills with electrons. *States are filled up to Fermi energy*.
- Uses: the filling level of the electron bands determines whether a material is a conductor, insulator or semiconductor.

### 5.5.1 Filling bands (insulators v.s. conductors)

"An empty band conducts no charge" and "A filled band conducts no charge". Only **partially filled bands** contribute to electrical conduction as there are **nearby states available** so the Fermi sphere can be displaced on application of an E-field.

$$\Delta k = \frac{m^* v_{\text{drift}}}{\hbar}$$

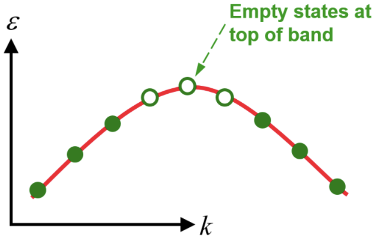


#### How many electron states are there?

Separation of free-electron states in k-space $= \frac{2\pi}{A}$, where $A = na$ is size of crystal.
Size of $1^{st}$ Brillouin zone $= \frac{2\pi}{a}$.
Total number of states in the zone $= \frac{A}{a}$.
So, there are n k-states or 2n electron states in the $1^{st}$ BZ.

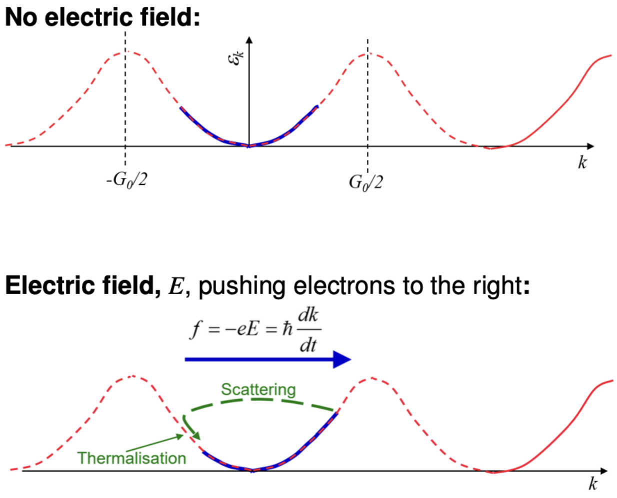
#### Where to find empty states?

Empty states exist near the **top of a band**.



**Valance band**: lower almost full band.
**Conduction band**: upper almost empty band.

### 5.5.2 Band structure and process of conduction



When there is no electron field, all the electrons are in the ground state and there is equal number of electrons moving forward and backward. There is no net current.

When an E-field is applied,

- E field causes electrons move to higher k-states (greater momentum), electrons are **pushed to the right**.
- Phonons and defects **scatter** electrons into empty states of comparable energy.
- Scattered electrons **thermalise** (lose energy) by further phonon-interactions, until they reach the occupied states.
- Result is a **net current**; more electrons are moving forwards than backwards. The group velocity (gradient of dispersion curve)

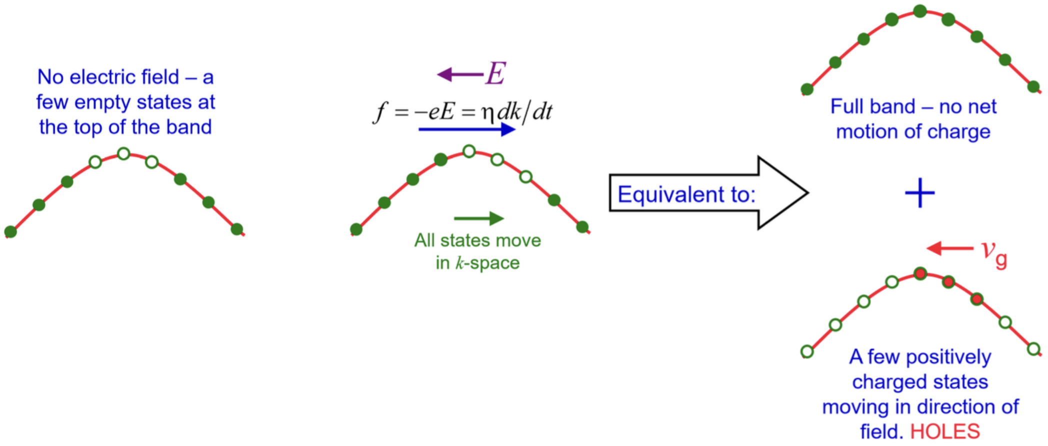
## 5.6 Conduction by holes

We can represent the few empty states at the top of a band as a 'holes' moving in the top of a full band.

Treat each empty state as containing a particle with:

- positive charge, $+|e|$
- positive mass, $m_h$
- positive energy, $\frac{\hbar^2 k_e^2}{2m_h}$

Hole band looks just like a free particle band.



An empty state (net positive charge) travels in exactly the same way as a filled state in the presence of an applied field.

Energy to create hole by transferring an electron into the conduction band:

$$\Delta\epsilon = E_{gap} + \frac{\hbar^2 k^2}{2m_e} + \frac{\hbar^2 k^2}{m_h}$$

The energy $\epsilon_e$ and momentum $k_e$ of electron in the valence band is measured with respect to the top of the valence band.

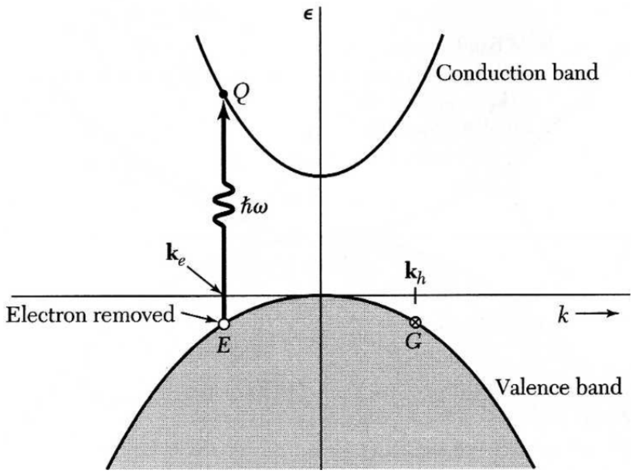


Figure 9: Absorption of a photon of energy $\hbar\omega$ and negligible wavevector takes an electron from E in the filled valence band to Q in the conduction band. If $k_e$ was the wavevector of the electron at E, it becomes the wavevector of the electron at Q. The total wavevector of the valence band after the absorption is $-k_e$ , and this is the wavevector we must ascribe to the hole if we describe the valence band as occupied by one hole. Thus $k_h = -k_e$; the wavevector of the hole is the same as the wavevector of the electron which remains at G. For the entire system the total wavevector after the absorption of the photon is $k_e + k_h = 0$, so that the total wavevector is unchanged by the absorption of the photon and the creation of a free electron and free hole.

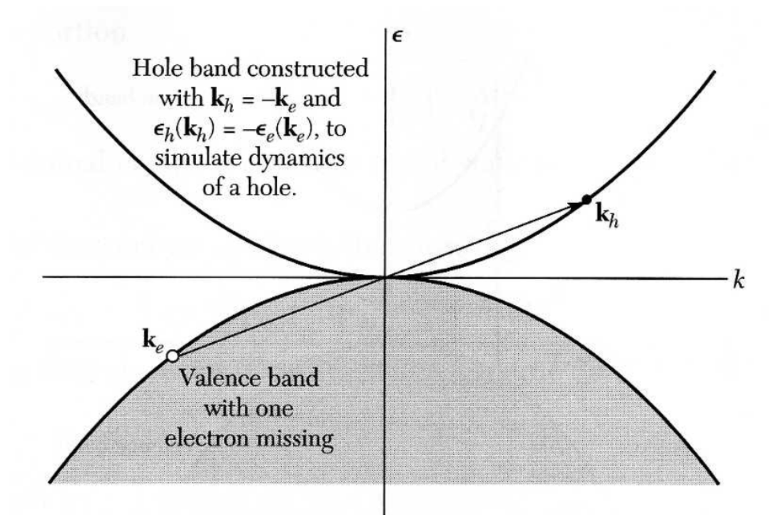


Figure 10: he upper half of the figure shows the hole band that simulates the dynamics of a hole, constructed by inversion of the valence band in the origin. The wavevector and energy of the hole are equal, but opposite in sign, to the wavevector and energy of the empty electron orbital in the valence band. We do not show the disposition of the electron removed from the valence band at $k_e$

Representing missing electron in a corresponding hole band.

$$\epsilon_h = -\epsilon_e$$

$$k_h = -k_e$$

### 5.6.1 Observation of holes

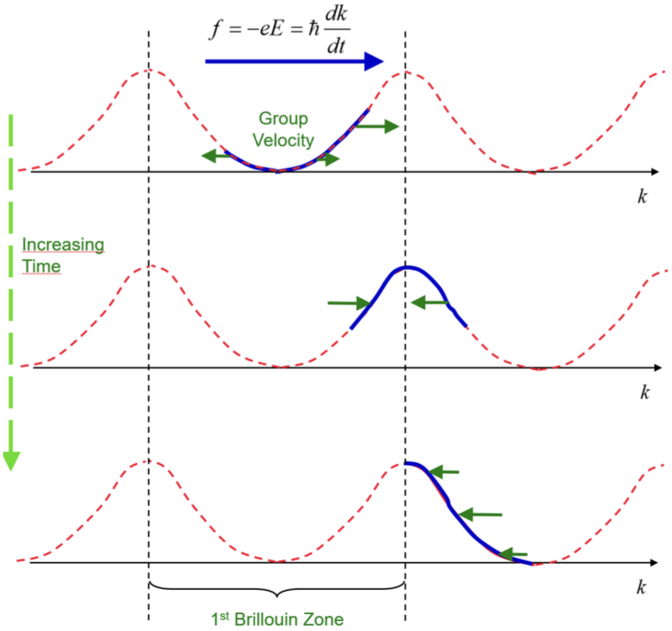
Both electrons and holes contributes to electrical conduction.

$$\sigma_e = \frac{n_e e^2 \tau_e}{m_e^*} \quad \text{and} \quad \sigma_h = \frac{n_h e^2 \tau_h}{m_h^*}$$

$$\mathbf{j} = (\sigma_e + \sigma_h)\mathbf{E}$$

## 5.7 Bloch Oscillations

An extreme situation where occupied states **move continuously** through k-space, which happens if the **electric field is strong** and the **scattering processes are weak**.



Strong E-field + weak scattering $\longrightarrow$ occupied states steadily increase in k $\longrightarrow$ filled states cross into 2nd BZ $\longrightarrow$ direction of electron group velocity reverse $\longrightarrow$ backfolding means process is continuous $\longrightarrow$ group velocity, and hence position of electrons, oscillates.

Bloch oscillation is observed in both condensed matter and ultracold Cs atoms.

## 5.8 Effective mass, $m^*$

Remember this!

$$m^* = \frac{\hbar^2}{\frac{d^2\epsilon}{dk^2}}$$

Memory aid: $\epsilon = \frac{\hbar^2 k^2}{2m}$.

This shows that the curvature of the band structure explains the origin of the effective mass.

**Derivation:**
By Newton's Law:

$$f = \underbrace{m^* \frac{dv}{dt}}_{} = \underbrace{\frac{d(\hbar k)}{dt} = \hbar \frac{dk}{dt}}_{}$$

$$\Rightarrow \frac{dv}{dt} = \frac{\hbar}{m^*}\frac{dk}{dt}$$

Using dispersion relations to express speed $v$ of electron:

$$\frac{dv}{dt} = \frac{d}{dt}\left(\frac{d\omega}{dk}\right) = \frac{dk}{dt}\frac{d}{dk}\left(\frac{d\omega}{dk}\right) = \frac{dk}{dt}\frac{d^2\omega}{dk^2} = \frac{1}{\hbar}\frac{d^2\epsilon}{dk^2}\frac{dk}{dt}$$

Equating:

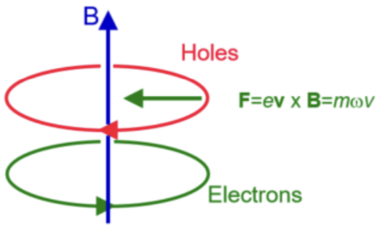
$$\boxed{m^* = \frac{\hbar^2}{d^2\epsilon/dk^2}}$$

Effective mass depends on the second derivative of $\epsilon(k)$.

Consequences:
1. Electron behaves with different effective mass for particular band structure and particular bands we are talking about
2. Different effective mass for different values of k
3. Depending on where the Fermi energy is, we might have more than 1 effective mass contributing to conduction.

### 5.8.1 Observation of effective mass: Cyclotron resonance

Cyclotron resonance can be used to measure effective mass.



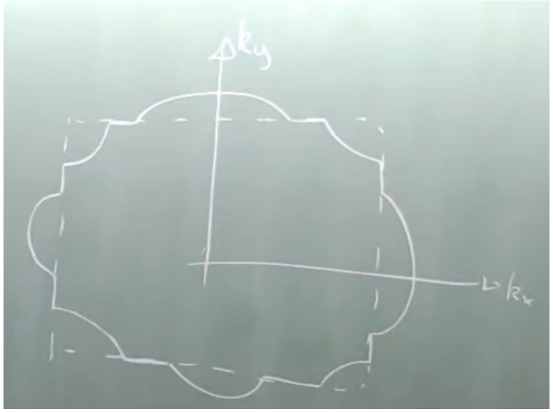
Principle: in a B-field, charged particles perform circular orbits around the field lines with the cyclotron frequency, $\omega = \frac{eB}{m}$.

Detection: At certain frequencies, we can observe resonances via strong absorption of radio waves. From the frequencies, $m_e^*$ or $m_h^*$ can be determined.

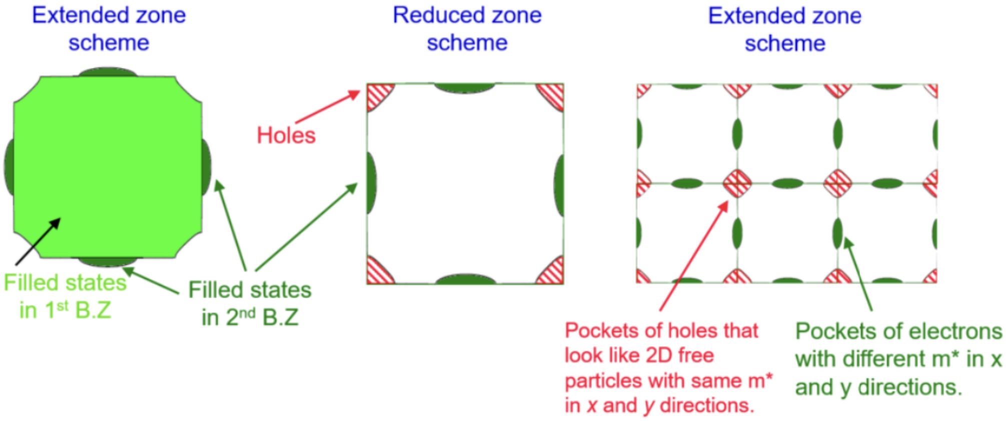
Conditions: Need strong B field and very low temperatures.
To be able to measure resonance, charged particle must travel at least $\sim 1$ rads, so $\omega\tau > 1 \longrightarrow \omega$ must be very high (10s of GHz)

## 5.9 Divalent metals

- At $T = 0$, both electrons and holes exist.
- Carriers originate from Fermi contour crossing 1st BZ boundary.



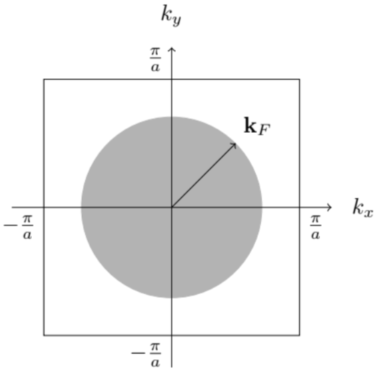
There are half-filled states in both the 1st and 2nd band. Electrons in the 2nd BZ and holes in the 1st BZ. They have different effective masses, due to differing band curvature.



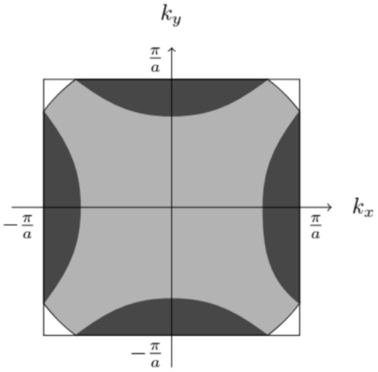
## 5.10 Tripos Q & A

Q1: (2011 P1 A5) Sketch the first Brillouin zone and the Fermi surface of a 2D square lattice of (a) a monovalent and (b) a divalent metal.

A1: (a) Just fill to the Fermi level. So a circle.



(b) There is backfolding.



The double shaded parts are backfolded regions

Q2:

# 6 Semiconductors

**What is a semiconductor and what differentiates it from a metal?**

Semiconductor:

- A semiconductor is a material where the electronic bandstructure of the material has a gap in it.
- The electrons completely fill states below the gap, and the band above the gap is completely empty, i.e. the Fermi level is in the gap.
- Semiconductors differ from insulators in that the bandgap is sufficiently small that either thermal or optical excitation can promote electrons from the valence band to the conduction band and therefore the material will conduct.

Metal:

- In a metal, there will either be some overlap of the bandstructure such that electrons are always available for conduction in the conduction band or a not completely filled band structure.

## 6.1 Doping

**Explain the concept of doping in semiconductors, including the difference between p and n type**.

- Doping in semiconductors allows for either electrons (n type) or holes (p type) to be added to the material in states that lie close to either the conduction or valance bands respectively.
- This is achieved by adding impurities to the sample which are either lacking an electron compared to the number needed to bond into the surrounding lattice (p type, valence 3 Al atoms), or which have an additional electron (n type, valence 5 P atoms).
- This allows for much greater conductivity in the samples, and also a degree of control over this.

1. Add in $P^+$ ions:

- $P^+$ has same electronic structure as Si. The system is no different than pure Si.
- VB full and CB empty.

2 Add in extra electron:

- The extra electrons all sit in the CB, but it can be in two states: ionised or hydrogenic.

1. **Ionised state** - electron and ion are well separated
    - More likely higher temperatures and **contributes to conductivity**.
2. **Bound (hydrogenic) state** - electron and ion form a 'hydrogen-like' structure
    - Electrostatic potential results in binding energy between the electron and the ion so bound states are formed below the base of the conduction band.
    - Low temperature state, and **does not contribute to conductivity**.

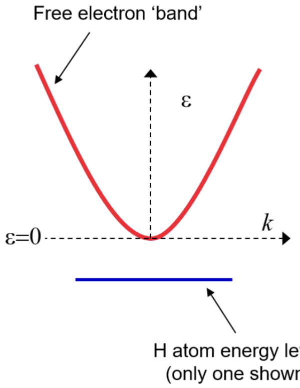


Figure 11: The state has no k-dependence so appear as a straight line

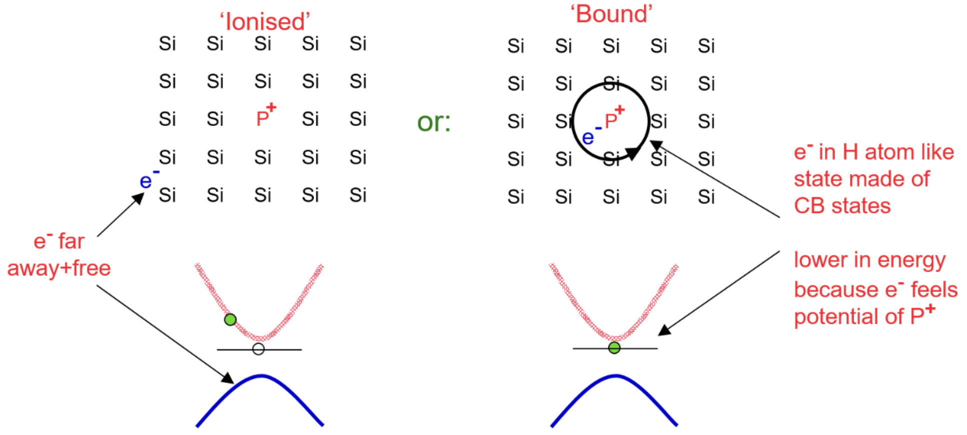
- Energy below the bottom of the conduction band and mean radius of orbit are given by the H-atom formulae but using $\epsilon_r$ and $m^*$.

$$\boxed{\Delta E = -13.6 \times \frac{(m^*/m_e)}{\epsilon_r^2}\, eV \quad \text{and} \quad r_{\text{orbit}} = 0.53 \times \frac{\epsilon_r}{(m^*/m_e)} \text{Å}}$$

- For each defect state created, we take of the states out of the bottom of the band it was created from.

### 6.1.1 n-type & p-type doping

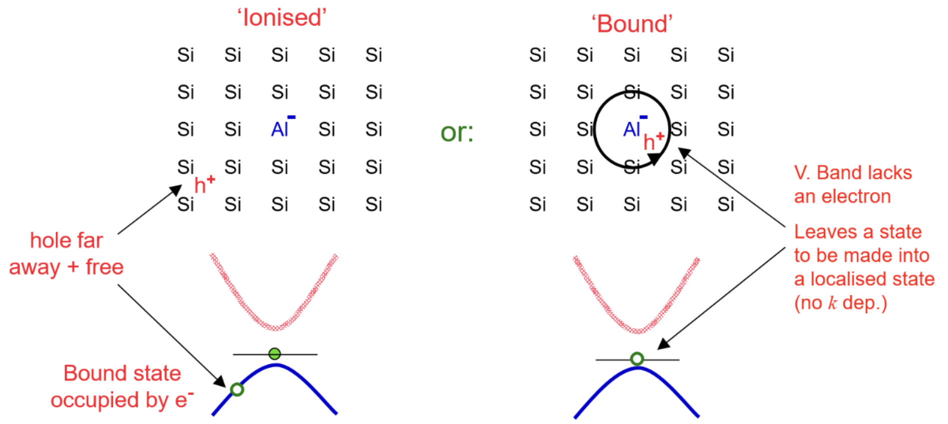
**n-type doping (donor states)**
Using a dopant with an extra electron (e.g. P atoms)



In n-type material, the majority carriers are electrons and they sit in the conduction band. Otherwise, they could form hydrogenic states just below the conduction band. Hydrogenic state has slightly lower energy because the electron feels the potential of the positive ion.

### p-type doping (acceptor states)

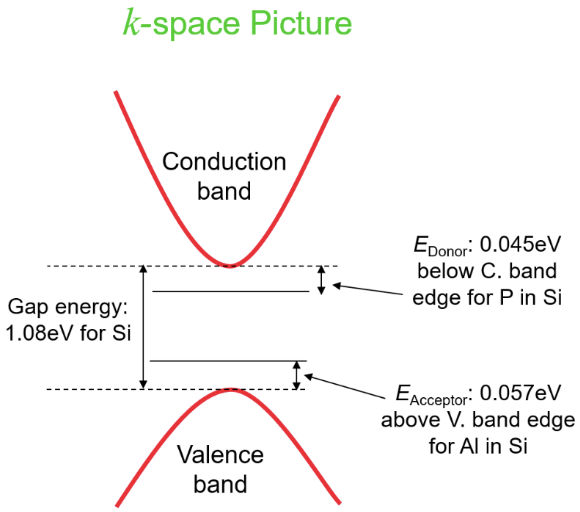
Using a dopant with a lack of an electron, extra one hole (e.g. Al atoms)

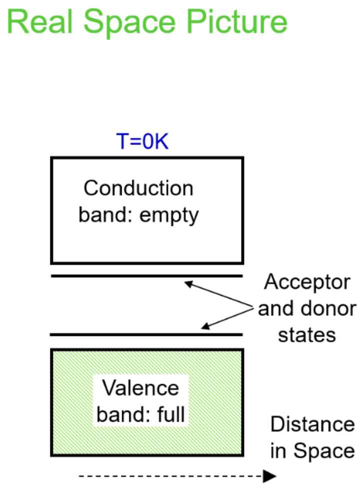


**Note:** The empty electron state and full valence band are upside down to the 'full hole state and empty hole band' picture.

In p-type material, the majority carriers are holes and they sit in the valence band, so the chemical potential leans towards the valence band. But overall, the conduction and valence band have more energy than in n-type as trivalent impurities exert lower forces (fewer protons) on the outer shell electron so electron orbits are slightly larger and have greater energy.

### 6.1.2 The picture so far...



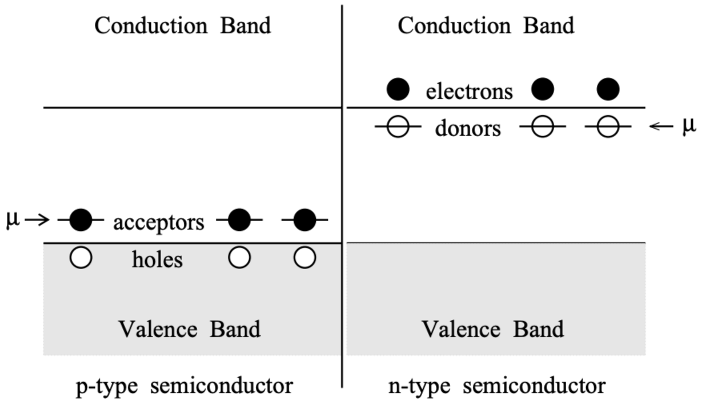


Compare with $k_B T \sim 25meV$ at room temperature, to see if there are significant excitations possible.

### 6.1.3 Chemical potential of doped semiconductor

$$\text{Fermi-Dirac distribution: } p(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1} = \frac{1}{2} \quad \text{when} \quad \epsilon = \mu$$

To find where $\mu$ is, look for the half-occupation level of the states



Key idea: chemical potential close to conduction band in n-type material and close to valence band in p-type material.

Valence and conduction band in p-type material is higher than valence and conduction band in n-type material.

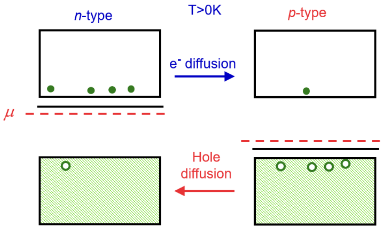
For n-type: at $T > 0$, can excite a small number of carriers from the valence band into the conduction band (intrinsic) + excite a larger number of carriers from donor states into conduction band (extrinsic) → shift distribution up → chemical potential drops down slightly, **shifting towards the middle of the gap**.

For p-type: acceptor states are empty at first i.e. full of holes. At higher temperatures, add in thermal excitations, generating majority and minority carriers. By the same argument, chemical potential shift towards the middle.

## 6.2 p-n junction

At the p-n junction, carriers diffuse to balance $\mu$ and a depletion region is formed with particular characteristics.

Bring p-type and n-type material into intimate contact.



Electrons are filled to higher energy levels in the n-type material, so they flow from n-type (high concentration) into the p-type (low concentration) material. Similarly, holes flow from the p-type to the n-type.

In the contact region, they cancel each other out, creating a **depletion region** where there are no carriers. Electric field between opposite charges there. For electrons to go through it, must have p.d. greater than barrier potential.

The diffusing carriers leave their associated ions behind. Resultant charge separation produces an electric field at the junction that stops further carrier diffusion and establish an **electrostatic potential equal to the difference in $\boldsymbol{\mu}$**.

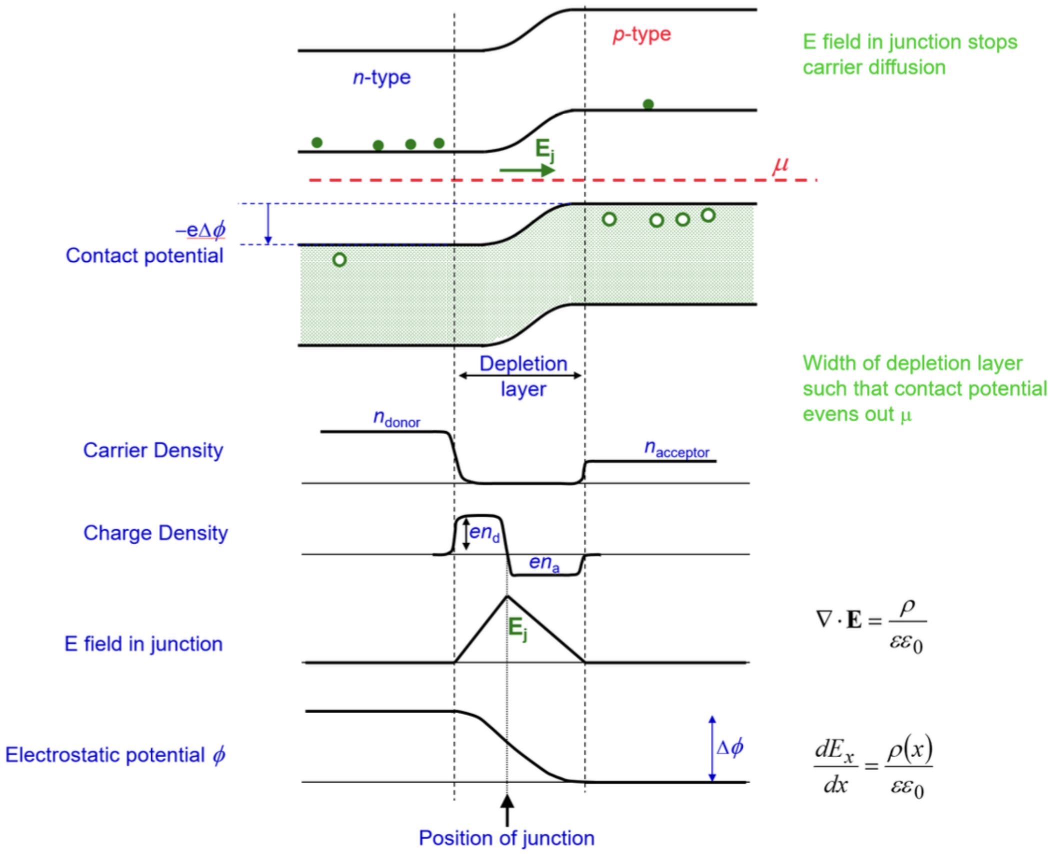


Figure 12: Very important diagram

Electrons want to go down from n-type conduction band to p-type valence band while holes want to float up from p-type valence band to n-type conduction band.

### 6.2.1 Applying the bias

**Forward bias**: apply a field to force the majority carriers towards the junction by reducing contact potential. Leads to good conduction.

**Reverse bias**: apply a field that forces majority carriers away from the junction, increasing the width of depletion layer. Leads to poor conduction.

### 6.2.2 Generation and recombination currents

Forward bias: pushes the majority carrier towards the junction, creating a **steady recombination current** as they recombine with majority carriers coming the other way to maintain the equilibrium number densities (F.D. distribution). Conducts well.

Reverse bias: pushing majority carriers away from junction and minority carriers towards the junction, creating a **small generation current** → the diffusion of majority carriers away from the junction widens the depletion region as well. Do not conduct well.

### Quantifying how the applied bias alters number of charge carriers

$$p_0(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_BT}+1} \approx e^{-(\epsilon-\mu)/k_BT}$$

If $\mu$ increases to $\mu + eV$ when we add a bias:

$$\begin{aligned} p_V(\epsilon) &\approx e^{-(\epsilon-\mu-eV)/k_BT} \\ &= e^{-(\epsilon-\mu)/k_BT} e^{eV/k_BT} \\ &= p_0(\epsilon)\, e^{eV/k_BT} \end{aligned}$$

### I-V characteristic graph

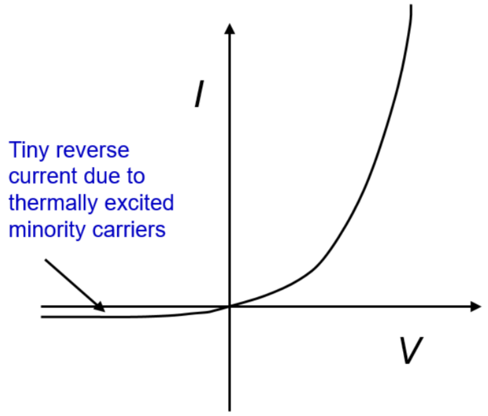
For no bias, recombination current = generation current.

Bias does not change generation current, $I_{e,0}$.

The number of electrons in the n-type region that can cross the junction varies with $e^{eV/k_BT}$

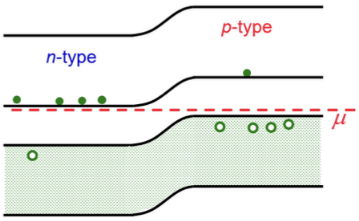
So, overall current through diode:

$$I = I_0 \left( e^{\frac{eV}{k_BT}} - 1 \right)$$



Diode act as a one-way conductor, with low resistance in forward bias and high resistance in reverse bias.

## 6.3 Diodes



### 6.3.1 p-n junction diode

**Uses**: one way conductor.

**Operational principle**: With forward bias, majority carriers pushed towards junction - good conduction. With reverse bias, minority carriers pushed towards junction - poor conduction.

**I-V characteristic**:

$$I_e = I_{e,0}(e^{eV/k_BT} - 1)$$

**Applications**: in electronics such as AC-to-DC rectification / protection from large voltage generated.

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Pushing diodes to their **breakdown** limit. With sufficient reverse bias, p-n junction can break down and conduct in the reverse direction.

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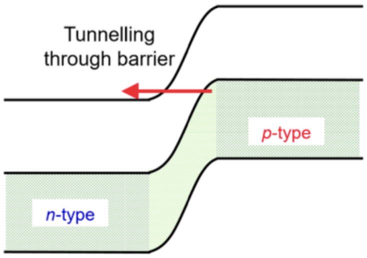
### 6.3.2 Zener diode



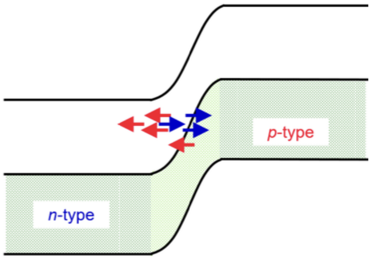
**Uses**: voltage reference in electronic circuits.

**Operational principle**: Zener breakdown caused by tunneling.

- Tunneling of electrons at the top of p-type valence band through energy barrier to unoccupied states at the bottom of the n-type conduction band.
- Sufficiently large bias causes the energy at the top of the valence band in the p-type material to overlap the bottom of the conduction band in the n-type.

- Can be deliberately engineered to **happen at a particular bias** by using heavily doped materials.
- Heavy doping puts $\mu$ near the band edge and reduces the voltage needed for breakdown (so Zener breakdown occurs before other breakdown).

### 6.3.3 Avalanche diode

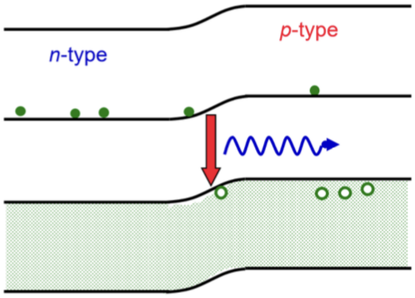


**Uses**: voltage references, protection devices, single photon detectors.

**Operational principle**: Avalanche breakdown caused by successive generation of carriers.

- Thermally excited carriers within junction gain energy between collisions.
- These create further electron-hole pairs, which gain energy and so form even more carriers.
- Large reverse current can flow and can dissipate a lot of heat; potential to damage the device.

### 6.3.4 Light emitting diode

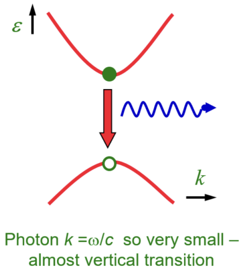


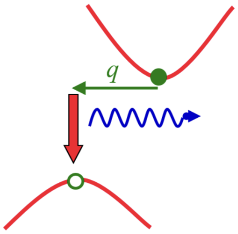
**Uses**: communications, efficient lighting.

**Operational principle**: recombine electron-hole pair and liberate photons.

- When a forward bias is applied, majority carriers flow into the junction and the electron-hole can recombine, releasing energy.
- Use ‘direct band gap’ material, so the emission of energy as photons/light is the most favorable process.
- The size of the band-gap determines the wavelength of the photons emitted.

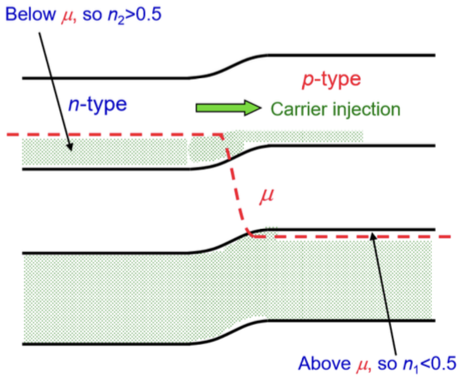
**Band Gap Requirements**: direct band-gap material e.g. gallium arsenide (GaAs). The bands are located above each other in k space, allowing a photonic transition between the two states as photons have very little momentum.





Indirect bandgap material (e.g. silicon): states are displaced in k-space and so addition of momentum from a phonon is required to effect a transition from one band to the other. Light emission much less likely and a lot of energy dissipated as heat.

## 6.4 Semiconductor laser



**Uses**: telecommunications

**Operational principle**: maintain population inversion by driving carriers directly from the n-type material to higher relative states in the p-type material.

- Normal population of energy levels at equilibrium is given by Boltzmann distribution, where higher energy states less populated than lower states.

- In population reversion, higher energy states more populated than lower states. This is not at equilibrium so needs to be continuously pumped by using a very large forward current to have carrier injection.
- Need photon that matches energy levels. Photon stimulates electron transitions, leading to further photon emission: Light Amplification by Stimulated Emission of Radiation.
- The junction is surrounded by an optical cavity (partially reflecting surfaces) to reflect photons backwards and forwards through the gain region. Some photons are transmitted at the interface, to form the laser beam.

**Working Requirements**:

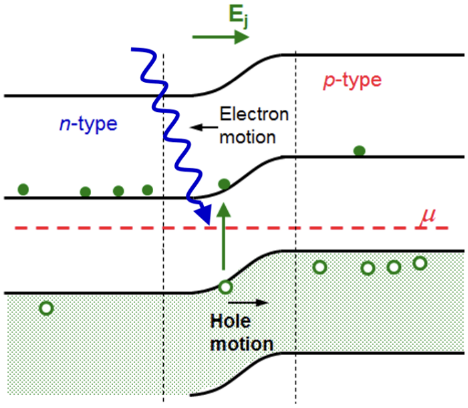
1. Very heavy doping to place $\mu$ in the conduction band (n-type) / valence bands (p-type).
2. Use strong forward bias.
3. Carrier injection: carriers can be injected from n-type conduction band to p-type conduction band to maintain the population inversion.

## 6.5 Solar cells

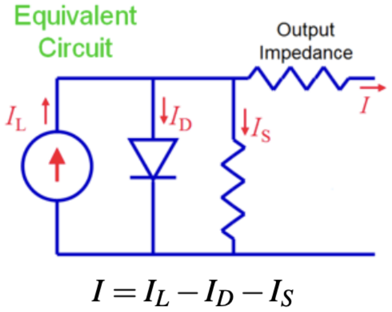
The reverse of LEDs or semiconductor laser. Photons are absorbed and generate electron hole pairs in the junction, which can drive an external current.

**Uses**: renewable energy (20-30% efficiency)

**Operational principle**: photocurrent.

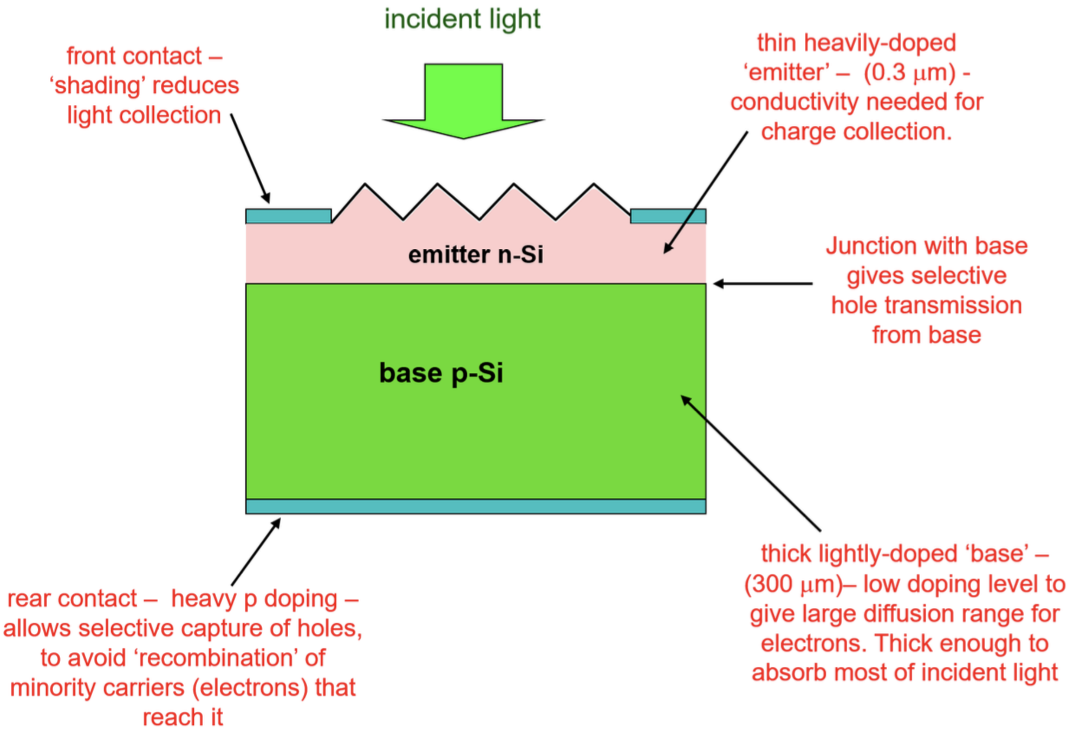


- Send photon in and create an electron-hole pair at the junction.
- An electric field is applied at the junction so they are swept out of the junction, creating a photo-current, $I_L$.
- Photocurrent acts to forward bias the junction, so some of the current leaks back again.
- Equivalent circuit: looks like a current source in parallel with diode and a shunt resistor (resistive leakage). The greater the output voltage (across the diode), the greater the leakage.



Equivalent circuit of solar cell

**Optimised design**:



~ End of Notes ~