

# PHY2009 - Physics Of Crystals

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## 1 Inter-atomic Bonding in Solids

### 1.1 Ionic Bonding

The atom consists of a sphere of net positive charge made up of the nucleus and inner core electrons, and a shell of out valence electrons orbiting which are involved in bonding.

Involves the complete transfer of electrons from one atom to another (compounds only, not elemental solids). E.g. Sodium Chloride (NaCl).

- Bond is strong (due to electrostatic attraction), so ionic compounds have a high melting point and a large elastic modulus.
- Not directional (because of omnidirectional electric attraction), so ionic compounds have co-ordination number (number of bonded atoms per atom) and a high density.
- Ionic compounds are never elemental solids (as the ionization requires a difference in electron affinity between the atoms)
- Good insulators (except near melting point) as the electrons cannot move from the bonds
- Transparent up to UV as the strong bonds mean the electrons require a lot of energy to become free
- Energy is on the order of  $\frac{1}{r}$

### 1.2 Covalent Bonding

Sharing of electrons between atoms. Occurs in elemental solids such as Diamond (Carbon). Note that there is a continuum between ionic and covalent behaviour depending on the electron affinity of the atoms involved.

E.g. III-V compounds GaAs and InSb are partially covalent and partially ionic.

- Strong bonds, so covalent molecules have high melting points and a high elastic modulus
- Directional bonds (due to the orientation of the orbitals)
- Saturable bonds so there is a limited number of bonds per atom. This means covalent molecules usually have a low density.
- Good insulators as there are no mobile electrons.

### 1.3 Metallic Bonding

Positive ions in a sea of electrons. This can be considered as the limiting case of ionic bonding in which the negative ions are electrons. However due to the uncertainty principle the electrons cannot sit at the lattice points and so are mobile.

- Non-directional bonds (due to omnidirectional electrostatic attraction), and so metallic compounds have a high density, a high co-ordination number and are malleable and ductile.
- Non-saturable bonds so high density.

- Variable strength
- Free electrons and metallic compounds are highly conductive and shiny. (They are shiny due to the electric field from the incident light causing the electrons on the surface to move back and forth, re-radiating the light as a reflected beam.)

## 1.4 Van der Waals Bonding

Created by fluctuations in the charge distribution in neutral particles. The dipole interaction is always attractive. E.g. solid inert gases (Argon, Neon) and molecular solids (solid Oxygen).

- Weak bonds so these compounds have low melting points, a low bulk modulus and a large expansion co-efficient.
- Non-directional so a high co-ordination number **BUT**
- long bond lengths and so a low density (despite the high co-ordination number)

## 1.5 Hydrogen Bonding

Hydrogen is relatively easily ionized (as it has only one electron) and so the region of a molecule around a hydrogen atom is often positive, which allows an electrostatic bond to form between it and the negative parts of neighbouring molecules. E.g. the strength of hydrogen bonding explains the high melting point of ice.

## 1.6 Central Core Repulsion

Orbital overlap hugely increases the energy of the electrons due to the Pauli Exclusion Principle (no two fermions may have the same set of quantum numbers, so no two electrons can occupy the same space). This repulsion is necessary to provide the equilibrium separation for bond lengths, it is characterised by high power laws or an exponential functions but these are determined empirically.

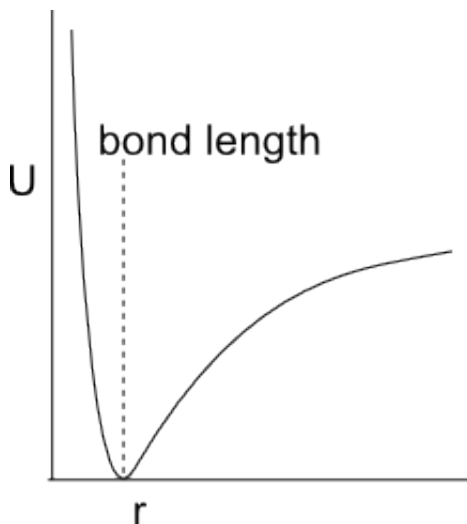


Figure 1: A plot of the potential energy,  $U$ , against atomic separation,  $r$ . The minimum in the potential well is the equilibrium bond length.

## 2 Crystal Lattices

The crystal structure is described by the lattice and the basis. To find the lattice structure first identify the atoms in identical environments and then define co-ordinate axes between these atoms. Note the axes need not be perpendicular and are not unique.

Note that every atom on the lattice points must be identical or else the crystal will not remain invariant as the lattice is translated.

The **primitive unit cell** is the smallest possible area which can be repeated to fill the whole space. The primitive unit cell only contains one lattice point within it (though it may share many with neighbouring cells). The area is given by  $\vec{a} \times \vec{b}$  for 2d co-ordinates and  $\vec{a} \cdot (\vec{b} \times \vec{c})$  (note that this is the scalar triple product).

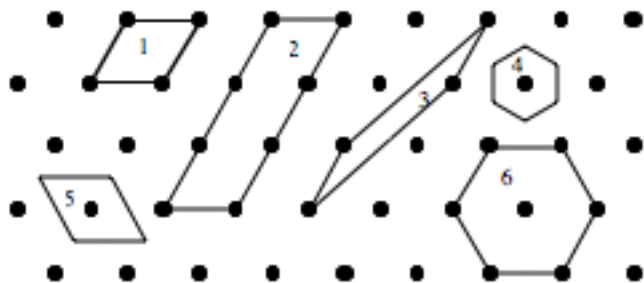
And so the position vector of any lattice point is given by:  $\vec{r} = u\vec{a} + v\vec{b}$  where  $u$  and  $v$  are integers. That is to say, any lattice point can be described by an integer translation along the lattice array. Areas which are larger than the primitive unit cell, but can still be translated to fill all the space, are known as non-primitive lattice vectors.

**Unit cell:** When repeated through space without rotation and without gaps or overlaps, reconstructs the pattern to infinity.

**Primitive unit cell:** Is the smallest possible unit cell.

**Non-Primitive unit cell:** Contain extra lattice points not at the corners.

- 1) The diagram shows a portion of a 2D lattice. Which of the outlines represent (i) primitive unit cells, (ii) non-primitive unit cells; (iii) not unit cells at all.



1, 3, 4 and 5 are primitive unit cells, 2 is a non-primitive unit cell (as it does not enclose the smallest area) and 6 is not a unit cell at all (as it cannot be repeated to fill all space without overlapping). 4 is the Wigner-Seitz primitive unit cell.

## 2.1 The Wigner-Seitz unit cell

The Wigner-Seitz cell is found by choosing a lattice point and drawing lines from it to its nearest neighbours. The drawing perpendicular bisects to these vectors, then repeat this to the next nearest neighbours until an area is fully enclosed. This area is the Wigner-Seitz primitive unit cell. It can also be found by drawing points half-way between the lattice point and each of its neighbours, and then joining these points up. That is to say it is the region of space that is closer to the chosen lattice point than to any other.

## 2.2 The basis

The lattice alone does not fully describe the crystal structure, the basis is necessary too, to describe what atoms are attached to the lattice and how they are arranged. The lattice only describes the periodicity of the pattern.

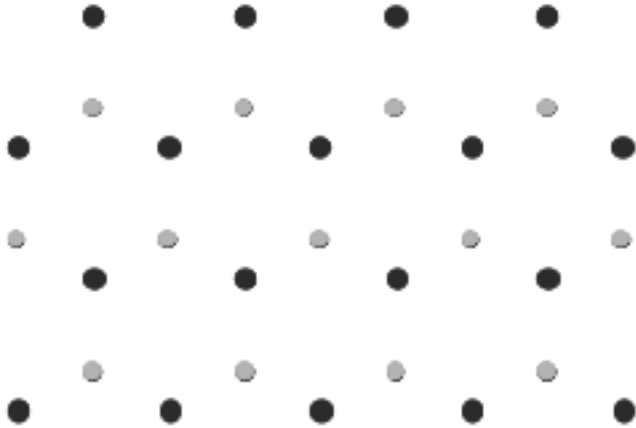


Figure 2: The black points could be part of the the lattice whilst the grey points would be described by the basis. Note that the black points' position on the lattice is also specified by the basis (even if they are only at the origin). The roles could also be reversed with no consequences.

In this case the basis would be two carbon atoms (in the case of graphite) at  $C(0,0)$  and  $C(\frac{2}{3}, \frac{1}{3})$ . A basis of two atoms means that each lattice point has two atoms associated with it.

## 2.3 Lattice symmetries

A **Bravais Lattice** is an infinite array of points that looks the same from any point. There are a finite number of distinct Bravais lattices and so they serve as template lattices for all crystals.

All lattices possess translational symmetry - i.e. the lattice remains the same when moved through integer numbers of lattice vectors. Note this means that all the atoms on lattice points must be of the same type, or else the crystal would not be invariant during translation.

There are other types of symmetry:

**Reflectional:** The lattice is the same when reflected through a line through the lattice.

**Rotation:** The lattice is the same when rotated a certain number of degrees about a lattice point. Six-fold would be  $60^\circ$  (e.g. in the Wigner-Seitz cell for the graphite crystal), Four-fold would be  $90^\circ$  (e.g. in the square lattice) etc.

**Inversion:** The lattice is the same when lattice points are moved from their relative position to one lattice point, to the opposite side of the point.

## 2.4 Types of lattices:

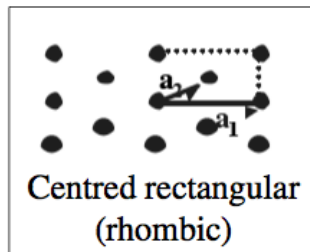
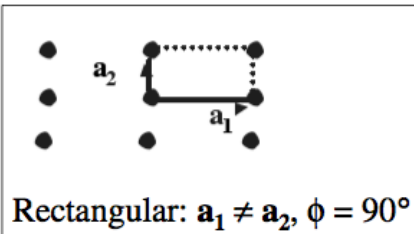
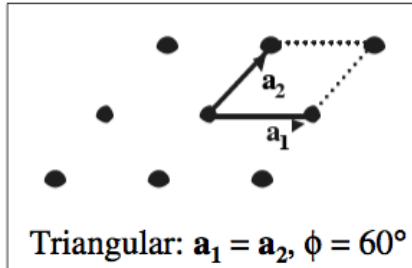
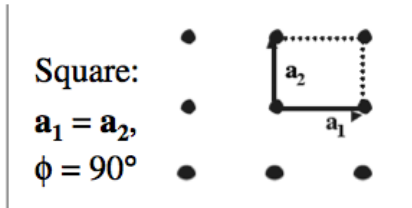
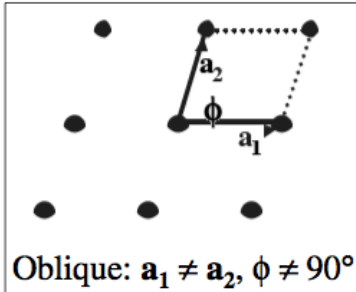
There are five distinct 2D lattices and 14 distinct 3D lattices.

### 2.4.1 2D lattices:

π  
k

## 2. 2D and 3D lattices

Five distinct 2D lattices:



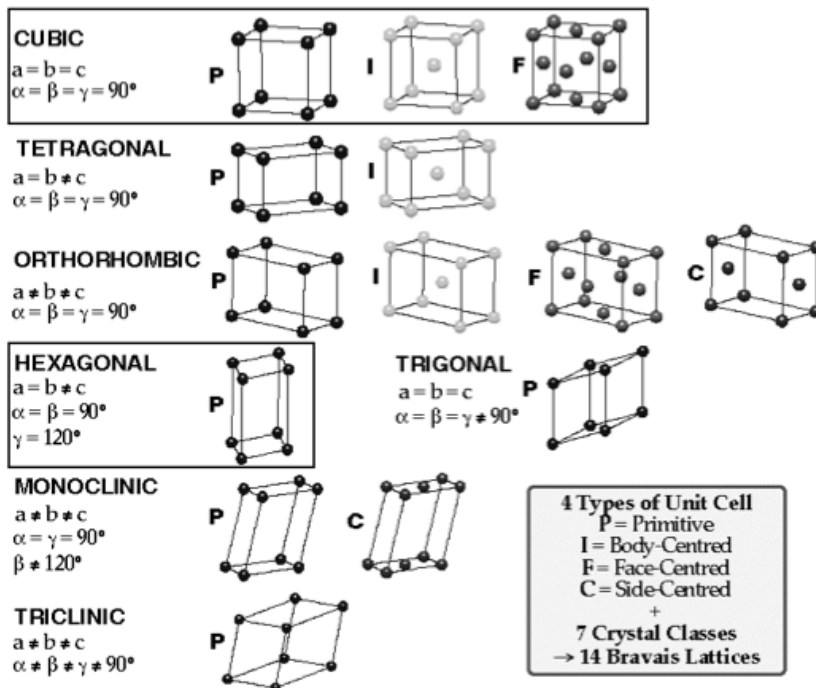
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The oblique lattice has the least symmetry as there is no link between  $a_1$ ,  $a_2$  and  $\phi$ . Whilst the square and triangular lattices are the most symmetrical.

### 2.4.2 3D lattices:

## 2. 2D and 3D lattices

...and 14 distinct 3D lattices:



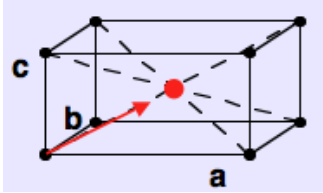
Where the top lattices have the most symmetry (cubic) and the bottom lattices have the least. We will only study the cubic and hexagonal lattices.

## 3 Miller Indices

### 3.1 Defining position and direction

The position of any lattice point is given by  $\mathbf{r} = u\mathbf{a} + v\mathbf{b} = w\mathbf{c}$ , where  $u, v$  and  $w$  are integers (a general point in space is written the same way but when  $u, v$  and  $w$  need not be integers).

Directions are defined in terms of the vector  $\mathbf{r}$  from the origin, in the direction required.



E.g. for a point at the centre of an orthorhombic lattice. It has fractional co-ordinates  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , and the associated direction passing through the point (from the origin) is given by  $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$ .

### 3.2 Defining sets of planes

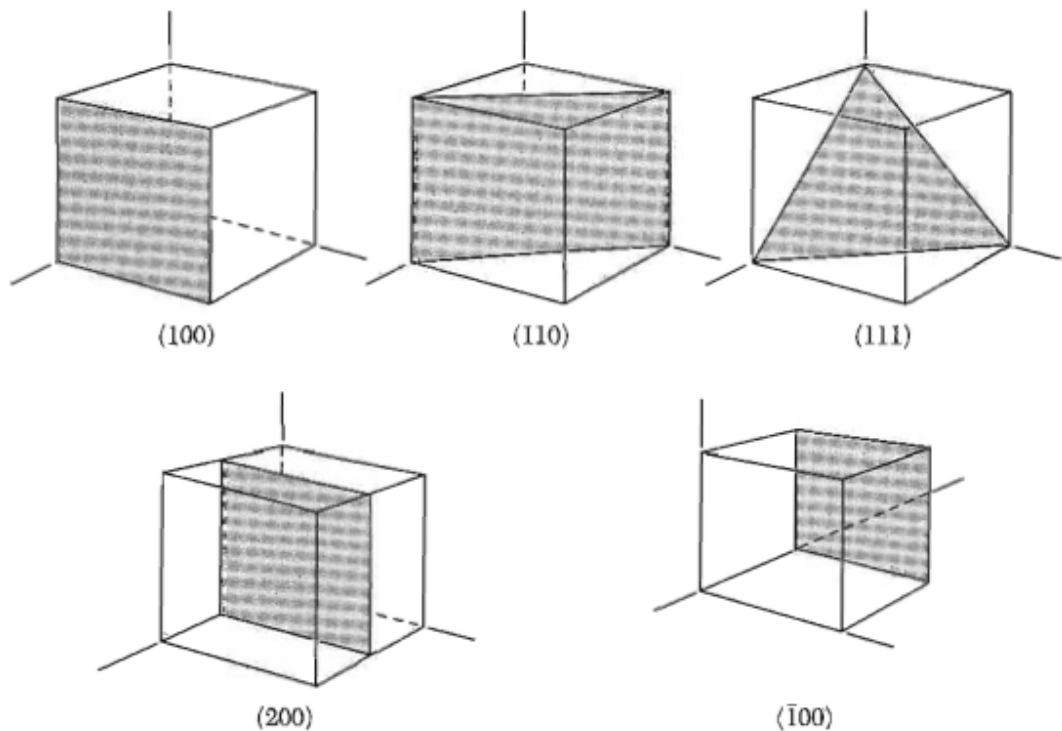
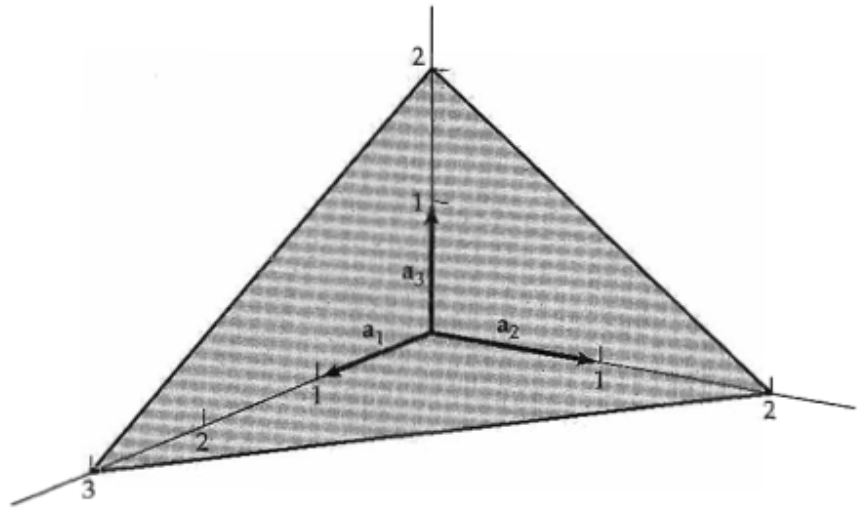
Miller indices are used to define sets of planes. To find the Miller indices associated with a set of planes:

1. Identify the plane in the set which passes closest to the origin without actually passing through it.
2. Determine the positions at which the chosen plane crosses each of the co-ordinate axes defined by the primitive lattice vectors, writing them in fractional co-ordinates.
3. The Miller indices are the reciprocals of these fractional co-ordinates.

Note that:

- A bar above a number, in the Miller indices, designates it as negative.
- The indices represent a set of planes (with the same ratio of co-ordinate intercepts), not just one.
- Sets of 2D lines in a lattice can be represented similarly.
- In crystals of high symmetry, several sets of planes may be equivalent. E.g. in a cubic crystal (100), (010) and (001) are equivalent (all defining faces). These would be referred to as a group as  $\{100\}$ . The same thing can be done for a set of equivalent directions, which would be written as  $\langle 100 \rangle$ .

**Figure 13** This plane intercepts the  $a_1$ ,  $a_2$ ,  $a_3$  axes at  $3a_1$ ,  $2a_2$ ,  $2a_3$ . The reciprocals of these numbers are  $\frac{1}{3}$ ,  $\frac{1}{2}$ ,  $\frac{1}{2}$ . The smallest three integers having the same ratio are 2, 3, 3, and thus the indices of the plane are (233).



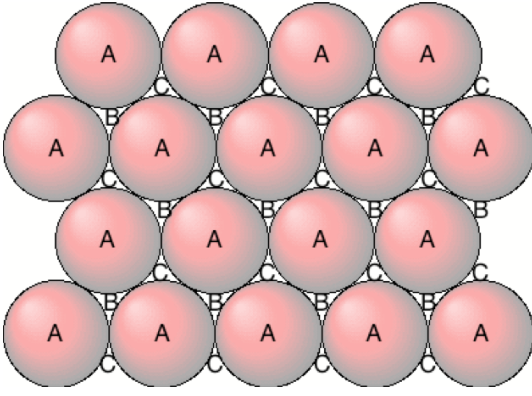
**Figure 14** Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to (100).

## 4 Typical crystal structures: Close-Packed Structures

Structures with similar-sized atoms (such as the elemental solids) and non-directional/non-saturable bonds like to have the highest co-ordination number possible (as every bond lowers the energy). For a set of rigid spheres in a plane, this is achieved by a triangular lattice (consider snooker balls). Note that A, B and C are all triangular lattices slightly displaced from one another. The length of the primitive lattice vectors is equal to the diameter of the spheres.

As layers are added they can be added on to either the B or C sites, for the first layer it matters not which sites are chosen. However, the next choice over whether to lay the third layer either back on the A sites or on to the C sites leads to two distinct lattice types.

The ABCABC pattern creates a face-centered cubic (FCC or “cubic close packed”) lattice. This is

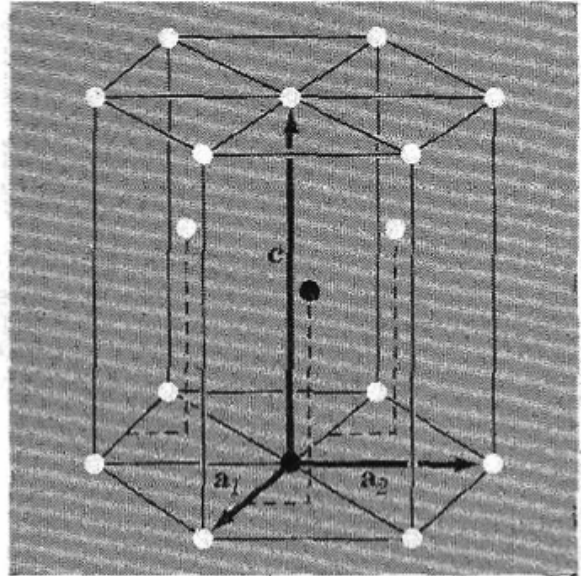


more common.

The ABABAB pattern produces a hexagonal close-packed structure.

## 4.1 The Hexagonal Close-Packed structure

The primitive unit vector is hexagonal with a two atom basis. One is at  $(0,0,0)$ , the other is at  $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$ . Note that the unit vectors  $\mathbf{a}$  and  $\mathbf{b}$  are not perpendicular and that the second atom is **not** centered.



**Figure 21** The primitive cell has  $a_1 = a_2$ , with an included angle of  $120^\circ$ . The  $c$  axis (or  $\mathbf{a}_3$ ) is normal to the plane of  $\mathbf{a}_1$  and  $\mathbf{a}_2$ . The ideal hcp structure has  $c \approx 1.633 a$ . The two atoms of one basis are shown as solid circles. One atom of the basis is at the origin; the other atom is at  $\frac{2}{3}\frac{1}{3}\frac{1}{2}$ , which means at the position  $\mathbf{r} \approx \frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{1}{2}\mathbf{a}_3$ .

Finding the value of  $\mathbf{c}$  in terms of  $\mathbf{a}$ :

$$\left| \frac{2}{3}\vec{a} + \frac{1}{3}\vec{b} + \frac{1}{2}\vec{c} \right| = a \quad \therefore \quad \left( \frac{2}{3}\vec{a} + \frac{1}{3}\vec{b} + \frac{1}{2}\vec{c} \right) \cdot \left( \frac{2}{3}\vec{a} + \frac{1}{3}\vec{b} + \frac{1}{2}\vec{c} \right) = a^2$$

Since  $\vec{a}$  and  $\vec{b}$  are not perpendicular:  $\therefore \frac{4}{9}a^2 + \frac{1}{9}a^2 + \frac{1}{4}c^2 + 2 \cdot \frac{2}{9}(\vec{a} \cdot \vec{b}) = a^2$

$$\therefore \frac{4}{9}a^2 + \frac{1}{9}a^2 + \frac{1}{4}c^2 + \frac{4}{9}a^2 \cos(120^\circ) = a^2 \quad \therefore \frac{4}{9}a^2 + \frac{1}{9}a^2 + \frac{1}{4}c^2 - \frac{2}{9}a^2 = a^2$$

$$\therefore c = 2a\sqrt{\frac{2}{3}} = 1.63a$$

## 4.2 The Packing Fraction

The packing fraction is the fraction of the volume actually taken up by the spheres (atoms). To calculate the packing fraction we use the primitive unit cell since its volume is easy to calculate and we know how many atoms are in the volume.

For the primitive unit cell:  $V = \vec{a} \cdot (\vec{b} \times \vec{c})$



For the Hexagonal CP structure:

$$\vec{a} = a\vec{i}, \vec{b} = -a\vec{i}\sin(30^\circ) + a\vec{j}\cos(30^\circ), \vec{c} = 2\sqrt{\frac{2}{3}}a\vec{k}$$

$$\begin{aligned} \text{So } \vec{a} \cdot (\vec{b} \times \vec{c}) &= a\vec{i} \cdot \left( (-a\vec{i}\sin(30^\circ) + a\vec{j}\cos(30^\circ)) \times \left( 2\sqrt{\frac{2}{3}}a\vec{k} \right) \right), \text{ taking cross-product of unit-vectors:} \\ &= 2\sqrt{\frac{2}{3}}a^3\vec{i} \cdot ((-\vec{i}\sin(30^\circ) + \vec{j}\cos(30^\circ)) \times \vec{k}) = 2\sqrt{\frac{2}{3}}a^3\vec{i} \cdot (\vec{j}\sin(30^\circ) + \vec{i}\cos(30^\circ)) \\ &= 2\sqrt{\frac{2}{3}}a^3\cos(30^\circ) = \sqrt{2}a^3 \end{aligned}$$

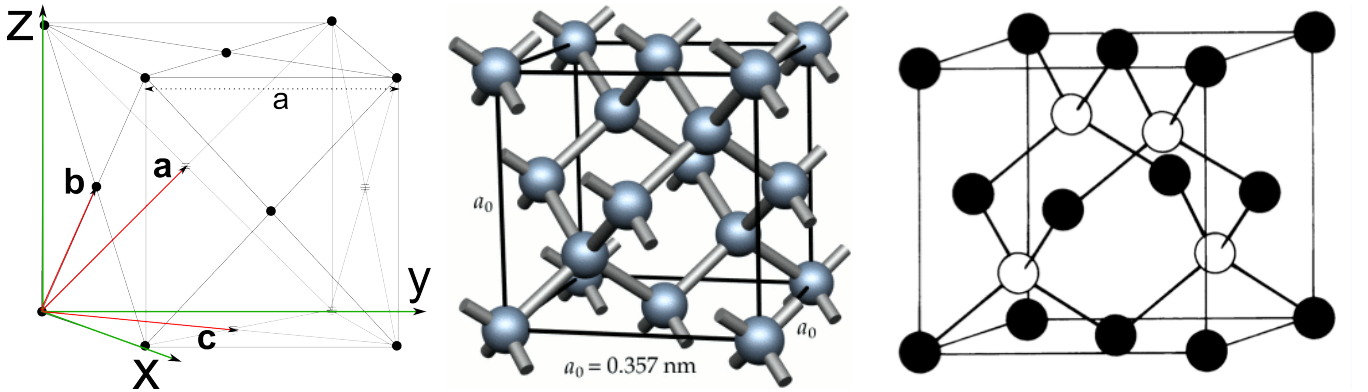
$$\begin{aligned} \text{So to calculate the packing fraction: Packing Fraction} &= \frac{\left( \text{Volume of two spheres, radius } \frac{a}{2} \right)}{\text{Volume of primitive unit cell}} \\ &= \frac{2 \times \frac{4\pi \left( \frac{a}{2} \right)^3}{3}}{\sqrt{2}a^3} = \frac{\pi}{3\sqrt{2}} = 0.740 \end{aligned}$$

This value is the largest packing fraction possible for rigid spheres, and is the same for the Face-Centred Cubic structure (ABCABC).

**To solve for the packing fraction in general:**

1. Calculate the smallest distance between atoms, i.e. the distance to the nearest neighbour specified in the basis.
2. Use this distance as the diameter of the spheres, and so calculate the radius (remember to take the modulus if in multiple directions).
3. Use the radius to calculate the volume per atom and multiply this by the number of atoms (lattice points multiplied by basis) to obtain the numerator of the packing fraction, the denominator is the total volume of the lattice cell.

Applying this to Diamond:



Diamond has an FCC structure with a diatomic basis of carbon atoms at  $(0, 0, 0)$  and  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ . The total number of lattice points is  $\frac{1}{8} \cdot 8 + \frac{1}{2} \cdot 6 = 4$ .

But there is a two-atom basis and so the number of atoms per lattice cell is  $2 \cdot 4 = 8$ .

Let  $a$  be the side length of the cube. We will let the diameter of the spheres be equal to the distance to the nearest neighbour, and so  $2r = \sqrt{\left(\frac{1}{4}a\right)^2 + \left(\frac{1}{4}a\right)^2 + \left(\frac{1}{4}a\right)^2}$

$$\therefore 2r = \frac{a\sqrt{3}}{4} \quad \therefore r = \frac{a\sqrt{3}}{8}$$

$V_{\text{cell}} = a^3$  as it is a cubic lattice.

$$\therefore \text{Packing Fraction} = \frac{8 \cdot \frac{4}{3} \pi \left( \frac{\sqrt{3}}{8} a \right)^3}{a^3} = 8 \cdot \frac{4}{3} \pi \cdot \frac{3^{\frac{3}{2}}}{8^3} = 0.34$$

### 4.3 Co-ordination number

The co-ordination number is the number of nearest neighbours. For the HCP structure there are 6 in the same plane, plus three in each of the neighbouring planes, providing a total of 12 nearest neighbours, and so the co-ordination number of HCP structures is 12.

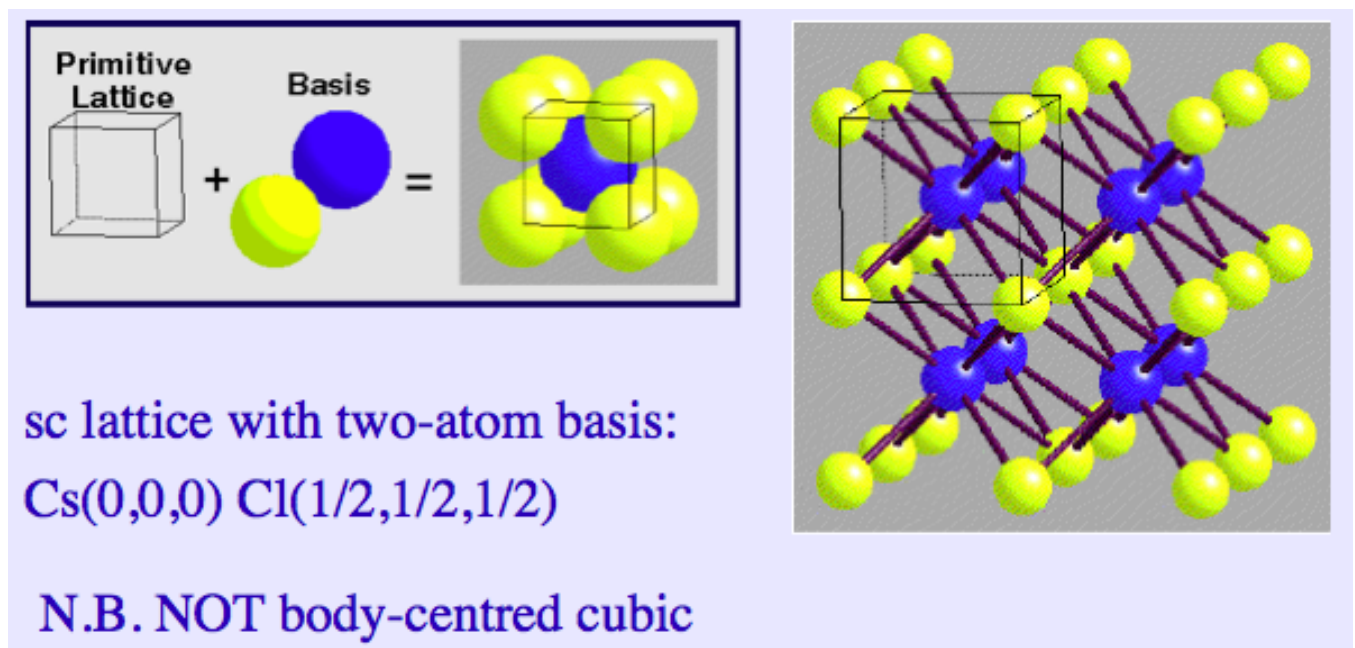
Co, He, Be, Mg, Zn and many other metals all crystallize in the HCP structure.

## 5 Cubic Structures

A cube has 9 planes of reflection symmetry, three four-fold rotation axes, four three-fold rotation axes and six two-fold rotation axes.

### 5.1 The Simple Cubic (sc) or cubic-P structure

This structure is relatively rare, but Caesium Chloride is an example:



Note it is **not** the same as a body-centred cubic since the Caesium atoms cannot be translated on to the Chlorine atom lattice points without changing the crystal. This is why the additional atom in the basis is necessary. This is not a close-packed structure.

The primitive unit cell is a cube and the primitive lattice vectors run along the edges of this cube.

## 5.2 The Body-Centred Cubic (bcc) or Cubic-I Structure:

Each lattice point has 8 nearest neighbours. This is fewer than with close-packed structures.

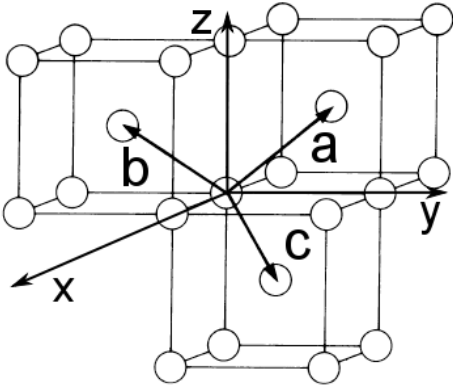
The nearest neighbour is at a distance of  $\frac{\sqrt{3}}{2}a$  (where  $a$  is the length of a side of the cube).

The cubic unit cell is the conventional unit cell but it is **NOT** primitive, as it contains more than one lattice point.

The 6 next nearest neighbours are at a distance of  $a$  away (1.15 times the nearest neighbour distance).

Remember HCP has 12 nearest neighbours, but only 2 next nearest neighbours at a distance of 1.63 times the nearest neighbour distance.

It is important to note that the most stable structure is not necessarily close-packed. It depends on the nature of the bonds involved as in reality, even “metallic” bonds have some covalent character which will influence the equilibrium.



The conventional choice of primitive lattice vectors is:

$$\vec{a} = \frac{1}{2}a(-\vec{i} + \vec{j} + \vec{k})$$

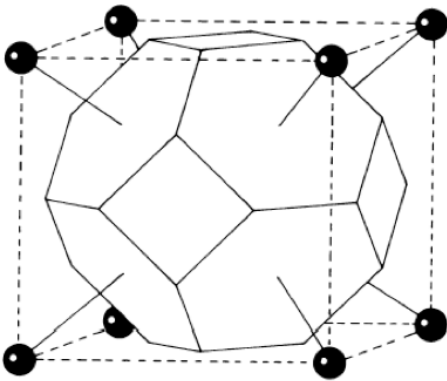
$$\vec{b} = \frac{1}{2}a(\vec{i} - \vec{j} + \vec{k})$$

$$\vec{c} = \frac{1}{2}a(\vec{i} + \vec{j} - \vec{k})$$

Note that these vectors are not orthogonal (perpendicular) and so the primitive unit cell is a parallelepiped.

**The BCC Wigner-Seitz primitive unit cell**

A “truncated octahedron”.

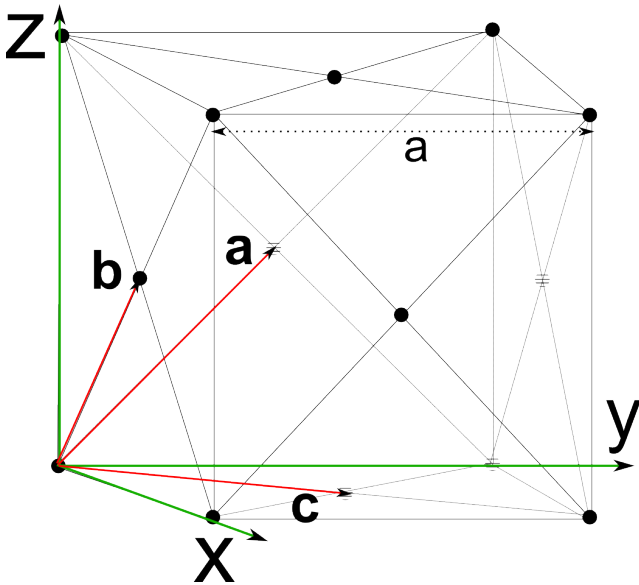


The first perpendicular bisecting planes produce an octahedron but the bisectors to the next nearest neighbours chop off each of the corners.

The shape has eight hexagonal faces and six square faces. Examples of BCC crystals include Lithium, Sodium and Chromium.

### 5.3 Face-centred cubic (FCC) or cubic-F lattice

The close-packed planes are along the (111) direction, i.e. they go diagonally through the cubic lattices.



The conventional primitive lattice vectors are:

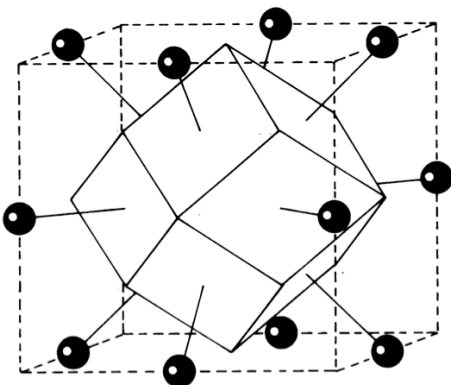
$$\vec{a} = \frac{1}{2}a(\vec{j} + \vec{k})$$

$$\vec{b} = \frac{1}{2}a(\vec{i} + \vec{k})$$

$$\vec{c} = \frac{1}{2}a(\vec{i} + \vec{j})$$

#### The FCC Wigner-Seitz primitive unit cell

The cell is a rhombic dodecahedron with 12 sides from the 12 nearest neighbours (the next nearest neighbours do not contribute).

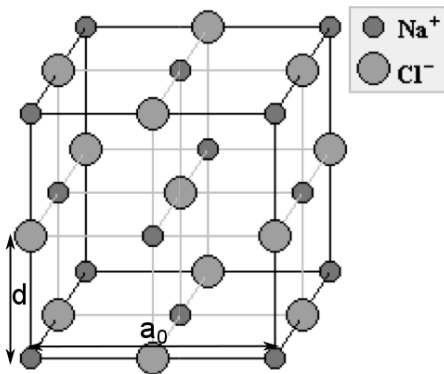


### 5.4 Crystal structures based on the FCC Lattice

#### Sodium Chloride NaCl

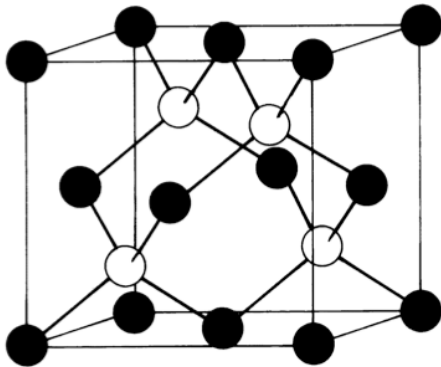
Sodium chloride is an FCC lattice with a basis of  $Na^+$  at  $(0, 0, 0)$  and  $Cl^-$  at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ .

Each ion has a co-ordination number of 6 (there are 3 lattice points, diatomic basis), the electrostatic bond will “try” to give as large a co-ordination number as possible but 6 is the largest number of anions that can cluster around a cation for these particular ion sizes.



### Diamond and zincblende (ZnS)

For diamond all the atoms are the same. The atoms are tetrahedrally co-ordinated, so there are only four nearest neighbours, this is a result of the covalent bonding.



Note that a tetrahedral structure is **NOT** a Bravais lattice as all the positions are not equivalent (as the white atoms are not in the same environment, like the two environments in graphite).

The structure is an FCC lattice with a basis of two identical atoms at  $(0, 0, 0)$  and  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ .

For zincblende there are two different atoms on the black and white positions as the two atoms in the basis are different. This structure is also used by GaAs and most semiconductors.

## 5.5 Bonding of ionic solids

In ionic solids the co-ordination number will aim to be as high as possible (as the bond is non-directional and non-saturable).

In the case where the ions are of similar size this leads to a close packed structure such as HCP or FCC.

However, **usually** the anion (negative ion) is larger than the cation (because the anion has a weakly bound outer electron), and so the structure is determined by how many anions can be packed tightly around each cation.

In NaCl we see that this number is 6, whereas in CsCl it is 8, as Cs is larger than Na and so more anions can pack around it.

## 6 Elastic Scattering of Waves

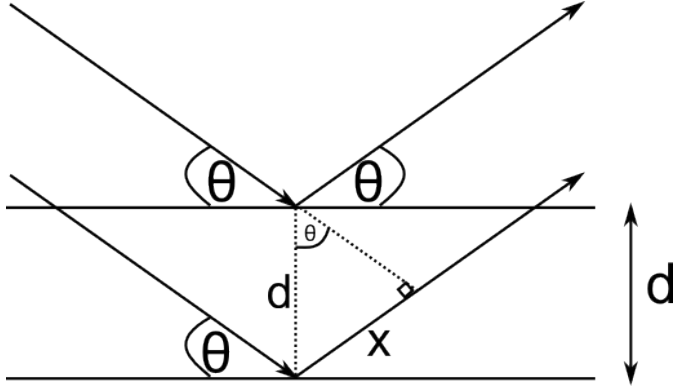
The Elastic scattering means that the incident wavelength is the same as the reflected wavelength i.e. there is no change in wavelength due to the collision.

The crystals consist of parallel planes of atoms and waves reflect from these planes. This means that waves from successive planes will interfere (either constructively or destructively) depending on the wavelength, grazing angle and plane spacing.

These waves could be electrons, X-rays or lattice vibrations (phonons).

## 6.1 Simple derivation of Bragg Condition

Note that  $\theta$  is the grazing angle **not** the angle of incidence (which would be to the normal).



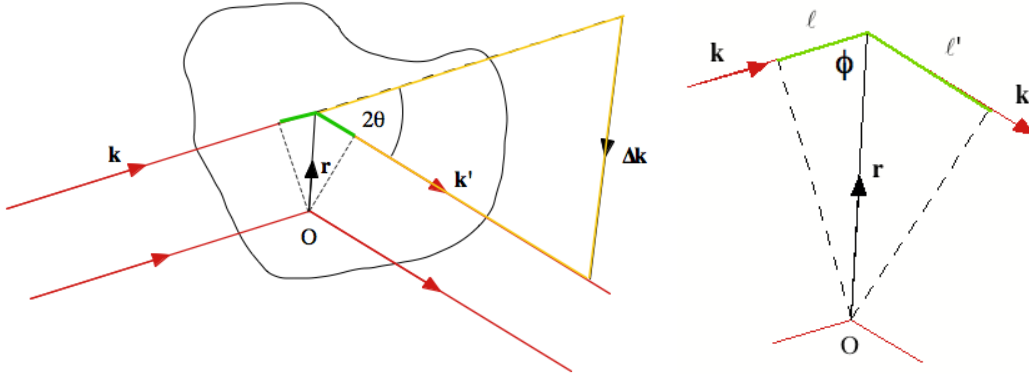
The path difference is  $2d\sin(\theta)$ , for constructive interference to occur the path difference must be an **integer** number of wavelengths and so:

$$2d\sin(\theta) = n\lambda$$

Note that this becomes destructive for very small deviations from this condition as since there are many planes present, the phase difference is magnified at lower planes.

## 6.2 Complicated derivation

This is more general derivation, recall elastic scattering so  $|k| = |k'|$ , this means the path difference forms an isosceles triangle.



The path difference between the wave reflected from point  $\vec{r}$  and the wave reflected from the origin is  $l' + l$ .

$$l + l' = \frac{\vec{k} \cdot \vec{r}}{|\vec{k}|} - \frac{\vec{k}' \cdot \vec{r}}{|\vec{k}'|}$$

Note that:  $l = r\cos(\phi)$  and  $\vec{k} \cdot \vec{r} = |\vec{k}||\vec{r}|\cos(\phi)$ . The phase difference is equal to the path difference multiplies by the wavenumber  $\vec{k}$ . And so:

$$\text{Phase difference} = -\Delta\vec{k} \cdot \vec{r}$$

where  $\Delta\vec{k} = \vec{k}' - \vec{k}$

And so the total amplitude of the reflected wave when the entire blob is illuminated uniformly is:

$$A = \int n(\vec{r}) e^{-i\Delta\vec{k} \cdot \vec{r}} d^3\vec{r}$$

Where  $n(r)$  is a weighting function describing the amount of 'stuff' causing the scattering at position  $\vec{r}$ .

This is obtained since the wave equation is

$$E \sim e^{i(\vec{k} \cdot \vec{r} - \omega t + \phi)}$$

Where the wave travels in the  $\vec{k}$  direction and  $\phi$  is the phase difference.

And so summing across all space:

$$\sum e^{i(\vec{k} \cdot \vec{r} - \omega t - \Delta\vec{k} \cdot \vec{r})}$$

But  $\vec{k} \cdot \vec{r} - \omega t$  is the same for all points and so can be discarded.

But in crystals only the atoms reflect and the structure is regular and so the equation can be simplified since we need only do a sum over all lattice points (for a monatomic basis).

So we obtain:

$$A \propto \sum_{\vec{R}} e^{i\Delta\vec{k} \cdot \vec{R}}$$

where  $\vec{R}$  is the lattice equation  $\vec{R} = u\vec{a} + v\vec{b} + w\vec{c}$  where  $\vec{a}, \vec{b}, \vec{c}$  are the primitive lattice vectors.

These complex exponentials can be expressed in a sum of sin and cos terms from De Moivre's Theorem. In general the sum of this would be zero however if the condition:

$$\Delta\vec{k} \cdot \vec{R} = 2n\pi$$

holds for all  $\vec{R}$  (where  $n$  is any integer) then there is constructive interference between all the wavelets and a diffraction maximum results.

## 7 The Reciprocal Lattice

The set of values of the scattering wave vector  $\Delta\vec{k}$  which have this property are denoted  $\vec{G}$ . The  $\vec{G}$ -points form a lattice - the Reciprocal Lattice.

The properties of the wave  $e^{i(\vec{G} \cdot \vec{r})}$  satisfying the condition  $\vec{G} \cdot \vec{R} = 2n\pi$  are:

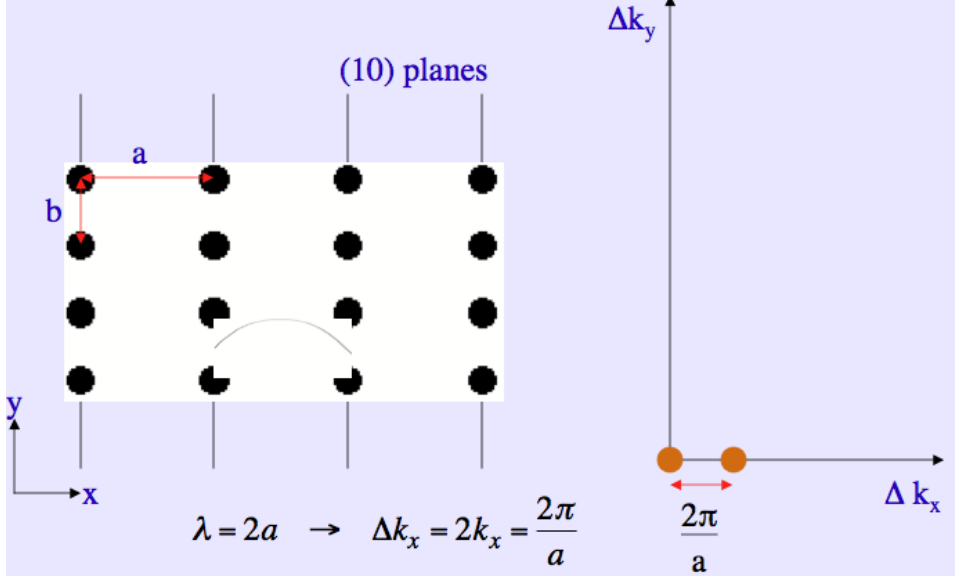
- Travelling plane wave (in  $\vec{G}$  direction).
- Wave has same phase at every lattice point (has a multiple of  $2\pi$ ).

The values of  $\vec{G}$  are wave vectors of all waves having the same periodicity of the lattice  $\vec{R}$ .

## 7.1 Drawing the Reciprocal lattice

$n\lambda = 2d\sin(\theta)$  letting  $\theta = 90^\circ, n = 1$  we obtain  $\lambda = 2a$  and so  $\Delta k_x = 2k_x = \frac{2\pi}{a}$

For  $n = 2$  we obtain  $\lambda = a$  and so  $\Delta k_x = \frac{4\pi}{a}$  and so we obtain a series of points equally spaced by  $\frac{2\pi}{a}$ .



We can do this in the y-direction (the (01) planes) as well:  $\lambda = 2b \therefore \Delta k_y = 2k_y = \frac{2\pi}{b}$  And again obtain a series of equally spaced points.

Doing this across all planes we obtain a lattice.

## 8 Laue Conditions for diffraction

An alternative way to state the condition:

$$\Delta \vec{k} \cdot \vec{R} = \vec{G} \cdot \vec{R} = 2n\pi$$

given that  $\vec{R} = u\vec{a} + v\vec{b} + w\vec{c}$  is to say:

$$\vec{G} \cdot \vec{a} = 2\pi h, \quad \vec{G} \cdot \vec{b} = 2\pi k, \quad \vec{G} \cdot \vec{c} = 2\pi l$$

where  $h, k$  and  $l$  are integers.

These three equations are the Laue conditions, and we shall see that the integers  $h, k$  and  $l$  are the Miller indices of the scattering planes.

This condition is satisfied if we define that:

$$\vec{G}_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

where:

$$\begin{aligned} \vec{a}^* \cdot \vec{a} &= 2\pi & \vec{a}^* \cdot \vec{b} &= 0 & \vec{a}^* \cdot \vec{c} &= 0 \\ \vec{b}^* \cdot \vec{b} &= 2\pi & \vec{b}^* \cdot \vec{c} &= 0 & \vec{b}^* \cdot \vec{a} &= 0 \\ \vec{c}^* \cdot \vec{c} &= 2\pi & \vec{c}^* \cdot \vec{a} &= 0 & \vec{c}^* \cdot \vec{b} &= 0 \end{aligned}$$

We need to find values of  $\vec{a}^*, \vec{b}^*$  and  $\vec{c}^*$  that satisfy these 9 conditions as this will satisfy the Laue conditions.

We can show this will work since:

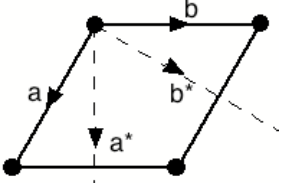
$$\vec{G} \cdot \vec{R} = (h\vec{a}^* + k\vec{b}^* + l\vec{c}^*) \cdot (u\vec{a} + v\vec{b} + w\vec{c}) = 2\pi(hu + kv + lw) = 2\pi \times \text{integer}$$



## 8.1 Geometric interpretation

$\vec{a}^*$  is perpendicular to the primitive lattice vectors  $\vec{b}$  and  $\vec{c}$  of the direct lattice, and the same for  $\vec{b}^*$  and  $\vec{c}^*$  with the other vectors.

So for a 2D triangular lattice:



From the dot product we see that the projection of  $\vec{a}^*$  in the direction of  $\vec{a}$  is  $\frac{2\pi}{a}$ .

## 8.2 Mathematical Derivation

We need to construct a vector  $\vec{a}^*$  which is perpendicular to  $\vec{b}$  and  $\vec{c}$  and satisfying  $\vec{a}^* \cdot \vec{a} = 2\pi$ .

To obtain a perpendicular vector we take the cross product and then must divide by the triple scalar product to cancel out the other one that will form (to get 1), and so multiply this by  $2\pi$  to satisfy the condition.

By considering this we obtain:

$$\vec{a}^* = 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$\vec{b}^* = 2\pi \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$\vec{c}^* = 2\pi \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

Note the cyclic pattern in the changing cross product order for the different vectors, the triple scalar product remains unchanged since this is constant regardless of the order of the vectors. Note that the dimensions are  $\frac{1}{\text{Length}}$  and the term in the denominator is the volume of the primitive unit cell of the real space lattice.

## 8.3 For 2D lattices:

$\vec{a}^*$  must be perpendicular to  $\vec{b}$  and  $\vec{b}^*$  must be perpendicular to  $\vec{a}$ .

We can either:

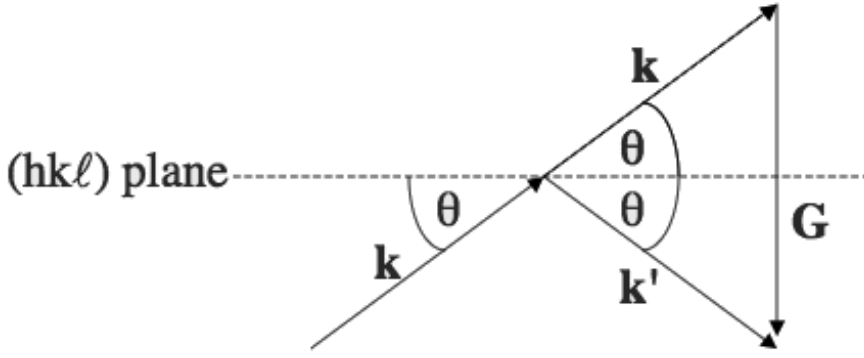
- Set  $\vec{c}$  to be a unit vector perpendicular to the plane and ignore the third reciprocal lattice vector  $\vec{c}^*$ .
- Or:
- Let  $\vec{c}$  be perpendicular to the plane and let its length tend to infinity.

The latter method is preferable since it is more elegant. It works because if there is an infinite distance between planes in a certain dimension then in effect the other planes do not exist. The equations for  $\vec{a}^*$  and  $\vec{b}^*$  still work because the magnitude of  $\vec{c}$  cancels out, meanwhile the magnitude of  $\vec{c}$  is present in the denominator of the equation for  $\vec{c}^*$  and so  $\vec{c}^*$  tends to zero.

## 8.4 Relationship with diffracting planes

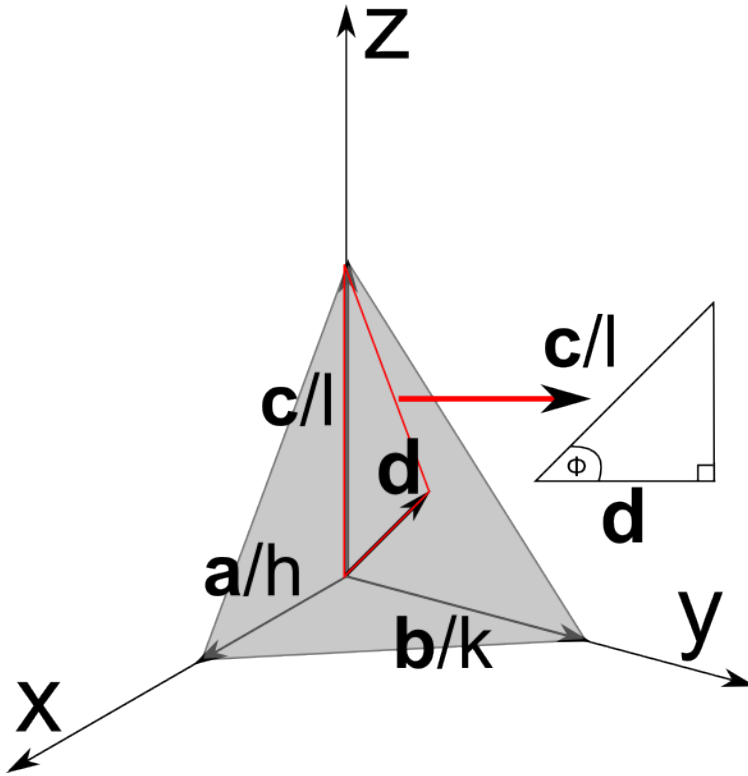
The expression  $\vec{k}' - \vec{k} = \vec{G}$  can be represented in the form of a vector triangle.

Note that  $\vec{G}$  is perpendicular to the scattering planes.



## 8.5 Connection with Miller indices

The  $(hkl)$  plane closest to the origin without passing through it, another  $hkl$  plane passes through the origin and so  $\vec{d}$  is a vector perpendicular to the planes with a length equal to the plane separation. The co-ordinates are found from the Miller indices since the co-ordinates are the reciprocals of the Miller indices, multiplied by the vector length.



Note that:

$$d \cdot \frac{c}{l} = d \left( \frac{c}{l} \cos(\phi) \right) = d^2$$

This is the same for other triangles and so:

$$d \cdot \frac{a}{h} = d \cdot \frac{b}{k} = d \cdot \frac{c}{l} = d^2$$

We note that this looks similar to the Laue condition which defined  $\vec{G}$ :

$$\begin{aligned} \vec{G} \cdot \vec{a} &= 2\pi h & \vec{d} \cdot \vec{a} &= d^2 h \\ \vec{G} \cdot \vec{b} &= 2\pi k & \vec{d} \cdot \vec{b} &= d^2 k \\ \vec{G} \cdot \vec{c} &= 2\pi l & \vec{d} \cdot \vec{c} &= d^2 l \end{aligned}$$

And so:

$$\vec{G}_{hkl} = \frac{2\pi}{d} \vec{d} = \frac{2\pi}{d} \hat{d}$$

This proves that  $\vec{G}$  is normal to the scattering planes and shows how the magnitude of  $\vec{G}$  is related to the plane spacing.

$\vec{G}$  is the scattering wave vector  $\vec{k}' - \vec{k}$  which gives rise to Bragg reflections involving planes having Miller indices  $(hkl)$ .

It's direction is **perpendicular** to these planes it's magnitude is  $\frac{2\pi}{d}$  where  $d$  is the distance between adjacent planes.

## 8.6 For a cubic lattice

Here:

$$\vec{a} = a\hat{i}, \quad \vec{b} = a\hat{j}, \quad \vec{c} = a\hat{k}$$

So:

$$\vec{a}^* = \frac{2\pi}{a}\hat{i}, \quad \vec{b}^* = \frac{2\pi}{a}\hat{j}, \quad \vec{c}^* = \frac{2\pi}{a}\hat{k}$$

$$\vec{G}_{hkl} = \left(\frac{2\pi}{a}\right) (h\hat{i} + k\hat{j} + l\hat{k})$$

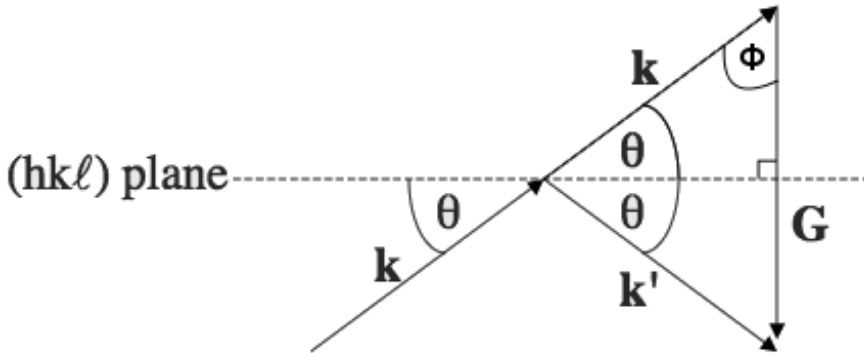
We can now find the distance between the neighbouring  $(hkl)$  planes:

$$d = \frac{2\pi}{|\vec{G}_{hkl}|} = \frac{2\pi}{\left(\frac{2\pi}{a}\right) \sqrt{h^2 + k^2 + l^2}}$$

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

## 8.7 Relationship with the Bragg Condition

The diffracting planes bisect  $\vec{G}$  perpendicularly. This means that:



$$\vec{k} \cdot \vec{G} = \frac{-1}{2} G^2$$

But:

$$\vec{k} \cdot \vec{G} = \frac{\cos(\phi)}{|\vec{k}||\vec{G}|}, \quad \text{but } \cos(\phi) = \sin(\theta)$$

So equivalently:

$$k \sin(\theta) = \frac{G}{2}$$

$$\begin{aligned}\therefore \frac{2\pi}{\lambda} \sin(\theta) &= \frac{1}{2} \cdot \frac{2\pi}{d} \\ \therefore 2d \sin(\theta) &= \lambda\end{aligned}$$

Note the usually present  $n$  term is effectively included in the  $d$  term since higher order diffraction is taken care of in the Miller indices. I.e. 2nd order reflection from (100) planes would be termed (200) reflection, and so the distance is halved (which is equivalent to having an  $n$  of 2 in the traditional equation  $n\lambda = 2d \sin(\theta)$ ).

## 8.8 Brillouin Zones

The Brillouin zones are related to the Wigner-Seitz cell of the reciprocal lattice.

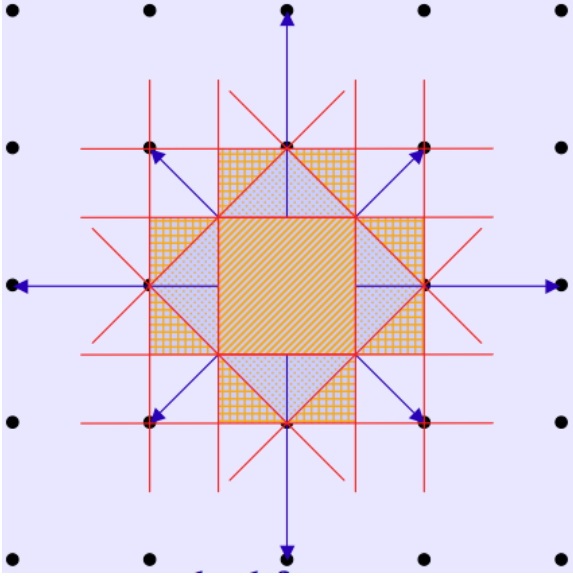


Figure 3: The first Brillouin zone is the central rectangle, the second Brillouin zone is the blue triangles, the third Brillouin zone is the checkered triangles.

The first Brillouin zone is simply the Wigner-Seitz cell of the reciprocal lattice, whilst the second Brillouin zone is the area covered when taken to the next nearest neighbours, minus the first Brillouin zone area.

In general the  $n$ th Brillouin zone is the region of reciprocal space reached from the chosen lattice point by crossing exactly  $n - 1$  perpendicular bisectors.

This has the consequence that all Brillouin zones must have the same area (in 2D) or volume (in 3D).

The significance of the Brillouin zone is that any vector  $\vec{k}$  that ends at the edge of a Brillouin zone (i.e. the boundary) satisfies the Bragg condition and so gives rise to a diffracted beam.

## 8.9 Information in the reciprocal lattice

The reciprocal lattice is the lattice of points in reciprocal space ( $k$ -space) which represents waves with the same periodicity as the direct lattice.

Note that:

- The reciprocal lattice vector  $\vec{G}_{hkl}$  is the scattering wave vector  $\vec{k}' - \vec{k}$  which gives rise to Bragg reflections involving planes having Miller indices  $(hkl)$ .
- Its direction is perpendicular to these planes and its magnitude is  $\frac{2\pi}{d}$  where  $d$  is the perpendicular distance between adjacent planes.

The reciprocal lattice tells us:

- All the scattering wavevectors  $\Delta\vec{k}$  that give rise to Bragg reflections.
- The orientation (Miller indices) of the scattering planes.
- The separation between adjacent scattering planes.
- Through the construction of Brillouin zones, the incident wavevectors  $\vec{k}$  that will produce Bragg reflections.

## 8.10 X-ray Crystallography

In X-ray crystallography we know the details of the incident waves but wish to analyse the structure of the sample crystal.

The diffraction gives a series of peaks at certain angles ( $2\theta$ , where  $\theta$  is the grazing angle) from the incident beam.

These allow us to construct the reciprocal lattice:

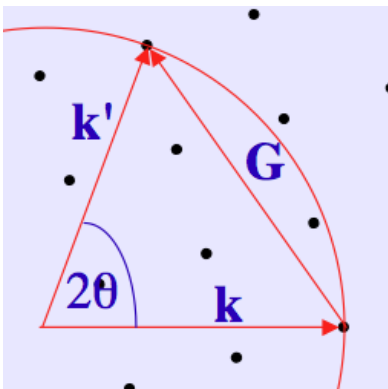
- Get the magnitude  $\frac{2\pi}{d}$  from the Bragg condition:  $2d\sin(\theta) = n\lambda$ .
- The orientation is in the direction of  $\vec{k}' - \vec{k}$ .

Once we know the reciprocal lattice we can derive the direct lattice since the reciprocal of the reciprocal lattice is the direct lattice.

## 8.11 Ewald Sphere construction

The Ewald sphere is a graphical way of determining whether a wavevector  $\vec{k}$  satisfies the Bragg condition (and so produces Bragg reflection).

1. Draw reciprocal lattice.
2. Draw wavevector  $\vec{k}$  such that it ends on a reciprocal lattice point.
3. Draw a sphere (or circle in 2D) of radius  $k$ , centred at the start of the wave vector  $\vec{k}$ .
4. Diffraction will occur if the Ewald sphere passes through any other lattice points.



## 8.12 Example of reciprocal lattice: Simple cubic direct lattice

In this case:

$$\vec{a} = a\hat{i}, \quad \vec{b} = a\hat{j}, \quad \vec{c} = a\hat{k}$$

$$\therefore \vec{a}^* = 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})} = 2\pi \frac{a^2(\hat{j} \times \hat{k})}{a^3(\hat{i} \cdot (\hat{j} \times \hat{k}))}$$

Recalling that (note the cyclic order):

$$\hat{i} \times \hat{j} = \hat{k}, \quad \hat{j} \times \hat{k} = \hat{i}, \quad \hat{k} \times \hat{i} = \hat{j}$$

$$\therefore \vec{a}^* = \frac{2\pi}{a} \hat{i}$$

And similarly for the other reciprocal lattice vectors:

$$\vec{b}^* = \frac{2\pi}{a} \hat{j}, \quad \vec{c}^* = \frac{2\pi}{a} \hat{k}$$

And so the reciprocal lattice is also a simple cubic lattice with side length  $\frac{2\pi}{a}$ .

## 8.13 Example of reciprocal lattice: Face-Centred Cubic direct lattice

In this case:

$$\vec{a} = \frac{a}{2}(\hat{j} + \hat{k}), \quad \vec{b} = \frac{a}{2}(\hat{k} + \hat{i}), \quad \vec{c} = \frac{a}{2}(\hat{i} + \hat{j})$$

So:

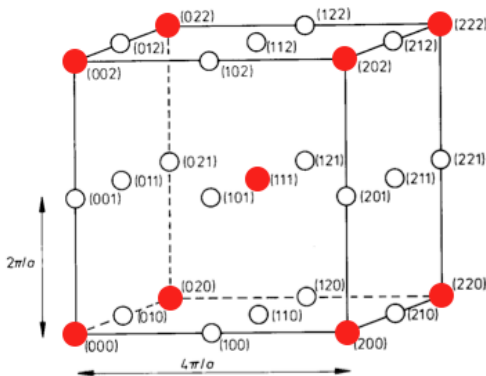
$$\vec{a}^* = \frac{4\pi}{a} \frac{(\hat{k} + \hat{i}) \times (\hat{i} + \hat{j})}{(\hat{j} + \hat{k}) \cdot ((\hat{k} + \hat{i}) \times (\hat{i} + \hat{j}))} = \frac{4\pi}{a} \frac{(\hat{j} - \hat{i} + \hat{k})}{(\hat{j} + \hat{k}) \cdot (\hat{j} - \hat{i} + \hat{k})} = \frac{2\pi}{a} (\hat{j} + \hat{k} - \hat{i})$$

$$\therefore \vec{b}^* = \frac{2\pi}{a} (\hat{k} + \hat{i} - \hat{j}), \quad \vec{c}^* = \frac{2\pi}{a} (\hat{i} + \hat{j} - \hat{k})$$

Note the cyclic order, that the first reciprocal lattice vector has the first unit vector as negative, whilst the second reciprocal lattice vector has the second unit vector as negative, etc.

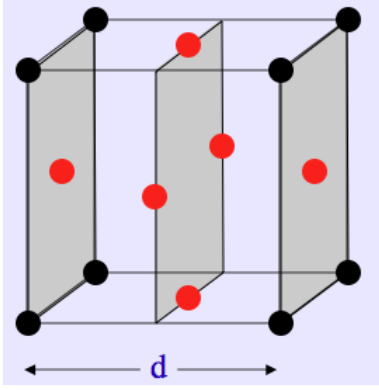
And so the reciprocal lattice is a body-centred cubic with side length  $\frac{4\pi}{a}$ .

Note that  $\vec{c}^*$  is perpendicular to both  $\vec{a}$  and  $\vec{b}$ , and lies in the  $[111]$  direction.



So the allowed reflections for the FCC direct lattice form a BCC lattice with cube side  $\frac{4\pi}{a}$ . Note that the points all have  $h, k, l$  either all even (on the vertices) or all odd (the body-centric point).

Note that some sets of planes which gave Bragg reflections in the simple cubic (SC) lattice do not do so for the FCC lattice. e.g. the  $\{100\}$  planes.



This is because the FCC lattice has more lattice points which halve the effective plane separation, which causes destructive interference, as the path difference is then a half-integer multiple of the wavelength.

$$n\lambda = 2d\sin(\theta)$$

Note that constructive interference is still observed when  $n$  is even.

### 8.14 Example of reciprocal lattice: Body-Centred Cubic direct lattice

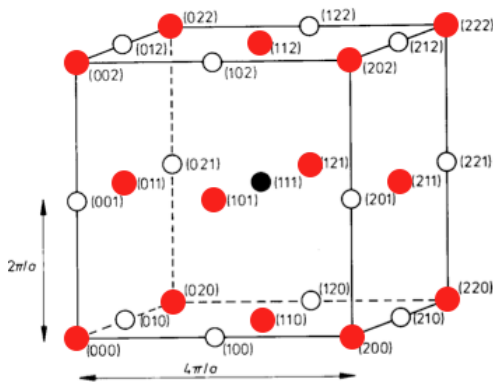
In this case:

$$\vec{a} = \frac{a}{2} (\hat{j} + \hat{k} - \hat{i}), \quad \vec{b} = \frac{a}{2} (\hat{k} + \hat{i} - \hat{j}), \quad \vec{c} = \frac{a}{2} (\hat{i} + \hat{j} - \hat{k})$$

And so using the same method as previously:

$$\vec{a}^* = \frac{2\pi}{a} (\hat{j} + \hat{k}), \quad \vec{b}^* = \frac{2\pi}{a} (\hat{k} + \hat{i}), \quad \vec{c}^* = \frac{2\pi}{a} (\hat{i} + \hat{j})$$

And so the reciprocal lattice is Face-Centred Cubic with a side length of  $\frac{4\pi}{a}$ .



Note that all the allowed points have the property that:  $h + k + l$  is even.

Note that the Miller indices are the reciprocals of the co-ordinates of intersection for the real space lattice and so they are the *actual* fractional co-ordinates for the reciprocal lattice.

## 9 Structure Factor

The expression:

$$A \propto \sum_{\vec{R}} e^{i\Delta\vec{k} \cdot \vec{R}}$$

used previously in the derivation of the Bragg condition, assume that there is one point-like atom positioned at each lattice point.

### 9.1 Atoms are not points

This complication means that waves scattered from one side of an atom will not quite be in phase with waves scattered from the other side.

Following the same argument for the blob, we arrive at the equation for the **atomic form factor**:

$$f = \int_{V_{\text{atom}}} n(\vec{r}) e^{(-i\vec{G} \cdot \vec{r})} dV$$

Where the integral is over the volume of the atom,  $\vec{r}$  describes positions within the atom, and  $n(\vec{r})$  is the density of “stuff” in the atom that is responsible for the scattering. E.g. this would be the electron/charge density for X-ray scattering.

### 9.2 Basis of more than one atom

This means that not all the atoms are on lattice points.

So for each term in the sum for A there must be as many terms as there are atoms in the basis.

So we multiply A by a sum over the atoms in the basis, this yields the **Structure Factor**:

$$S_{\vec{G}} = \sum_j f_j e^{(-i\vec{G} \cdot \vec{r}_j)}$$

Where  $f_j$  is the atomic form factor of the  $j$ th atom, and  $\vec{r}_j$  is the position of the  $j$ th atom in the basis relative to the lattice point.

For reflection involving the  $(hkl)$  planes:

$$\vec{G}_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

i.e. the coefficients of the primitive reciprocal lattice vectors are the Miller indices of the diffracting planes.

So letting the  $j$ th atom in the basis have fractional co-ordinates  $(u_j, v_j, w_j)$  such that:

$$\vec{r}_j = u_j\vec{a} + v_j\vec{b} + w_j\vec{c}$$

then:

$$S(hkl) = \sum_j f_j e^{(-i2\pi(hu_j + kv_j + lw_j))}$$

Where  $j$  increases to the number of basis atoms.

We can use the structure factor to derive the rules for the Miller indices of the reflecting planes that we derived directly from the reciprocal lattice previously.

### 9.3 Structure factor of the BCC lattice

If we consider the BCC lattice to be a Simple Cubic lattice with a 2-atom basis (remember that there is only really one lattice point since they are shared between adjacent cells) at fractional co-ordinates  $(0, 0, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  (putting the basis atom as close to the origin as possible) then the structure factor becomes:

$$S(hkl) = f (1 + e^{(-i\pi(h+k+l))})$$

By substituting  $(0, 0, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  for  $u_j$ ,  $v_j$  and  $w_j$ . Where  $f$  is the atomic form factor.

This means that:



$$S(hkl) = \begin{cases} 0 & \text{if } h + k + l \text{ is odd, so there is no diffraction} \\ 2f & \text{if } h + k + l \text{ is even, so there is strong diffraction} \end{cases}$$

As expected, this is the same result as when we considered the lattice as BCC with a one-atom basis and used the reciprocal lattice directly.

Note that you don't *need* to do it this way, but it is likely easier to use the structure factor method than to deduce the reciprocal lattice.

## 9.4 Structure factor of the FCC lattice

If we consider the FCC lattice as a Simple Cubic lattice with a 4-atom basis at fractional co-ordinates  $(\frac{1}{2}, \frac{1}{2}, 0)$ ,  $(\frac{1}{2}, 0, \frac{1}{2})$ ,  $(0, \frac{1}{2}, \frac{1}{2})$  and  $(0, 0, 0)$ . then the structure factor is:

$$S(hkl) = f (1 + e^{-i\pi(h+k)} + e^{-i\pi(h+l)} + e^{-i\pi(k+l)})$$

This means that:

$$S(hkl) = \begin{cases} 4f & \text{if } h, k \text{ and } l \text{ are all even or all odd, so there is strong diffraction} \\ 0 & \text{otherwise (e.g. } h \text{ and } k \text{ even but } l \text{ odd), so there is no diffraction} \end{cases}$$

Again we obtain the same result as we did from calculating the reciprocal lattice directly.

## 10 X-ray Diffraction Questions

To solve the X-ray diffraction questions you must remember that:

$$\lambda = 2d \sin(\theta)$$

as the  $n$  is taken in to the  $d$  as part of the Miller indices.

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where  $a$  is the lattice constant and  $h, k, l$  are the Miller indices of the reflecting planes.

Bravais Lattice	Conditions on Miller Indices	From these equations we see that:
Simple Cubic	All $h, k, l$ combinations allowed	
Body Centred Cubic	$h + k + l$ must be even	
Face Centred Cubic	$h, k$ and $l$ must be all even or all odd	

$$\sin(\theta) \propto \sqrt{h^2 + k^2 + l^2}$$

So this means that the ratios of the  $\sin(\theta)$  values will be different depending on the allowed  $hkl$  values (as these will change the rate of change of the square rooted function).

Direct Lattice	Simple Cubic		Body-Centred Cubic	Face-Centred Cubic
Reciprocal Lattice (cube lattice parameter)	Simple Cubic ( $2\pi/a$ )		Face-Centred Cubic ( $4\pi/a$ )	Body-Centred Cubic ( $4\pi/a$ )
Planes, spacing	(100)	a	No	No
	(110)	$a/\sqrt{2}$	Yes	No
	(111)	$a/\sqrt{3}$	No	Yes
	(200)	$a/2$	Yes	Yes
	(210)	$a/\sqrt{5}$	No	No
	(211)	$a/\sqrt{6}$	Yes	No
	(220)	$a/\sqrt{8}$	Yes	Yes
	(221)	$a/3$	No	No
	(300)	$a/3$	No	No
	(310)	$a/\sqrt{10}$	Yes	No
	(311)	$a/\sqrt{11}$	No	Yes
	(222)	$a/\sqrt{12}$	Yes	Yes
	(320)	$a/\sqrt{13}$	No	No
	(321)	$a/\sqrt{14}$	Yes	No
	(400)	$a/\sqrt{16}$	Yes	Yes
Rule:	All h, k, l		Sum (h + k + l) even	h, k, l all odd or all even
Ratio of sines of Bragg angles	1: $\sqrt{2}$ : $\sqrt{3}$ :2: $\sqrt{5}$ : $\sqrt{6}$ : $\sqrt{8}$ :...		1: $\sqrt{2}$ : $\sqrt{3}$ :2: $\sqrt{5}$ : $\sqrt{6}$ : $\sqrt{7}$ : $\sqrt{8}$ :...	1:2: $\sqrt{3}$ : $\sqrt{8}$ : $\sqrt{3}$ :...

So for the BCC lattice the ratio of the  $\sin(\theta)$  of the second reflecting plane to the first is:

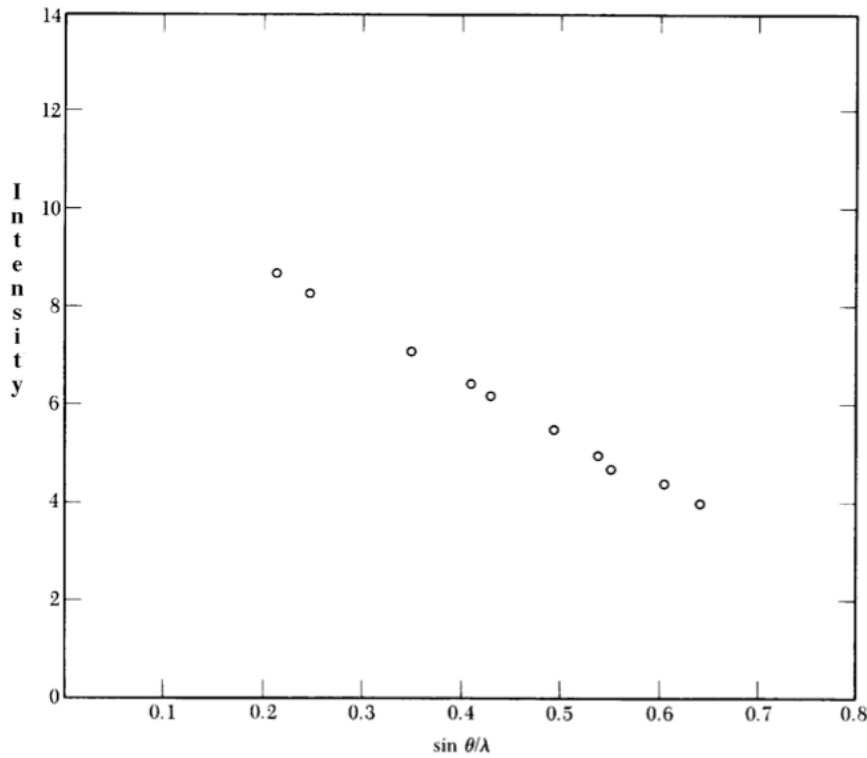
$$\frac{\sqrt{2^2 + 0^2 + 0^2}}{\sqrt{1^2 + 1^2 + 0^2}} = \frac{2}{\sqrt{2}} = \sqrt{2} = 1.414$$

Whilst for the FCC lattice the ratio of the  $\sin(\theta)$  of the second reflecting plane to the first is:

$$\frac{\sqrt{2^2 + 0^2 + 0^2}}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{2}{\sqrt{3}} = 1.155$$

Note that the ratios of the second to first peaks for BCC and SC are the same, and so we would have to go to the third and second peak ratios to distinguish these.

So using the following example:



We observe that the first peak is at approximately 0.21 whilst the second is at 0.24. This a ratio of  $\frac{0.24}{0.21} = 1.14$  which is closest to 1.155 and thus we deduce that the Bravais lattice is Face-Centred Cubic.

It is then easy to label each of the peaks with the corresponding reflecting plane since we know that they will increase in the order of  $\sqrt{h^2 + k^2 + l^2}$ , so in this case it will go (111), (200), (220), etc.

Finally given that the wavelength used was  $0.713 \text{ \AA}$  (though in this case this information is unnecessary as the horizontal scale is  $\frac{\sin(\theta)}{\lambda}$ ) we can determine the lattice constant,  $a$ :

$$a = \frac{\lambda}{2\sin(\theta)}\sqrt{h^2 + k^2 + l^2} = \frac{1}{2}\sqrt{3}\frac{1}{0.21} = 4.12 \text{ \AA}$$

## 11 Atomic Vibrations

So far we have considered the atoms to be located at fixed positions, however they actually oscillate about these positions due to thermal motion (even at absolute zero).

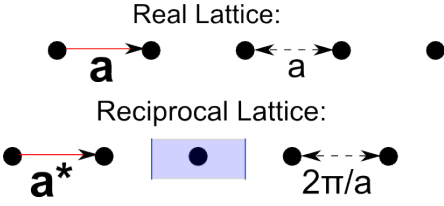
This is interesting because the coupled oscillators means we get waves (with associated normal modes).

These waves are:

- are quantized (and are termed phonons)
- undergo Bragg reflections (this is important for scattering, as the scattering from the conduction electrons is related to the resistivity).
- are responsible for thermal conduction in insulators (in metals there is the conduction due to the conduction electrons also).
- Scatter X-rays or neutrons with **inelastic scattering** this leads to Raman scattering.

## 12 Lattice vibrations of a monatomic linear chain

Assume atoms are of mass  $M$  and spaced  $a$  apart.



Now model the atoms as being connected via springs of spring constant  $C$ . The  $s$ th atom has equilibrium position  $x_{s0} = sa$ , where the 0th atom is at the origin.

Let us assume there is only:

- Only nearest neighbour interactions.
- Harmonic approximation so  $F \propto x$  (i.e. Hooke's Law stands)
- Longitudinal polarisation since 1-dimensional. Although we may draw this as transverse oscillation since it is easier.

Now if we displace each atom by a factor  $u$  such that the  $s$ th atom's position becomes  $u_s$ , etc. Then the force on the  $s$ th atom is:

$$F_s = C(u_{s+1} - u_s) + C(u_{s-1} - u_s) = C(u_{s+1} + u_{s-1} - 2u_s)$$

recall that:

$$F_{\text{net}} = Ma = M \frac{d^2 u_s}{dt^2}$$

$$\therefore M \frac{d^2 U_s}{dt^2} = C(u_{s+1} + u_{s-1} - 2u_s)$$

The solutions for this equation are travelling waves:

$$u_s = aE^{i(kx_{s0} - \omega t)} = Ae^{i(ksa - \omega t)}$$

Note that:

- All atoms oscillate with same angular frequency,  $\omega$ .
- But they oscillate with different phases, determined by  $s$ .
- $k$  is the wave vector (wave number for 1D) =  $\frac{2\pi}{\lambda}$ .

So for the  $s + 1$ th atom:

$$u_{s+1} = Ae^{i(k(s+1)a - \omega t)}$$

We want the dispersion relation, so substituting this solution for  $u_s$  back in to the equation of motion:

$$-\omega^2 MAe^{i(k(s)a - \omega t)} = CA [e^{i(k(s+1)a - \omega t)} + e^{i(k(s-1)a - \omega t)} - 2e^{i(k(s)a - \omega t)}]$$

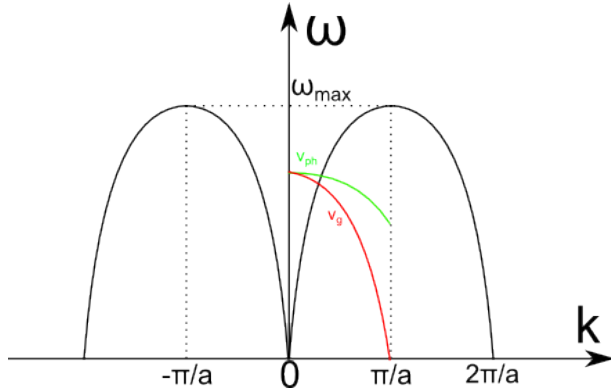
Dividing by  $Ae^{i(k(s)a - \omega t)}$ :

$$\begin{aligned} -\omega^2 M &= C(e^{ika} + e^{-ika} - 2) \\ \therefore \omega^2 M &= 2C(\cos(ka) - 1) \end{aligned}$$

Using the identity  $\cos(2\theta) = 1 - 2\sin^2(\theta)$ :

$$\omega^2 M = 4C \sin^2\left(\frac{ka}{2}\right)$$

$$\therefore \omega = 2\sqrt{\frac{C}{M}} \left| \sin\left(\frac{ka}{2}\right) \right|$$



Note from:

$$\omega = 2\sqrt{\frac{C}{M}} \left| \sin\left(\frac{ka}{2}\right) \right|$$

That  $\omega_{\max}$  is the amplitude of this equation and so:

$$\omega_{\max} = 2\sqrt{\frac{C}{M}}$$

Recall that:

$$v_{\text{phase}} = \frac{\omega}{k} \quad \text{and} \quad v_{\text{group}} = \frac{d\omega}{dk}$$

Note that:

- The wave is dispersive,  $v_{\text{ph}} > v_g$ .
- The **group velocity** is the velocity of energy transfer (and so information transfer).
- This acts as a low-pass filter as propagation only occurs for  $\omega < \omega_{\max}$ .
- $k$  is multi-valued - and the first Brillouin zone contains all the information.

## 12.1 Normal modes of a finite chain

In *Waves and Oscillators* we found the normal modes by:

- Fixing the string at both ends.
- Finding the waves that satisfied the resulting boundary condition that the amplitude must be zero at both ends.
- The results were standing waves.
- There were as many normal modes as there are atoms.

However, now we want to find the natural *travelling* wave modes:

We can remove the end effects by bonding the  $N$ th atom to the 1st to form a circular ring. If  $N$  is large enough then this is approximately linear.

This leads to the *periodic boundary condition* that  $u_n = u_{n+N}$  since they are the same atoms.

This in turn means that the  $n$ th atom must oscillate in phase with the  $N + n$ th since they are the same atoms. And this gives the following condition for the wavelength:

$$Na = p\lambda$$

where  $p$  is an integer and  $a$  is the distance between atoms. And so we obtain a quantized  $k$ :

$$k = \frac{2\pi p}{Na}$$

Taking an example of 10 atoms ( $N = 10$ ):

For  $p = \pm 1$  then  $\lambda = 10a$  and so  $k = \pm \frac{2\pi}{10a}$ .

For  $p = \pm 2$  then  $\lambda = 5a$  and so  $k = \pm \frac{2\pi}{5a}$ .

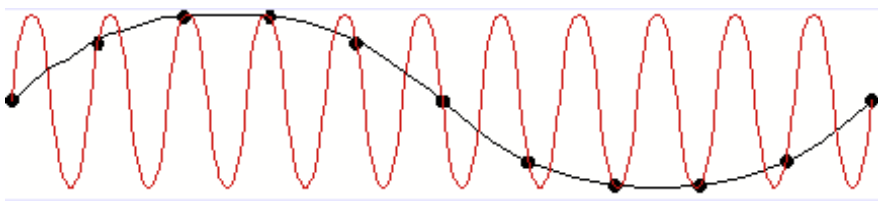
And so we obtain a series of equally spaced (in terms of  $k$ ) points on the dispersion relation graph.

However when  $p = \pm 5$  the point lies on the first Brillouin zone boundary (as  $\lambda = 2a \therefore k = \frac{2\pi}{a}$ ). At this point the wave describing the motion of the particles is a standing wave, and the wave will produce strong Bragg diffraction.

In general, for  $N$  atoms, at the first Brillouin Zone boundary  $p = \pm \frac{N}{2}$ . This is trivial to derive from the  $k = \pm \frac{\pi}{a}$  condition, and it is logical since this means that the atoms are spaced exactly half a wavelength apart, and so nearest neighbours are in antiphase with each other, this produces a standing wave.

At  $p = 6$  we find that the motion is equally well described by  $p = -4$ , as the same sine wave fits through all the points and matches the motion. This is a consequence of Nyquist's Theorem, which states that to accurately measure a signal (sine wave) of a certain frequency, the sample rate must be at least two samples per period.

Here the atoms are the sample rate, and at  $p = 6$  (i.e.  $\lambda = \frac{10a}{6}$ ) we don't have a high enough sampling rate to observe the additional complex behaviour, and so it is equivalent to  $p = -4$ .



Note that the negative sign is important since it signified that the wave is travelling leftwards whilst the  $p = 6$  wave will travel rightward (though the subsequent observed motion is the same).

From the graph of the dispersion relation we can see that the points  $p = -4$  and  $p = 6$  are the same, as they have the same values of  $\omega$  and  $\frac{d\omega}{dk}$ . All points outside the first Brillouin zone can be

equally represented by points within it, and so the first Brillouin zone contains all of the information.

All of the equivalent point are equally spaced, and so they can be reached by translating through a reciprocal lattice vector (i.e. in the  $k$  axis) of  $\frac{2n\pi}{a}$ .

However, if we recall that:

$$G = \frac{2n\pi}{a}$$

Then we see this can be expressed as the equivalent point  $k'$  for the point  $k$  is:

$$k' = k \pm G$$

## 12.2 Behaviour near the Brillouin zone centre ( $k = 0$ ):

- All displacements are the same at a given time, assuming  $N$  is large.
- Atoms oscillate (almost) in phase.
- Dispersion curver is linear with  $\omega = \sqrt{\frac{C}{M}}ka$  (from assuming that  $\frac{ka}{2} \rightarrow 0$  then  $\sin\left(\frac{ka}{2}\right) \rightarrow \frac{ka}{2}$ ).
- Dispersionless: as group velocity = phase velocity =  $a\sqrt{\frac{C}{M}}$  (i.e.  $\frac{\omega}{k} = \frac{d\omega}{dk}$ ).
- Compare to waves on a string - at large wavelengths, individual atoms “merge” and appear as a continuum.

## 12.3 Behaviour at the Brillouin zone boundary ( $k = \pm\frac{\pi}{a}$ ):

- Adjacent atoms oscillate  $180^\circ$  out of phase.
- Standing wave as:

$$v_g = \frac{d\omega}{dk} = \frac{d\left(2\sqrt{\frac{C}{M}}\left|\sin\left(\frac{ka}{2}\right)\right|\right)}{dk} = a\sqrt{\frac{C}{M}}\cos\left(\frac{ka}{2}\right) \text{ but } k = \frac{\pi}{a} \therefore v_g = 0$$

- Recall that the group velocity is the rate of energy transfer, and so when the group velocity is zero, there is no energy transfer and a standing wave is produced.

We could improve our model by adding interactions with next-nearest neighbour with different force constants, however this is not worth the effort as we find that, although the dispersion curve wil change:

- $\omega$  is still a periodic function of  $k$  with period  $\frac{2\pi}{a}$
- The group velocity is still zero at the Brillouin zone boundaries.
- It is still dispersionless in the small  $k$  limit.
- There are still  $N$  normal modes for a chain of  $N$  atoms.

## 13 Diatomic Linear Chain

Consider a linear chain with atoms of alternate masses  $M$  and  $m$ , here  $a$  is the separation between **like** atoms, as the structure repeats itself every  $a$ .

The underlying lattice is the same as for the monatomic lattice, and the first Brillouin zone is still between  $k = \pm \frac{\pi}{a}$

Note that to specify an atom we need to state both  $s$  *and* the atom's mass (though other sources may use a different convention).

If we assume there are only nearest neighbour interactions, and that the connecting springs obey Hooke's Law, as we did for the monatomic chain, we obtain the equations of motion (where  $u$  is the light mass ( $m$ ) displacement and  $v$  is the heavy mass ( $M$ ) displacement):

$$F_s = C(v_s - u_s) + C(v_{s-1} - u_s)$$

so:

$$m \frac{d^2 u_s}{dt^2} = C(v_s + v_{s-1} - 2u_s)$$

$$M \frac{d^2 v_s}{dt^2} = C(u_{s+1} + u_s - 2v_s)$$

From the derivation of the monatomic linear chain (the Taylor expansion, etc.), we know that the solutions are wavelike:

$$u_s = u e^{i(ksa - \omega t)}$$

$$v_s = v e^{i(ksa - \omega t)}$$

**but**  $v$  can be complex, allowing for a phase difference between each atom of mass  $M$  and its neighbouring atom of mass  $m$ .

To obtain the dispersion relation we substitute these equations back in to the equations of motion: For  $m$ :

$$-\omega^2 m u e^{i(ksa - \omega t)} = C (v e^{i(ksa - \omega t)} + v e^{i(k(s-1)a - \omega t)} - 2u e^{i(ksa - \omega t)})$$

After cancellation:

$$-\omega^2 m u = C v (1 + e^{-ika}) - 2C u$$

Similarly, for  $M$ :

$$-\omega^2 M v = C u (e^{ika} + 1) - 2C v$$

These two simultaneous equations in  $u$  and  $v$  can be solved by matrix methods, where the solution requires that:

$$\begin{vmatrix} 2C - m\omega^2 & -C(1 + e^{-ika}) \\ -C(1 + e^{ika}) & 2C - M\omega^2 \end{vmatrix} = 0$$

$$(2C - m\omega^2)(2C - M\omega^2) - C(1 + e^{-ika})C(1 + e^{ika}) = 0$$

Using that:

$$e^{\frac{ika}{2}} \left( e^{\frac{ika}{2}} + e^{-\frac{ika}{2}} \right) = 2e^{\frac{ika}{2}} \cos\left(\frac{ka}{2}\right)$$

$$mM\omega^4 - 2C(m + M)\omega^2 + 4C^2 - 4C^2 \cos^2\left(\frac{ka}{2}\right)$$

Using that  $1 - \cos^2(x) = \sin^2(x)$ :

$$mM\omega^4 - 2C(m + M)\omega^2 + 4C^2 \sin^2\left(\frac{ka}{2}\right)$$

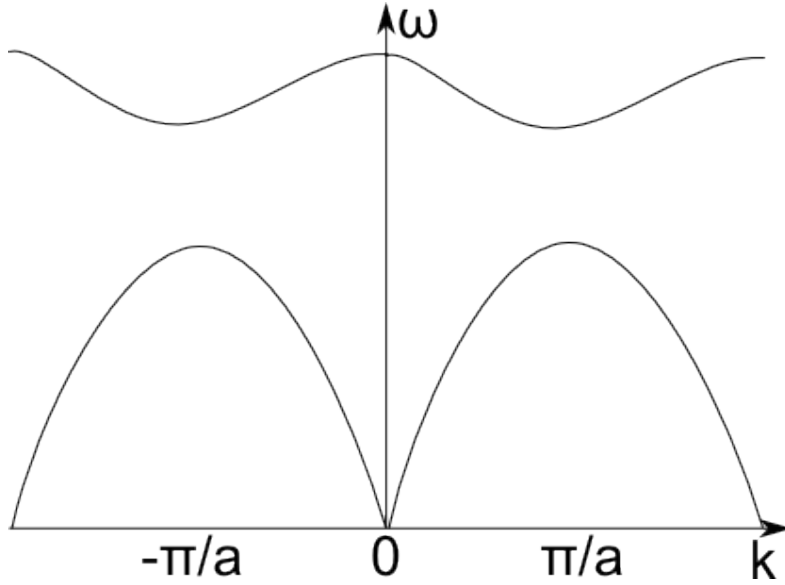


Solving this quadratic (in  $\omega^2$ ) gives the dispersion relation:

$$\omega^2 = \frac{2C(m+M) \pm \sqrt{4C^2(m+M)^2 - 4mM \left(4C^2 \sin^2 \left(\frac{ka}{2}\right)\right)}}{2mM}$$

$$\therefore \omega^2 = \frac{C(m+M)}{mM} \pm C \sqrt{\left(\frac{m+M}{mM}\right)^2 - \frac{4}{mM} \sin^2 \left(\frac{ka}{2}\right)}$$

Plotting this:



There are two values of  $\omega$  for each value of  $k$  (ignoring the physically meaningless negative values of  $\omega$ ). These give two branches to the dispersion curve: the upper branch called the **optical** branch, and the lower branch called the **acoustic** branch.

### 13.1 Behaviour near the centre of the Brillouin zone ( $k = 0$ )

At  $k = 0$ : the sin term vanishes and so:

for the (negative root) acoustic branch:  $\omega = 0$

For the optical branch (positive root):

$$\omega = \sqrt{\frac{2C(m+M)}{mM}}$$

This is the maximum frequency that the diatomic chain can support. Note that if we let  $m = M$  then this reduces to the maximum frequency equation for the monatomic chain as expected.

But in the limit  $k \approx 0$  then  $\sin \left(\frac{ka}{2}\right) \approx \frac{ka}{2}$  so:

$$\begin{aligned} \omega^2 &\approx \frac{C(m+M)}{mM} \pm C \sqrt{\left(\frac{m+M}{mM}\right)^2 - \frac{4}{mM} \frac{k^2 a^2}{4}} \\ &= \frac{C(m+M)}{mM} \left[ 1 \pm \sqrt{1 - \frac{k^2 a^2}{mM} \frac{(mM)^2}{(m+M)^2}} \right] \end{aligned}$$

But the whole square root term is small so we can use the Taylor expansion:  $\sqrt{1-x} \approx 1 - \frac{x}{2}$ :

$$\omega^2 = \frac{C(m+M)}{mM} \left[ 1 \pm \left( 1 - \frac{mM}{2(m+M)^2} k^2 a^2 \right) \right]$$

So to summarize, at  $k \approx 0$ :

Acoustic Branch (negative root):

$$\omega^2 = \frac{Ck^2 a^2}{2(m+M)}$$

So  $\omega \propto k$ , dispersion is linear as in monatomic chain.

For the Optical Branch (positive root):

$$\omega^2 = \frac{2C(m+M)}{mM} \left( 1 - \frac{mM}{4(m+M)^2} k^2 a^2 \right)$$

This is an upside down parabola, note that at  $k = 0$  the gradient is zero, i.e. there is zero group velocity, and so no energy transfer.

### 13.2 Behaviour at Brillouin Zone edge ( $k = \frac{\pi}{a}$ )

At the edge of the Brillouin zone boundary ( $k = \pm \frac{\pi}{a}$ ) the sin function reaches a maximum.

This means that at the boundary we have a maximum in the acoustic branch, and a minimum in the optical branch.

At this point the function inside the square root becomes:

$$\left( \frac{m+M}{mM} \right)^2 - \frac{4}{mM} = \frac{1}{(mM)^2} (m^2 + 2mM + M^2 - 4mM) = \left( \frac{M-m}{mM} \right)^2$$

And so for the optical branch (positive root):

$$\omega = \left( \frac{C(m+M)}{mM} + \frac{C(M-m)}{mM} \right)^{\frac{1}{2}} = \left( \frac{2CM}{mM} \right)^{\frac{1}{2}} = \sqrt{\frac{2C}{m}}$$

And by the same approach, for the acoustic branch:

$$\omega = \sqrt{\frac{2C}{M}}$$

### 13.3 The motion of atoms in the Diatomic Chain

Previously we saw that:

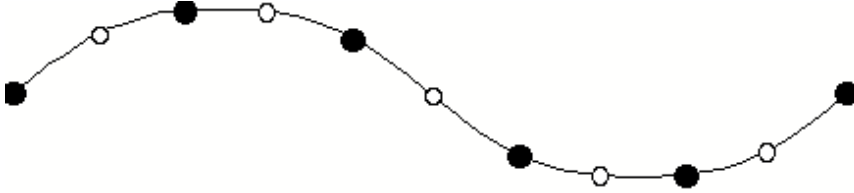
$$\begin{aligned} -\omega^2 mu &= Cv(1 + e^{-ika}) - 2Cu \\ -\omega^2 Mv &= Cu(e^{ika} + 1) - 2Cv \end{aligned}$$

**Near  $k = 0$  (zone centre):**

In the **acoustic branch** we obtain:

$$\omega_{k=0} = 0 \quad \therefore 0 = 2Cv - 2Cu \quad \therefore v = u$$

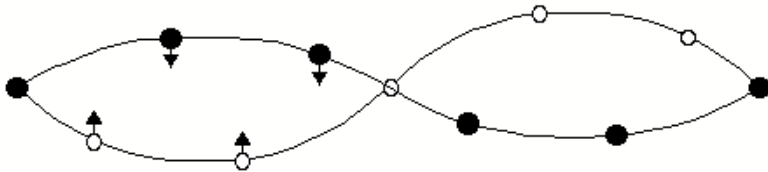
Atoms oscillate in phase (or approximately in phase nearby), with the same amplitude.



In the **optical branch** we obtain:

$$\begin{aligned} \omega_{k=0} &= \sqrt{\frac{2C(m+M)}{mM}} \quad \therefore -\left(\frac{2C(m+M)}{mM}\right)mu = 2Cv - 2Cu \\ \therefore v &= \left(1 - \frac{m+M}{M}\right)u \quad \therefore v = \frac{-m}{M}u \end{aligned}$$

The atoms of mass  $M$  oscillate out of phase with those of mass  $m$ , with a relative amplitude such that the centre of mass doesn't change in the motion (i.e. the heavier masses move less).

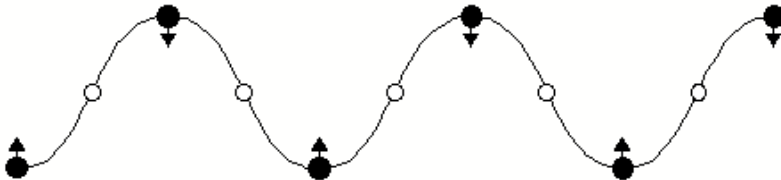


**Near  $k = \pm \frac{\pi}{a}$  (zone edge):**

In the **acoustic branch**:

$$\omega_{k=\pm\frac{\pi}{a}} = \sqrt{\frac{2C}{M}} \quad \therefore \frac{-2Cmu}{M} = -2Cu \quad \therefore u = 0$$

This means the light atoms are stationary.

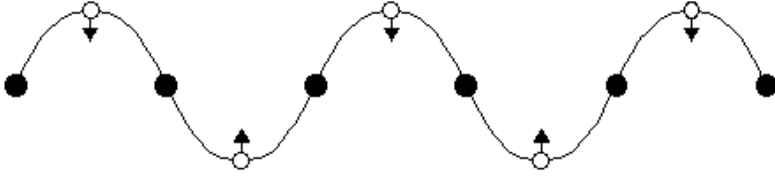


This is why  $\omega$  depends only on  $M$ . At the Brillouin zone edge the Bragg condition is satisfied and so we have a standing wave as we see here.

In the **optical branch**:

$$\omega_{k=\frac{\pm\pi}{a}} = \sqrt{\frac{2C}{m}} \quad \therefore \quad \frac{-2CMv}{m} = -2Cv \quad \therefore v = 0$$

This means that the heavy atoms are stationary.



And so this is why  $\omega$  depends only on  $m$ . The Bragg condition is satisfied and so we get a standing wave as shown.

## 14 Diatomic Chain summary

- In the optical branch, nearby atoms of different type tend to be moving in opposite directions, this is the way ionic compounds would respond to the light of EM waves, and so this is why it is called the **optical** branch.
- In the acoustic branch, nearby atoms of different type move in phase, this is how a solid responds to being struck, and hence the name **acoustic** branch.
- Normal modes: If we apply periodic boundary conditions to a chain with  $N$  atoms of each type, then:

$$Na = p\lambda \quad \therefore k = \frac{2\pi p}{Na}$$

Recall that within the first Brillouin zone there are  $N$  nodes for each branch, and so  $2N$  in total. Remember that  $N$  is the number of unit cells (i.e. the atoms of the same type) **not** the total number of atoms, and so the total number of nodes is equal to the total number of atoms.

- As for the monatomic chain, all modes outside the first Brillouin zone are equivalent to the ones inside.

Note that another common arrangement is the monatomic chain with alternative force constants or alternate spacings. However this just produces the same form of dispersion relation as the diatomic chain, with optical and acoustic branches.

## 15 Representing dispersion curves:

- The **Repeated Zone Scheme** contains surplus information as it extends past the first Brillouin zone, i.e. it is a complete plot.
- The **Reduced Zone Scheme** contains the first Brillouin zone only, and so it still contains all the information.
- The **Extended Zone Scheme** contains only the acoustic mode in the first Brillouin zone and only the optical mode in the second zone.

When  $M = m$  the extended zone scheme produces the monatomic dispersion curve, but with the Brillouin zone of twice the size. So the period of the lattice is now  $\frac{a}{2}$ .

## 16 Phonons

### 16.1 Quantisation of atomic vibrations

Classically the energy of a mode of oscillation with a certain frequency,  $\omega$ , will depend on the squared amplitude of the motion, and can take any value (i.e. it is continuous).

The crystal is a system of coupled harmonic oscillators, and from quantum mechanics we know these must have quantised energies:

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

The quantum of lattice vibration is called a **phonon**. When the vibrational mode of frequency  $\omega$  is excited to the energy,  $E_n$  (shown above) it is said to be occupied by  $n$  phonons.

### 16.2 Lattice vibrations in three dimensions

For three dimensions the equations of motion are similar but are more complicated:

$$M_b \frac{d^2 u_{l,b,i}}{dt^2} = - \sum_{l',b',j} C_{ij} (lb : l'b') u_{l',b',j}$$

where  $i$  and  $j$  represent spatial co-ordinates ( $x$ ,  $y$  or  $z$ ) and  $l$  and  $b$  label the  $l$ th unit cell and the  $b$ th basis atom in the crystal structure.

Note that displacing an atom in the  $x$ -direction can lead to a force in the  $y$  or  $z$  direction.

If there are  $N$  unit cells with  $p$  basis atoms then there are 3 acoustic and  $3p - 3$  optical modes for each value of the wavevector, and there are  $N$  distinct values of the wavevector. So the total number of modes is  $3pN$ .

For an isotropic medium and directions parallel to the  $[100]$ ,  $[110]$  and  $[111]$  directions in cubic crystals the allowed modes separate into pure longitudinal and transverse modes.

### 16.3 Experimental determination of phonon dispersion curves

#### Inelastic Light Scattering: Photon Absorption

This is the extreme case, a far-infrared photon can be fully absorbed to produce a phonon. But both energy and momentum must be conserved, so what is the momentum of this photon with the right energy?

$$E = pc \quad \therefore E = \frac{p}{c} \approx \frac{0.02\text{eV} \cdot 1.6 \times 10^{-19}}{3 \times 10^8} = 1.1 \times 10^{-29} \text{kgms}^{-1}$$

This momentum is small and so the photons can only detect zone-centre (i.e.  $k \approx 0$ ) optic phonons, as these phonons have a small enough momentum.

#### Inelastic Light Scattering: Raman Scattering

This uses visible light which is inelastically scattered rather than completely absorbed. However this still only detects zone-centre phonons.

We could also attempt giving the photon the right momentum (and so much more energy) by using X-ray photons. However, the energy of the scattered X-rays only differ by 30meV. This is a very small fraction of the total photon energy and so we need a detector with a resolution of at least 1 part in  $10^4$ . There is also the problem that the elastic scattering is far more common and so we need a very good frequency filter to ignore the elastically scattered photons, these problems make this approach very impractical.

## Inelastic Neutron Scattering

Thermal neutrons have both the right energy and the right momentum:

$$E = \frac{p^2}{2m} = 30\text{meV}, \quad p = 4 \times 10^{-24} \text{kgms}^{-1}$$

And so they can be used to probe the dispersion relation.

### 16.4 Phonon Momentum

We can consider the scattering of phonons by neutrons either in terms of waves or in terms of particles.

$$\hbar\vec{k} \rightarrow \hbar\vec{q} + \hbar\vec{k}'$$

From the conservation of momentum we see that:

$$\vec{k}' - \vec{k} = \vec{q} + \vec{G}$$

Note the  $\vec{G}$  is added since the dispersion relation is periodic, and so  $\vec{k} = \vec{k} + \vec{G}$ .

This addition to the conservation of momentum has strange consequences when we consider phonons scattering off each other. I.e. two phonons colliding and combining to produce a third phonon.

$$\vec{q}_1 + \vec{q}_2 \rightarrow \vec{q}_3$$

if  $\vec{q}_1$  and  $\vec{q}_2$  are such that  $\vec{q}_3$  is outside the first Brillouin zone, then  $\vec{q}_3$  can be equally well described by a point within the first Brillouin zone travelling in the opposite direction (i.e. negative  $\vec{k}$ ).

This means that two forward-travelling phonons combine to produce a third backward-travelling phonon. I.e. two points with a positive group velocity combine to produce a point with a negative group velocity.

This is called the **Umklapp process** and it is important in determining the thermal conductivity of an insulator, as the conductivity will decrease at high phonon densities (as phonon-phonon collisions become more common).

Note that this is not possible in 1-Dimensional systems, as  $\vec{q}_1$  and  $\vec{q}_2$  cannot be co-linear. This is because two phonons placed on the same dispersion curve cannot produce a third on the same curve. This means that in 1-D systems that phonons cannot combine in this fashion.

Note that we must not take the concept of phonon momentum too literally:

- Phonons have a quantity  $\hbar\vec{q}$  associated with them which is conserved in a similar (not identical) way to momentum in collisions. This quantity is often called **crystal momentum**.
- It is not normal kinematic momentum as there are no masses moving (net) distances as the phonon passes through a crystal. Indeed for a transverse wave, even the oscillatory movements that do occur are perpendicular to  $\vec{q}$ .
- There is one phonon mode that does carry real momentum, this is the  $\vec{q} = 0$  mode, this means the entire crystal must be moved to conserve momentum as there is no phonon scattering.

## 17 Electrons in Crystals

In the early 20th century the electrons in a solid were thought to behave as a classical gas, with a mean energy of  $\frac{3}{2}kT$ . This gave good agreement with electrical conductivity  $\sigma = \frac{n_e e^2 \tau}{m}$  where  $\tau$  is the average time between scattering events (the relaxation time). And taking  $\tau$  to be the mean free path divided by the thermal velocity this obtained a mean free path of the order of a lattice spacing. So the electrons were scattering off ions and everything seemed okay.

However, this model gave a prediction for the heat capacity of  $N_e$  electrons as:  $C = \frac{3}{2}N_e k$  but when the heat capacity was measured it was found to be approximately 100 times smaller. This discrepancy required a new model.

The basic ideas are:

- Electrons are confined within the crystal, like a particle in a box in Quantum Mechanics.
- Electrons are Fermions and so only one electron can occupy each state (including spin).
- Electrons have a dispersion relation of energy against momentum (since  $E = \hbar\omega$ ,  $p = \hbar k$ ) or  $E$  against  $k$ , which contains information such as the group velocity and effective mass.

## 18 The Free-Electron Model

Here we neglect potential energy, and so the electrons are free except for the confinement within the crystal.

The dispersion relation is given by:

$$E = \frac{p^2}{2m} \quad \therefore \quad \omega = \frac{\hbar k^2}{2m}$$

The particle velocity is the group velocity:

$$v_g = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{dE}{dk} = \frac{\hbar k}{m} = \frac{p}{m} = v$$

The mass is inversely proportional to the curvature:

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

The electrons are confined in a crystal with sides  $L_x$ ,  $L_y$  and  $L_z$ . By considering with one dimension:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = E\Psi$$

with a boundary condition that  $\Psi$  is zero at the walls, the solution is:

$$\Psi = A \sin(k_x x) = A \sin\left(\frac{n\pi x}{L_x}\right)$$

where  $n$  is an integer.

In 2D:

$$\Psi = A \sin(k_x x) \sin(k_y y) = A \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right)$$

In 3D:

$$\Psi = A \sin(k_x x) \sin(k_y y) \sin(k_z z) = A \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

When we work out the quantized values of  $k$  we find there is  $\left(\frac{\pi}{L}\right)^3$  volume of  $k$ -space per allowed point in 3D,  $\left(\frac{\pi}{L}\right)^2$  area of  $k$ -space per allowed point in 2D and  $\frac{\pi}{L}$  length of  $k$ -space per allowed point in 1D.

The **Pauli Exclusion Principle** states that only two electrons (one spin-up and one spin-down) can go into each of these states, and so the states get filled up to some energy, called the **Fermi Energy**,  $E_F$ .

The Fermi Energy,  $E_F$ , and the number of allowed states within  $kT$  of  $E_F$  both affect the properties of the solids.

## 18.1 The Density Of States

We have a cubic (or square or equally spaced) array of allowed states in 3D (or 2D or 1D)  $k$ -space. We want to know the number of allowed states in a given energy range (between  $E$  and  $E + dE$ ), and so in 3D:

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m}$$

So we use the allowed states between  $k$  and  $k + dk$ , the individual components don't matter so long as  $|\vec{k}|$  is in this range.

This produces a sphere of radius  $k$  in 3D, a circle of radius  $k$  in 2D and a line up to  $k$  in 1D (so a length of  $2k$ ).

However we can ignore the negative  $k$ -components, as these do not produce new quantum states (they are not measurable as distinct from positive  $k$ -components) and so we deal with only the positive octant of the sphere (or the positive quadrant of the circle or positive half of the line), as using the whole sphere would overcount.

We know there are two allowed states for every  $\left(\frac{\pi}{L}\right)^3$   $k$ -space in 3D,  $\left(\frac{\pi}{L}\right)^2$   $k$ -space in 2D and  $\frac{\pi}{L}$   $k$ -space in 1D).

We also know that the volume of the positive octant of the sphere, area of the positive quadrant of the circle and length of the positive half space are given by:

$$V = \frac{\frac{4\pi k^3}{3}}{8} = \frac{\pi k^3}{6}$$

$$A = \frac{\pi k^2}{4}$$

$$L = k$$

So the number of states from 0 to  $k$  is given by:

$$\frac{\text{space from 0 to } k}{\text{space per state}}$$

Note that this includes two possible spin orientations.

So the number of states from 0 to  $k$  is:

3D	2D	1D
$N(0 \rightarrow k) = \frac{\frac{\pi k^3}{6}}{\frac{1}{2}\left(\frac{\pi}{L}\right)^3} = \frac{Vk^3}{3\pi^2}$	$N(0 \rightarrow k) = \frac{\frac{\pi k^2}{4}}{\frac{1}{2}\left(\frac{\pi}{L}\right)^2} = \frac{Ak^2}{2\pi}$	$N(0 \rightarrow k) = \frac{k}{\frac{\pi}{2L}} = \frac{2Lk}{\pi}$

Using that:

$$E = \frac{\hbar^2 k^2}{2m} \therefore k = \sqrt{\frac{2mE}{\hbar^2}}$$



3D	2D	1D
$N(0 \rightarrow E) = \frac{V}{3\pi^2} \left( \frac{2mE}{\hbar^2} \right)^{\frac{3}{2}}$	$N(0 \rightarrow E) = \frac{A}{2\pi} \left( \frac{2mE}{\hbar^2} \right)$	$N(0 \rightarrow E) = \frac{2L}{\pi} \left( \frac{2mE}{\hbar^2} \right)^{\frac{1}{2}}$

And so the density of states is the number of states per unit energy range:

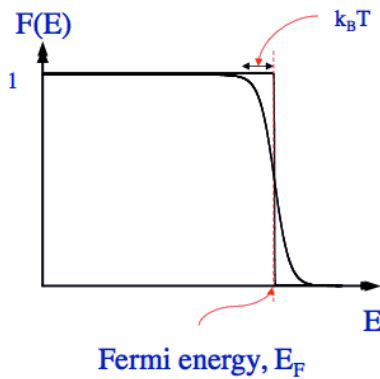
3D	2D	1D
$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}}$	$D(E) = \frac{dN}{dE} = \frac{A}{2\pi} \left( \frac{2m}{\hbar^2} \right)$	$D(E) = \frac{dN}{dE} = \frac{L}{\pi} \left( \frac{2m}{\hbar^2} \right)^{\frac{1}{2}} E^{-\frac{1}{2}}$

## 18.2 The Fermi Distribution

So  $D(E)$  tells us how many states we have available, however it does not specify which states are occupied by electrons, to do this we require a probability distribution function.

At  $T = 0$  the electrons will fill the lowest energy states available. But there are only two electrons allowed per state (due to spin) and so the probability of the state being occupied is 1 up to a certain energy,  $E_F$  and 0 beyond this (as all the electrons are distributed).

However, at  $T > 0$  electrons can be thermally excited to higher energy states if there are **empty** states within  $kT$  of the Fermi energy,  $E_F$ .



The function that describes this behaviour is:

$$F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

Where  $F(E)$  is the probability of the state being occupied. As  $T \rightarrow 0$  then if  $E > E_F$  then  $F(E) \rightarrow 0$  whilst if  $E_F > E$  then  $F(E) \rightarrow 1$ , which is the simple Fermi distribution described earlier.

## 18.3 Fermi Energy Estimation

The total number of states from  $E = 0$  to  $E = E_F$  must be equal to the total number of electrons in the system.

In 3D:

$$N_e = \frac{V}{3\pi^2} \left( \frac{2mE_F}{\hbar^2} \right)^{\frac{3}{2}} \quad \therefore E_F = \frac{\hbar^2}{2m} \left( 3\pi^2 \frac{N_e}{V} \right)^{\frac{2}{3}}$$

In 2D:

$$N_e = \frac{A}{2\pi} \left( \frac{2mE_F}{\hbar^2} \right) \quad \therefore E_F = \frac{\pi \hbar^2 N_e}{Am}$$

For a metal there is usually one free electron for every atom and so usually one electron for every  $(3 \times 10^{-10})^3 \text{ m}^3$  of volume (the typical volume of a primitive unit cell).

So as an estimate:

$$\frac{N_e}{V} = \frac{1}{(3 \times 10^{-10})^3} = 4 \times 10^{-28} \text{ m}^{-3} \quad \therefore E_f = 4 \text{ eV}$$

This is over 100 times  $kT$  at room temperature, and so the step like  $t = 0$  behaviour of the Fermi function appears to be a good approximation. Electrons at  $E_F$  have velocities between  $10^6$  and  $10^7$   $\text{ms}^{-1}$  (at which relativistic effects begin to become significant).

The Fermi temperature is given by:

$$T_F = \frac{E_F}{k} \approx 50,000 \text{ K}$$

## 18.4 When is a thin film 2D or 3D?

If  $L_z$  is very small in comparison to  $L_x$  and  $L_y$  (i.e. it is a thin film) then the energy levels associated with x and y are more closely spaced than those associated with z, since  $k_x = \frac{n_x \pi}{L_x}$ .

This means that the electrons will fill the increasing  $n_x$  and  $n_y$  values whilst at  $n_z = 1$  until the number of electrons or temperature is increased significantly to provide enough energy for them to fill the  $n_z = 2$  state. I.e. they will fill up in a staircase manner.

## 18.5 Heat Capacity

In the classical gas *every* particle acquires extra thermal energy as the temperature is increased, and so *every* particle contributes to the heat capacity:

$$C = \frac{3}{2} N_e k$$

Whilst in the Fermi gas, only electrons within  $kT$  of  $E_F$  acquire extra thermal energy. This is approximately a fraction  $\frac{T}{T_F}$  of  $N$ .

So we expect something like:

$$C = \frac{3}{2} N_e k \frac{T}{T_F}$$

At room temperature  $\frac{T}{T_F} \approx \frac{1}{100}$ . This is what is observed and it explains the previous problem of the classical heat capacity being 100 times larger than the observations.

## 18.6 Electrical Conductivity

In equilibrium we now know that the electrons of a solid will fill up the allowed states in k-space up to an energy  $E_F$ . If we apply an electric field then the equation of motion is:

$$\frac{d\vec{p}}{dt} = -e\vec{E} \quad \therefore \quad \frac{d\vec{k}}{dt} = \frac{-e\vec{E}}{\hbar}$$

since  $\vec{p} = \hbar\vec{k}$ .

After a time  $t$ , an electron with wavevector  $\vec{k}$  will obtain an extra  $\Delta\vec{k}$  from the electric field:

$$\Delta\vec{k} = \frac{-e\vec{E}t}{\hbar}$$

obtained by integrating the earlier expression with respect to time.

The electric field causes all the electrons to transfer from k-state to k-state in unison. I.e. they all move to an adjacent k-state in the direction of the electric field at once.

If the electrons were in a vacuum, or an infinite perfect crystal at absolute zero then the Fermi sphere would continue to shift this way forever as the electrons are accelerated indefinitely.

However, in a real solid it is assumed that the electrons scatter, on average, after a time  $\tau$  called the **relaxation time**.

So each electron acquires *on average*:

$$\Delta \vec{k} = \frac{-e\vec{E}\tau}{\hbar}$$

The electrical conductivity is defined by the equation:

$$\vec{j} = \sigma \vec{E}$$

where  $\vec{j} = n_e q \vec{v}_d$  and  $n_e = \frac{N_e}{V}$  and  $\sigma$  is the inverse of the electrical resistivity.

Where  $\vec{v}_d$  is the drift velocity - the extra velocity due to the field which is related to  $\Delta \vec{k}$  by:

$$\begin{aligned} \vec{v}_d &= \frac{\Delta \vec{p}}{m} = \frac{\hbar \Delta \vec{k}}{m} = \frac{-e\vec{E}\tau}{m} \\ \therefore \vec{j} &= \frac{n_e e^2 \vec{E} \tau}{m} \quad \therefore \sigma = \frac{n_e e^2 \tau}{m} \end{aligned}$$

This is the same formula as for the classical gas model, however the mean free path will be different.

In the classical model, the mean free path was calculated from:

$$M.F.P. = v_{\text{thermal}} \tau$$

where electrons were assumed to move at the thermal velocity and so:

$$\frac{1}{2} m v_{\text{thermal}}^2 = \frac{3}{2} kT \quad \therefore v_{\text{thermal}} = \sqrt{\frac{3kT}{m}} \approx 10^5 \text{ ms}^{-1}$$

Remember this gave a mean free path approximately equal to a lattice constant using a typical room temperature of value  $\sigma$ .

Note that the drift velocity caused by the electric field is very small compared with this, only a few mm s<sup>-1</sup>.

In the free-electron fermi-gas model the velocity to use is the Fermi velocity:

$$M.F.P. = v_F \tau$$

where  $\frac{1}{2} m v_F^2 = E_F$  and so  $v_F = \sqrt{\frac{2E_F}{m}} = 10^6 \text{ ms}^{-1}$ .

Consequently the value of  $\tau$  obtained from the measurement of electrical conductivity gives a mean free path of approximately 10-100 lattice constants.

If we measure low temperature conductivity in very pure crystals we obtain a mean free path approximately equal to the size of the crystal, that is to say that the only scattering is from the edges of the crystal! (The scattering from the lattice disappears for some reason I didn't write down, I guess it's due to the long  $\tau$  or something).

Pauli paramagnetism is another example of the success of the free electron model however I don't think it is examined.

So in summary the free-electron model succeeds in explaining:

- The small heat capacity with linear  $T$  dependence.
- Predicts contribution to the paramagnetic susceptibility (Pauli paramagnetism) in metals.
- Gives the same successful formula for the electrical conductivity as the classical theory

**BUT** it gives an unexpectedly long mean free path (which is correct however) and provides no explanation for insulators, which have no free electrons (which the free-electron model does not explain).

## 19 The Nearly-Free Electron Model

Electrons in crystals are waves travelling in a periodic potential, we know that waves should undergo reflection if their wavevectors lie on the edges of Brillouin zones.

We now know that the electrons will fill up to the Fermi energy in discrete  $k$ -states, but how many electrons are necessary before their  $k$ -vectors approach the edge of the Brillouin zone?

The Brillouin zone boundary is at  $k = \pm \frac{\pi}{a}$ , and so

$$E_{BZ} = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2}{2ma^2}$$

Recall that the allowed states form a cubic array in  $k$ -space, where the volume per allowed state is  $\frac{1}{2} \left(\frac{\pi}{L}\right)^3$  (including spin).

The volume of the Brillouin zone in  $k$ -space (assuming a simple cubic lattice, with lattice constant  $a$ ) is  $\left(\frac{\pi}{a}\right)^3$ .

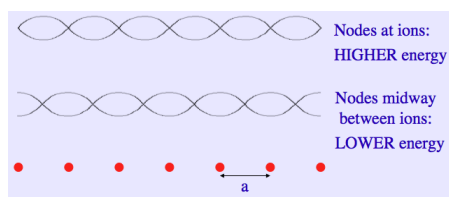
And so the number of allowed states in the Brillouin zone is:

$$\frac{2 \left(\frac{\pi}{a}\right)^3}{\left(\frac{\pi}{L}\right)^3} = 2 \frac{L^3}{a^3}$$

Note that  $\frac{L^3}{a^3}$  is the number of primitive unit cells in the lattice.

If we assume a monatomic basis then we reach the edge of the Brillouin zone boundary by having two electrons per atom (e.g. Calcium).

Consider an electron in a travelling wave quantum state, moving through the crystal, with  $k = \frac{\pi}{a}$ , and so  $\lambda = 2a$ . This wave keeps Bragg-reflecting which eventually produces a counter-propagating travelling wave. These standing waves have the same wavevector  $k$ , but their energies are different due to the position of the nodes relative to the positive ions.

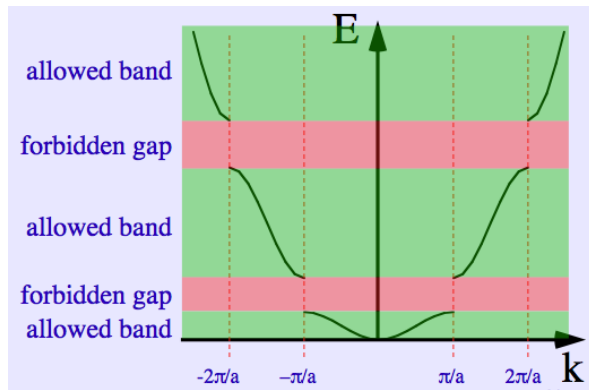


So the standing wave with zero probability of existing at the ions, has a **high energy** as the electrons are furthest from the positive ions they will be attracted to, whilst the standing wave with

the maximum probability of existing at the ions has a **low energy** as on average they will be very close to the ions.

This means that for the dispersion relation there are **two** possible energies at the Brillouin zone boundary. The standing waves mean this point has zero group velocity and  $\frac{d\omega}{dk} = 0$  and so  $\frac{dE}{dk} = 0$ . This means this point is a turning point in the dispersion relation.

This produces band gaps:



As we increase the number of electrons per atom (or primitive unit cell) the Fermi energy,  $E_F$ , moves up the dispersion relation. At 1 electron per atom it sits halfway up the first allowed band, whilst for 2 electrons per atom it sits halfway between the first and second allowed bands (as on average some electrons will be in the above state and some below), at 3 electrons per atom it is halfway up the next allowed state, etc.

When  $E_F$  is far away from a gap, the dispersion is similar to the free electron case but with a slight change in curvature. Recall that the mass is inversely proportional to curvature and so the behaviour of these electrons is described by replacing the mass with an “*effective mass*”.

Remember the description of electrical conduction in a metal:

That as an electric field is applied the electrons on the right move in to states just above the equilibrium Fermi energy. The *tiny* energy required to do this is supplied by the electric field.

The rest of the electrons then step from left to right filling the steps made vacant.

## 19.1 Insulators

If  $E_F$  lies in a forbidden gap, then there are no states near the Fermi energy for the electrons to be excited in to by the field. And so there is zero electrical conductivity and the material is an **insulator**.

Whilst if  $E_F$  lies in a band of allowed states then the electric field can excite the electrons as described previously, and so there is high electrical conductivity and the material is a **metal**.