

3C25: Solid State Physics

Part 1: Structural Properties of Solids

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Autumn Term 2001

1. Order and Disorder

Atoms can condense to form solids and liquids – since they attract at large separations, and repel at short.

Typical interatomic spacing $\sim 1\text{\AA}$

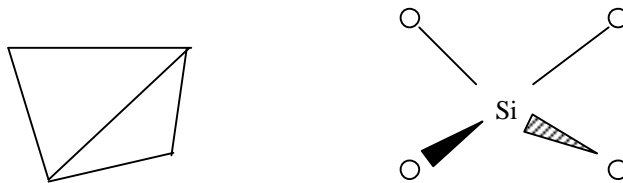
What structures can result on the microscopic scale?

a) Disordered matter.

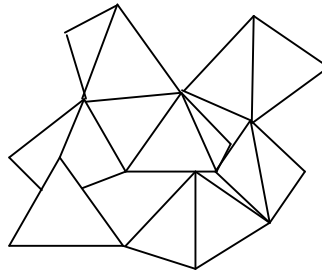
e.g. amorphous solids (glass), liquids. Each atom has a different environment.

- There can be short-range order, but no long-range order.

Silica glass (SiO_2): basic building block is tetrahedron.



The structure is formed by sharing oxygens between tetrahedra:



There is short-range order (at tetrahedral level), but none at larger distances. This is the Zacharaisen model of a glass.

b) Partial long-range order.

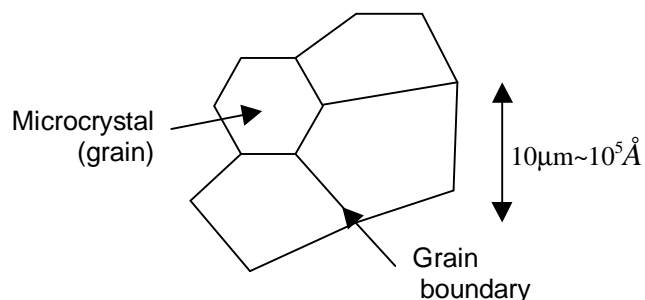
e.g. liquid crystals

- Alignment of molecules can be ordered, while spatial position can remain disordered.

c) Regular arrays of atoms (or molecules).

i.e. crystals (e.g. quartz).

- Order extends indefinitely (position and orientation). Many materials are polycrystalline, with crystals of size $\sim 10\mu\text{m}$.



Symmetry is important in classifying structures, and phases (gases, liquids, and solids)
This course is about crystals, which are easiest to understand, due to the high symmetry.

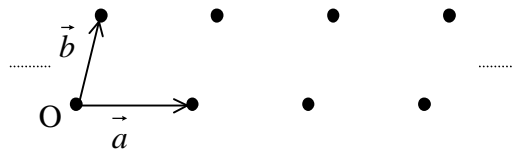
2. Crystalline Structures

The geometrical arrangement of atoms in an ideal crystal (one that extends to infinity) can be described using 2 elements – a lattice and a basis.

2.1 Lattices

2.1.1 Geometric Preliminaries and 2d Lattices

A lattice is a mathematical abstraction. It is a set of points with discrete translational symmetry. The surroundings of each point are identical.
 e.g. in 2d: the so-called “oblique lattice”.

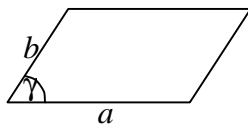


The positions of these points with respect to an origin O , are defined using Lattice Vectors. The choice is arbitrary, but a conventional set is usually chosen. The positions of the lattice points are: $\vec{R} = n\vec{a} + m\vec{b}$ where n and m are integers.

Lattice vectors must “span the space” – cannot be colinear.

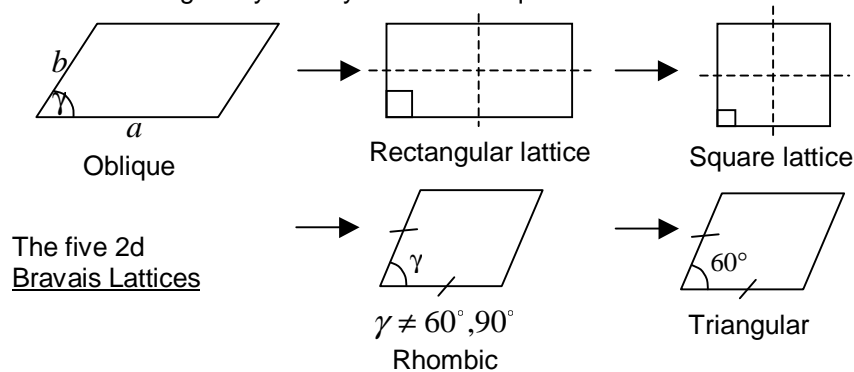
Lengths of \vec{a} and \vec{b} are written a and b – the lattice parameters.

The area $ab \sin \gamma$ is called the unit cell.



It can be repeated to fill space, mapping out the lattice.

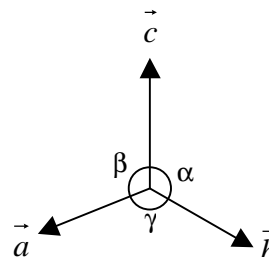
Identify 2d lattices with higher symmetry than the oblique lattice.

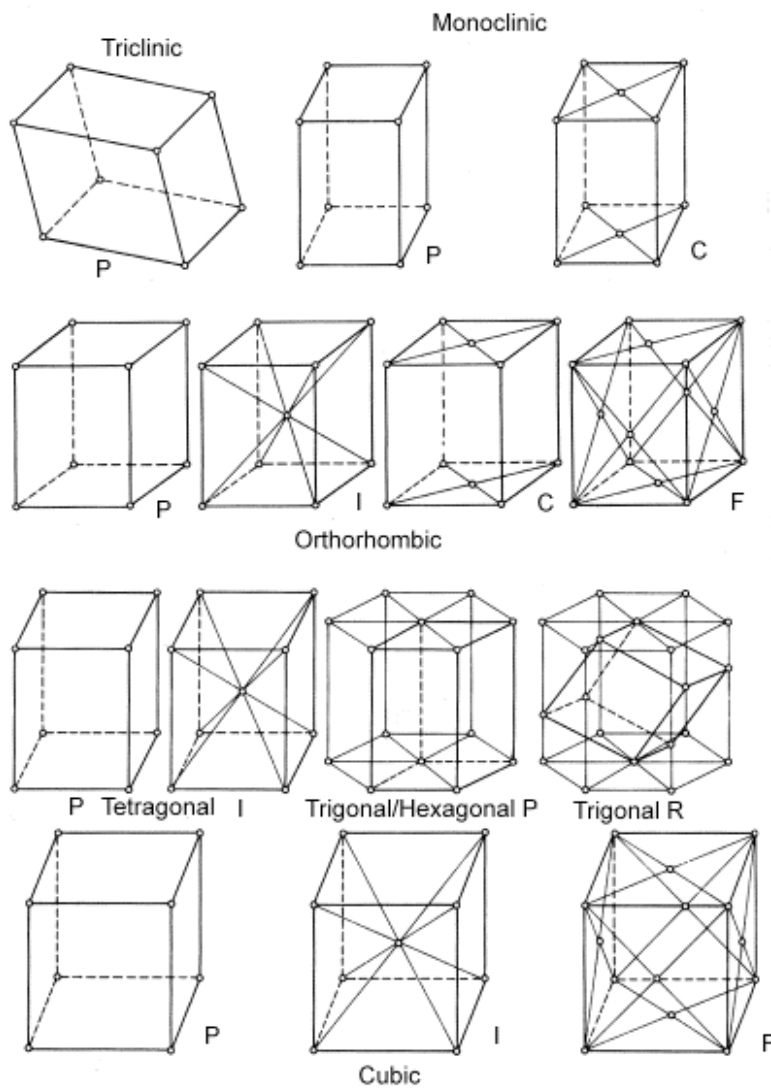


In 3d there are 14 Bravais lattices (see overleaf). Need 3 lattice vectors $\vec{a}, \vec{b}, \vec{c}$ to describe positions: they cannot be coplanar. Lattice points (with respect to an origin) at positions given by combinations of these.

3d unit cell is a parallelepiped with volume $|\vec{a} \cdot (\vec{b} \times \vec{c})|$.

The general 3d lattice is called triclinic.



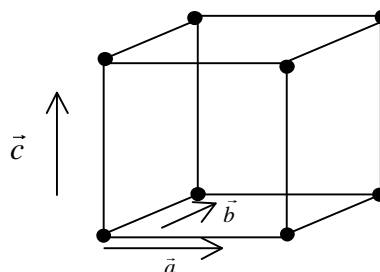


2.1.2 Important 3d Bravais Lattices

(a) Simple cubic (sc).

$$a = b = c, \alpha = \beta = \gamma = 90^\circ$$

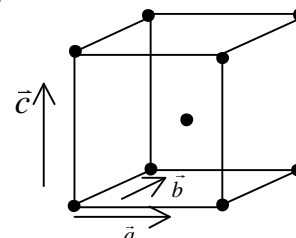
Conventional unit cell:



Contains one lattice point: eight vertices each shared by eight adjacent unit cells.

(b) Body centred cubic (bcc).

Extra lattice point at centre. There are 2 points in the conventional cell. $8 \times \frac{1}{8} + 1 = 2$

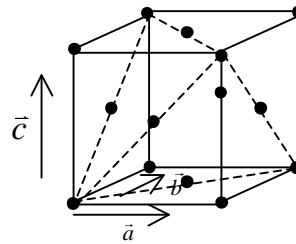


(c) Face centred cubic (fcc).

Extra points on faces.

There are 4 lattice points per cell.

$$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$



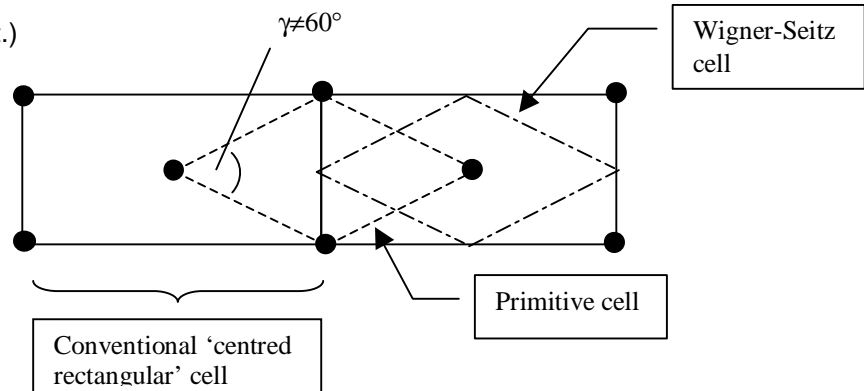
2.1.3 Primitive Unit Cell

This is a unit cell which contains one lattice point. Sometimes used as an alternative description. It is defined by primitive lattice vectors.

The three lattices so far were described using a primitive cell for sc, and non-primitive cells for bcc and fcc. These conventional cells demonstrate the symmetry of the lattice better.

(See 'Primitive cells' handout.)

The rhombic unit cell is the primitive unit cell of a "centred rectangular" lattice in 2d.



A particular primitive cell is called the Wigner-Seitz cell. This is centred on a lattice point and denotes the volume of space which is closest to that lattice point rather than any other. Useful for ascribing a "zone of influence" around a lattice point.

2.2 The Basis – and Derived Structures

An ideal crystal structure consists of a lattice with a group of atoms associated with each lattice point. This group is the basis (or motif), : it is said to *decorate* the lattice.

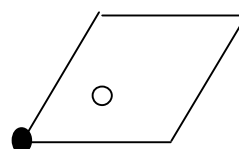
The basis could be a single atom (lattice and structure then equivalent)

- copper is a fcc structure.
- low temperature iron is a bcc structure.
- polonium is a sc structure.

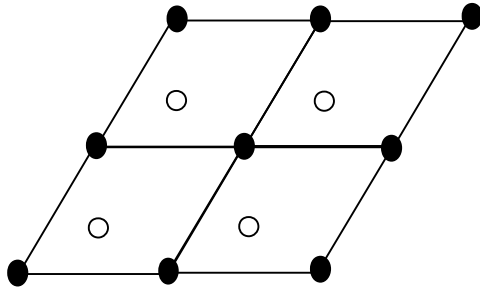
But there can be larger (non-trivial) bases:

(i). In 2d, consider the triangular lattice with a diamond-shaped unit cell. Apply a basis of 2 atoms.

- : one at the origin of the cell. (Filled circle)
- : one at $\frac{1}{3}(\vec{a} + \vec{b})$ (Open circle)



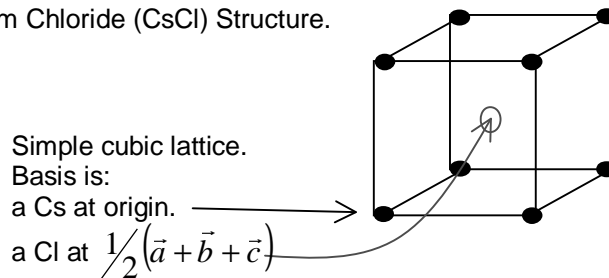
Now put several together:



If you join the nearest neighbours, you get a hexagonal sheet! Now disregard difference between open and filled symbols, and it looks like the sheet structure of graphite.

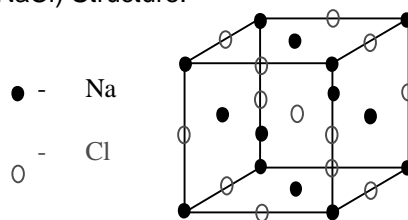
The lattice in graphite is either subset of open or closed symbols. The hexagonal structure of a sheet of graphite requires a basis of two atoms to be associated with each lattice point. The surroundings of all the atoms in the sheet are not identical.

(ii). Caesium Chloride (CsCl) Structure.



Similar to bcc, but different, since central atom is not the same as atoms at vertices.

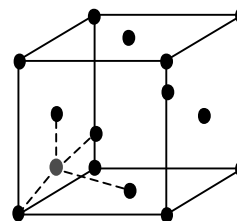
(iii). Sodium Chloride (NaCl) Structure.



An fcc lattice decorated by a basis of Na at the origin and Cl at $\frac{\vec{a}}{2}$

(iv). Diamond.

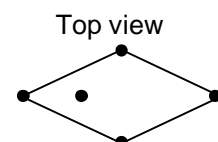
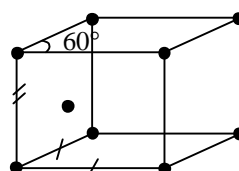
An fcc lattice decorated by a basis of two atoms, one at the origin, one at $\frac{1}{4}(\vec{a} + \vec{b} + \vec{c})$



If the two atoms in the basis differ, then the structure is known as zinc blende, or ZnS, instead of diamond.

(v). Hexagonal Close Packed hcp

Simple hexagonal Bravais lattice.



$$a=b \neq c$$

$$\gamma=60^\circ$$

Basis: one atom at origin, one at $\frac{1}{3}(\vec{a} + \vec{b}) + \frac{1}{2}\vec{c}$

Also requires $c = \sqrt{\frac{8}{3}}a$ in order that the central atom is at a distance a from the origin: then all atoms in the structure have twelve equidistant nearest neighbours.

2.3 Coordination Number and Coordination Polyhedra

Each structure can be characterised by the number of nearest neighbours possessed by each atom – the coordination number.

Also, joining up the nearest neighbours gives the coordination polyhedron.

Structure	Coordination Number	Coordination Polyhedron
Hexagonal sheet	3	Triangle
Diamond and ZnS	4	Tetrahedron
sc and NaCl	6	Octahedron
bcc and CsCl	8	Cube
fcc	12	Cuboctohedron
hcp	12	Rhombic dodecahedron

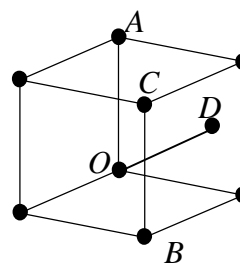
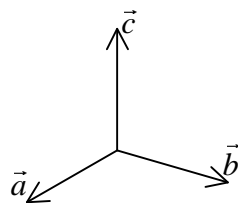
2.4 Crystal Directions and Planes

2.4.1 Directions

Specify a direction using the lattice vectors.

$$\vec{v} = h\vec{a} + k\vec{b} + l\vec{c}$$

hkl : Miller indices – integers with no common denominator. Notation $[h k l]$
e.g. in sc structure.



Direction OA is written $[0 0 1]$
 Direction OB is written $[1 1 0]$
 Direction OC is written $[1 1 1]$
 Direction DC is written $[2 1 1]$

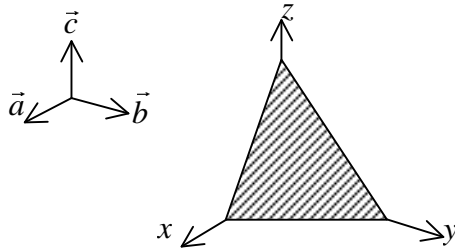
Negative indices are written with an overbar.

OD is written $[\bar{1} 0 0]$

Further notation: a family of directions that are equivalent under the symmetries of the structure.

$\langle 100 \rangle \equiv [1 0 0], [0 1 0], [0 \bar{1} 0]$ etc...

2.4.2 Planes



Place the origin on one plane, and examine where the next plane up intersects the axes.

Intercepts on axes:

$$\frac{a}{h} \text{ on the } x\text{-axes.}$$

$$\frac{b}{k} \text{ on the } y\text{-axes.}$$

$$\frac{c}{l} \text{ on the } z\text{-axes.}$$

The equation of the plane is: $\frac{h}{a}x + \frac{k}{b}y + \frac{l}{c}z = 1$

Orientation of the plane is uniquely defined by hkl .

If the plane we select is not the next plane up, then we might come out with indices which are not integers, or which have a common factor. Convention is to choose integers with no common factors. These specify the orientation of a plane uniquely. hkl = Miller indices of a plane.

Notation of one orientation is (hkl) . A family of equivalent orientations is written $\{hkl\}$.
 $(110), (011), (101), \dots = \{110\}$

N.B. If a plane does not intersect an axis (e.g. z-axis), $l = 0$

Why such a system? For cubic structures, plane (hkl) is perpendicular to direction $[hkl]$. Also relates to *reciprocal space* description of structures (not covered in this course).

Miller indices can be used to calculate angles between faces – for cubic crystals.

Unit vector normal to (hkl) :

$$\hat{n}_{hkl} = \frac{h\vec{a} + k\vec{b} + l\vec{c}}{a(h^2 + k^2 + l^2)^{1/2}}$$

$$\hat{n}_{hkl} \cdot \hat{n}_{h'k'l'} = \cos \theta$$

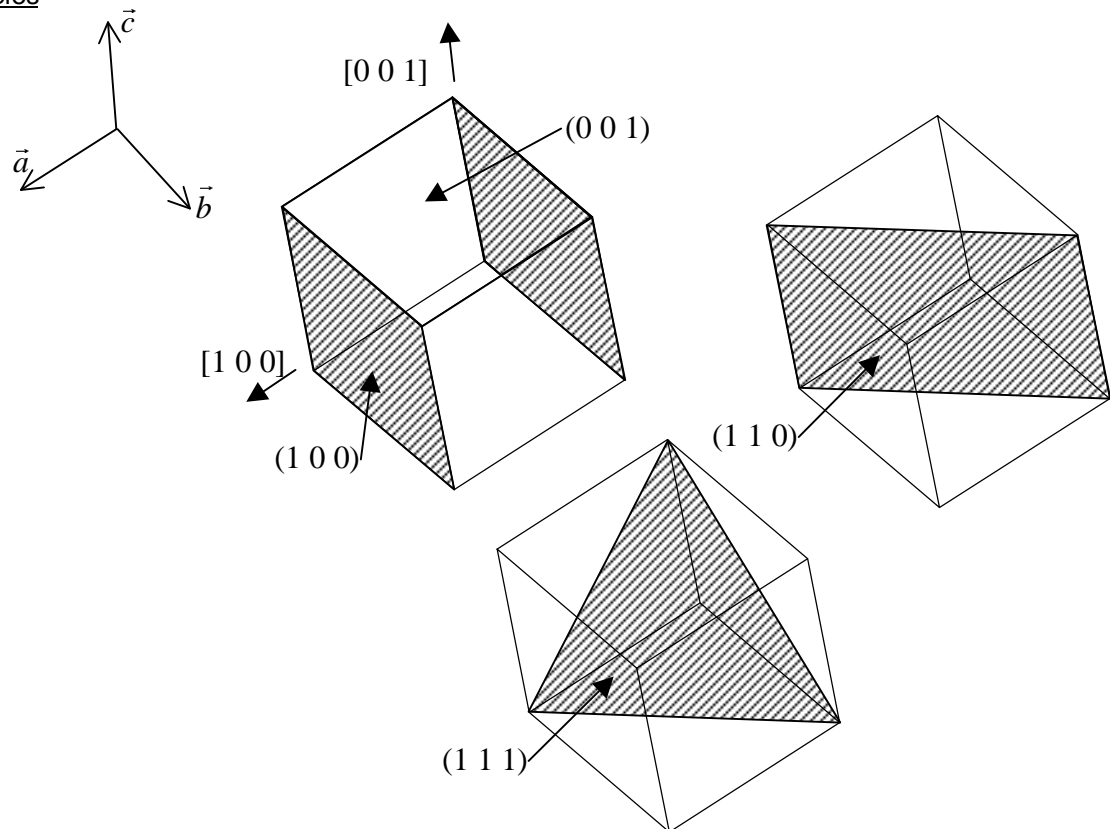
θ = Angle between the (hkl) and $(h'k'l')$ planes.

$$\cos \theta = \frac{hh' + kk' + ll'}{(h^2 + k^2 + l^2)^{1/2} (h'^2 + k'^2 + l'^2)^{1/2}}$$

for cubic crystals only.

Again for cubic crystals, the separation between (hkl) planes is $d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$

- check with following examples!

Examples**2.5 Stacking of close-packed planes in fcc and bcc**

See handout

2.6 Summary

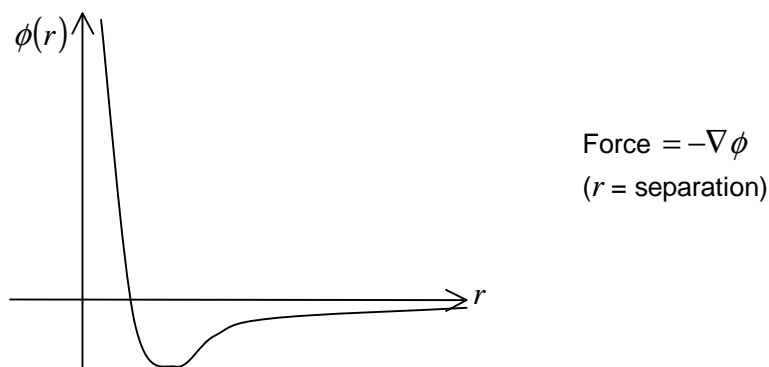
1. A crystal consists of a lattice of points each decorated by a basis of atoms. Each lattice point has an identical environment. Atoms in the basis need not.
2. Symmetry is important for classification of structures.
3. Unit cells fill space by repetition. (Various sorts: conventional, primitive, Wigner-Seitz)
4. Atoms in a structure have characteristic co-ordination numbers and coordination polyhedra.
5. Planes and directions can be specified using Miller indices.

3. Cohesion

How atoms bind together.

3.1 The Interatomic Potential

Simplest models of cohesion divide interactions in a solid into pairwise forces. More sophisticated treatments involve 3-body forces etc. There are attractive and repulsive terms. A pairwise interatomic potential will have the minimal form:



All this is due to forces between the electrons and nuclei on one atom, and those on the other.

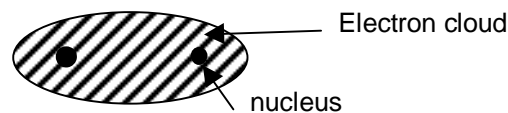
3.1.1 Attractive Forces between Atoms

- (i). Electron transfer between atoms – ionic bonding (e.g. ceramics, and minerals, sodium chloride).

Na transfers an electron to Cl, fills shells of electrons on each atom, producing spherical electron clouds, with net +ve or –ve charges. Electrostatic forces: isotropic or non-directional.

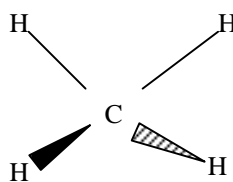
- (ii). Electron sharing – covalent bonding.

e.g. In H_2 electrons “orbit” both atoms, which produces a lower energy state
– See material later in course.



Quantum mechanics tells us that these bonds are directional. The orientation of one bond determines a preferred orientation of others.

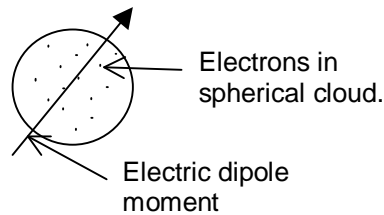
⇒ Methane with tetrahedrally arranged bonds



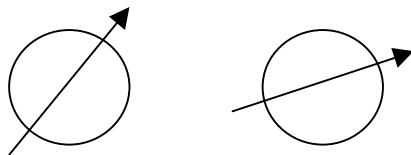
- (iii). Electron correlation on separate atoms: van der Waals bonding.

Classical picture (although QM is better):
Each atom has a filled electron shell – no opportunities for electron transfer or sharing.

Also known as London force, dispersion force.
- non-directional



Mean moment is zero.

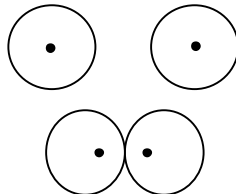


- orientations are correlated.
- Correlations lead to a reduction in energy.

3.1.2 Repulsive Force

- (i). Ionic repulsion – see above.
- (ii). Pauli exclusion principle forbids electrons to occupy the same state.

When filled electron shells are made to approach each other, we are effectively demanding that they violate this exclusion principle, and they resist by increasing their kinetic energy.



Repulsion as though atoms were “hard spheres”. Sometimes called hard-core repulsion, or Pauli repulsion.

- This repulsion is due to localised, core electrons (those in filled shells). Short range repulsive potential. The same principles applied to the delocalised (‘free’) electrons in metals produce a long range repulsion – see material in Part 2).

3.1.3 Model Interatomic Potential

$$\phi(r) = \frac{A}{r^n} - \frac{B}{r^m} \quad \text{(Mie potential)}$$

Hard core repulsion	$n=12$	} Lennard-Jones potential
Van der Waals attraction	$m=6$	
Ionic attraction	$m=1$	
Pauli repulsion in metals	$n=2$	

Covalent bonding cannot be represented using a non-directional pairwise potential: constraints on bond angles have to be introduced.

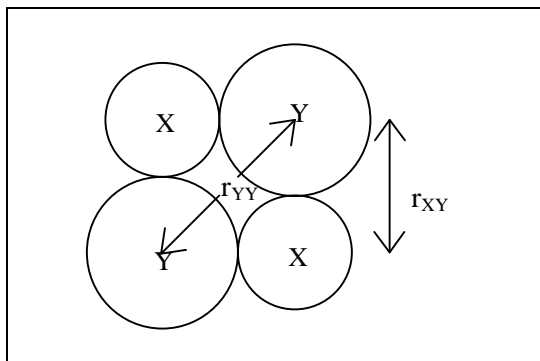
3.2 Selection of structure by geometry: packed arrays of spheres.

If we know the atomic or ionic 'radii', we can determine the feasibility of different structures simply by geometry in some cases. The atomic radius is the radius at which the hard core repulsion acts strongly: the radius of the filled electron shells. The procedure is very simple.

For example, consider the X^+Y^- class of ionic solids. You've seen two structures named after such materials, namely the NaCl and CsCl structures, with coordination numbers six and eight respectively. Which of these is taken by a given material?

We simply build a structure and check that the spheres fit together. In cases where the atomic radii are very different, this is not always possible. The procedure is to assume that the nearest neighbours are separated by the sum of their atomic radii, i.e. the spheres are touching. Then we check that the separation between second nearest neighbours is greater than or equal to the sum of their radii, etc.

Consideration of the NaCl and CsCl structures tells us that the first nearest neighbours of an ion are of the opposite type, and the second nearest neighbours are the same type. For example, the following is part of a (100) plane in NaCl:



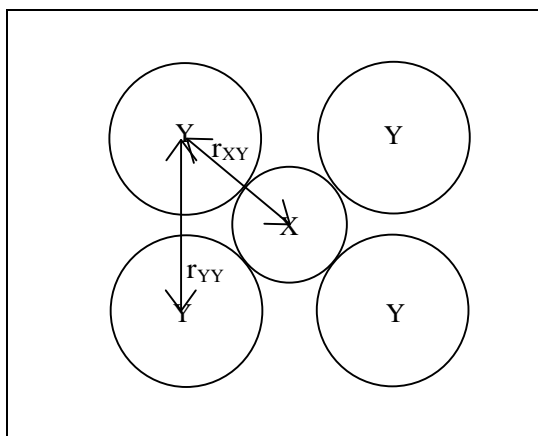
We have $r_{XY} = r_X + r_Y$

and $r_{YY} = \sqrt{2} (r_X + r_Y)$ which must be $\geq 2r_Y$

so $r_Y/r_X \leq 1/(\sqrt{2}-1)$

is the geometric condition for the ions to form the NaCl structure.

Now consider the (110) plane in the CsCl structure, which contains the first and second nearest neighbour separations.



The nearest neighbour distance is still $r_{XY} = r_X + r_Y$, but the second nearest neighbour is not the same as in NaCl. As a result, the same arguments lead to a different condition which must be met by the atomic radii to allow this structure to occur. Simple geometry can be used to show that it is

$$r_Y/r_X \leq 1/(\sqrt{3}-1)$$

3.3 Selection of structure through thermodynamic arguments

This is more general than geometric considerations. In thermal equilibrium at constant temperature and pressure, Nature selects the structure which minimises the Gibbs free energy.

$$G = E - TS + pV$$

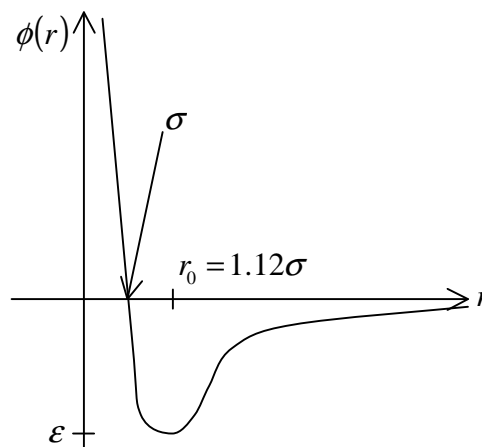
Simplify matters, work with $T = 0$, and $p = 0$. Furthermore neglect kinetic energy.

- left with the minimisation of potential energy (and neglect quantum effects for now). Later we shall include entropy.

3.3.1 Van der Waals Solids

- Van der Waals attraction, hard core repulsion – the L-J potential.
- Solid noble gases (Ne, Ar, Kr, Xe) and halogens (F, Cl, Br, I).

$$\text{and } \phi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad \begin{array}{l} \varepsilon = \text{depth of potential,} \\ \sigma = \text{scale distance.} \end{array}$$



$\varepsilon =$ dimer binding energy.

Place origin at a particular atom. Contribution to potential energy of a structure due to pairwise interactions involving this atom is:

$$V_1 = \sum_i \phi(r_i) \quad i \text{ labels atoms in the structure, at a distance } r_i.$$

Total PE of the structure:
$$V = \frac{1}{2} NV_1$$

$N =$ number of atoms in the structure.

$\frac{1}{2}$ to avoid double counting [ϕ is a pair potential]

write $r_i = \alpha_i a$

where: $a =$ nearest neighbour distance.

$\alpha_i =$ dimensionless number ≥ 1

So
$$\phi(r_i) = 4\epsilon \left(\frac{1}{\alpha_i^{12}} \left(\frac{\sigma}{a} \right)^{12} - \frac{1}{\alpha_i^6} \left(\frac{\sigma}{a} \right)^6 \right)$$

and
$$V = 2\epsilon N \left(A_{12} \left(\frac{\sigma}{a} \right)^{12} - A_6 \left(\frac{\sigma}{a} \right)^6 \right)$$

where
$$A_{12} = \sum_i \frac{1}{\alpha_i^{12}}$$

$$A_6 = \sum_i \frac{1}{\alpha_i^6}$$

These are called "lattice sums" – dimensionless numbers, depend on structure.
(See handout sheet 3.3.1.1)

e.g. for 2-d square structure:

$$A_{12} = \frac{4}{1^{12}} + \frac{4}{\sqrt{2}^{12}} + \frac{4}{2^{12}} + \frac{4}{\sqrt{5}^{12}} + \frac{4}{2\sqrt{2}^{12}} \approx 4.064$$

and $A_6 \approx 4.634$ by similar computation

Now minimise V with respect to a .

$$\frac{dV}{da} = \frac{2\epsilon N}{\sigma} \left(-12A_{12} \left(\frac{\sigma}{a} \right)^{13} + 6A_6 \left(\frac{\sigma}{a} \right)^7 \right) = 0$$

$$\Rightarrow a_o = \left(\frac{2A_{12}}{A_6} \right)^{\frac{1}{6}} \sigma \quad (\text{equilibrium nearest neighbour distance})$$

$$V(a_o) = -\frac{A_6^2}{2A_{12}} \epsilon N = -V_{coh} \quad V_{coh} - \text{cohesive energy.}$$

Need to look at a variety of 3-d structures to find the maximum cohesive energy.

	sc	bcc	fcc
A_6	8.4	12.25	14.45
A_{12}	6.2	9.11	12.13
$\frac{V(a_o)}{N\epsilon}$	-5.69	-8.24	-8.61

So, Van der Waals bonded materials will take the fcc structure (for single atomic species).

3.3.2 Ionic Solids

Ionic attractive and repulsive forces, and hard core repulsions. Van der Waals attractions neglected.

Consider NaCl, or CsCl structures.

Pair potential:
$$\phi(r) = \pm \frac{e^2}{4\pi\epsilon_0 r} + \frac{4\epsilon\sigma^{12}}{r^{12}}$$

(It is assumed that the hard core repulsive term between the same sign ions is the same as between opposite sign ions)

As, before,
$$V = \frac{N}{2} \sum_i \phi(r_i)$$

$$\frac{V}{N} = \frac{\gamma e^2}{8\pi\epsilon_0 a} + 2\epsilon A_{12} \left(\frac{\sigma}{a}\right)^{12} \quad \text{where: } \gamma = \sum_i \frac{\pm 1}{\alpha_i} \quad \begin{array}{l} (+ \text{ for like charges,} \\ - \text{ for unlike charges)} \end{array}$$

e.g. linear chain of ions.



$$\begin{aligned} \gamma &= \sum_i \frac{1}{\alpha_i} = \left[-2 + \frac{2}{2} - \frac{2}{3} + \frac{2}{4} - \dots \frac{2}{n} \dots \right] \\ &= -2 \ln 2 \end{aligned}$$

γ is called the Madelung constant. It depends upon the structure.

e.g. NaCl : $\gamma = 1.748$
CsCl : $\gamma = 1.763$

We can determine structure by minimising the PE, as before.

3.3.3 Hydrogen bonded materials

Can be thought of as an electrostatic attraction between charge distributions in covalent bonds on different atoms. Important in liquid water and ice. Can be modelled with suitable potentials.

3.3.4 Covalent Materials

Electrons are shared amongst all atoms in a structure, but tend to congregate between atoms, forming directional bonds. Structures tend to be 'open' (low coordination numbers). Needs a quantum mechanical description [See Part 2].

3.3.5 Metals

Extreme form of covalency. Electrons are shared between all atoms in a near-uniform cloud, or "gas". Bonds tend to be non-directional. Structures tend to be close-packed. [See Part 2]

4. Experimental Determination Of Structure

Most common technique is to scatter particles or radiation off a sample, and analyse the results. Use a crystal as a 3-d diffraction grating.

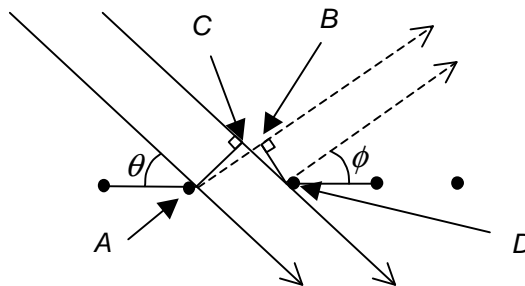
Probe	Energy	λ	Scattered by	Penetration length
x-ray	10^4 eV	1.2 Å	electrons	~10 cm
neutron	10^{-2} eV	2.8 Å	nuclei	~10 cm
electron	50 eV	1.7 Å	electrons	~1 μm

Analyse the scattered rays using various theoretical techniques
 \Rightarrow lattice parameters + structures.

4.1 Bragg's Law

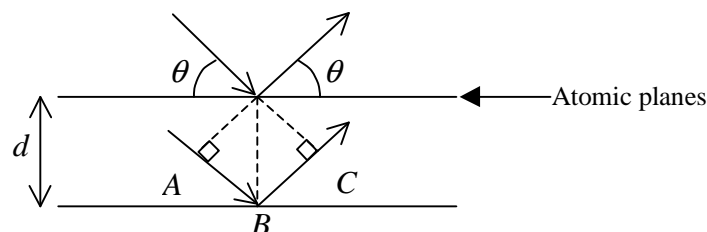
Simple version of full diffraction theory (Laue theory).

- (i). Consider first a single plane of scatterers, illuminate with radiation at glancing angle θ .



Zeroth order diffraction requires $AB=CD$, so $\theta=\phi$ a "reflection".

- (ii). Now consider a stack of planes.



Only if $ABC = n\lambda$ will the "reflections" off planes interfere constructively.

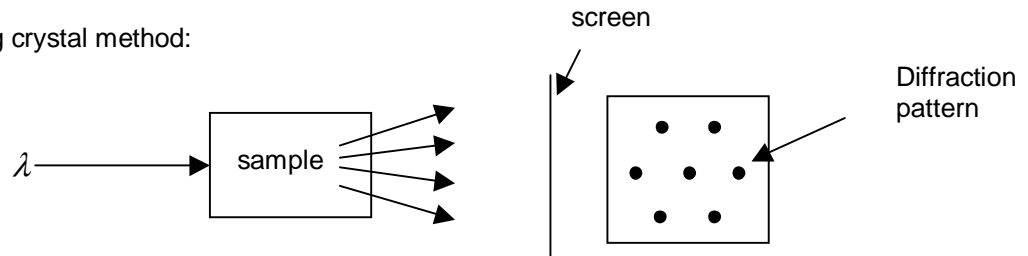
$$ABC = 2d \sin \theta = n\lambda \quad \text{Bragg's Law.}$$

Define scattering angles 2θ for n^{th} order diffractions off the planes with separation d .

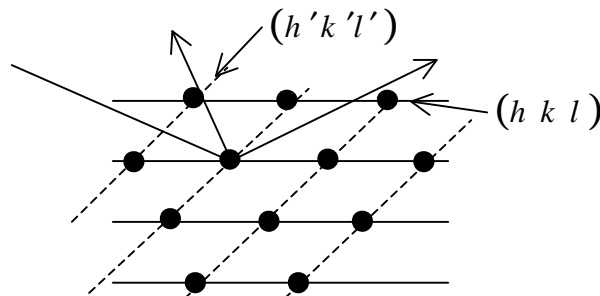
4.2 Experimental Methods

Methods are similar for x-ray, neutrons, electrons.

(i). Rotating crystal method:



Single wavelength probe beam, single crystal sample. Rotate the sample to the glancing angle upon a set of planes that satisfies the Bragg condition is met. There is then a strong deflection peak.



If a plane $(h k l)$ satisfies the Bragg condition with $n > 1$, i.e.

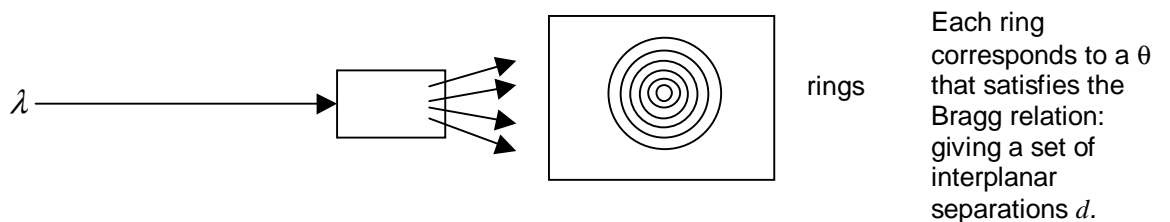
$$2d_{hkl} \sin \theta_{hkl} = n\lambda$$

it written as the $(nh nk nl)$ 'reflection', or diffraction.

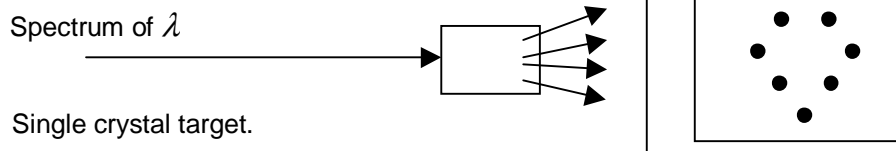
Use theoretical methods in scattering theory to determine the structure from the scattering angles.

(ii). Powder Photograph (Debye-Scherrer method).

Single wavelength source, finely divided powder target. All orientations of the sample are presented simultaneously. No need to rotate the sample.



(iii). Laue Photograph.



Useful for determination of symmetry of structure. Entire structure obtained if wavelengths of diffracted beams can be determined.

4.3 Interpretation of Intensities of the Diffracted Beams

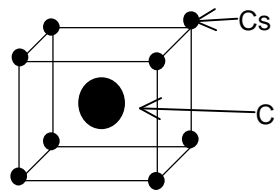
We've assumed the scatterers are 'point-like'. In reality, it is the basis of atoms at each lattice point that scatters the radiation.

Scattered rays are anisotropic in general, and with various strengths from different atoms.

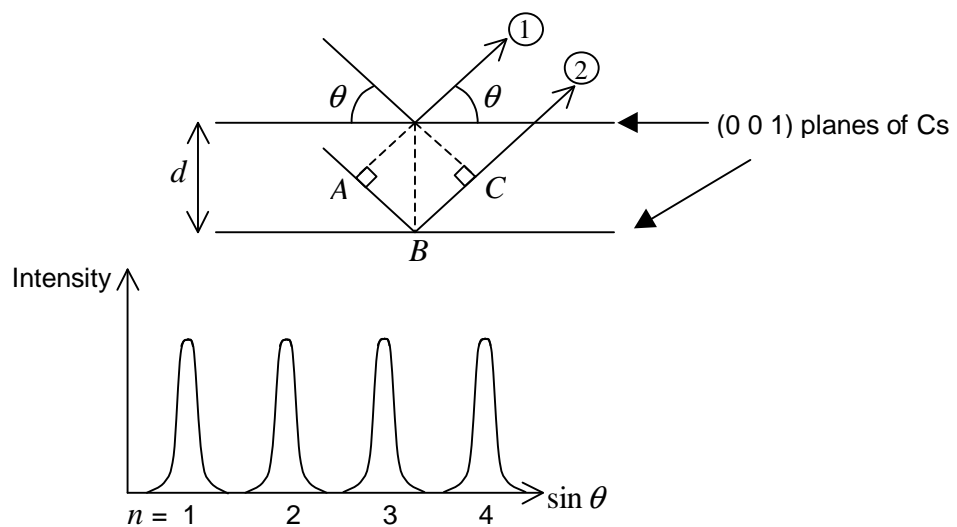
- ⇒ Intensities tell us the structure of the basis
- ⇒ Techniques for determining molecular structure (e.g. DNA, proteins)

Simple example

CsCl structure



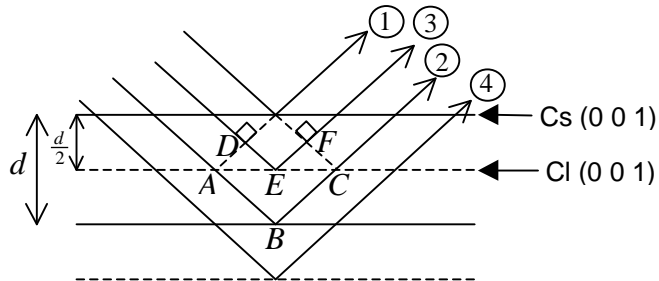
- (i). First ignore scattering from Cl.
 Bragg condition: $ABC = n\lambda = 2d \sin \theta$



Order of diffraction

(ii). Now switch on Cl scattering.

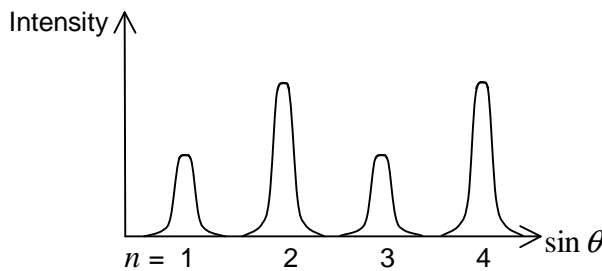
$$DEF = 2 \frac{d}{2} \sin \theta = \frac{n\lambda}{2}$$



If rays ① and ③ have amplitudes A_1 and A_3 , the intensity of the superposition will be:

$$|A_1 + A_3|^2 \text{ if } n \text{ is even. (constructive interference).}$$

$$|A_1 - A_3|^2 \text{ if } n \text{ is odd. (destructive interference).}$$

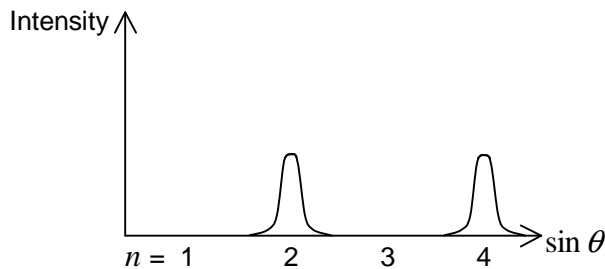


① and ③ in phase if n is even, out of phase if n is odd.

So, pattern of intensities tells us something about the basis.

(iii). Now regard the Cl planes as equal in scattering strength to the Cs planes.

⇒ complete destructive interference if n is odd.



“Missing orders” due to interference. This is a property of the bcc structure, when the atoms occupying Cs and Cl are identical.

4.4 Surface probe microscopy

4.4.1 Scanning tunnelling microscope

Measure quantum mechanical tunnelling current between an extremely sharp tip and a surface. Gives image of the electron density distribution in the surface.

4.4.2 Atomic force microscope

Drag tip across the surface, or make it oscillate above the surface. Measure the force on the tip, which is a reflection of the force between atoms in the tip and atoms in the surface. Gives an image of the atomic distribution in the surface.