MP464: Solid Sate Physics

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1. Introduction

Broadly speaking there are three common states of matter: solid, liquid and gas, though plasmas and other more exotic states can also be legitimately called different states of matter. Thermodynamics studies all states of matter in general terms while fluid dynamics deals with properties specific to liquids and gases. Solid State physics describes the properties of solids.

Examples of solids at room temperature are: rocks, metals (except mercury), ice, glass and wood. This course will deal exclusively with one type of solid — crystals (rocks and metals are made up of crystals, glass and wood are not crystals). The regular structure of crystals makes it easier to construct realistic mathematical models of them, the cellular structure of wood is much more complicated at a microscopic level than a crystal. While this restriction to crystals may seem rather narrow it is in fact more general than one might think: metals and rocks are in fact made up of an agglomeration of large numbers of small crystals. While the crystal structure is obvious in some rocks, such as the sample of Iron Pyrites shown below, it is not obvious in metals where the crystals are usually too small to see without a microscope.

Some crystals can be very large, metres across like the ones shown here from a mine in Mexico[1]

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[1] It has even been suggested by some geologists, based on analysis of seismic data and computer modelling of the quantum mechanical properties of iron at high pressure, that the inner core of the Earth might be a single crystal of iron more than 2400 km in size — but this is speculative.

2. Lattices and crystals

A **crystal** is a periodic array of atoms or molecules in a regular lattice structure. Mathematically a **lattice** is a rigid, periodic array of points that looks exactly the same from every point and is infinite in extent. Putting an atom, a group of atoms or a molecule (a **basis**) at every point of a lattice gives a crystal structure.

> **Crystal structure = Lattice + Basis.**

Below is a two dimensional representation of this concept. The blue and green dots represent atoms, *e.g.* Zn and S for a crystal of Zinc Sulphide. A lattice is an abstract mathematical structure that is completely determined by a set of basis vectors, $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ below, which, when combined with the basis, gives a representation of a crystal,[2]

Lattice   +   Basis   =   Crystal Structure
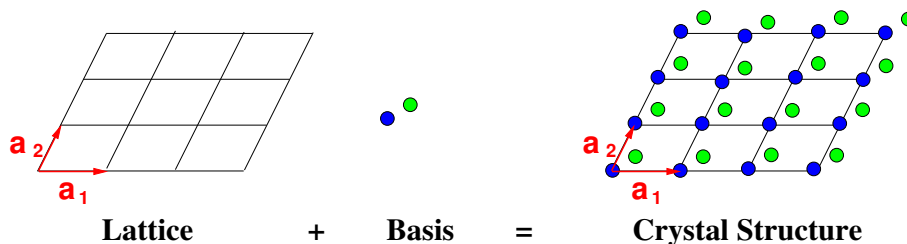
A lattice is defined by a set of **primitive lattice vectors**, such as $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ in the two dimensional example. The definition of a set of primitive lattice vectors is that any lattice vector $\mathbf{L}$ can be expressed as a linear combination of primitive lattice vectors, $\mathbf{L} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2$, with integer co-efficients. Primitive lattice vectors describe a **primitive cell** of the lattice, a parallelogram in this case,

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[2] Real crystals do not have infinite extent, of course, but even small crystals of a milligramme can have 10^{20} atoms in them so it not unreasonable to model them with a lattice of infinite extent.
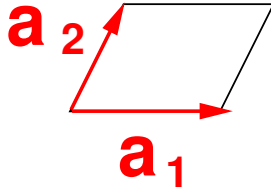
It may be useful to think of a two-dimensional lattice as a tiling of the two-dimensional plane by primitive cells. A primitive cell need not be a parallelogram. By definition a primitive cell contains one complete lattice point and only one complete lattice point.

A general point in a two dimensional lattice is described by a **lattice vector**

$$\mathbf{L} = n_1 \boldsymbol{a}_1 + n_2 \boldsymbol{a}_2$$

defined by two integers n_1 and n_2.

Primitive lattice vectors and primitive cells are not unique, the pairs $(\boldsymbol{a}_1, \boldsymbol{a}_2)$, $(\boldsymbol{a}_1', \boldsymbol{a}_2')$ and $(\boldsymbol{a}_1'', \boldsymbol{a}_2'')$ in the figure below are all primitive lattice vectors and the green shapes are all possible primitive cells,
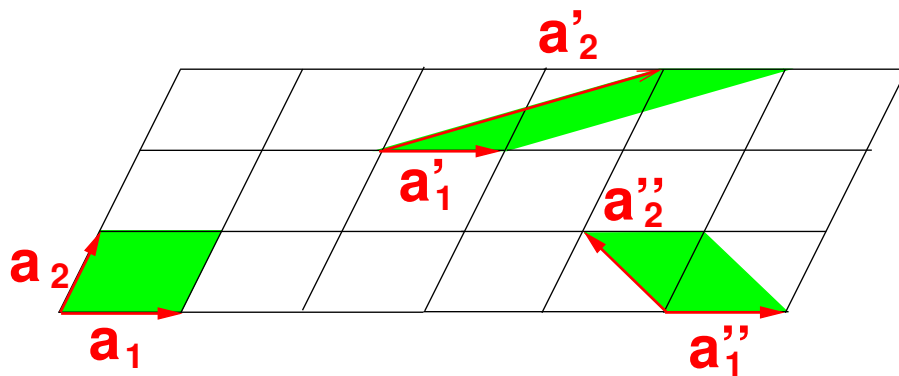
The three green shapes in the figure above all have the same area,

$$|\boldsymbol{a}_1 \times \boldsymbol{a}_2| = |\boldsymbol{a}_1' \times \boldsymbol{a}_2'| = |\boldsymbol{a}_1'' \times \boldsymbol{a}_2''|.$$

A three-dimensional lattice is described by three primitive lattice vectors $(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)$, lattice vectors are defined by three integers, n_1, n_2 and n_3,

$$\mathbf{L} = n_1 \boldsymbol{a}_1 + n_2 \boldsymbol{a}_2 + n_3 \boldsymbol{a}_3,$$

and all primitive three dimensional cells have the same volume

$$V_c = |\boldsymbol{a}_1 . (\boldsymbol{a}_2 \times \boldsymbol{a}_3)|.$$

Symmetries

The set of all possible lattices can be classified by their symmetries:

- All lattices are symmetric under translations by any lattice vector (all lattice points move under such a translation);

- Symmetries leaving at least one lattice point fixed are called **point symmetries** — the set of all point symmetries is called the **point group** of the lattice. Point symmetries are: rotations about a lattice point; reflections in lines or planes containing a lattice point and inversion about a lattice point (any given lattice might not have all of these symmetries).

- The combination of all lattice translations and the point group of the lattice is called the **space group** of the lattice.

As an example in 2-dimensions, consider the pattern below and imagine it to be infinitely extended in both directions:
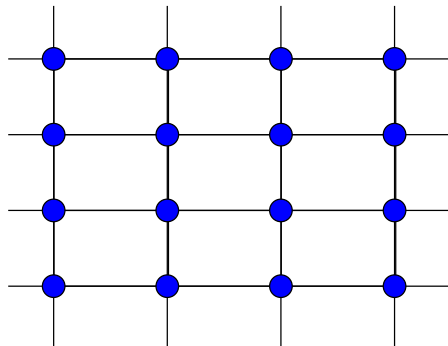
When extended this rectangular pattern is symmetric under rotations through π about any point and, of course, rotations though 2π which just brings the pattern back to its original orientation. The pattern is also symmetric under reflections about any of the marked horizontal lines, we shall represent such reflections by the symbol M_1 (M for mirror), and reflections about any of the vertical lines, which we shall represent by M_2. The rotations leave precisely one point fixed while the reflections leave an entire line of points fixed, these operations are part of the point group. Combining any two symmetry operations that leave the same point fixed should also be a symmetry of the point group: for example we could perform M_1 followed by a rotation through π, this does not give a new symmetry operation because it is completely equivalent to M_2 (convince yourself of this).

To understand the point group in more detail it is useful to draw up a table that shows the result of combining any two symmetry operations, this is called a *group multiplication table*. Denote a clockwise rotation though an angle θ by θ itself and the result of doing nothing at all (or rotating through 2π) by **1** then the table below shows the result obtained by first applying the operation in the top row and then applying the operation in the first column. We get a 4×4 table because we must include **1** in order to complete the table.

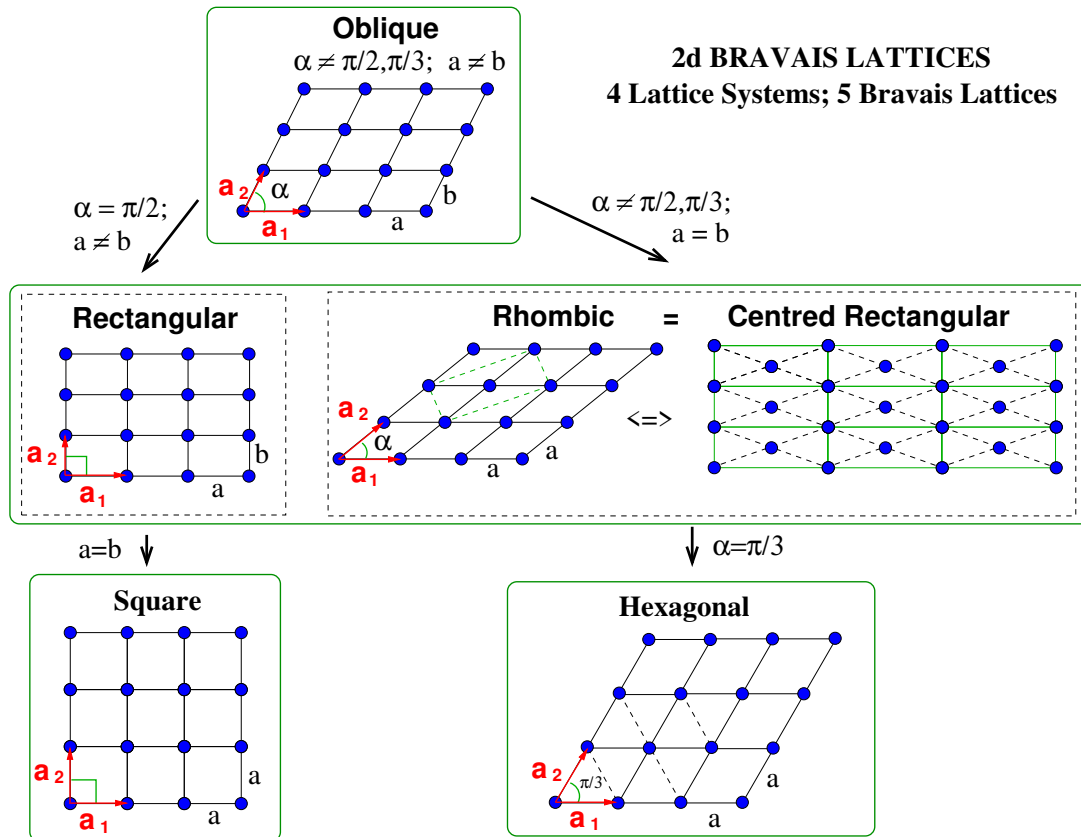|	**1**	π	M_1	M_2
1	**1**	π	M_1	M_2
π	π	**1**	M_2	M_1
M_1	M_1	M_2	**1**	π
M_2	M_2	M_1	π	**1**

Note that any symmetry multiplied by **1** just reproduces the symmetry itself, so **1** is called the *identity* operation. Also each row and each column contains a **1**, any two operations that combine to produce a **1** are called inverses of each other and every entry has an inverse. The requirement that applying any two symmetry operation must produce another symmetry and that every operation has an inverse in the multiplication table puts very strong restrictions on the number of consistent multiplication tables that can be constructed. All possible point groups have a finite number of elements and have been classified and listed by mathematicians.

Space groups have a (countably) infinite number of elements, because there are an infinite number of lattice vectors available for translations, but nevertheless all possible space groups can also be classified and listed. This means that all possible lattice structures can be classified and in three dimensions this was first achieved by the French physicist Bravais in 1850. For this reason these lattices are called Bravais lattices. Sometimes there is more than one space group with the same point group as we shall see below.

Two dimensional lattices

For simplicity we start with two dimensional lattices. In two dimensions there are 4 possible point groups (giving rise to 4 lattice systems) and 5 possible space groups (giving rise to 5 inequivalent lattices). The possibilities are shown below (lattice points are indicated by blue dots for clarity):

Oblique

$\alpha \neq \pi/2, \pi/3$; $a \neq b$

2d BRAVAIS LATTICES
4 Lattice Systems; 5 Bravais Lattices

$\boldsymbol{a_2}$ α b $\boldsymbol{a_1}$ a

$\alpha = \pi/2$;
$a \neq b$

$\alpha \neq \pi/2, \pi/3$;
$a = b$

Rectangular

$\boldsymbol{a_2}$ b $\boldsymbol{a_1}$ a

Rhombic = **Centred Rectangular**

$\boldsymbol{a_2}$ α a a $\boldsymbol{a_1}$ a <=>

$a=b$ ↓

$\alpha=\pi/3$ ↓

Square

$\boldsymbol{a_2}$ a $\boldsymbol{a_1}$ a

Hexagonal

$\boldsymbol{a_2}$ $\pi/3$ a $\boldsymbol{a_1}$ a

In two dimensions the only possible point symmetries are:

i) Rotations by $\frac{\pi}{3}$, $\frac{\pi}{2}$ and multiples of these, namely $\frac{2\pi}{3}$, π, $\frac{4\pi}{3}$, $\frac{3\pi}{2}$ and $\frac{5\pi}{3}$.

ii) Reflection in a line.

All two-dimensional lattices have rotations by π as part of their space group, the complete set of possibilities is:

$$
\begin{array}{l}
\text{4 lattice systems} \\
\text{(point groups)}
\end{array}
\left\{
\begin{array}{ll}
\pi \text{ only} & \text{Oblique} \\
\pi + \text{reflections} & \left\{\begin{array}{l}\text{Rectangular} \\ \text{Centred Rectangular}\end{array}\right. \\
\text{multiples of } \frac{\pi}{2} + \text{reflections} & \text{Square} \\
\text{multiples of } \frac{\pi}{3} + \text{reflections} & \text{Hexagonal}
\end{array}
\right\}
\quad \text{5 Bravais lattices.}
$$

Although the rectangular and centred rectangular lattices share the same point group they are different because they have different space groups, as can be seen by combining reflections with translations. If M_1 represents reflection in the x-axis and M_2 reflection in the y-axis then, for the rectangular lattice

$$
M_1 : \begin{cases} \boldsymbol{a_1} \to \boldsymbol{a_1} \\ \boldsymbol{a_2} \to -\boldsymbol{a_2} \end{cases}
\qquad
M_2 : \begin{cases} \boldsymbol{a_1} \to -\boldsymbol{a_1} \\ \boldsymbol{a_2} \to \boldsymbol{a_2}, \end{cases}
$$

while, for the centred rectangular lattice

$$
M_1 : \begin{cases} \boldsymbol{a_1} \to \boldsymbol{a_2} \\ \boldsymbol{a_2} \to \boldsymbol{a_1} \end{cases}
\qquad
M_2 : \begin{cases} \boldsymbol{a_1} \to -\boldsymbol{a_2} \\ \boldsymbol{a_2} \to -\boldsymbol{a_1}. \end{cases}
$$

6
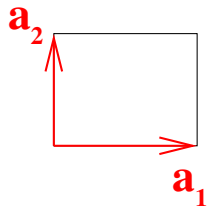
Rectangular   Centred Rectangular
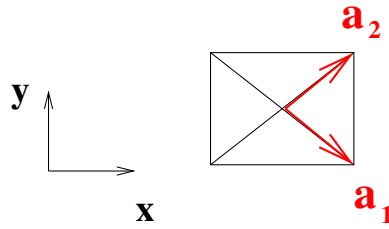
Thus M_1 interchanges $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ for the centred rectangular lattice, and this is a symmetry. There is no such symmetry for a general rectangular lattice, unless $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ have the same length in which case the a lattice is square and has a different space group with more rotational symmetries.

Note that rotations by $\frac{2\pi}{5}$ is not a possibility — it is not possible to tile a two dimensional plane with a single shape with 5-fold symmetry, the figure below shows the kind of thing that goes wrong if we try to do so,
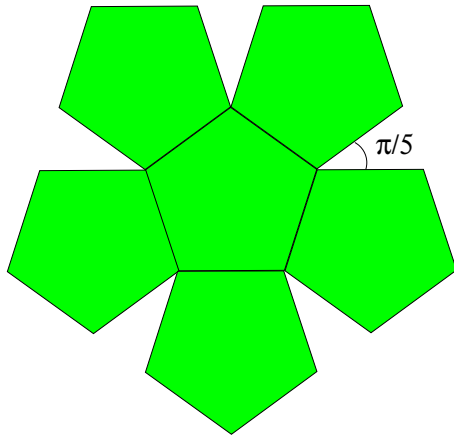

Curiously it is possible to tile the two dimensional plane with a 5-fold symmetric pattern (point group consisting of rotations by $\frac{2\pi}{5}$) but which has *no* translational symmetries at all: the pattern *never* repeats, and so does not fall into the category of crystals by our definition. This pattern requires two different rhombic tiles for its construction and is called a **Penrose tiling**,

7
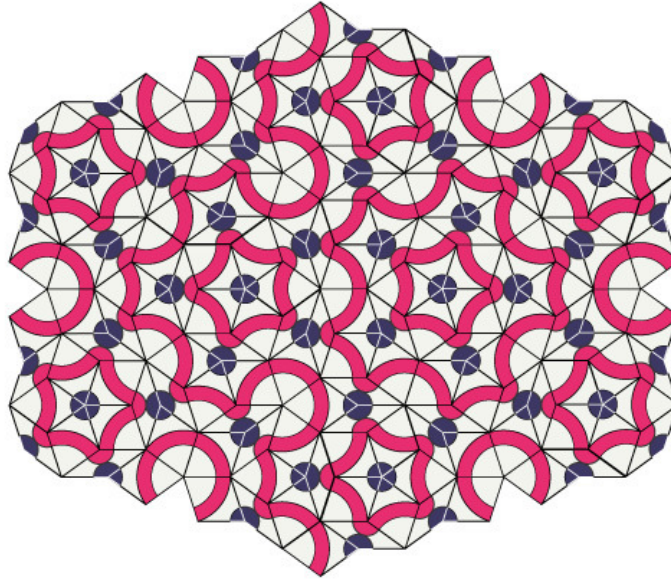
Structures similar to this have been seen in Nature, they are called quasi-crystals, but we shall not be describing these any further in this course.

Before going on to describe the classification of three-dimensional lattices we first describe the construction of a special primitive cell, called a **Wigner-Seitz cell**. To construct a Wigner-Seitz cell first pick any lattice point and draw lines connecting it to all its neighbours. Bisect these lines at right-angles and the bisectors enclose a Wigner-Seitz cell.
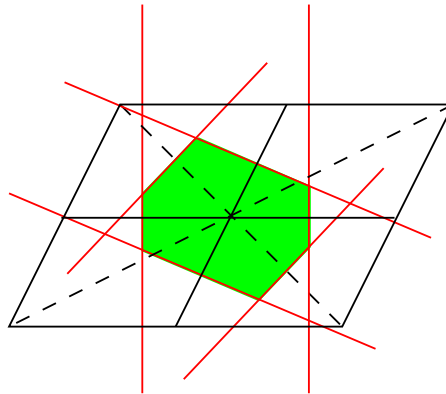
In the figure above solid black lines enclose primitive cells, the parallelograms described earlier, and dotted black lines link other neighbours to the chosen lattice point, at the centre of the green shape. Red lines represent perpendicular bisectors of all the black lines, both solid and dashed. The red lines enclose the six-sided green shape, which is a Wigner-Seitz cell for this lattice — it has the same area as one of the parallelograms.

Three dimensional lattices

In three dimensions the only possible allowed rotations of a crystal are the same set as in 2-dimensions, but around any one of three axes. There can be up to three reflection planes and inversion in an origin corresponds to a reflection plus a rotation of π radians (in 2-dimensions reflection in the origin is completely equivalent to a rotation through π).

There are 7 possible point groups in 3-dimensions, giving different 7 lattice systems, with 14 different space groups and hence 14 inequivalent Bravais lattices:

3d BRAVAIS LATTICES

## 7 Lattice Systems; 14 Bravais Lattices
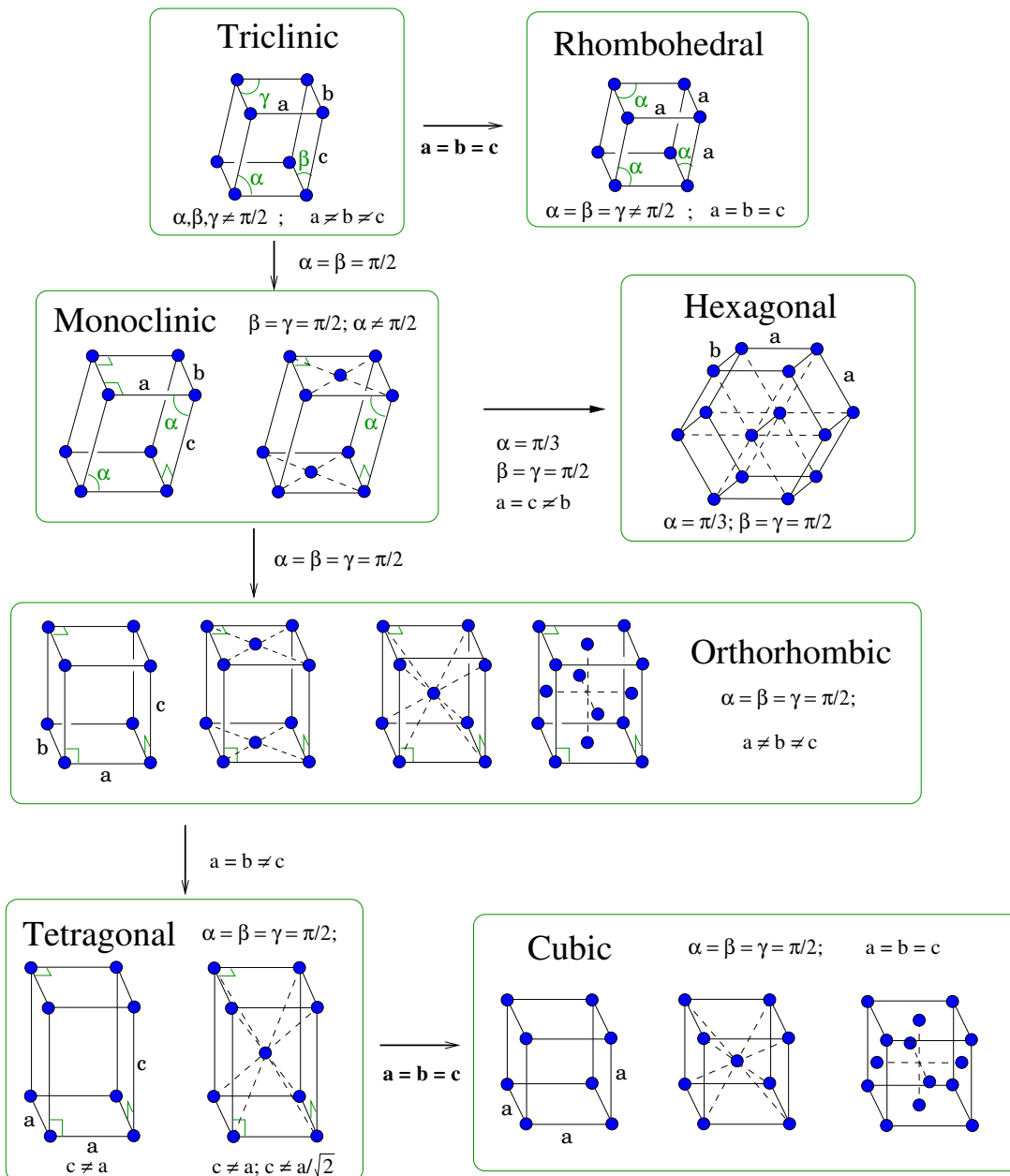
We shall consider four of the simpler cases in more detail. Firstly the three cubic lattices all have space groups which are the symmetries of a cube, which include rotations,

Symmetries of a cube (Octahedral group)

$\pi/2, \pi, 3\pi/2$

$2\pi/3, 4\pi/3$

3x3=9

4x2=8

6x1=6

π
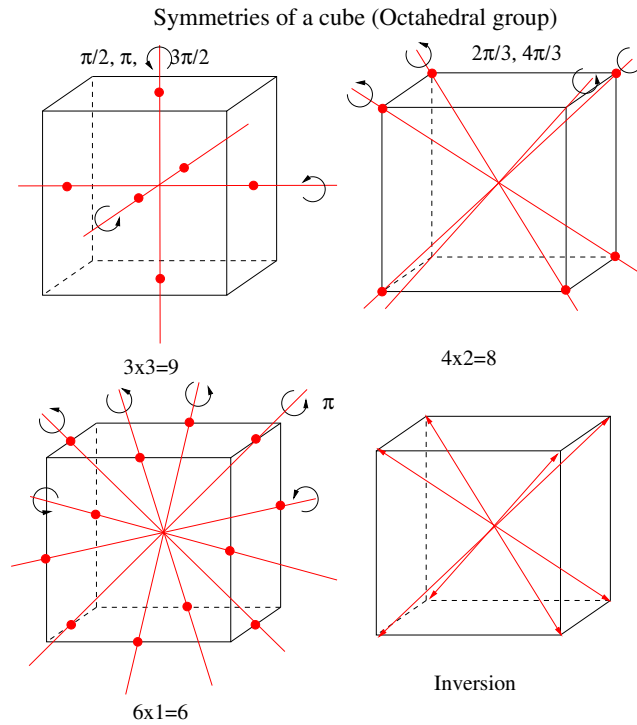
Inversion

Including the identity gives 24 proper (chiral) operations;
Including inversion gives 24 achiral operations = 48 in total.
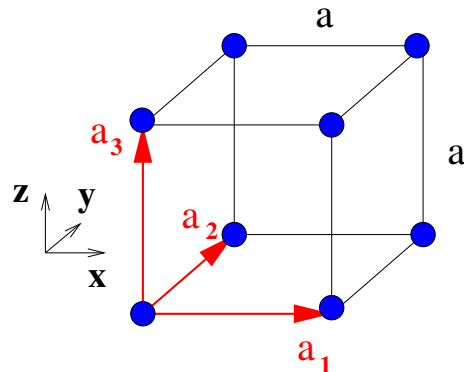
and reflections in various planes,

Examples of mirror (achiral) symmetries of a cube, reflection in a plane
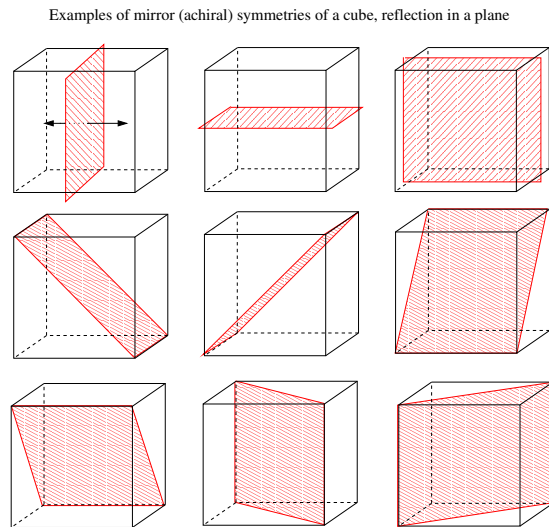
1. Simple cubic lattice

For the simple cubic lattice we can choose primitive lattice vectors to be

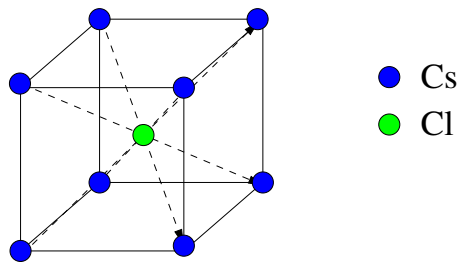$$\boldsymbol{a}_1 = a\hat{\mathbf{x}}, \qquad \boldsymbol{a}_2 = a\hat{\mathbf{y}}, \qquad \boldsymbol{a}_3 = a\hat{\mathbf{z}}.$$
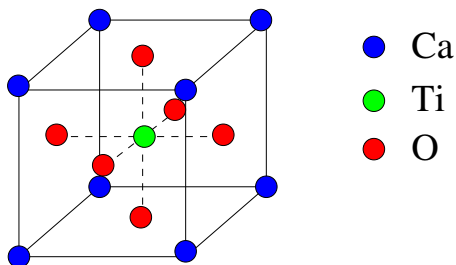
The volume of a primitive cell is

$$V_c = |\boldsymbol{a}_1.(\boldsymbol{a}_2 \times \boldsymbol{a}_3)| = a^3.$$

Examples of materials that crystallise in simple cubic form are Nitrogen (at $20°$ K), Caesium Chloride (CsCl with $a = 0.411\mathring{A}$) and the mineral Perovskite (CaTiO$_3$ with $a = 2.94\mathring{A}$). *

Ceasium Chloride

Perovskite

There is one full Caesium atom in each primitive cell of a CsCl crystal, there are eight blue dots at the vertices of the cube, but only one-eighth of each dot is inside the primitive cell. Similarly there are six red dots on the faces of the cube for CaTiO$_3$ but only half of each dot is inside the cube, so there are three Oxygen atoms in each primitive cell.

Note that CsCl and CaTiO$_3$ have different crystal structures, but the same lattice structures — their bases are different.

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* Perovskite is an important ingredient in geology: it is believed that the lower part of the Earth's mantle, between 700 and 2,500 km down, could be more than 90% Perovskite.

2. Body centred cubic

Putting an extra lattice point at the centre of every primitive cell of a simple cubic lattice gives a distinct lattice structure called **body centred cubic**. A body centred cubic lattice can be viewed as two interwoven simple cubic lattices, as shown on the right below.
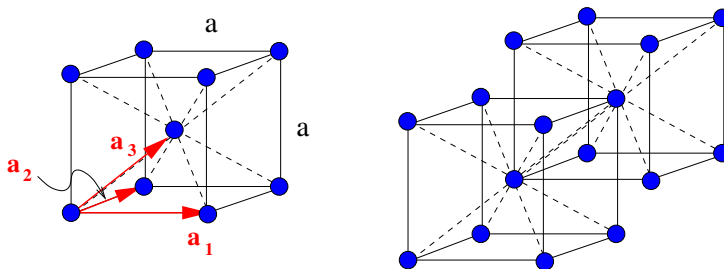
The picture on the left above is not a primitive cell, it contains two lattice points, but is still a useful way of visualising a body centred cubic lattice — it is called a **conventional cell**. A set of primitive lattice vectors is shown above,

$$\boldsymbol{a}_1 = a\hat{\mathbf{x}}, \qquad \boldsymbol{a}_2 = a\hat{\mathbf{y}}, \qquad \boldsymbol{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}).$$

The volume of a primitive cell is

$$V_c = |\boldsymbol{a}_1.(\boldsymbol{a}_2 \times \boldsymbol{a}_3)| = \frac{a^3}{2}.$$

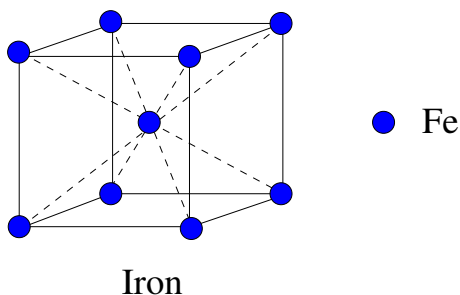An alternative set, which is more symmetric, is

$$\boldsymbol{a}_1' = \frac{a}{2}(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \qquad \boldsymbol{a}_2' = \frac{a}{2}(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}) \qquad \boldsymbol{a}_3' = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}),$$

with has the same volume,

$$V_c = |\boldsymbol{a}_1'.(\boldsymbol{a}_2' \times \boldsymbol{a}_3')| = \frac{a^3}{2},$$

as it must do if it is to be a primitive cell.

Examples of materials that crystallise in body centred form are iron, Fe, potassium, K, and Sodium, Na.

Iron

Note that CsCl is *not* a body centred lattice: the Cl atom at the centre of the cell is different to the Ce atoms at the vertices, so the central point is not equivalent to the

vertices — it is not a lattice point. Do not confuse the lattice structure of CsCl with that of Iron — they are different.

The Wigner-Seitz cell for a body centred cubic lattice is a truncated octahedron:

BCC Lattice Cell

Conventional Cell

Wigner–Seitz Cell
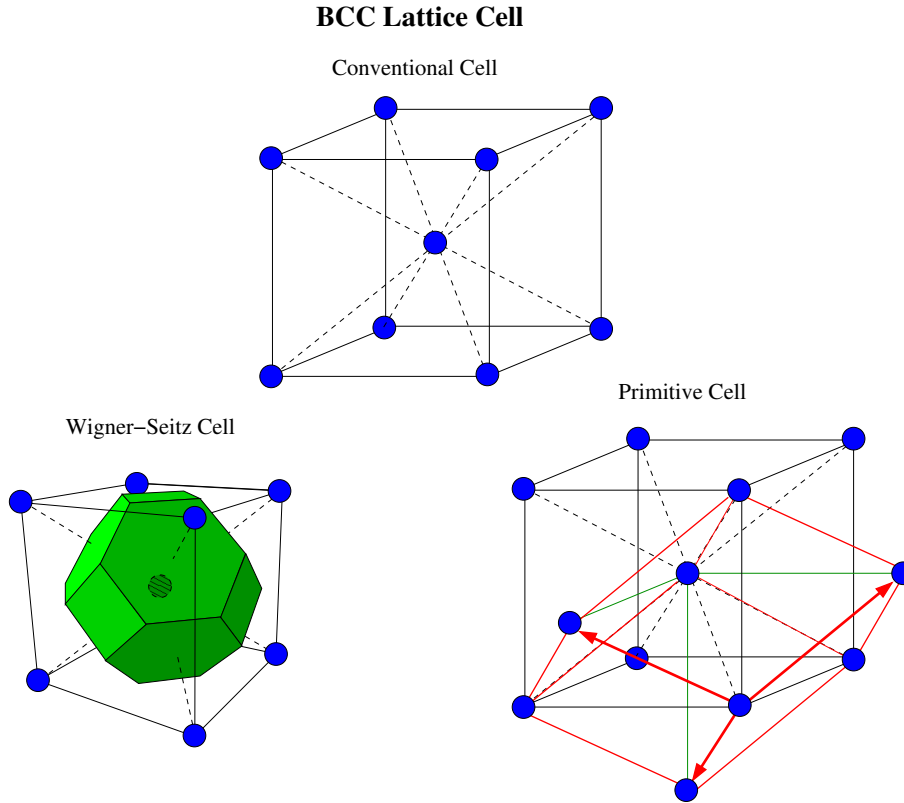
Primitive Cell

3. Face centred cubic

Putting an extra lattice point at the centre of the faces of a primitive cell of a simple cubic lattice gives another distinct lattice structure called **face centred cubic**. A face centred cubic lattice can be viewed as four interwoven simple cubic lattices.
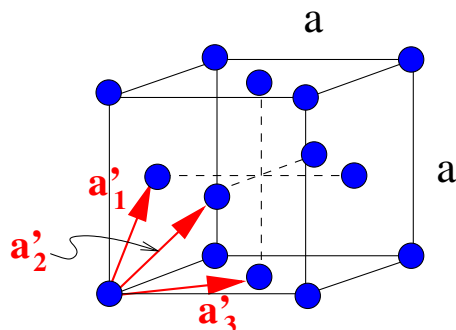
The picture above is not a primitive cell because it contains four lattice points, it is a **conventional cell** of the face centred lattice. A set of primitive lattice vectors, as shown above, is
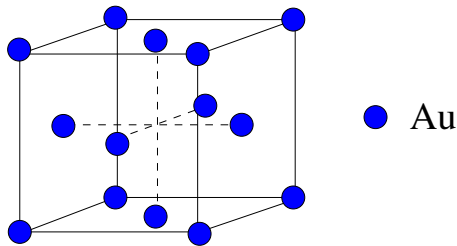
$$\boldsymbol{a}'_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}) \qquad \boldsymbol{a}'_2 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}}) \qquad \boldsymbol{a}'_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}),$$

The volume of a primitive cell is

$$V_c = |\boldsymbol{a}_1.(\boldsymbol{a}_2 \times \boldsymbol{a}_3)| = \frac{a^3}{4},$$

where a is the size of a conventional cell.

Examples of metals that crystallise in face centred form are aluminium, gold and lead, with bases consisting of a single atom at every lattice site.


Salt, NaCl, is face centred, with $a = 3.56\overset{\circ}{A}$, it is *not* simple cubic!
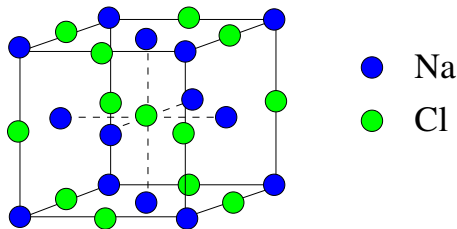
Diamond has a face centred structure with a basis consisting of two carbon atoms, one at the origin (front-bottom-left corner) and one at $\frac{a}{4}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$, and a identical pair at all lattice sites of course. This structure allows each carbon to be linked to its four nearest neighbours, each a distance $\frac{\sqrt{3}a}{4}$ away, by covalent bonds. Si, Ge and Sn have the same structure as diamond.
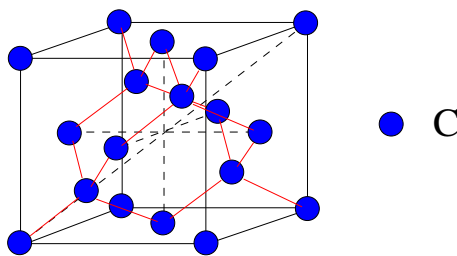
Zinc sulphide, ZnS, has a similar structure, except the base pair is ZnS rather than two identical carbon atoms,
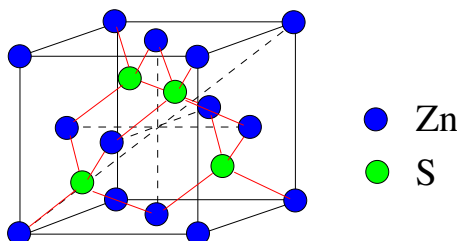
Carbon 60 (buckyballs) has also been found to crystallise in face centred cubic form — in this case the basis consists of sixty carbon atoms!
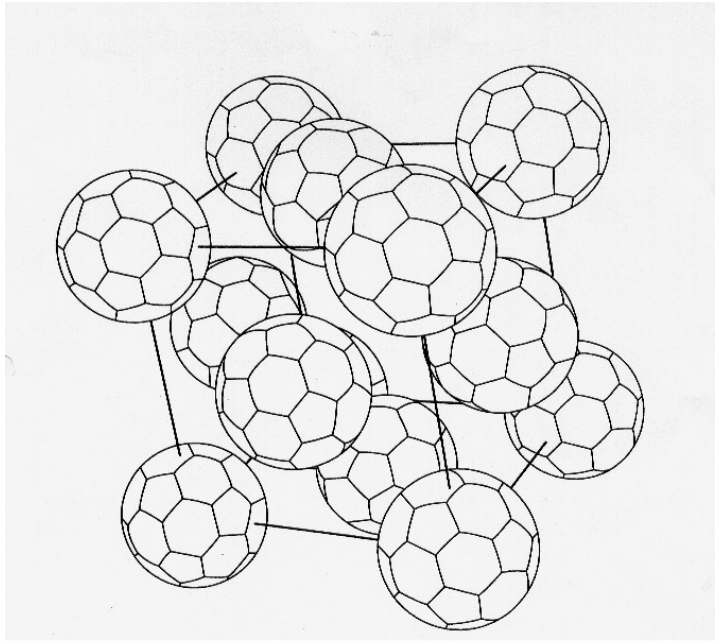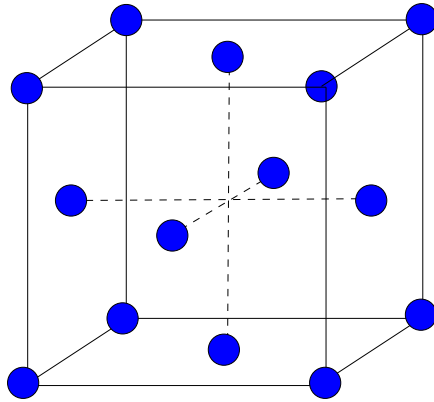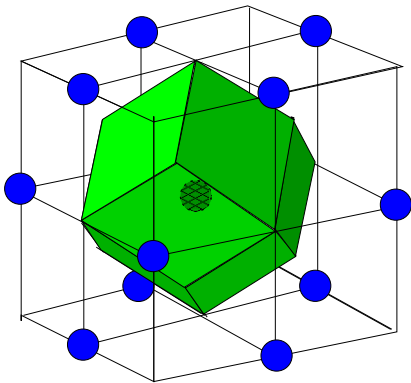

The Wigner-Seitz cell for a face centred cubic lattice is a truncated rhombic dodecahedron:
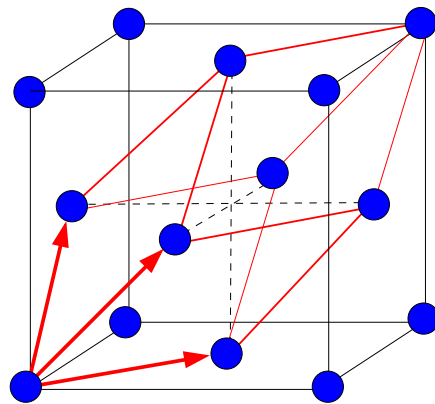
FCC Lattice Cell

Conventional Cell

Wigner−Seitz Cell

Primitive Cell

4. Hexagonal close packed structure

Strictly speaking this is not a Bravais lattice, but it is nevertheless a useful structure to consider as it not infrequently occurs in Nature, *eg.* Mg, Ti, Zn. The hexagonal close packed structure consists of two interwoven 3-dimensional hexagonal lattices and, like diamond, it is really a Bravais lattice (3-d hexagonal) with a basis consisting of two identical atoms. It is constructed by stacking 2-dimesnional hexagonal lattices on top of each other in the sequence ABAB... as shown in the upper figure below:

Hexagonal Close Packed Structure

2nd layer at B

3rd layer at A

2−d hexagonal lattice
array of spheres, radii a/2

ABABA....

ABCABC...
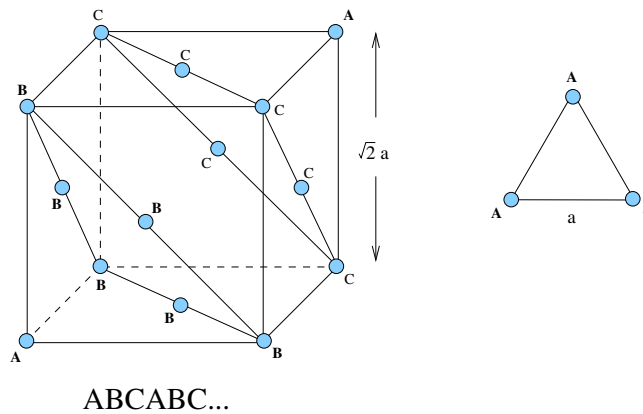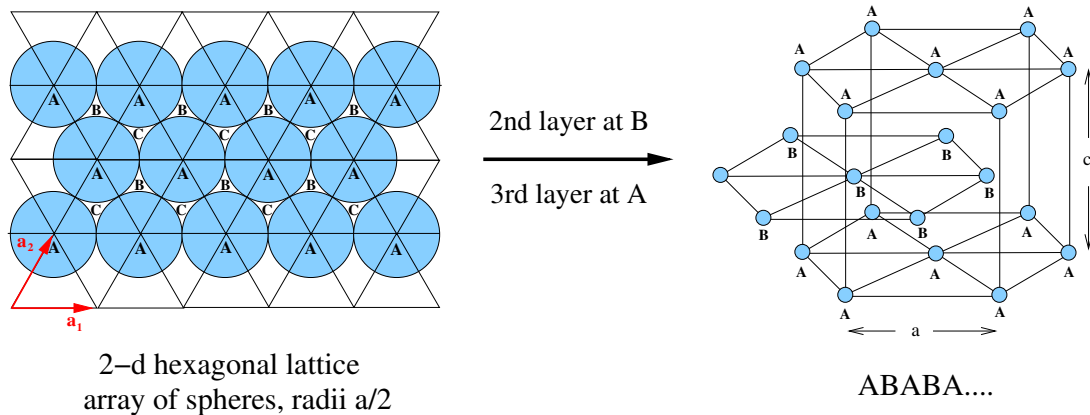
For optimal close packing with identical spheres $c = \sqrt{\frac{8}{3}}a$. Magnesium for example crystallises in a hexagonal close packed structure with $a = 3.21\mathring{A}$ and $c = 5.21\mathring{A}$, giving $\frac{c}{a} = 1.62$.

Different sequences of stacking hexagonal lattices give different structures. For example, as shown in the lower picture above, ABCABC... is equivalent to face centred cubic. Other sequences are possible, *e.g* ABACABAC... for some rare earth metals.

Filling fractions

Solids have higher densities than liquids or gases, because their atoms are closely packed. For example we can calculate the fraction of space filled by a spherical monatomic basis in a simple cubic crystal. For a cell size a the basis atoms just touch if their radius is $\frac{a}{2}$.
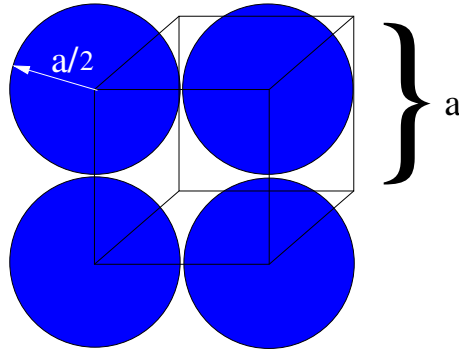
Each primitive cell has a volume $V_c = a^3$ and contains one complete sphere with volume $\frac{4\pi}{3}\left(\frac{a}{2}\right)^3 = \frac{\pi}{6}a^3$, so the fraction of space that is filled by solid spheres of radius $\frac{a}{2}$, the **packing fraction** is

$$\frac{V_{Sphere}}{V_c} = \frac{\pi}{6} = 0.524...$$

For some other structures the packing fractions are:

$$\mathbf{FCC}: \frac{\sqrt{2}\pi}{6} = 0.740...$$

$$\mathbf{BCC}: \frac{\sqrt{3}\pi}{8} = 0.68...$$

$$\mathbf{Diamond}: \frac{\sqrt{3}\pi}{16} = 0.34...$$

(the first two are for a monatomic spherical basis).

We finish this section with a couple of observations. First, note that the decomposition `Crystal = Lattice + Basis` is not necessarily unique. For example a body centred cubic lattice with a single monatomic basis (*e.g.* iron) is identical to a simple cubic lattice with a basis consisting of two identical atoms, one at the origin and one at the centre, $\frac{a}{2}(\hat{\mathbf{x}}+\hat{\mathbf{y}}+\hat{\mathbf{z}})$,
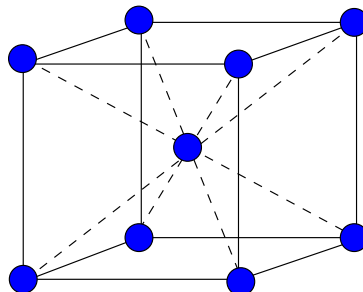
Secondly we observe that, once the basis is included, the symmetry of the crystal might be smaller than that of the lattice. The list of possible crystal point groups and space groups is larger than those of lattices:

Lattices: 7 point groups; 14 space groups
Crystals: 32 point groups; 230 space groups

We shall not list all possible crystal space groups here. In four dimensions there are 52 Bravais lattices (different lattice space groups).

3. Reciprocal Lattices

Bragg Law

Experimentally crystal structure can be determined by **diffraction** experiments. Typical atomic separations in a crystal are of the order of $1\mathring{A} = 10^{-10}\ m$ so we need wavelengths of this order to resolve the structure. For electromagnetic radiation this corresponds to X-rays, though we can also use electrons or neutrons whose de Broglie wavelength is $\lambda \approx 1\mathring{A}$.

For concreteness let's consider X-rays reflecting off 2-dimensional planes in a crystal. Generically the X-rays experience partial reflection — part of the wave is transmitted and the remainder reflected. The reflected wave can experience interference between lattice planes, either constructive or destructive depending on the angle of incidence. In the figure below there is constructive interference when the path difference between the two waves shown is an integral multiple N of the wavelength,
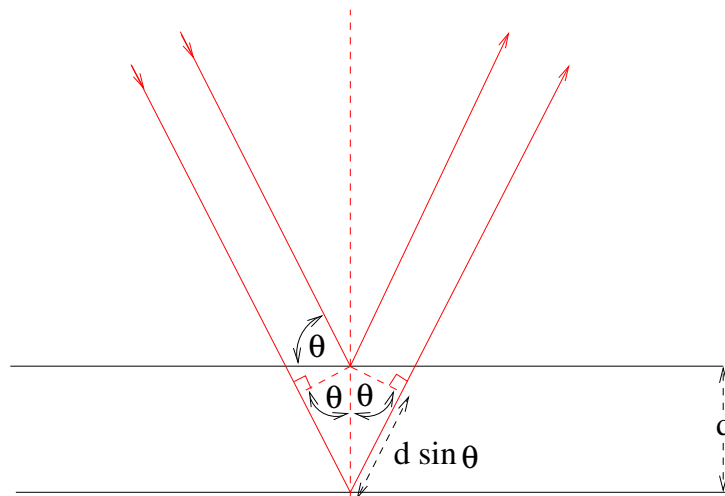
There is constructive interference when

$$2d\sin\theta = N\lambda.$$
(1)

This is known as **Bragg's Law**. Since N is an integer only some specific angles, given by $\sin\theta = \frac{N\lambda}{2d}$, will give strong reflection — angles of incidence that do not satisfy this criterion for any integer N will tend to be transmitted rather than reflected. There will be peaks in intensity, **Bragg peaks**, for special directions such that angle θ satisfies (1) — other directions will receive no scattered X-rays. Bragg peaks manifest themselves as bright spots as seen in this X-ray diffraction pattern for a crystal of Alum (hydrated potassium aluminium sulfate, $\mathrm{K\,Al\,(SO_4)_2.12H_2O}$).
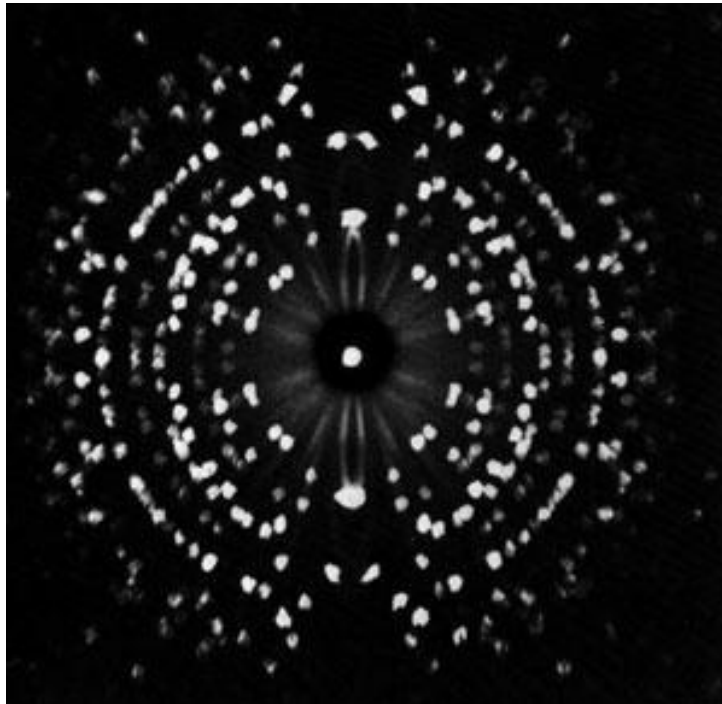
This simple derivation of the Bragg law assumes that X-rays scatter off smooth 2-dimensional planes, like partially transparent mirrors, but in reality they scatter off the electrons in atoms which are localised near points in the plane. To make further progress we need a more realistic mathematical model of the diffraction process. First we define a **lattice plane**.

Lattice planes and Miller indices

A lattice plane is a two-dimensional plane passing through any three non-colinear points of a three-dimensional lattice. Due to periodicity of the original lattice a lattice plane always contains an infinite number of points. A lattice plane is in fact always one of the five two-dimensional Bravais lattices.

For example consider an orthorhombic lattice with primitive lattice vectors $\boldsymbol{a}_1 = a\,\hat{\mathbf{x}}$, $\boldsymbol{a}_2 = b\,\hat{\mathbf{y}}$ and $\boldsymbol{a}_3 = c\,\hat{\mathbf{z}}$. A general lattice point can be represented by the lattice vector

$$\mathbf{L} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3 = n_1 a\,\hat{\mathbf{x}} + n_2 b\,\hat{\mathbf{y}} + n_3 c\,\hat{\mathbf{z}},$$

with n_1, n_2 and n_3 three integers. So $\mathbf{L}$ has Cartesian co-ordinates $x = n_1 a$, $y = n_2 b$ and $z = n_3 c$.

A linear relation between x, y and z defines a plane, *e.g.*

$$\frac{h}{a}x + \frac{k}{b}y + \frac{l}{c}z = p, \tag{2}$$

with h, k, l and p fixed constants. If we allow p to vary, equation (2) defines a family of parallel planes. So, if (x, y, z) is a lattice point, the constraint

$$hn_1 + kn_2 + ln_3 = p \tag{3}$$

defines a family of parallel planes, one for each value of p (the plane with $p = 0$ contains the origin). To describe this family of parallel planes it is sufficient to consider $p = 0$, since we can always choose the origin to lie in any given lattice plane. So we need only consider

$$hn_1 + kn_2 + ln_3 = 0. \tag{4}$$

For an infinite number of solutions to this equation, (n_1, n_2, n_3), which are not co-linear, h, k and l must be rational numbers, and we can always multiply (4) by the least common multiple of their denominators to make them integers — so we can choose h, k and l to be integers without any loss of generality. The smallest three integers (h, k, l) that define a family of parallel lattice planes are called **Miller indices**.

Note:
  i) If a lattice plane is parallel to one of the primitive lattice vectors then the corresponding co-efficient in (3) is infinity and the Miller index is 0.
 ii) When there is no possibility of confusion, commas are omitted from the triple (h, k, l) and (hkl) denotes either a single lattice plane or the set of equally spaced parallel planes, one for each value of p.
iii) By convention the Miller indices associated with a negative co-efficient in (3) is indicated with a bar above it, e.g. $(hk\bar{l})$.
 iv) Another convention is that square brackets, $[hkl]$, denotes the direction normal to the plane (hkl). For simple cubic lattices $[hkl]$ is in the same direction as some lattice vector $\mathbf{L}$, but this is not the case for all of the Bravais lattices.

Examples of Miller indices for lattice planes in a simple cubic lattice

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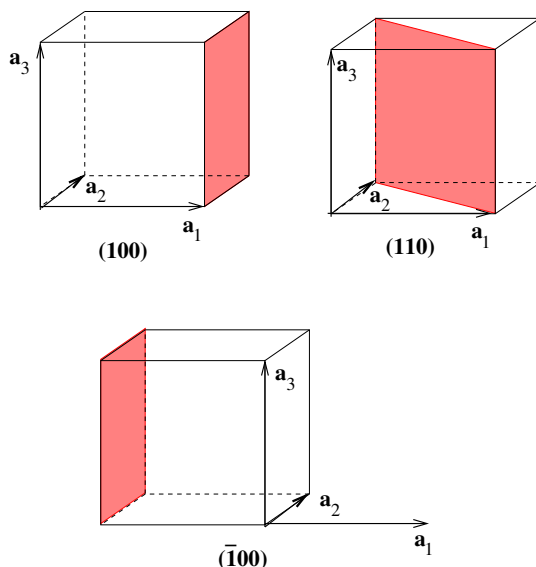
Reciprocal Lattice

The above simple derivation of Bragg's law ignores the periodic structure of the lattice planes and we have to be more sophisticated in order to understand fully the kind of X-ray diffraction pattern shown above. X-rays scatter elastically off electrons in the atoms that make up the crystal. Denote the density of electrons at a point $\mathbf{r}$ by $\rho(\mathbf{r})$ (with dimensions of $1/length^3$). Since the crystal is periodic $\rho(\mathbf{r})$ should be a periodic function, $\rho(\mathbf{r} + \mathbf{L}) = \rho(\mathbf{r})$ for any lattice vector $\mathbf{L}$. Since $\rho(\mathbf{r})$ is periodic we can write it as a three-dimensional Fourier series.

As a warm-up exercise, first consider the simple case of a one dimensional monatomic lattice, *i.e.* a line of periodically spaced atoms, each a distance a from its nearest neighbours on either side, so the one dimensional electron density is a periodic function of its argument x,

$$\rho(x) = \rho(x + a).$$

Periodic functions can be expanded as a Fourier series

$$\rho(x) = \rho_0 + \sum_{m=1}^{\infty} A_m \cos\left(\frac{2\pi m x}{a}\right) + \sum_{m=1}^{\infty} B_m \sin\left(\frac{2\pi m x}{a}\right).$$

$$\rho_0 = \frac{1}{a} \int_0^a \rho(x) dx$$

is just the average density over a single period and the co-efficients A_m and B_m can be calculated from $\rho(x)$ in the standard way

$$A_m = \frac{2}{a} \int_0^a \cos\left(\frac{2\pi m x}{a}\right) \rho(x) dx$$

$$B_m = \frac{2}{a} \int_0^a \sin\left(\frac{2\pi m x}{a}\right) \rho(x) dx.$$

It will be convenient to re-express the Fourier series as a sum of complex exponentials,

$$\rho(x) = \sum_{m=-\infty}^{\infty} \rho_m e^{\frac{2\pi i m x}{a}},$$

where the Fourier co-efficients $A_m = \rho_m + \rho_{-m}$ and $B_m = i(\rho_m - \rho_{-m})$ for $m \geq 1$ are real numbers. The Fourier co-efficients in exponential form, ρ_m and ρ_{-m}, are complex in general but must satisfy $\rho_m^* = \rho_{-m}$ since $\rho(x)$ is real. In fact $\rho_m = \frac{1}{2} A_m + \frac{1}{2i} B_m$ and $\rho_{-m} = \frac{1}{2} A_m - \frac{1}{2i} B_m$ for $m \geq 1$. The co-efficients ρ_m are obtained from

$$\rho_m = \frac{1}{a} \int_0^a \rho(x) e^{-\frac{2\pi i m x}{a}} dx$$

for all integral m.

We seek a similar decomposition for all of the three dimensional Bravais lattices. Consider first a simple cubic lattice, with lattice spacing a. This is very like three copies of the one dimensional lattice and we can write

$$\rho(\mathbf{r}) = \sum_{m_1=-\infty}^{\infty} \sum_{m_2=-\infty}^{\infty} \sum_{m_3=-\infty}^{\infty} \rho_{m_1,m_2,m_3} e^{\frac{2\pi i m_1 x}{a}} e^{\frac{2\pi i m_2 y}{a}} e^{\frac{2\pi i m_3 z}{a}} \tag{5}$$

The only subtlety is that this *cannot* be written as

$$\left(\sum_{m_1=-\infty}^{\infty} \rho_{m_1} e^{\frac{2\pi i m_1 x}{a}} \right) \left(\sum_{m_2=-\infty}^{\infty} \rho_{m_2} e^{\frac{2\pi i m_2 y}{a}} \right) \left(\sum_{m_3=-\infty}^{\infty} \rho_{m_3} e^{\frac{2\pi i m_3 z}{a}} \right)$$

because there is no reason to assume that ρ_{m_1,m_2,m_3} can be factorised into $\rho_{m_1}\rho_{m_2}\rho_{m_3}$, and in general it cannot. Equation (5) can be written more compactly as

$$\rho(\mathbf{r}) = \sum_{\{m_1,m_2,m_3\}} \rho_{m_1,m_2,m_3} e^{\frac{2\pi i \mathbf{m}.\mathbf{r}}{a}} = \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G}.\mathbf{r}}$$

where $\mathbf{r} = x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}}$,

$$\mathbf{G} = \frac{2\pi}{a}(m_1\hat{\mathbf{x}} + m_2\hat{\mathbf{y}} + m_3\hat{\mathbf{z}}),$$

and the sum means the sum over all integer triples (m_1, m_2, m_3).

We can write a similar decomposition for $\rho(\mathbf{r})$ for any three dimensional Bravais lattice

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G}.\mathbf{r}}, \tag{6}$$

where $\rho_{\mathbf{G}}$ are independent of $\mathbf{r}$ and the sum is over all vectors $\mathbf{G}$ for which

$$\rho(\mathbf{r}) = \rho(\mathbf{r} + \mathbf{L}) \quad \Rightarrow \quad \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G}.\mathbf{r}} = \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G}.(\mathbf{r}+\mathbf{L})} \tag{7}$$

for any lattice vector $\mathbf{L}$.

As for one-dimensional Fourier transforms the Fourier co-efficients $\rho_{\mathbf{G}}$ are derivable from the original electron density function $\rho(\mathbf{r})$

$$\rho_{\mathbf{G}} = \frac{1}{V_c} \int_{\substack{Primitive \\ Cell}} \rho(\mathbf{r}) e^{-i\mathbf{G}.\mathbf{r}} dV.$$

The set of all allowed $\mathbf{G}$'s satisfying (7) can be found as follows: define three vectors $\boldsymbol{b}_1$, $\boldsymbol{b}_2$ and $\boldsymbol{b}_3$ in terms of primitive lattice vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ and $\boldsymbol{a}_3$

$$\boldsymbol{b}_1 = 2\pi \frac{\boldsymbol{a}_2 \times \boldsymbol{a}_3}{\boldsymbol{a}_1.(\boldsymbol{a}_2 \times \boldsymbol{a}_3)}, \qquad \boldsymbol{b}_2 = 2\pi \frac{\boldsymbol{a}_3 \times \boldsymbol{a}_1}{\boldsymbol{a}_1.(\boldsymbol{a}_2 \times \boldsymbol{a}_3)}, \qquad \text{and} \qquad \boldsymbol{b}_3 = 2\pi \frac{\boldsymbol{a}_1 \times \boldsymbol{a}_2}{\boldsymbol{a}_1.(\boldsymbol{a}_2 \times \boldsymbol{a}_3)}. \tag{8}$$

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With this definition it is automatic that

$$\boldsymbol{b}_i . \boldsymbol{a}_j = 2\pi \delta_{ij}$$

where δ_{ij} is the Kronecker δ, equal to 1 if $i = j$ and zero otherwise. Then, for any three integers m_1, m_2 and m_3,

$$\mathbf{G} = m_1 \boldsymbol{b}_1 + m_2 \boldsymbol{b}_2 + m_3 \boldsymbol{b}_3 \tag{9}$$

satisfies

$$e^{i\mathbf{G.L}} = e^{2\pi i(n_1 m_1 + n_2 m_2 + n_3 m_3)} = 1 \tag{10}$$

for any lattice vector $\mathbf{L} = n_1 \boldsymbol{a}_1 + n_2 \boldsymbol{a}_2 + n_3 \boldsymbol{a}_3$, so (7) is automatic.

The set of all vectors $\mathbf{G}$ satisfying (9) itself constitutes a lattice, called the **reciprocal lattice**, with primitive lattice vectors $\boldsymbol{b}_1$, $\boldsymbol{b}_2$, $\boldsymbol{b}_3$.

For a 2-dimensional lattice, just set $\mathbf{a}_3 = \hat{\mathbf{z}}$ and use

$$\boldsymbol{b}_1 = \frac{2\pi(\boldsymbol{a}_2 \times \hat{\mathbf{z}})}{|\boldsymbol{a}_1 \times \boldsymbol{a}_2|}, \qquad \boldsymbol{b}_2 = -\frac{2\pi(\boldsymbol{a}_1 \times \hat{\mathbf{z}})}{|\boldsymbol{a}_1 \times \boldsymbol{a}_2|}.$$

Examples:

i) **Simple Cubic:** primitive lattice vectors,

$$\boldsymbol{a}_1 = a\hat{\mathbf{x}}, \qquad \boldsymbol{a}_2 = a\hat{\mathbf{y}}, \qquad \boldsymbol{a}_3 = a\hat{\mathbf{z}};$$

the reciprocal lattice has primitive lattice vectors

$$\boldsymbol{b}_1 = \frac{2\pi}{a}\hat{\mathbf{x}}, \qquad \boldsymbol{b}_2 = \frac{2\pi}{a}\hat{\mathbf{y}}, \qquad \boldsymbol{b}_3 = \frac{2\pi}{a}\hat{\mathbf{z}}.$$

It is a simple cubic lattice with lattice spacing $\frac{2\pi}{a}$.

ii) **FCC:** conventional cell size a, primitive cell volume $V_c = \frac{a^3}{4}$,

$$\boldsymbol{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}), \qquad \boldsymbol{b}_1 = \frac{2\pi}{(a^3/4)}\left(\frac{a}{2}\right)^2 \left((\hat{\mathbf{x}} \times \hat{\mathbf{y}}) + (\hat{\mathbf{z}} \times \hat{\mathbf{x}}) + (\hat{\mathbf{z}} \times \hat{\mathbf{y}})\right) = \frac{2\pi}{a}(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}});$$

$$\boldsymbol{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}}), \qquad \boldsymbol{b}_2 = \frac{2\pi}{a}(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}});$$

$$\boldsymbol{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}), \qquad \boldsymbol{b}_3 = \frac{2\pi}{a}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}).$$

The reciprocal lattice is body centred cubic, with conventional cell lattice spacing $\frac{4\pi}{a}$.

iii) **BCC:** with conventional cell size a the reciprocal lattice is face centred cubic with conventional cell size $\frac{4\pi}{a}$ (the proof is left as an exercise).

When necessary the original lattice will be referred to as the **direct lattice**, to distinguish it from the reciprocal lattice.

Suppose we have a family of lattice planes, (hkl), with minimal separation d_{hkl}. If $\mathbf{L}$ is a lattice vector in one plane and $\widetilde{\mathbf{L}}$ a lattice vector in another plane, a distance $s\,d_{khl}$ away from the first (with s any positive integer), then

$$(\mathbf{L} - \widetilde{\mathbf{L}}).\hat{\mathbf{n}} = sd_{hkl}$$

where $\hat{\mathbf{n}}$ is a unit normal to the planes.
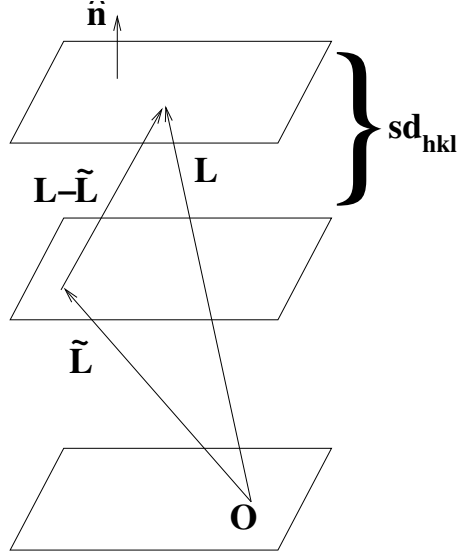
This implies that

$$e^{\frac{2\pi i}{d_{hkl}}\hat{\mathbf{n}}.(\mathbf{L}-\widetilde{\mathbf{L}})} = e^{2\pi is} = 1$$

for all $\mathbf{L} - \widetilde{\mathbf{L}}$ (by varying s, $\mathbf{L}$ and $\widetilde{\mathbf{L}}$ this will include all direct lattice vectors). From the definition (10) this in turn implies that $\mathbf{G} = \frac{2\pi}{d_{hkl}}\hat{\mathbf{n}}$ is a reciprocal lattice vector. It is in fact the shortest reciprocal lattice vector that is normal to the (hkl) planes, hence

$$\mathbf{G}_{hkl} = \frac{2\pi}{d_{hkl}}\hat{\mathbf{n}}$$

has length $\frac{2\pi}{d_{hkl}}$, where d_{hkl} is the distance between neighboring planes among the (hkl) set of planes.

Von Laue condition

We can now derive a more powerful version of the Bragg condition, called the Von Laue condition, which takes into account the fact that lattice planes are collections of lattice points. Consider a beam of X-rays scattering elastically off identical atoms sitting at two lattice points separated by a lattice vector $\mathbf{L}$. Elastic scattering means that the energy, and hence wavelength λ, of the X-rays does not change, only their direction changes. If the incoming beam has wavevector $\mathbf{k} = |\mathbf{k}|\hat{\mathbf{k}}$ in the $\hat{\mathbf{k}}$ direction and the outgoing beam has $\mathbf{k}' = |\mathbf{k}|'\hat{\mathbf{k}}'$ in the $\hat{\mathbf{k}}'$ direction then $|\mathbf{k}| = |\mathbf{k}'| = \frac{2\pi}{\lambda}$ ($\hat{\mathbf{k}}$ and $\hat{\mathbf{k}}'$ are unit vectors in the directions $\mathbf{k}$ and $\mathbf{k}'$).
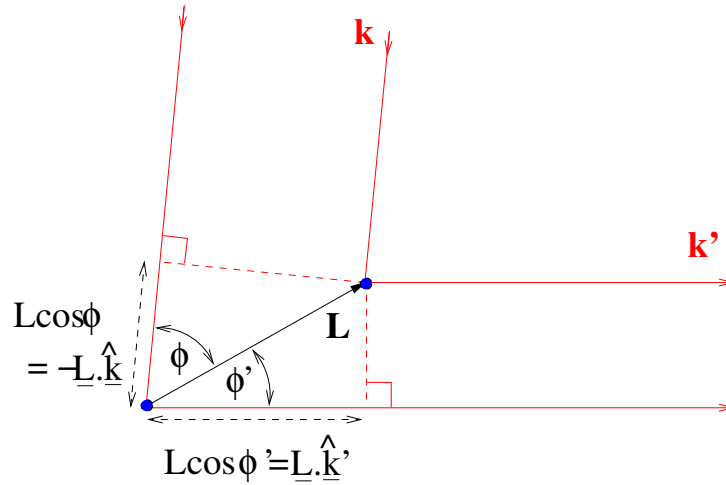
From the diagram above the path difference between two X-rays scattering off the two atoms is $\mathbf{L}.(\hat{\mathbf{k}}' - \hat{\mathbf{k}})$. Constructive interference requires

$$\mathbf{L}.(\hat{\mathbf{k}}' - \hat{\mathbf{k}}) = N\lambda$$

where N is an integer. Hence

$$\mathbf{L}.(\mathbf{k}' - \mathbf{k}) = 2\pi N,$$

since $k = k' = \frac{2\pi}{\lambda}$. There will be a huge enhancement in the intensity of the scattered wave if this is true for all lattice vectors $\mathbf{L}$, that is if

$$e^{i\mathbf{L}.(\mathbf{k}-\mathbf{k}')} = 1 \tag{11}$$

for all $\mathbf{L}$, which is equivalent to the statement that

$$\mathbf{G} = \mathbf{k} - \mathbf{k}'$$

is a reciprocal lattice vector, (10). From this follows

$$-\mathbf{k}' = \mathbf{G} - \mathbf{k} \qquad \Rightarrow \qquad |\mathbf{k}'|^2 = \mathbf{G}^2 - 2\mathbf{G}.\mathbf{k} + |\mathbf{k}|^2,$$

giving

$$\boxed{\mathbf{G}^2 = 2\mathbf{G}.\mathbf{k}} \tag{12}$$

since $|\mathbf{k}'|^2 = |\mathbf{k}|^2$. This is the **von Laue condition**, a scattered X-ray will show a peak in intensity if the incoming wavevector $\mathbf{k}$ satisfies this condition for some reciprocal lattice vector $\mathbf{G}$.

This is related to the Bragg condition (1) as follows. Since $\mathbf{G}$ is a reciprocal lattice vector and it is an integral multiple, $\mathbf{G} = N\mathbf{G}_{hkl}$, of some shortest reciprocal lattice vector,

$\mathbf{G}_{hkl}$, for three integers h, k and l. If (hkl) have no common divisor[3] then $\mathbf{G}_{hkl} = \frac{2\pi}{d_{hkl}}\hat{\mathbf{n}}$ has magnitude $|\mathbf{G}_{hkl}| = \frac{2\pi}{d_{hkl}}$ where d_{hkl} is the distance between neighbouring (hkl) lattice planes. The von Laue condition is

$$\frac{|\mathbf{G}|}{2} = \hat{\mathbf{G}}.\mathbf{k} = |\mathbf{k}|\sin\theta$$

where the angle θ is defined in the figure below,
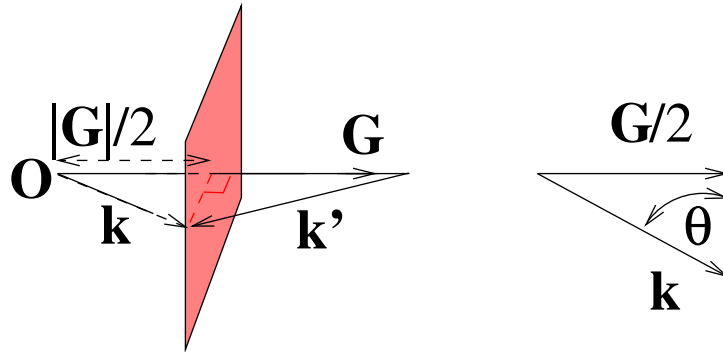
Hence

$$\frac{|\mathbf{G}|}{2} = \frac{\pi N}{d_{hkl}} = |\mathbf{k}|\sin\theta = \frac{2\pi}{\lambda}\sin\theta \qquad \Rightarrow \qquad 2d_{hkl}\sin\theta = N\lambda,$$

which is the Bragg condition (1) with $d = d_{hkl}$.

From the figure above it can be seen that the maximum intensity in the scattered ray is achieved when the tip of the wavevector $\mathbf{k}$ lies in a plane which is the perpendicular bisector of a reciprocal lattice vector $\mathbf{G} = N\mathbf{G}_{hkl}$ for some (hkl) — this called the **Bragg plane** for the incoming wave. Most $\mathbf{k}$ will not lie in a Bragg plane and so will not give peak intensity for the scattered wave.

Ewald construction

A neat way of visualising the von Laue condition is the **Ewald construction**. Choose an origin $\mathbf{O}$ at a point in the reciprocal lattice and place the tail of $\mathbf{k}$ at $\mathbf{O}$. Draw a circle of radius $|\mathbf{k}|$ centred on the tip of $\mathbf{k}$, so it passes through the tail of $\mathbf{k}$. $\mathbf{k}$ will generate a Bragg peak if and only if another reciprocal lattice point $\mathbf{G}$ (other than $\mathbf{O}$) lies on the circle.


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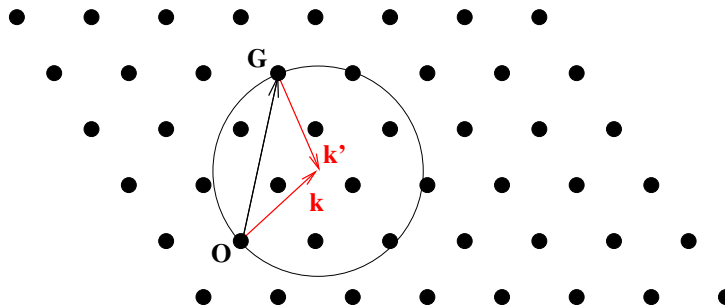
[3] The k in (hkl) here is an integer describing reciprocal lattice planes, *not* the wave number of the incoming X-ray!

Three common methods of observing diffraction peaks are:

1) **Laue method:** fix the direction of **k** relative to the crystal and allow |**k**| to vary (*i.e.* vary the wave-length), effectively thickening the circle in the Ewald construction above so that it encompasses some **G**

2) **rotating crystal method:** fix **k** and rotate the crystal, equivalent to rotating the lattice points in the Ewald construction about the origin.

3) **powder method:** use a powder consisting of many small crystals, in random orientations, with **k** fixed. There will always be some small crystals with the lattice in the correct orientation to give a peak.

The Ewald construction makes it clear that if |**k**| is less than the reciprocal lattice spacing there will be no Bragg peaks, *i.e.* the wavelength is too long. If |**k**| is very large compared to the reciprocal lattice spacing, *i.e.* very short wave-lengths, there will be very many such **G**'s and very many allowed directions **k**′, when this happens the Bragg peaks wash out and the pattern is lost. A clear pattern is only seen if |**k**| is larger than the reciprocal lattice spacing, but not too large, corresponding to wavelengths of the order of the direct lattice spacing which, for most crystals, is of the order of a few $\overset{\circ}{A}$. For electromagnetic radiation this corresponds to X-rays, but electrons or neutrons with velocities momenta corresponding to de Broglie wavelengths of a few $\overset{\circ}{A}$ can also be used.

Below is the X-ray diffraction pattern for diamond, taken using the von Laue method. Note the 4-fold symmetry which reflects the underlying cubic structure of diamond:
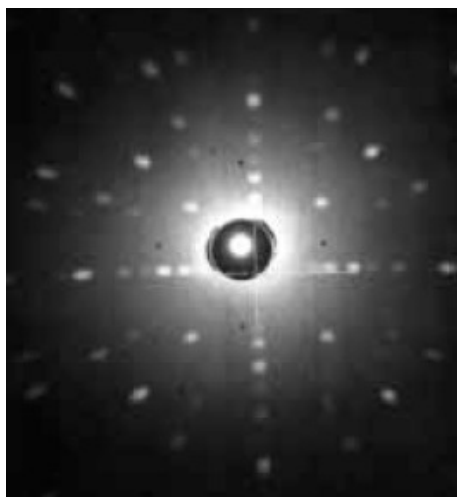
Brillouin zones

A Wigner-Seitz cell of the reciprocal lattice is called a **Brillouin zone**. Brillouin zones are another very useful way of understanding how X-ray diffraction patterns can arise — they will also play a central rôle in understanding crystal vibrations and the movement of electrons through crystals to be studied later. For a one-dimensional lattice for example, with lattice spacing a, the reciprocal lattice has lattice spacing $\frac{2\pi}{a}$ and the region between $-\frac{\pi}{a}$ and $\frac{\pi}{a}$ is a Brillouin zone.

Brillouin
Zone

$2\,\pi/a$
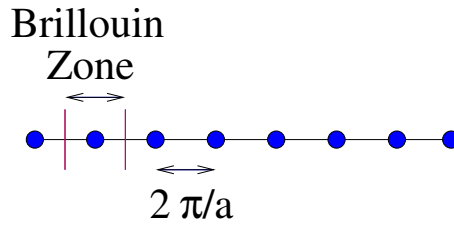
In two or three dimensions the von Laue condition requires that the tip of $\mathbf{k}$, the wavevector of the incoming X-ray, lie on a plane which is the perpendicular bisector of a reciprocal lattice vector $\mathbf{G}$. Consider first a 2-dimensional square lattice, with primitive lattice vectors $\boldsymbol{a}_1 = a\hat{\mathbf{x}}$ and $\boldsymbol{a}_2 = a\hat{\mathbf{y}}$. The reciprocal lattice is also square, with primitive lattice vectors $\boldsymbol{b}_1 = \frac{2\pi}{a}\hat{\mathbf{x}}$ and $\boldsymbol{b}_2 = \frac{2\pi}{a}\hat{\mathbf{y}}$ and reciprocal lattice vectors have the form $\mathbf{G} = m_1\boldsymbol{b}_1 + m_2\boldsymbol{b}_2$, with m_1 and m_2 integers. In the figure below the blue square is bounded by four red lines, each is a perpendicular bisector of a reciprocal lattice vector. The four lattice vectors that are used to construct the blue square are $\pm\boldsymbol{b}_1$ and $\pm\boldsymbol{b}_2$ ($m_1 = \pm 1$, $m_2 = \pm 1$). The blue square is a Wigner-Seitz cell for the reciprocal lattice and is called the **first Brillouin zone**. An incoming X-ray whose wavevector $\mathbf{k}$ has its tail on the central reciprocal lattice point and its head anywhere on the boundary of the blue square will generate a Bragg peak.

Brillouin Zones for Square Lattice
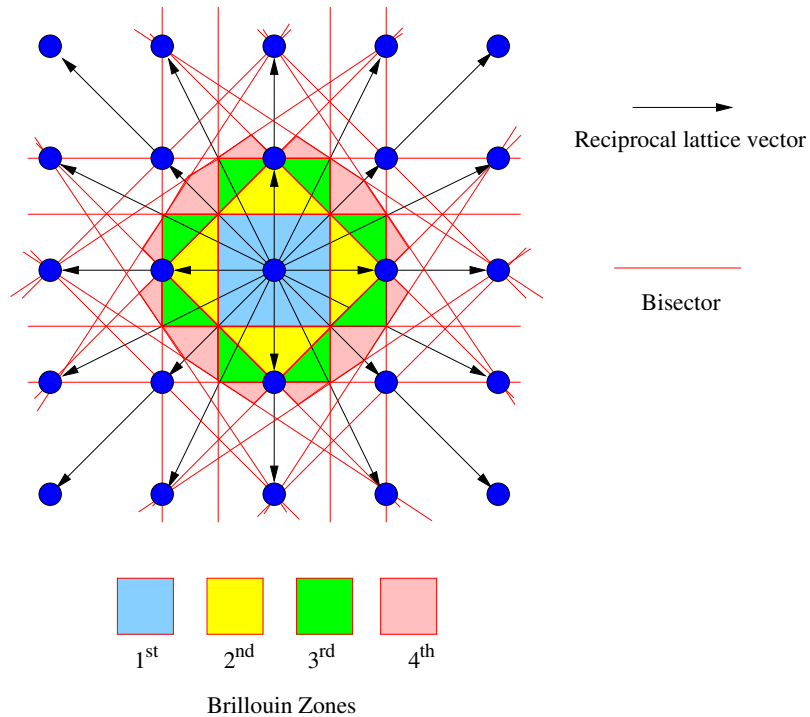
The yellow triangles are bounded on the outside by perpendicular bisectors of the four reciprocal lattice vectors

$$\mathbf{G} = \boldsymbol{b}_1 + \boldsymbol{b}_2, \qquad \mathbf{G} = \boldsymbol{b}_1 - \boldsymbol{b}_2, \qquad \mathbf{G} = -\boldsymbol{b}_1 + \boldsymbol{b}_2, \qquad \mathbf{G} = -\boldsymbol{b}_1 - \boldsymbol{b}_2,$$

and on the inside by the first Brillouin zone, the blue square. They can be pieced together to make a yellow square which is also a Wigner-Seitz cell of the reciprocal lattice, identical in size and shape to the first Brillouin zone. This cell is called the **second Brillouin zone**. An incoming X-ray whose wavevector **k** has its tail on the central reciprocal lattice point and its head anywhere on the boundary of the yellow triangles will generate a Bragg peak.

The green triangles can be pieced together to make a square identical to the blue one — this is the **third Brillouin zone** (can you work out which reciprocal vectors are bisected by the red boundaries?). The pink shapes constitute the fourth Brillouin zone, and so on.

Blue arrows in the figure below give examples of **k**-directions that generate Bragg peaks from the boundary of the first Brillouin zone. The tip if the wavevector is rotated to give the blue circle, only the specific directions where this circle intersects the boundary of a Brillouin zone (red lines) corresponds to an incident direction that gives a Bragg peak. The reflected waves $\mathbf{k}'$ are shown in a lighter blue and, for clarity, they have been extended by dotted blue arrows and labelled by the Miller indices of the reciprocal vector that is bisected by the relevant red line.

Bragg peak directions for square lattice

for fixed |**k**| extending into 2nd Brillouin zone
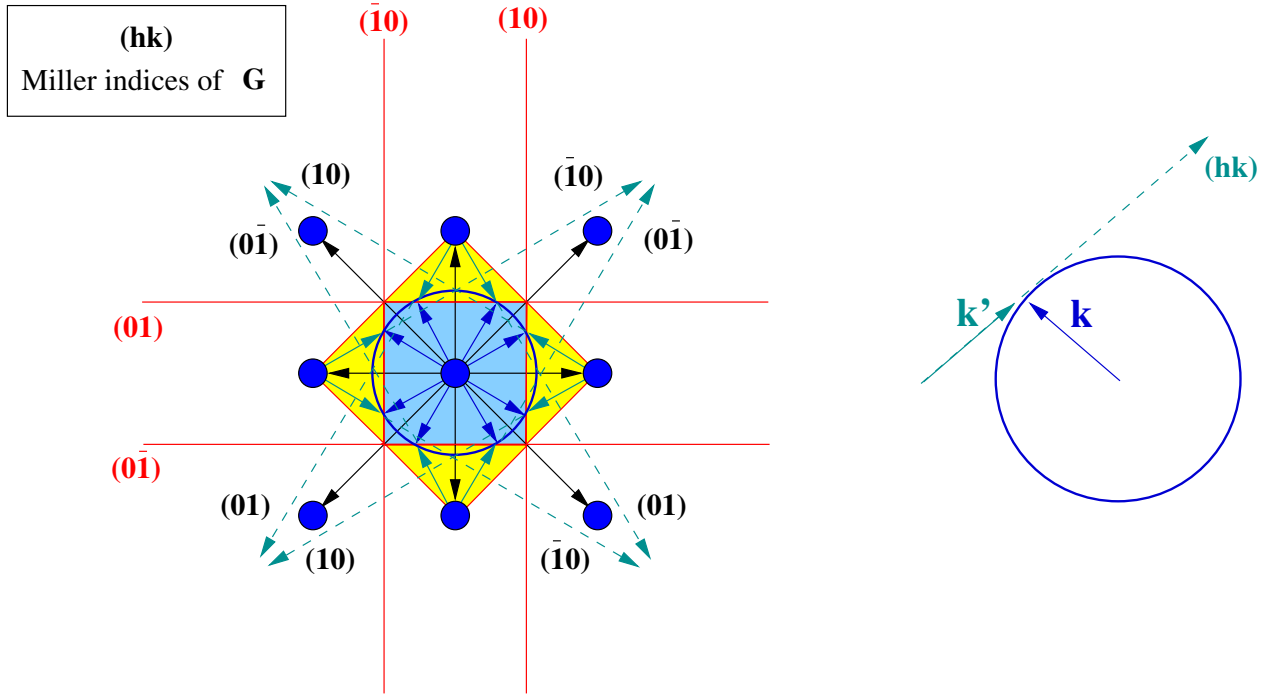
Shorter wavelengths (longer **k**) can scatter off more Brillouin zones: the following figure shows incident directions that give Bragg peaks by scattering off second and even third Brillouin zone boundaries. The second figure below shows the direction of the outgoing (scattered) wave for the same length of **k**.

Bragg peak k−directions for square lattice

(extended
for clarity)

(hk)
Miller indices of **G**
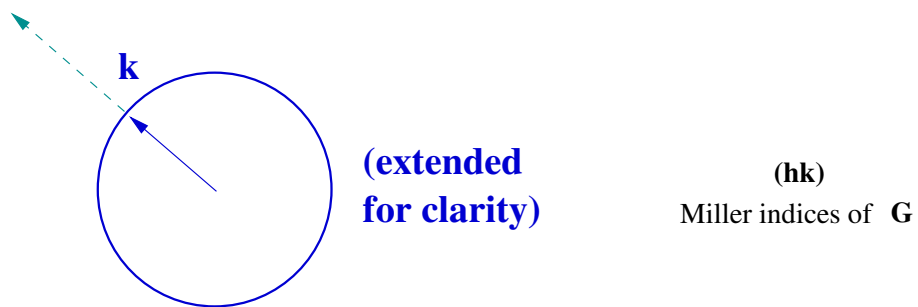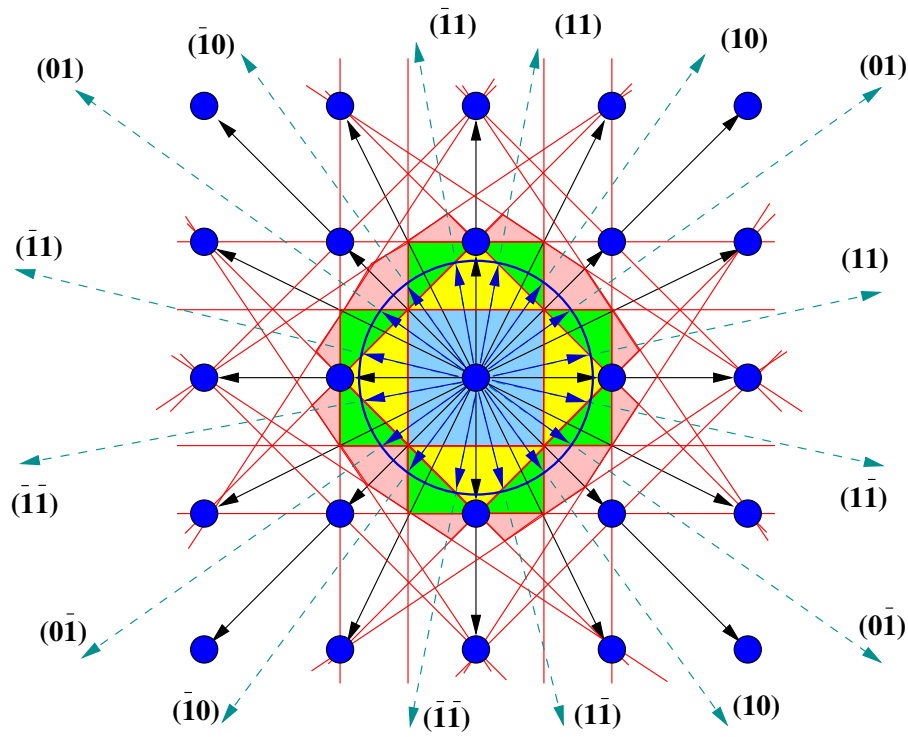
Bragg peak k'−directions for square lattice
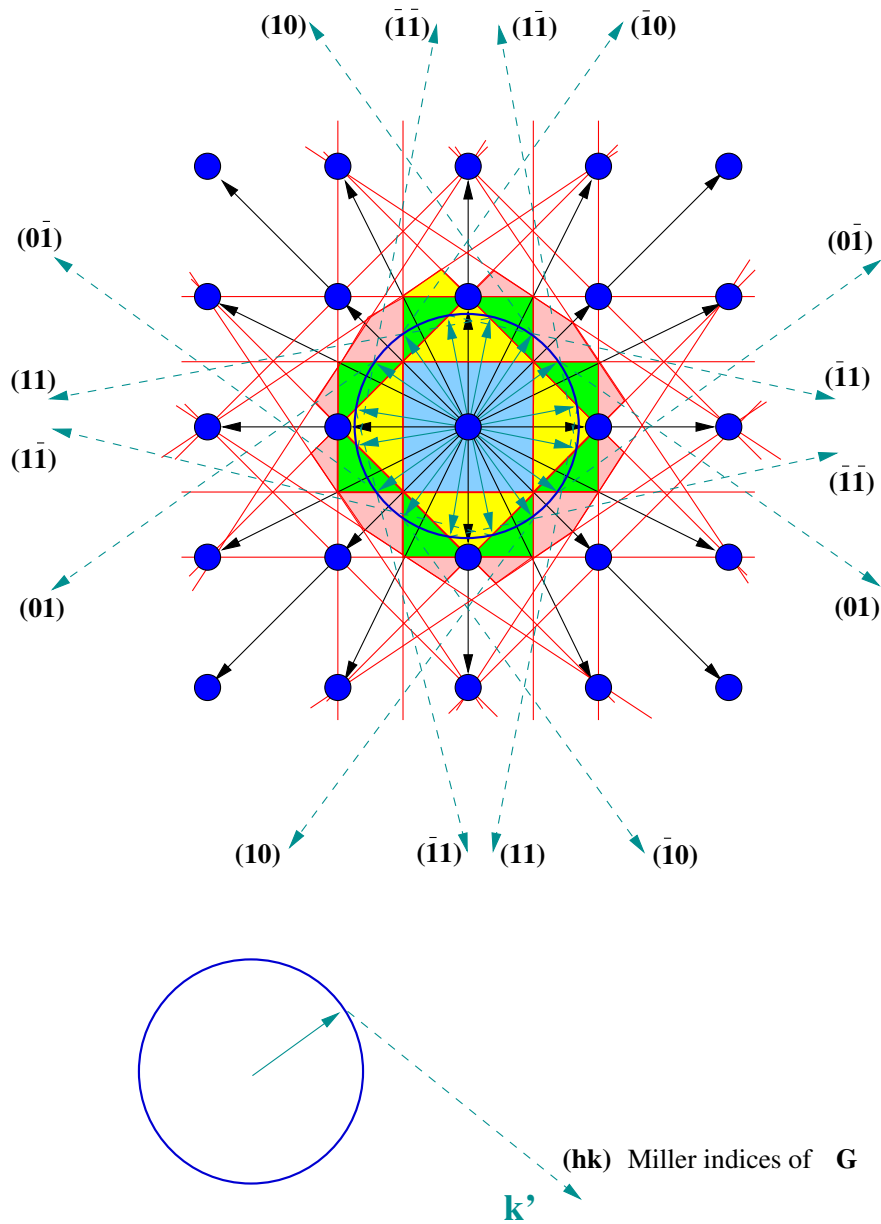
In summary, a Bragg peak is present if and only if the tip of **k** lies on the boundary of a Brillouin zone in the above construction.

Structure factors

So far we have assumed that lattice sites, and only lattice sites, act as point scatterers. Representing the scattered wave by a complex number (the physical wave is the real part) each lattice site $\mathbf{L}$ contributes $e^{i(\mathbf{k}-\mathbf{k'}).\mathbf{L}}$ to the scattered wave, so the total scattered amplitude is proportional to[4] $\sum_{\mathbf{L}} e^{i(\mathbf{k}-\mathbf{k'}).\mathbf{L}}$. If $\mathbf{k} - \mathbf{k'} = \mathbf{G}$ is a reciprocal lattice vector then $e^{i(\mathbf{k}-\mathbf{k'}).\mathbf{L}} = 1$ for every lattice site and every term in the sum adds coherently. If $\mathbf{k} - \mathbf{k'}$ is not a reciprocal lattice vector every term in the sum has a different phase and they combine destructively to give a total of zero.

For a crystal with anything other that a monatomic basis the true story is a little more complicated. Electromagnetic waves scatter predominantly off electrons (electrons react to an incoming wave much more readily than positive ion cores, as they are much lighter and more responsive). Denote the electron density $\rho(\mathbf{r})$ then, in general, the scattered amplitude is proportional to

$$F(\mathbf{k} - \mathbf{k'}) := \int dV \rho(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k'}).\mathbf{r}},$$

where the integral is over the volume of the crystal.

For a monatomic crystal the electron density resides only at lattice sites and we can write

$$\rho(\mathbf{r}) = n_0 \delta(\mathbf{r} - \mathbf{L})$$

where n_0 is the number of electrons in the atom free to respond to the incoming wave and $-e$ is the charge on an electron, but ρ will be more complicated than this for a more general crystal type. With the von Laue condition, $\mathbf{k} - \mathbf{k'} = \mathbf{G}$, we have

$$F = \int_{Crystal} dV \rho(\mathbf{r}) e^{i\mathbf{G}.\mathbf{r}} = \mathcal{N}_c \int_{Cell} dV \rho(\mathbf{r}) e^{i\mathbf{G}.\mathbf{r}},$$

where $\mathcal{N}_c$ is the number of cells in the crystal. The integral over a single cell,

$$S_{\mathbf{G}} = \int_{Cell} dV \rho(\mathbf{r}) e^{i\mathbf{G}.\mathbf{r}},$$

is called the **structure factor** — a dimensionless number, in general complex.

If the basis consists of s atoms at points $\mathbf{r}_j$ in the unit cell, where $j = 1, \ldots, s$, and $\rho_j(\mathbf{r})$ is the electron density of the j-th atom then

$$S_{\mathbf{G}} = \sum_{j=1}^{s} \int_{Cell} dV \rho_j(\mathbf{r}) e^{i\mathbf{G}.\mathbf{r}} = \sum_{j=1}^{s} e^{i\mathbf{G}.\mathbf{r}_j} \int_{Cell} dV \rho_j(\mathbf{r}) e^{i\mathbf{G}.(\mathbf{r}-\mathbf{r}_j)} = \sum_{j=1}^{s} f_j e^{i\mathbf{G}.\mathbf{r}_j},$$

where

$$f_j := \int_{Cell} dV \rho_j(\mathbf{r}) e^{i\mathbf{G}.(\mathbf{r}-\mathbf{r}_j)}$$

---

[4] Remember (11), $e^{i(\mathbf{k}-\mathbf{k'}).\mathbf{L}}=1$ for constructive interference — if it is not unity for all $\mathbf{L}$ different lattice points will give different complex phases and the sum will be zero.

is called the **atomic structure factor**. To a good approximation f_j is independent of $\mathbf{r}_j$ and $\mathbf{G}$, since we expect $\rho_j(\mathbf{r})$ to be strongly localised about $\mathbf{r} = \mathbf{r}_j$, $\rho_j(\mathbf{r}) \approx n_j \delta(\mathbf{r} - \mathbf{r}_j) \Rightarrow f_j \approx n_j$ where n_j is the number of electrons in atoms j that are free to respond to the incoming X-ray.

Example 1: Caesium Chloride has a simple cubic structure with a basis consisting of two atoms ($s = 2$), which we take to be a Caesium atom at $\mathbf{r}_1 = 0$ and a Chlorine atom at $\mathbf{r}_2 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$, using a conventional cell basis $\boldsymbol{a}_1 = a\hat{\mathbf{x}}$, $\boldsymbol{a}_2 = a\hat{\mathbf{y}}$, $\boldsymbol{a}_3 = a\hat{\mathbf{z}}$. Sodium and Chlorine have different electronic structures and we expect them respond differently to X-rays, so $f_1 \neq f_2$. The reciprocal lattice is also cubic, with

$$\mathbf{G} = \frac{2\pi}{a}(h\hat{\mathbf{x}} + k\hat{\mathbf{y}} + l\hat{\mathbf{z}}).$$

This gives

$$S_{hkl} = f_1 + e^{i\frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \cdot \mathbf{G}} f_2 = f_1 + e^{i\pi(h+k+l)} f_2 = \begin{cases} f_1 - f_2 & \text{for } h + k + l \text{ odd;} \\ f_1 + f_2 & \text{for } h + k + l \text{ even.} \end{cases}$$

Indeed experimentally reflections from (200) and (110) planes are stronger than from (100) and (300) planes.

Example 2: Sodium has a BCC structure with a monatomic basis, but we can also think of this a simple cubic structure with a diatomic basis, $s = 2$, consisting of identical atoms of sodium at $\mathbf{r}_1 = 0$ and at $\mathbf{r}_2 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$. This is similar to CsCl, but now $f_1 = f_2$ and we expect all Bragg peaks corresponding to $h + k + l$ odd to be completely absent, and indeed this is the case.

The absence of $h + k + l$ odd planes for BCC crystals can be understood intuitively in a simple two-dimensional example with adjacent lines of atoms off-set from one another,
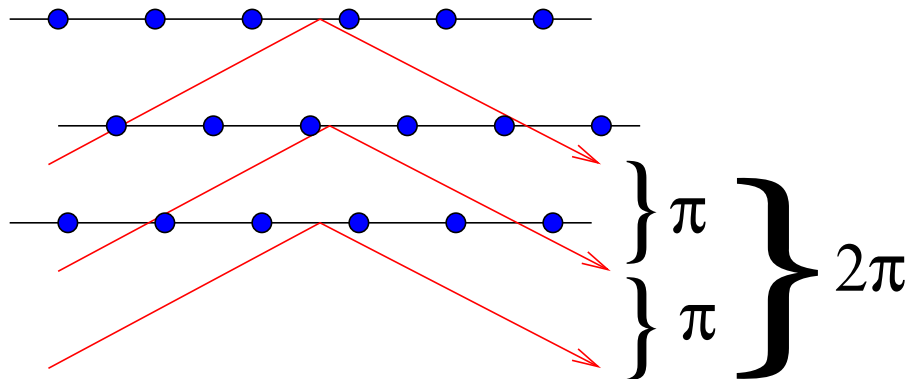
When the phase of the wave reflected from adjacent layers differ by π they interfere destructively, but then the next to adjacent layers must necessarily differ in phase by 2π and interfere constructively.

Diffraction experiments on crystals require wavelengths of a few $\mathring{A}$ corresponding to X-rays for electromagnetic radiation, but we can also use electrons or neutrons with de

Broglie wavelength of similar size. For X-rays the scatters are electrons in the crystal, but for neutrons it is the atomic nuclei that cause scattering while for electrons it is the combined electrostatic potential of the crystal electrons plus the positively charged atomic nuclei that cause scattering. We therefore get different information about the crystal from X-rays, neutron and electron scattering.

4. Crystal Binding

The way in which atoms are bound together to form crystals depends in detail on inter-atomic forces between the atoms making up the crystal. We shall discuss two cases in some depth: inert elements and ionic crystals, but you should bear in mind that there are other cases, such as covalent bonding, that will not be covered in this course.

Inert elements: (*i.e.* noble gases: Ne, Ar, Kr, Xe). These gases tend to form face centred cubic crystals when they solidify, with a monatomic basis. (The physics of solid Helium is very different and will not be covered here.)

To understand their structure we model the force between two atoms separated by $\mathbf{r}$ using the **Lennard-Jones** potential,

$$U(\mathbf{r}) = \frac{B}{r^{12}} - \frac{A}{r^6} = 4\varepsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right\},$$

where A and B are two constants which can be traded for an energy ε and a length σ. The second term above represents an attraction between atoms due to dipole-dipole interactions while the first term is a repulsion due to quantum effects — when the atoms get so close to one another that their outermost electronic orbitals start to overlap the Pauli exclusion principle wants to prevent the electron wave-functions from overlapping too much.

The energy ε and the length σ are characteristics of each element and they can be determined from experiments performed on the gaseous phase, determining the equation of state by measuring virial co-efficients and viscosity,

	Melting Point ($°K$)	$\varepsilon(10^{-23}J)$	$\sigma(\mathring{A})$
Ne	24	50	2.74
Ar	84	167	3.40
Kr	117	225	3.65
Xe	161	320	3.98

The total binding energy of the crystal is obtained by summing the interactions over all pairs of atoms, remembering to divide by 2 to avoid over-counting. For a crystal with $\mathcal{N}$ atoms,

$$U_{Tot} = \left(\frac{\mathcal{N}}{2}\right) 4\varepsilon \sum_{\mathbf{L} \neq 0} \left\{ \left(\frac{\sigma}{|\mathbf{L}|}\right)^{12} - \left(\frac{\sigma}{|\mathbf{L}|}\right)^6 \right\}.$$

A stable configuration requires that the crystal is at a minimum of the potential energy. If the lattice spacing is varied then the lattice vectors $\mathbf{L}$ will change length. Let $\widetilde{\mathbf{L}}$ be lattice

vectors for a lattice with primitive cells having unit volume. Then a lattice with primitive cells having volume R^3 will have lattice vectors $\mathbf{L} = R\widetilde{\mathbf{L}}$. For a monatomic crystal based on a simple cubic lattice R is the same thing as the inter-atomic spacing, but for other Bravais lattices it is not necessarily exactly the same as the inter-atomic spacing though it will be proportional to it. In any case the potential energy of the whole crystal is

$$U_{Tot} = 2\mathcal{N}\varepsilon \left\{ A_{12} \left(\frac{\sigma}{R}\right)^{12} - A_6 \left(\frac{\sigma}{R}\right)^6 \right\}, \tag{13}$$

where

$$A_n := \sum_{\mathbf{L} \neq 0} \frac{1}{|\widetilde{\mathbf{L}}|^n}.$$

Varying R is the same as varying the nearest neighbour separation.

For example in a one-dimensional crystal there is an atom at each lattice site, labelled by an integer k, $\widetilde{\mathbf{L}} = k\hat{\mathbf{x}}$ with $\hat{\mathbf{x}}.\hat{\mathbf{x}} = 1$, and $\mathbf{L} = kR\hat{\mathbf{x}}$ so $|\mathbf{L}| = kR$ and

$$A_n = \sum_{k \neq 0} \frac{1}{k^n} = 2 \sum_{k=1}^{\infty} \frac{1}{k^n}.$$

The sum $\zeta(n) = \sum_{k \neq 0} \frac{1}{k^n}$ is known as the Riemann ζ-function, and it can be calculated analytically when n is even, for example $\zeta(12) = \frac{691\pi^{12}}{638512857}$.

For three dimensional crystals the sums will depend on the lattice type and must be carried out numerically. For FCC lattices the results are

$$A_6 = 14.45392 \cdots, \qquad A_{12} = 12.13188 \cdots$$

(any lattice point in a FCC lattice has 12 nearest neighbours and successive terms in the sum fall off very rapidly, particularly for A_{12} for which by far the greatest contribution to the sum comes from just the nearest neighbors). The equilibrium separation R_0 is obtained by setting

$$\frac{dU_{Tot}}{dR} = 0 \qquad \Rightarrow \qquad -12A_{12}\frac{\sigma^{12}}{R_0^{13}} + 6A_6\frac{\sigma^6}{R_0^7}$$

giving

$$R_0^6 = 2\left(\frac{A_{12}}{A_6}\right)\sigma^6 \qquad \Rightarrow \qquad R_0 = 1.090\sigma.$$

The experimentally measured values of R_0 in real crystals are

	Ne	Ar	Kr	Xe
$\frac{R_0}{\sigma}$	1.14	1.11	1.10	1.09

The increasing discrepancies in Kr, Ar and Ne are due to quantum effects as the outer electron shells are more and more tightly bound in the smaller atoms.

Using $\frac{R_0}{\sigma} = 1.09$ in (13) gives the binding energy per atom in equilibrium

$$\frac{1}{\mathcal{N}} U_{Tot}(R_0) = -8.6\varepsilon.$$

Note that values of ε given above, and hence the binding energy per atom, are proportional to the melting point of the crystals.

Ionic crystals: (*e.g.* NaCl, CsCl, ZnS). Crystals made up of positive and negative ions, such as salt, in a regular array are called *ionic* crystals. The binding force for ionic crystals is due to the Coulomb interaction of the positive and negative charges on the ions. Assuming the atoms are singly ionised the binding energy is obtained from the Coulomb energy between particles of charge $\pm e$ a distance r apart, $\frac{e^2}{4\pi\epsilon_0 r}$. This is a much longer range force than that arising from the Lennard-Jones potential for inert elements. If the separation between nearest neighbour ion pairs of opposite charge is $\mathbf{R}$ and the total number of ion pairs (molecules) is $\mathcal{N}$ then the total electrostatic energy in the crystal is

$$U_{Col} = \frac{e^2 \mathcal{N}}{4\pi\epsilon_0} \left\{ -\frac{1}{|\mathbf{R}|} + \sum_{\mathbf{L} \neq 0} \left(\frac{1}{|\mathbf{L}|} - \frac{1}{|\mathbf{L} + \mathbf{R}|} \right) \right\}. \tag{14}$$

The sum over $\frac{1}{L}$ comes from like sign ions at each lattice point and is positive because like sign ions repel each another.

For example in a one-dimensional crystal, consisting of a regular line of molecules a distance a apart, the nearest neighbour ionic separation is $R = \frac{a}{2}$,

● = +ve ion
● = −ve ion
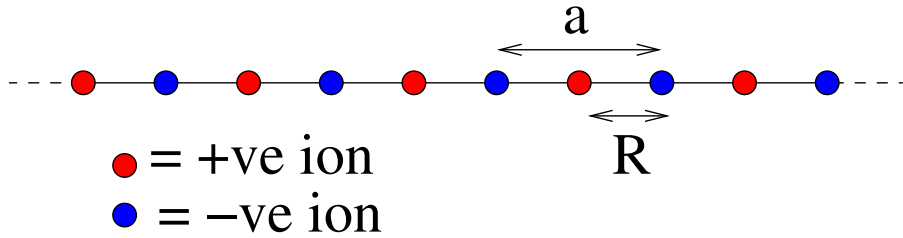
and

$$\begin{aligned}
U_{Col} &= \frac{e^2 \mathcal{N}}{4\pi\epsilon_0} \left(\cdots - \frac{1}{3R} + \frac{1}{2R} - \frac{1}{R} - \frac{1}{R} + \frac{1}{2R} - \frac{1}{3R} + \cdots \right) \\
&= \frac{e^2 \mathcal{N}}{2\pi\epsilon_0} \left(-\frac{1}{R} + \frac{1}{2R} - \frac{1}{3R} + \cdots \right) = -\frac{e^2 \mathcal{N}}{2\pi\epsilon_0 R} \left(1 - \frac{1}{2} + \frac{1}{3} - \cdots \right).
\end{aligned}$$

Note that we use $\mathcal{N}$ here, rather than $\frac{\mathcal{N}}{2}$ as for the inert elements, because we are summing over $2\mathcal{N}$ ions and, dividing by one-half to avoid over-counting just reduces this to $\mathcal{N}$.

We need the sum

$$1 - \frac{1}{2} + \frac{1}{3} - \cdots = \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k}.$$

This is a convergent series,

$$\sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k} = \ln 2, \tag{15}$$

as is seen by Taylor expanding[5]

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \cdots$$

$$\underset{x=1}{\Rightarrow} \quad \ln 2 = 1 - \frac{1}{2} + \frac{1}{3} - \cdots. \tag{16}$$

Thus

$$U_{Col} = -\frac{e^2 \mathcal{N} \alpha}{4\pi\epsilon_0 R}$$

with $\alpha = 2\ln 2 = 1.386294\ldots$.

For a three dimensional crystal the sum over lattice points in (14) must be carried out numerically and the dimensionless number

$$\alpha = -1 + R \sum_{\mathbf{L} \neq 0} \left(\frac{1}{L} - \frac{1}{|\mathbf{L} + \mathbf{R}|} \right) \tag{17}$$

is called the **Madelung constant**. Again it depends on the sequence in which the crystal is put together and it is best to compute it by first assembling small neutral blocks and then putting them together to form the crystal.

The Madelung constant depends on the lattice structure:

Structure	α	Example
SC	1.762675	CsCl
BCC	1.747565	
FCC	1.6381	NaCl

The total energy includes repulsion of the atoms when they get too close to one another, due to the exclusion principle and electron wave-function overlap — this is the same effect as for inert elements. It can be modelled as a $\frac{1}{R^m}$ repulsive potential (for noble gases $m = 12$) but, unlike the inert element case, it is not possible to obtain the form from experiments on the gaseous phase. With this assumption the total potential is

$$U_{Tot} = \mathcal{N} \left(\frac{C}{R^m} - \frac{e^2 \alpha}{4\pi\epsilon_0 R} \right), \tag{18}$$

---

[5] While (15) is correct, the infinite series is convergent, it's value depends on the order in which it is summed, it is said to be *conditionally convergent*. Physically this means, for an infinite crystal, the Coulomb energy stored in the crystal would depend on how the crystal is assembled — real crystals however are never truly infinite and the sums will always really be finite with unambiguous values.

where C is a positive constant. The equilibrium separation, R_0, is obtained by demanding

$$\frac{\partial U_{Tot}}{\partial R}\bigg|_{R_0} = 0 \qquad \Rightarrow \qquad -\frac{mC}{R_0^{m+1}} + \frac{e^2\alpha}{4\pi\epsilon_0 R_0^2} = 0,$$

giving

$$R_0^{m-1} = \frac{4\pi\epsilon_0 mC}{e^2\alpha}.$$

Putting this value of R_0 into (18) gives the binding energy per ion par

$$\frac{U_{Tot}(R_0)}{\mathcal{N}} = -\frac{e^2\alpha}{4\pi\epsilon_0}\left(\frac{m-1}{m}\right)\frac{1}{R_0}.$$

The value of m does not affect the result much, as long as m is large.

5. Crystal Vibrations – Phonons

A real crystal is not a perfect lattice, the atoms and molecules making up the crystal will vibrate about their equilibrium positions. These vibrations will propagate through the crystal at definite speeds, as sound waves. There will also be vibrations due to thermal motion — a warm crystal is continuously humming!

One-dimensional crystal (monatomic basis)

To illustrate the concepts, consider again a one-dimensional monatomic crystal consisting of identical atoms a distance a apart. For small amplitude vibrations we can model the atomic vibrations by thinking of each pair of atoms being linked with a spring with identical spring constant $C > 0$ for each pair, with the spring relaxed when the atoms are a distance a apart. The restoring force on the n-th atom due to the $(n+1)$-th atom on its right is $F = C(x - a)$ (the force is to the right if $x > a$).
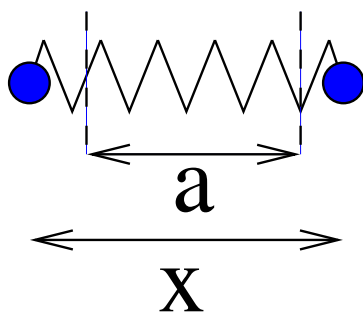

In a chain of such atoms, which are vibrating around their equilibrium positions, denote the position of the n-th atom by x_n. The equilibrium position of the n-th atom is na but when the crystal vibrates $x_n \neq na$ in general. To construct a specific mathematical model we need to specify boundary conditions: we choose[6] $\mathcal{N} + 1$ atoms and fix $x_0 = x_{\mathcal{N}} = 0$. If the atoms are vibrating x_n is a function of time $x_n(t)$. Denote the displacement of the n-th atom from its equilibrium position by $u_n(t)$,

$$u_n(t) = x_n(t) - na,$$

then the total force on the n-th atom is the sum of the forces due to the atoms on either side,

$$F_n = C(x_{n+1} - x_n - a) - C(x_n - x_{n-1} - a) = C(u_{n+1} - 2u_n + u_{n-1}).$$

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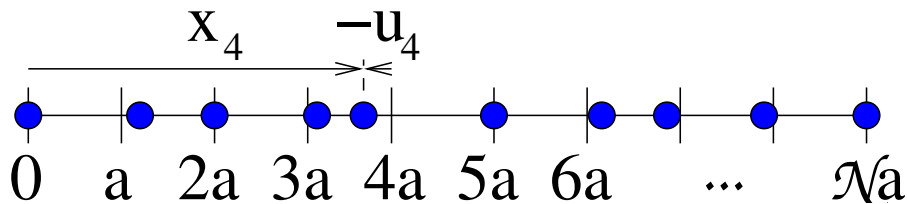
[6] Alternatively we could use periodic boundary conditions on $\mathcal{N}$ atoms and set $x_0 = x_{\mathcal{N}}$ without specifying its value. For very large $\mathcal{N}$ which boundary conditions we choose makes little difference.

If the mass of each atom is M, then Newton's second law implies

$$M\ddot{u}_n = C(u_{n+1} - 2u_n + u_{n-1}). \tag{19}$$

This gives a set of $\mathcal{N}$ coupled linear ODE's for the $u_n(t)$, which we can solve. The solutions are oscillating. Using a complex notation write

$$u_n(t) = \varepsilon_0 e^{-i(\omega t - Kna)} \tag{20}$$

with ω, K and ε_0 constants (the actual displacements are the real part of these complex u_n). ω is an angular frequency, K is a wave-number ($K > 0$ represents waves moving to the right and $K < 0$ waves moving to the left) and ε_0 the amplitude of the displacement. Using this form in (19) gives

$$-\omega^2 M = C(e^{iKa} + e^{-iKa} - 2) = 2C(\cos Ka - 1) = -4C\sin^2\left(\frac{KA}{2}\right).$$

Taking the positive square root we get a relation between ω and K

$$\boxed{\omega = 2\sqrt{\frac{C}{M}} \sin\left|\frac{Ka}{2}\right|.} \tag{21}$$

Since the wavenumber $|K| = \frac{2\pi}{\lambda}$ is related to the wavelength λ equation (21) relates the frequency to the wavelength $\omega(K)$ — it is an example of a *dispersion relation*.
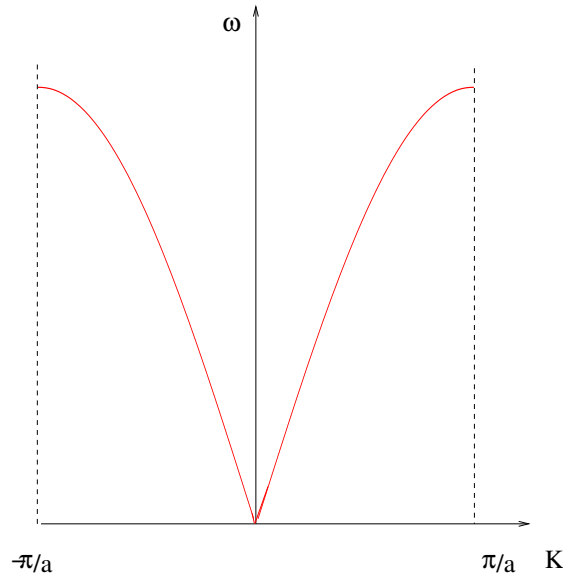
Since in (20) $\frac{u_{n+1}(t)}{u_n(t)} = e^{iKa} = e^{i\left(K + \frac{2p\pi}{a}\right)a}$, for any integer p, we need only consider K in the range $-\frac{\pi}{a} < K \leq \frac{\pi}{a}$, or equivalently $\lambda = \frac{2\pi}{|K|} \geq 2a$, wavelengths with $\lambda < 2a$ are meaningless! This can be visualised using the figure below.
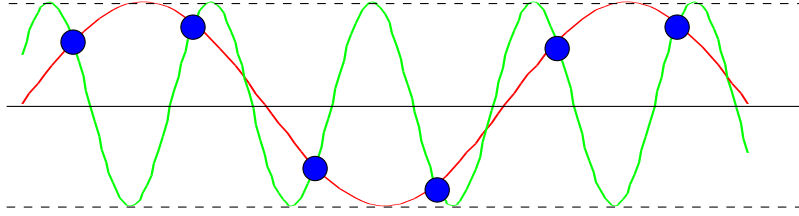
For ease of visualisation the displacements u_n at one instant of time are represented vertically here and the horizontal displacement represents the equilibrium position of the atoms, na. The green curve has a wavelength one-third of the red curve, but the red curve is perfectly adequate for representing the displacements, there is nothing to be gained by considering the shorter wavelength.

The range of wavevectors $|K| \leq \frac{\pi}{a}$ is precisely the First Brillouin zone of the one-dimensional crystal. For $\mathcal{N}$ large, but still finite, we can decompose a general vibration of the crystal into a linear superposition of normal modes. With periodic boundary conditions, $u_0 = u_{\mathcal{N}} \Rightarrow e^{iK\mathcal{N}a} = 1$ and so we must have $K\mathcal{N} = \frac{2\pi p}{a}$ with p an integer. So $K = \frac{2p}{\mathcal{N}}\left(\frac{\pi}{a}\right)$ and $-\frac{\pi}{a} \leq K \leq \frac{\pi}{a} \Rightarrow p = \pm 1, \pm 2, \cdots, \frac{\mathcal{N}}{2}$. There is a finite number, $\mathcal{N}$, of modes ($p = 0$ corresponds to a rigid translation of the whole crystal and is uninteresting). In other words the allowed values of K,

$$K = \pm \frac{2\pi}{\mathcal{N}a}, \pm \frac{4\pi}{\mathcal{N}a}, \pm \frac{6\pi}{\mathcal{N}a}, \cdots, \pm \frac{\pi}{a},$$

are *discrete* for $\mathcal{N}$ finite — we get a continuum of K-values only in the $\mathcal{N} \to \infty$ limit. Note that:

- For K small and positive, $0 < K << \frac{\pi}{a}$, (21) gives $\omega \approx \sqrt{\frac{C}{M}} Ka$ leading to a linear relation between frequency and wavelength with velocity

$$v_p = \frac{\omega}{K} = \sqrt{\frac{C}{M}}\, a.$$

The larger the spring constant, C, *i.e.* the stiffer the crystal, the greater the speed of propagation of sound waves.

- More generally, away from small K, the velocity depends on the wavelength. A wave-packet made up of a combination of different wavelengths will tend to disperse because long wavelengths (small K) move faster than shorter wavelengths (with K near $\pm\frac{\pi}{a}$). Waves move with *group velocity*

$$v_g = \frac{d\omega}{dK} = \sqrt{\frac{C}{M}}\, a \cos\left(\frac{Ka}{2}\right).$$

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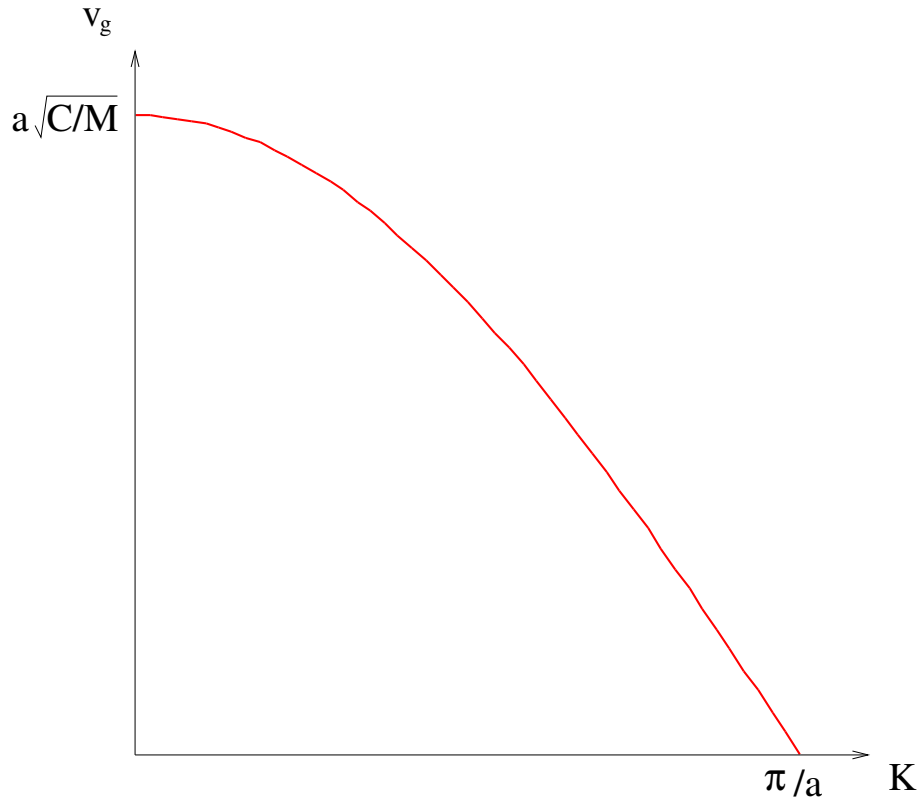
- For small K, $v_g \approx v_p$ and the group velocity is the same as v_p,[7] the dispersion relation is linear.
- For $K = \pm\frac{\pi}{a}$ the group velocity $v_g = 0$: we have **standing waves**. The displacements of neighbouring atoms are exactly out of phase

$$\frac{u_{n+1}(t)}{u_n(t)} = e^{i\pi} = -1.$$

Sound waves with these wavelengths are reflected off the Brillouin zone boundary.

**One-dimensional crystal (diatomic basis)**

For a basis consisting of two atoms (*e.g.* positive and negative ions in an ionic crystal) with different masses M_1 and M_2 there are further interesting phenomena. Again take the lattice spacing to be a and suppose that the equilibrium separation between M_1 and M_2 atoms is $\frac{a}{2}$ (in the picture below M_1 atoms are blue and M_2 atoms are red).

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[7] $v_p = \frac{\omega}{K}$, for any K, is called the *phase* velocity. An observer moving with speed v_p would see a constant phase in the atomic displacements — this is not necessarily a physical velocity. In most situations energy, and other physical quantities, are transported with the group velocity.
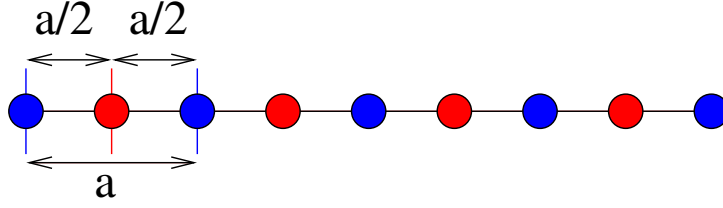
Denote the displacements of the n-th M_1 atom from equilibrium by u_n and that of the n-th M_2 atom by v_n. For small displacements we can model the forces as springs between nearest neighbour atoms and, for simplicity, we shall assume that the spring constants are all the same, C. In the picture below the vertical lines represent the equilibrium positions,
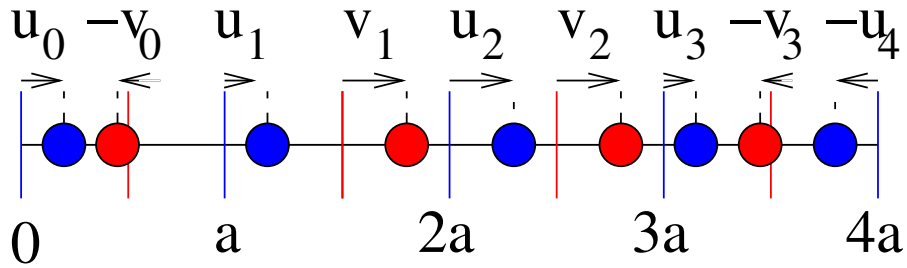
Then Newton's equations are

$$M_1 \ddot{u}_n = C(v_n - u_n) - C(u_n - v_{n-1}) = C(v_n + v_{n-1} - 2u_n)$$
$$M_2 \ddot{v}_n = C(u_{n+1} - v_n) - C(v_n - u_n) = C(u_{n+1} + u_n - 2v_n).$$

Looking for a (complex) solution of the form

$$u_n(t) = \varepsilon_1 e^{i(Kna - \omega t)}$$
$$v_n(t) = \varepsilon_2 e^{i(Kna - \omega t)} \qquad \Rightarrow \qquad
\begin{array}{l}
-M_1 \omega^2 \varepsilon_1 = C\big((1 + e^{-iKa})\varepsilon_2 - 2\varepsilon_1\big) \\
-M_2 \omega^2 \varepsilon_2 = C\big((e^{iKa} + 1)\varepsilon_1 - 2\varepsilon_2\big)
\end{array}$$

(again the physical displacements are the real parts of the complex $u_n(t)$ and $v_n(t)$.) This can be written in matrix form

$$\begin{pmatrix} M_1\omega^2 - 2C & C(1 + e^{-iKa}) \\ C(1 + e^{iKa}) & M_2\omega^2 - 2C \end{pmatrix} \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \end{pmatrix} = 0.$$

If the matrix is invertible the only solution is $\varepsilon_1 = \varepsilon_2 = 0$, a solution with ε_1 and ε_2 not both zero only exists if the matrix is not invertible *i.e.* the determinant is zero. This requires

$$M_1 M_2 \omega^4 - 2C(M_1 + M_2)\omega^2 + C^2(2 - e^{iKa} - e^{-iKa}) = 0,$$

or

$$\omega^2 = \frac{C(M_1 + M_2) \pm C\sqrt{(M_1 + M_2)^2 - 4M_1 M_2 \sin^2\left(\frac{Ka}{2}\right)}}{M_1 M_2}.$$

We see that there are now *two* different frequencies for each value of $-\frac{\pi}{a} \leq K \leq \frac{\pi}{a}$, corresponding to two different vibrational modes for each K. The lower sign (lower frequency) requires $\varepsilon_1 = \varepsilon_2$, so M_1 and M_2 are oscillating in phase, while the upper sign (higher frequency) requires $\varepsilon_1 = -\varepsilon_2$, so M_1 and M_2 are oscillating exactly out of phase — while M_1 is displaced to the left the adjacent M_2 is displaced to the right. These two possibilities are shown below, where the M_1 atoms are red and the M_2 atoms are blue (again, for clarity, the displacements u_n and v_n are represented vertically and the equilibrium positions, na and $\left(n + \frac{1}{2}\right)a$, horizontally)

● = negative ion
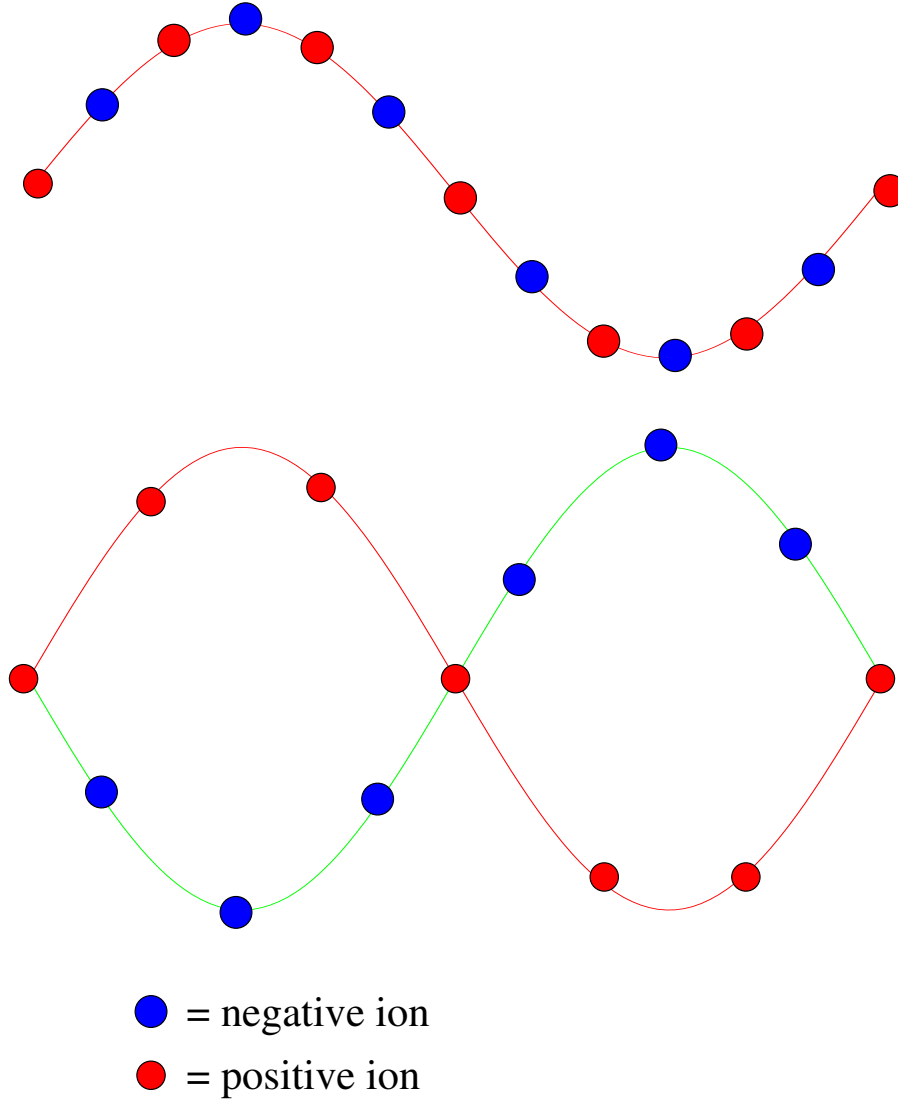
● = positive ion

Experimentally the different modes can be preferentially excited in an ionic crystal if M_1 are positive ions and M_2 are negative ions. Then a passing electromagnetic wave will push the positive and negative ions in different directions, because they are pushed in opposite directions by an electric field. However an acoustic vibration (hit the crystal with a hammer!) does not distinguish between positive and negative ions, they are both pushed in the same direction by a passing acoustic wave. For a given K the lower frequency mode

is called the *acoustic* mode, because it can be excited by a passing sound wave through the crystal, while the upper frequency is called the *optical* mode, because it can be excited by a passing electromagnetic wave (light) through the crystal.

The dispersion relation, shown below, has two *branches*, an acoustic branch and an optical branch.
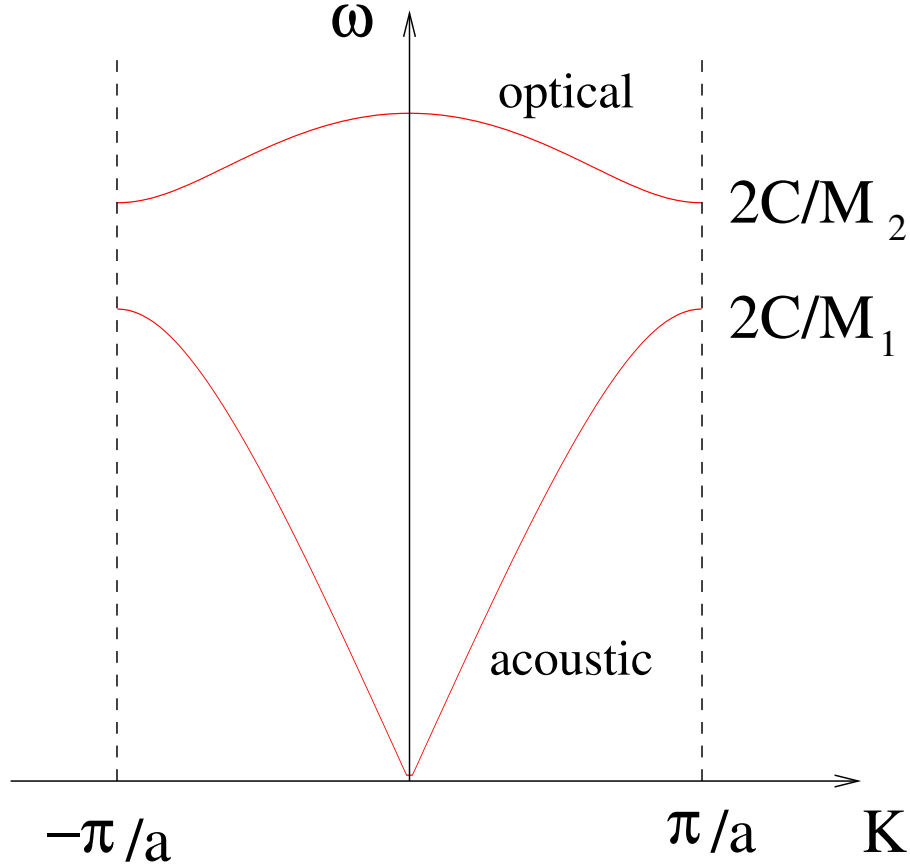
For K small, $0 < K << \frac{\pi}{a}$, $\sin^2\left(\frac{Ka}{2}\right) \approx \frac{K^2a^2}{4}$ and

$$\omega^2 = \begin{cases} \frac{2(M_2+M_2)C}{M_2M_2} - \frac{C(Ka)^2}{2(M_1+M_2)} + \cdots & \text{Optical branch } (\frac{\varepsilon_1}{\varepsilon_2} = -1); \\ \frac{C(Ka)^2}{2(M_1+M_2)} + \cdots & \text{Acoustic branch } (\frac{\varepsilon_1}{\varepsilon_2} = 1). \end{cases}$$

For the optical branch ω^2 is a maximum at $K = 0$, so $v_g = 0$ there, and the dispersion relation looks like an inverted parabola for small K, while the acoustic branch has a linear dispersion relation, $\omega \approx \sqrt{\frac{C}{2(M_1+M_2)}}\, aK$ and $v_g = v_p = \sqrt{\frac{C}{2(M_1+M_2)}}\, a$.

In two dimensions there are even more possibilities. For a monatomic basis, when there is only one mode in one dimension, there are two different modes in two dimensions, the atoms can be displaced in the *same* direction as the wavevector $\mathbf{K}$ as shown on the left in the picture below (a *longitudinal* mode) or at right-angles to the wavevector as shown on the right in the picture below (*transverse* mode).
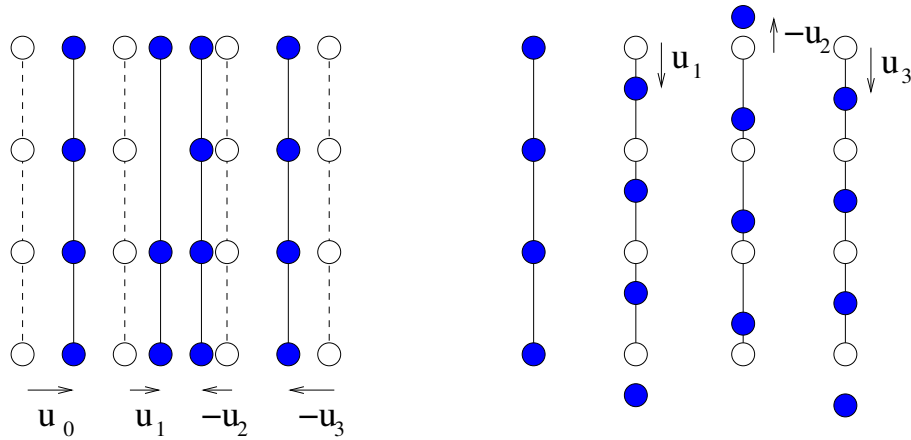
The amplitude ε_0 in one-dimension becomes a vector, $\underline{\varepsilon}_0$, in two-dimensions, with **K** parallel to $\underline{\varepsilon}_0$ in the longitudinal case and $\mathbf{K}.\underline{\varepsilon}_0 = 0$ in the transverse case. If the crystal is anisotropic and the spring constants are different in different directions, the dispersion relation will be different for the longitudinal and transverse modes.

For a diatomic 2-dimensional crystal there can be up to four modes: longitudinal optical (LO), transverse optical (TO), longitudinal acoustic (LA) and transverse acoustic (TA), each with a different dispersion relation
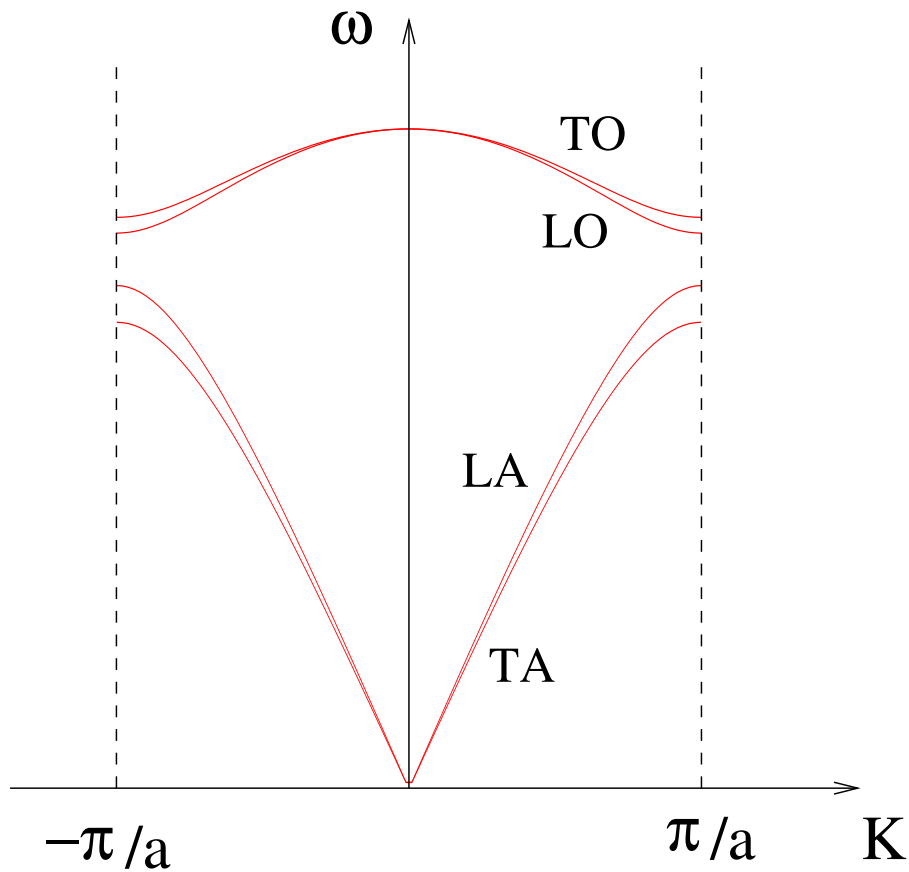
In three dimensions there can be two different transverse optical and transverse acoustic modes for each frequency, giving six different modes: one LO, two TO, one LA and two TA. The dispersion relation can become very complicated as it can be different for different directions $[hkl]$. For example the dispersion relations measured experimentally in lead (FCC), in various crystal directions, are shown below

(a)

(b)
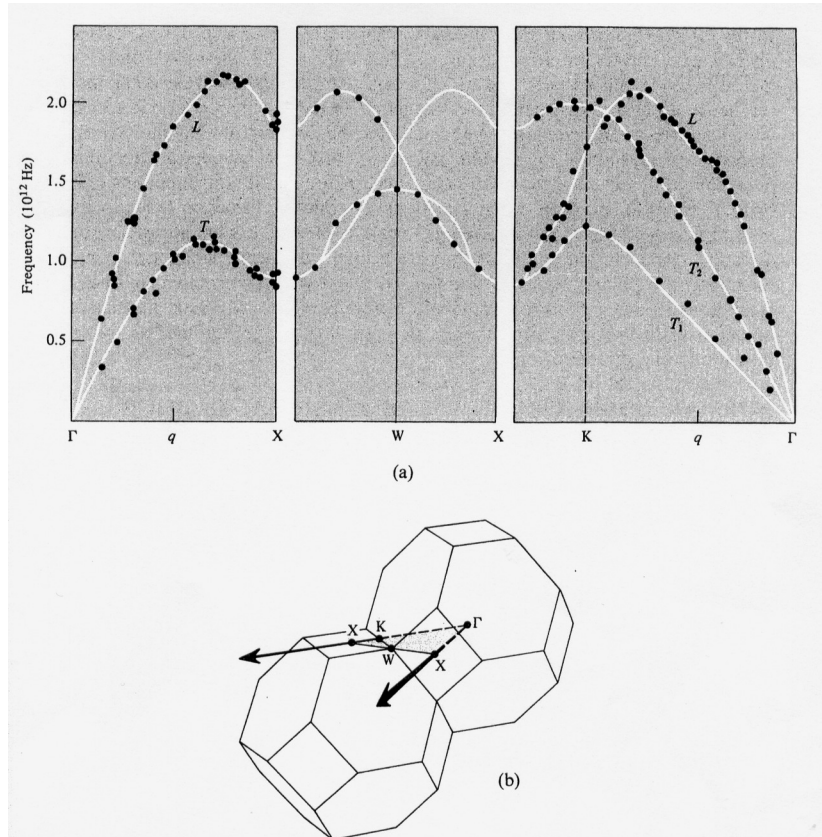
Data are shown for wavevectors in three different directions as indicated in the Wigner-Seitz cell of the reciprocal lattice in (b) (lead has a face centred cubic structure so the reciprocal lattice is body centred cubic and the Wigner-Seitz cell is a truncated octahedron). Γ marks the centre of the Wigner-Seitz and **K** traces out a triangle with sides $\Gamma - K - X$, $X - W - X$ and $X - \Gamma$. Lead is not an ionic crystal and only acoustic modes appear in the upper panel. On the line $\Gamma - X$ there is only one transverse acoustic branch and this bifurcates into two on $X - W - X$, which combine again into a single branch at the second X but bifurcates again before reaching K. The direction $\Gamma - X$ is $[100]$ and $\Gamma - K$ is $[110]$.

Quantisation

To understand fully the nature of crystal vibrations it is necessary to take quantum mechanical effects into account. In quantum mechanics a classical wave can sometimes best be described by particles in the quantum theory. A quantum of crystal vibration is called a **phonon** — a particle of sound.

The vibrations of the crystal atoms or molecules about their equilibrium positions

can be modelled using a harmonic oscillator. In quantum mechanics the energy levels of a harmonic oscillator are labelled by a non-negative integer $n = 0, 1, 2, 3, \ldots$ and are equally spaced

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

where ω is the characteristic frequency of the oscillator. In thermal equilibrium, in contact with a heat bath at temperature T, the probability of a given oscillator being in energy eigenstate n is given by the Boltzmann distribution

$$P_n = \frac{e^{-\frac{E_n}{k_B T}}}{\sum_{n=0}^{\infty} e^{-\frac{E_n}{k_B T}}} = \frac{e^{-\left(n+\frac{1}{2}\right)\frac{\hbar\omega}{k_B T}}}{\sum_{n=0}^{\infty} e^{-\left(n+\frac{1}{2}\right)\frac{\hbar\omega}{k_B T}}} = \frac{y^n}{\sum_{n=0}^{\infty} y^n},$$

where k_B is Boltzmann's constant and $y = e^{-\frac{\hbar\omega}{k_B T}}$ lies in the range $0 \leq y < 1$. The denominator in this expression for P_n is determined by the requirement that the probabilities sum to one, $\sum_{n=0}^{\infty} P_n = 1$. For y in this range

$$\sum_{n=0}^{\infty} y^n = \frac{1}{1-y} \qquad \Rightarrow \qquad P_n = y^n(1-y).$$

The expectation value of n, *i.e.* its most likely value, denoted by $< n >$, is the weighted sum

$$< n >= \sum_{n=0}^{\infty} n P_n = (1-y)\sum_{n=0}^{\infty} n y^n,$$

which can be evaluated using

$$\sum_{n=0}^{\infty} n y^n = y\frac{d}{dy}\left(\sum_{n=0}^{\infty} y^n\right) = y\frac{d}{dy}\left(\frac{1}{1-y}\right) = \frac{y}{(1-y)^2},$$

giving

$$< n >= \frac{y}{1-y} = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}.$$

This is the **Planck distribution**.

Label the possible crystal vibrational modes by their wavenumber K and a discrete variable s (denoting the different modes: TO, TA, *etc*), then the thermal energy in vibrational modes of the crystal, when it is at a temperature T, is the expectation value of the energy

$$U =< E > = \left\langle \sum_{K,s}\left(n_{K,s} + \frac{1}{2}\right)\hbar\omega_{K,s}\right\rangle = \sum_{K,s}\left(< n_{K,s} > +\frac{1}{2}\right)\hbar\omega_{K,s}$$

$$= \sum_K \sum_s \frac{\hbar\omega_{K,s}}{\left(e^{\frac{\hbar\omega_{K,s}}{k_B T}} - 1\right)} + \sum_K \sum_s \frac{\hbar\omega_{K,s}}{2}.$$

The last term on the right hand side here is a constant, independent of T, and can be ignored in the calculation of thermal properties of crystals below.

For simplicity first consider a monatomic one-dimensional crystal, where we can ignore s (there is only one mode for each K) and $K = \frac{2p}{\mathcal{N}}\left(\frac{\pi}{a}\right)$ with $p = \pm 1, \pm 2, \ldots$. The $\sum_K$ is equivalent to $\sum_p$ but for large $\mathcal{N}$ we can replace the sum with an integral, $\sum_K \to \int D(\omega)d\omega$, where $D(\omega)$ denotes the number of quantum states in the frequency range ω to $\omega + d\omega$. $D(\omega)$ is called the **density of states**, it is calculated below. Thus we get

$$U = \int_0^\infty \frac{D(\omega)\hbar\omega}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)} d\omega. \tag{22}$$

More generally, for a polyatomic basis and/or in higher dimensions when there is more than one mode for each K, the internal energy of the crystal is

$$\boxed{U = \sum_s \int_0^\infty \frac{D(\omega_s)\hbar\omega_s}{\left(e^{\frac{\hbar\omega_s}{k_B T}} - 1\right)} d\omega_s.}$$

Density of states

To calculate $\mathcal{D}(\omega)$, again initially in one dimension to simplify the demonstration, consider a one-dimensional crystal with lattice spacing a and periodic boundary conditions. The allowed wavevectors are $K = \frac{2p}{\mathcal{N}}\frac{\pi}{a}$ with $p \pm 1, \pm 2, \ldots$, so the spacing between successive wavevectors is $\frac{2}{\mathcal{N}}\frac{\pi}{a}$ and the number of modes in a range δK is $\frac{\mathcal{N}a}{2\pi}\delta K$. The number of modes δN in a frequency range $\delta\omega$ is therefore

$$\delta N = \frac{dN}{d\omega}\delta\omega = 2\left(\frac{\mathcal{N}a}{2\pi}\right)\frac{dK}{d\omega}\delta\omega = D(\omega)\delta\omega$$

(the extra factor of 2 here is inserted to allow for the fact that there are two modes for each ω, one moving to the left and one to the right). Since $\mathcal{N}a = L$, the length of the crystal, this gives

$$\left(\frac{L}{\pi}\right)\frac{dK}{d\omega}\delta\omega = D(\omega)\delta\omega \qquad \Rightarrow D(\omega) = \left(\frac{L}{\pi}\right)\frac{dK}{d\omega},$$

and we can calculate the density of states $D(\omega)$ if we know the dispersion relation $\omega(K)$.

For example the dispersion relation (19) for a one-dimensional crystal, with $\omega_0 = 2\sqrt{\frac{C}{M}}$, reads

$$\omega(K) = \omega_0 \sin\left|\frac{Ka}{2}\right| \qquad \Rightarrow \qquad \frac{d\omega}{dK} = \frac{a}{2}\omega_0\cos\left|\frac{Ka}{2}\right| \qquad (K \geq 0)$$

$$\Rightarrow \qquad D(\omega) = \frac{2L}{a\pi}\frac{1}{\omega_0}\frac{1}{\cos\left(\frac{|K|a}{2}\right)} = \frac{2\mathcal{N}}{\pi}\frac{1}{\sqrt{\omega_0^2 - \omega^2}}$$

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Note that at the Brillouin zone boundary, $K \to \frac{\pi}{a}$, $\omega \to \omega_0$ and $D(\omega) \to \infty$. A divergence in the density of states at certain characteristic frequencies is not uncommon and is called a **van Hove singularity**.

In three dimensions we can use the same ideas to get the density of states. Consider a crystal with simple cubic symmetry with $\mathcal{N}$ primitive cells and lattice spacing a. If the linear dimensions are L_1, L_2 and L_3 then the volume is $V = L_1 L_2 L_3 = \mathcal{N}a^3$. For simplicity we take $L_1 = L_2 = L_3 := L = \mathcal{N}^{\frac{1}{3}}a$ and assume $\mathcal{N}^{\frac{1}{3}}$ is an integer, for large $\mathcal{N}$ this is not a significant restriction, at least as far as intrinsic properties of the crystal are concerned. Imposing periodic boundary conditions implies

$$e^{i(K_x x + K_y y + K_z z)} = e^{i\left(K_x(x+L) + K_y(y+L) + K_z(z+L)\right)}$$

$$\Rightarrow \qquad K_x, K_y, K_z = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \dots, \pm\frac{\mathcal{N}^{\frac{1}{3}}\pi}{L}.$$

There is therefore one value of K per volume $\left(\frac{2\pi}{L}\right)^3 = \frac{8\pi^3}{V}$ in K-space. The number of quantum modes in a volume $d^3K = dK_x dK_y dK_z$ of K-space is therefore $d^3N = \frac{V}{8\pi^3}d^3K$. For large $\mathcal{N}$ we can approximate the discrete distribution of modes in K-space by a continuum and imagine integrating over a sphere of radius K and area $4\pi K^2$ in K-space, so the radius K is the only variable left,

$$\frac{V}{8\pi^3}d^3K = \frac{V}{8\pi^3}dK_x dK_y dK_z \quad \xrightarrow[\int d\Omega]{} \quad \frac{V}{2\pi^2}K^2 dK.$$

The number of modes inside such a sphere, with volume $\frac{4\pi}{3}K^3$ (*i.e.* with wavenumber less than K), is

$$N = \frac{V}{8\pi^3}\frac{4\pi}{3}K^3 = \frac{V}{6\pi^2}K^3.$$

This now gives the three-dimensional density of states as

$$dN = D(\omega)d\omega = \frac{dN}{d\omega}d\omega = \frac{dN}{dK}\frac{dK}{d\omega}d\omega = \frac{V}{2\pi^2}K^2\frac{dK}{d\omega}d\omega \qquad \Rightarrow$$

$$\boxed{D(\omega) = \frac{V}{2\pi^2}K^2\frac{dK}{d\omega}.} \tag{23}$$

which can be evaluated once the dispersion relation, $\omega(K)$, is known.

Debye model

The Debye model makes the simplifying assumption that the dispersion relation is linear, $\omega = vK$, where $v = \frac{d\omega}{dK}$, the speed of sound, is independent of ω. From this we get the density of states

$$D(\omega) = \frac{V}{2\pi^2}\frac{\omega^2}{v^3}.$$

If there are $\mathcal{N}$ primitive cells in the crystal then there is a maximum frequency ω_D, a cut-off frequency, determined by

$$\mathcal{N} = \int_0^{\omega_D} D(\omega)d\omega = \frac{V}{2\pi^2}\frac{1}{v^3}\int_0^{\omega_D}\omega^2 d\omega = \frac{V}{6\pi^2}\frac{\omega_D^3}{v^3} \qquad \Rightarrow \qquad \omega_D = \left(6\pi^2\frac{\mathcal{N}}{V}\right)^{\frac{1}{3}}v.$$

The maximum angular frequency ω_D is called the **Debye frequency**. With this cut-off the density of states for the Debye model looks like this:
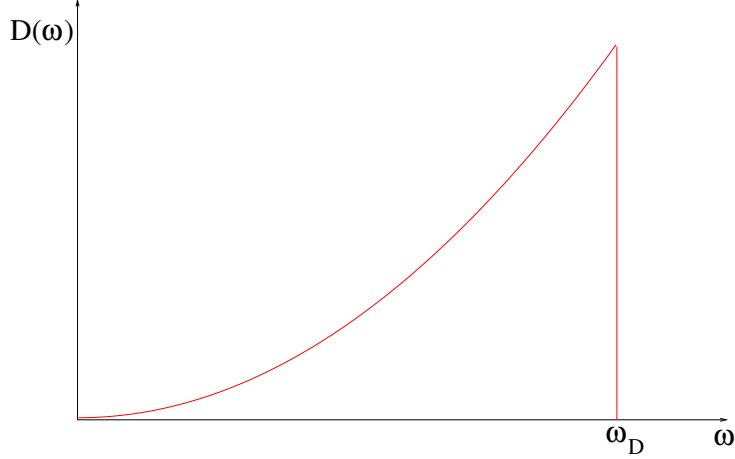
The contribution to the thermodynamic internal energy is

$$U = \int_0^{\omega_D}\frac{D(\omega)\hbar\omega}{e^{\frac{\hbar\omega}{k_BT}}-1}d\omega = \frac{V\hbar}{2\pi^2v^3}\int_0^{\omega_D}\frac{\omega^3 d\omega}{e^{\frac{\hbar\omega}{k_BT}}-1} \tag{24}$$

for each polarisation. For simplicity we shall just take v to be the same for each of the three acoustic modes, then the total internal energy is three times (24). Changing the integration variable from ω to $x = \frac{\hbar\omega}{k_BT}$ gives

$$U = \frac{3V(k_BT)^4}{2\pi^2v^3\hbar^3}\int_0^{x_D}\frac{x^3 dx}{e^x-1},$$

where $x_D = \frac{\hbar\omega_D}{k_BT}$.

It is conventional to define a temperature, Θ_D called the **Debye temperature**, by $k_B\Theta_D = \hbar\omega_D$,

$$\Theta_D = \frac{\left(6\pi^2\frac{\mathcal{N}}{V}\right)^{\frac{1}{3}}\hbar v}{k_B},$$

with $\frac{\mathcal{N}}{V} := n_c$ the number of primitive cells per unit volume. Then $x_D = \frac{\Theta_D}{T}$ and

$$U = 9\mathcal{N}k_BT\left(\frac{T}{\Theta_D}\right)^3\int_0^{\frac{\Theta_D}{T}}\frac{x^3 dx}{e^x-1}.$$

$U(T, V)$ depends on the volume through $\Theta_D \propto V^{-\frac{1}{3}}$.

Other thermodynamic quantities can be obtained from $U(T, V)$. The heat capacity of the crystal at constant volume, for example, is

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

This is most easily calculated from (24), multiplied by 3 to account for the three acoustic modes. The only T dependence in (24) is in $e^{\frac{\hbar\omega}{k_B T}}$, so

$$C_V = \frac{3V\hbar}{2\pi^2 v^3} \frac{\hbar}{k_B T^2} \int_0^{\omega_D} \frac{\omega^4 e^{\frac{\hbar\omega}{k_B T}} d\omega}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1 \right)^2} = \frac{3V}{2\pi^2 v^3} \frac{k_B^4 T^3}{\hbar^3} \int_0^{x_D} \frac{x^4 e^x dx}{(e^x - 1)^2}$$

$$= 9\mathcal{N} k_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} \frac{x^4 e^x dx}{(e^x - 1)^2}.$$

The specific heat, $c_V = \frac{C_V}{V}$, is plotted below:
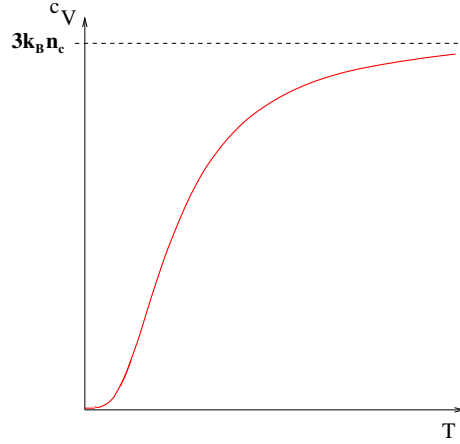
We can evaluate the integral in (24) in certain limits:

- Low temperatures: $k_B T << \hbar\omega_D$, $x_D \to \infty$,

$$\int_0^\infty \frac{x^3}{e^x - 1} = \sum_{n=1}^\infty \int_0^\infty x^3 e^{-nx} dx = \sum_{n=1}^\infty \frac{1}{n^4} \int_0^\infty u^3 e^{-u} du \qquad \text{where } u = nx$$

$$= \Gamma(4) \sum_{n=1}^\infty \frac{1}{n^4} = 3! \sum_{n=1}^\infty \frac{1}{n^4} = \frac{\pi^4}{15},$$

leading to thermal energy

$$U \approx \frac{3\pi^4}{5} \mathcal{N} k_B T \left(\frac{T}{\Theta_D} \right)^3$$

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and specific heat

$$c_V = \frac{C_V}{V} \approx \frac{12\pi^4}{5} \left(\frac{\mathcal{N}}{V}\right) k_B \left(\frac{T}{\Theta_D}\right)^3 = \frac{2\pi^2}{5} k_B \left(\frac{k_B T}{\hbar v}\right)^3. \tag{25}$$

There formula are only correct for T small, in particular

$$\lim_{T \to 0} \frac{C_v}{V T^3} = \frac{2\pi^2}{5} \frac{k_B^4}{(\hbar v)^3}$$

is constant. This is an important result from the Debye approximation, the specific heat due to crystal vibrations goes like $\sim T^3$ at low T. For a metallic crystal there is another contribution to the specific heat, due to electrons free to roam around the crystal, which we shall evaluate later. It may be necessary to go temperatures as low as $T < \frac{\Theta_D}{50}$ to see this T^3 behaviour.

- In the opposite limit, of high temperatures, $x_D \ll 1$, we can expand $\frac{1}{e^x - 1} = \frac{1}{x + \frac{x^2}{2} + \frac{x^3}{6} + \cdots} = \frac{1}{x} \left(1 - \frac{x}{2} + \frac{x^2}{12} - \cdots\right)$ and

$$U \approx 9\mathcal{N} k_B T \left(\frac{T}{\Theta_D}\right)^3 \frac{x_D^3}{3} = 3\mathcal{N} k_B T$$

is linear in T, hence the specific heat is constant

$$c_V = \frac{C_V}{V} \approx \frac{3\mathcal{N} k_B}{V}.$$

This is the classical result — constant specific is indeed observed at large T and is known as the **Dulong-Petit** result. The Dulong-Petit value for the specific heat of a crystal can be understood from the equipartition theorem: each degree of freedom in the crystal has the same energy $\frac{1}{2} k_B T$, each atom has 3 co-ordinates labelling its position and 3 momenta giving 6 degrees of freedom, hence the internal energy is $U = 6\mathcal{N} \frac{k_B T}{2} = 3\mathcal{N} k_B T$.[8] This classical result assumes that all degrees of freedom are excited but, if T is not very large $T \ll \Theta_D$, not all degrees of freedom can be excited and the specific heat is reduced

Values of Θ_D for some elements are: $158°K$ (Na); $400°K$ (Mg); $470°K$ (Fe); $2230°K$ (C).

Einstein model

The linear dispersion relation, $\omega = vK$, in the Debye model is a reasonable approximation for acoustic modes at small K, it is not a good model for optical modes in a crystal with a polyatomic basis. Einstein suggested a simplified density of states

$$D(\omega) = \mathcal{N}\delta(\omega - \omega_E)$$

---

[8] The internal energy of a monatomic gas is $\frac{3}{2}\mathcal{N} k_B T$, not $3\mathcal{N} k_B T$, because the degrees of freedom associated with the positions of the atoms in an ideal gas do not contribute to the energy and so do not contribute to the internal energy. In a crystal the position does contribute as it takes energy to move an atom away from its equilibrium position.

in this case, where ω_E is a fixed frequency and $\delta(\omega - \omega_E)$ is a Dirac δ-function, vanishing unless $\omega = \omega_E$. The integral over x in (24) is trivial in this case: if there are p optical modes, all with the same ω_E,

$$U = \frac{p\mathcal{N}\hbar\omega_E}{e^{\frac{\hbar\omega_E}{k_B T}} - 1}$$

and the specific heat is

$$c_V = \left(\frac{\mathcal{N}}{V}\right) \frac{(\hbar\omega_E)^2}{k_B T^2} \frac{p\, e^{\frac{\hbar\omega_E}{k_B T}}}{(e^{\frac{\hbar\omega_E}{k_B T}} - 1)^2} \quad \rightarrow \quad \begin{cases} p\left(\frac{\mathcal{N}}{V}\right) k_B, & T \to \infty \\ p\left(\frac{\mathcal{N}}{V}\right) \left(\frac{\hbar\omega_E}{k_B T}\right)^2 k_B e^{-\frac{\hbar\omega_E}{k_B T}}, & T \to 0. \end{cases}$$

The Einstein result is the same for large T as the Debye result, the specific heat approaches a constant at large T, but at low T the specific heat for optical modes in the Einstein model is much less than that of the acoustic modes in the Debye model. The two are compared below (with $p = 3$): the red curve is the Debye model and blue Einstein model,
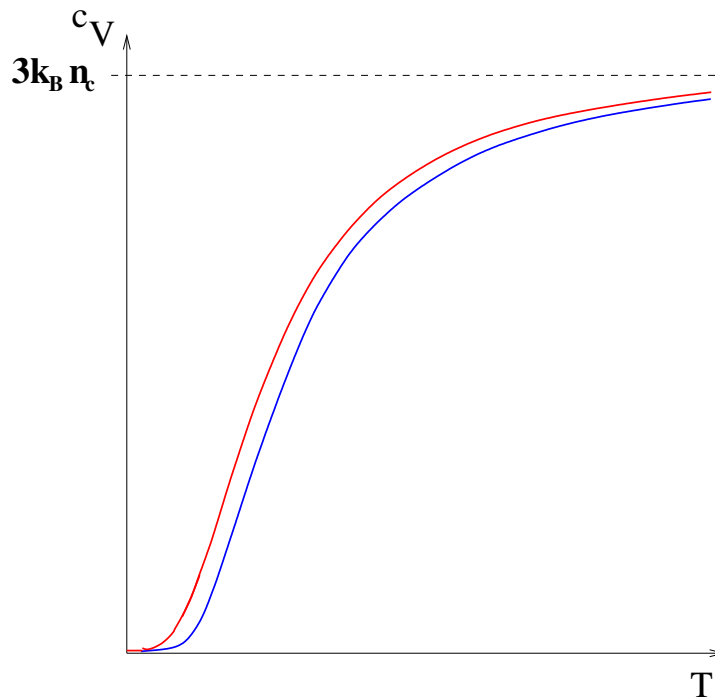

It is stressed that these calculations only take into account the vibrational modes of the crystal, any contribution from free electrons is ignored. The low T results are only valid for crystals that are electrical insulators, metallic crystals have an extra contribution to the specific heat coming from free electrons in the crystal. We shall see later that electrons contribute a linear term to the acoustic mode specific heat in a metallic crystal, giving $c_V \approx AT + BT^3$ at low T, with A and B constants. At very low temperatures the linear term dominates the cubic term and the metallic specific heat is linear in T.
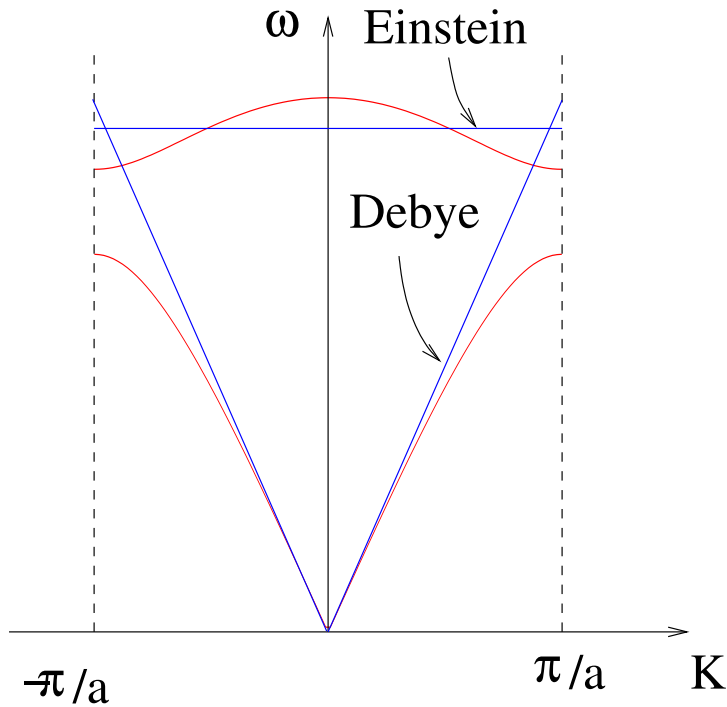
Both the Debye and the Einstein models are crude approximations to the dispersion relation in real crystals, they are plotted in blue above and compared to the one-dimensional diatomic results for acoustic and optical modes calculated earlier. Real crystals are more complicated: a real experimental dispersion relation for phonons, determined by neutron scattering, for acoustic modes in aluminium, is shown below,
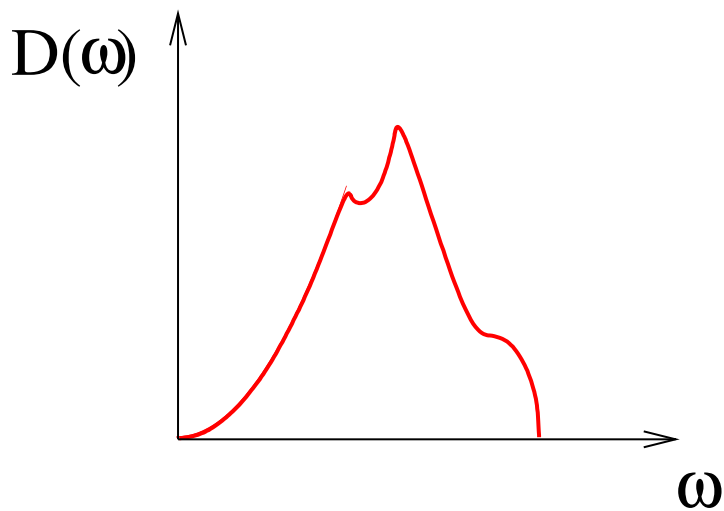
Thermal conductivity

Heat energy in a crystal is due to vibrating atoms and so we expect phonons to conduct heat. For simplicity consider a crystal with monatomic basis. Denote the equilibrium energy density in phonons (lattice vibrations) by $w(\mathbf{r})$ (so the internal energy is $\int_{crystal} w(\mathbf{r})dV$) and the phonon velocity by $\mathbf{v}$ (in the presence of a temperature gradient $w(\mathbf{r})$ will vary from place to place). Now introduce a temperature gradient $T(x)$ in

the x-direction and let the phonon mean free path (the average distance between phonon collisions) be l. Then the average time between phonon collisions is $\tau = \frac{l}{v}$. Any phonon arriving at a general point $\mathbf{r}_0$ of the crystal has, on average, come from a sphere of radius l centred on $\mathbf{r}_0$, this sphere represents the locus of points from which the phonons arriving at $\mathbf{r}_0$ last scattered and $w(\mathbf{r})$ will be different at different points on this sphere so, in the presence of a temperature gradient, phonons arriving from different directions will carry different energy — those coming from directions in which the temperature is hotter will have greater energy than those coming from directions in which the temperature is cooler. If $T(x)$ is constant in the y and z-directions then $w(\mathbf{r})$ will be too and $w(x)$ depends only on x.
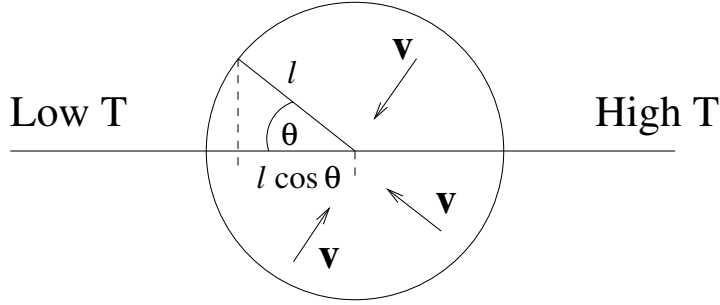
There will be a net flux of energy, a thermal current, in the direction of decreasing T as heat energy diffuses from regions of higher T to lower T. The x component of $\mathbf{v}$ is $v_x = v \cos \theta$ and, denoting an infinitesimal area element of the sphere by $dA = l^2 \sin \theta d\theta d\phi$ the thermal current is

$$
\begin{aligned}
J &= \frac{1}{4\pi l^2} \int_{sphere} v_x w(x) dA \\
&= \frac{2\pi}{4\pi l^2} \int_0^\pi (v \cos \theta) w(x_0 - l \cos \theta) l^2 \sin \theta d\theta \\
&\approx \frac{v}{2} \int_0^\pi \left\{ w(x_0) - l \cos \theta \left(\frac{dw}{dx} \right)_{x_0} \right\} \cos \theta \sin \theta d\theta \\
&= \frac{v}{2} \int_{-1}^1 \left\{ w(x_0) \alpha - \alpha l \left(\frac{dw}{dx} \right)_{x_0} \right\} \alpha d\alpha \qquad (\alpha = \cos \theta) \\
&= -\frac{vl}{3} \left(\frac{dw}{dx} \right)_{x_0}.
\end{aligned}
$$

Now $\frac{dw}{dx}$ is related to the thermal gradient, $\frac{dT}{dx}$, by the chain rule

$$
\frac{dw}{dx} = \frac{dw}{dT} \frac{dT}{dx}.
$$

Since there is a thermal gradient the system is not in thermal equilibrium but we still expect the thermal energy per unit volume $w(T, V)$ to depend on V as well as T, $\frac{dw}{dT}$ here

is more correctly written $\frac{\partial w}{\partial T}\big|_V$ which is the specific heat at constant volume, c_V, so

$$J = -\frac{c_V v l}{3}\frac{dT}{dx} = -\frac{c_V v^2 \tau}{3}\frac{dT}{dx},$$

where $\tau = \frac{v}{l}$ is average time between phonon collisions. The **thermal conductivity**, κ, is defined as the ratio of the thermal current to the thermal gradient,

$$J = -\kappa\frac{dT}{dx},$$

and we get the important result that the thermal conductivity

$$\boxed{\kappa = \frac{c_V v^2 \tau}{3}} \tag{26}$$

is proportional to the specific heat of the crystal.

Two limiting cases:

- At high T, $c_V = 3k_B n_c$ is a constant. It is reasonable to expect that the collision rate will be proportional to the phonon density,

$$\tau^{-1} \propto\; <n> = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \underset{T\to\infty}{\approx} \frac{k_B T}{\hbar\omega} \propto T,$$

  Since the phonon velocity is independent of the temperature (it is determined by the dispersion relation), we expect

$$\kappa \propto 1/T$$

  at high T. Experimentally $\kappa \propto \frac{1}{T^\nu}$ with ν between 1 and 2.

- For low T, $<n>\approx e^{-\frac{\hbar\omega}{k_B T}} \Rightarrow \tau \propto e^{\frac{\hbar\omega}{k_B T}} \to \infty$ as $T \to 0$. Hence $\kappa \to \infty$, except that the photon mean free path l is necessarily limited by the crystal size or, more realistically, the distribution of lattice imperfections or chemical impurities in the crystal, so τ tends to some finite value τ_0 as $T \to 0$ and $\kappa \to \frac{c_v v^2 \tau_0}{3}$. In the Debye approximation $c_V \propto T^3$ at low T, so

$$\kappa \propto T^3.$$

Crystal momentum and Umklapp processes

We can always map any wavevector into the first Brillouin zone by adding a reciprocal lattice vector. If $\mathbf{K}$ is not in the first Brillouin zone there always exists a reciprocal lattice vector $\mathbf{G}$ such that $\mathbf{K} + \mathbf{G}$ is. This is a three-dimensional generalisation of our earlier observation that, for a one-dimensional crystal with lattice spacing a, we need only consider wave-numbers $|K| \leq \frac{\pi}{a}$. If two phonons with wave-vectors $\mathbf{K}_1$ and $\mathbf{K}_2$, both in

the first Brillouin zone, collide and merge to give a single phonon with wave-vector $\mathbf{K}_3'$ then conservation of momentum says that

$$\hbar\mathbf{K}_1 + \hbar\mathbf{K}_2 = \hbar\mathbf{K}_3', \tag{27}$$

but $\mathbf{K}_3'$ may not be in the first Brillouin zone. However we can always find a reciprocal lattice vector $\mathbf{G}$ so that $\mathbf{K}_3 = \mathbf{K}_3' + \mathbf{G}$ is in the first Brillouin zone,

$$\hbar\mathbf{K}_1 + \hbar\mathbf{K}_2 = \hbar\mathbf{K}_3 + \hbar\mathbf{G}. \tag{28}$$

If $\mathbf{G} = 0$ then we obviously have

$$\hbar\mathbf{K}_1 + \hbar\mathbf{K}_2 = \hbar\mathbf{K}_3$$

identically, this called a **normal** process (N-process). Even if $\mathbf{G} \neq 0$ it still plays no role in the physics and equation (28) is completely equivalent to

$$\hbar\mathbf{K}_1 + \hbar\mathbf{K}_2 = \hbar\mathbf{K}_3. \tag{29}$$

As explained at the bottom of page 40 for a one-dimensional crystal wave-vectors outside the first Brillouin are not important for phonon physics and the same is true in three dimensions. (27) and (28) are indistinguishable physically. A $\mathbf{G} \neq 0$ process is called an **umklapp** process (U-process).[9] An umklapp process involves Bragg reflection of the final state phonon from a Brillouin zone boundary. The momentum $\hbar K$ is called the **crystal momentum** and it is not conserved absolutely in an umklapp process, it is only conserved up to a reciprocal lattice vector. Conservation laws in physics are a consequence of symmetries of the underlying dynamics and in free space conservation of momentum is a consequence of translation invariance. A crystal does not have translational invariance under arbitrary small displacements, it only has translational invariance under discrete translations by a direct lattice vector. This is a smaller symmetry than invariance under all possible translations of any magnitude and the resulting conservation law, conservation of crystal momentum, is less powerful than in free space — we only have conservation of momentum up to a reciprocal lattice vector.

At a temperature T we only expect phonons with $\hbar\omega \lesssim k_B T$ to be present and, if T is not too high, this means $\omega << \omega_D$ that $\mathbf{K}_1$ so $\mathbf{K}_2$ will be small and deep within the first Brillouin zone so that $\mathbf{K}_3$ is also well within the first Brillouin zone. Umklapp processes will then be very rare and conservation of crystal momentum is exact momentum conservation. If this is the case then there is no dissipation in phonon collisions, momentum and energy are conserved and we expect the thermal conductivity $\kappa \to \infty$ at low T (this argument assumes a perfect crystal and ignores impurities and imperfections in the crystal). As the temperature increases umklapp processes become more common and momentum leaks out of the phonons and through umklapp processes giving rise to dissipation and energy loss. Of course the total physical momentum is still conserved, $\hbar\mathbf{G}$ is absorbed by the crystal as it is buffeted about by the phonons.

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[9] "Umklapp" means "flip over" in German.