3C25

CRYSTAL STRUCTURES

Lecture 1

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1 Crystal Structures

FIGURE 1: Crystals of native copper.

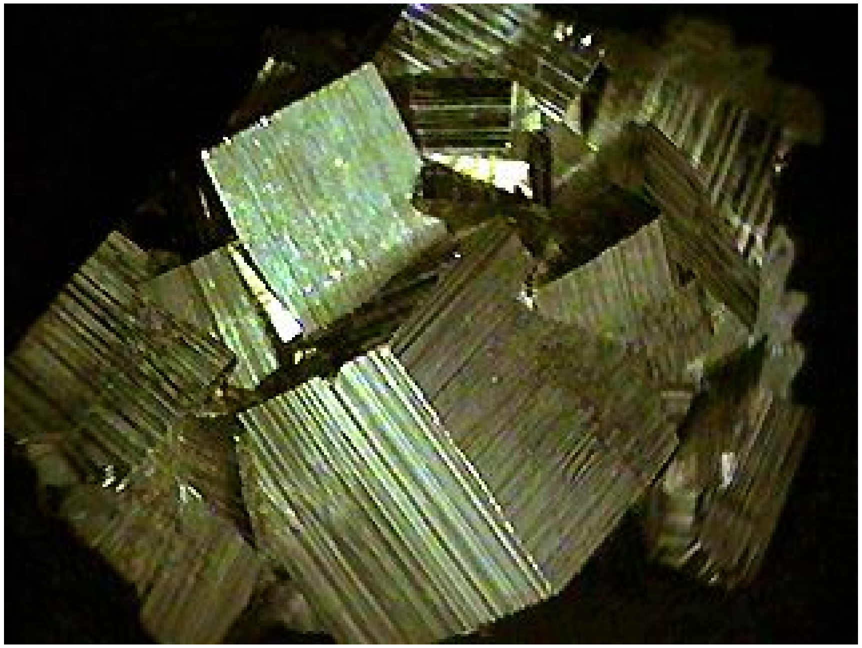


FIGURE 2: Crystals of pyrite (FeS_2).

FIGURE 3: Crystals of quartz ($\mathrm{SiO_2}$) - the original $\kappa\rho\upsilon\sigma\tau\alpha\lambda\lambda o\varsigma$.

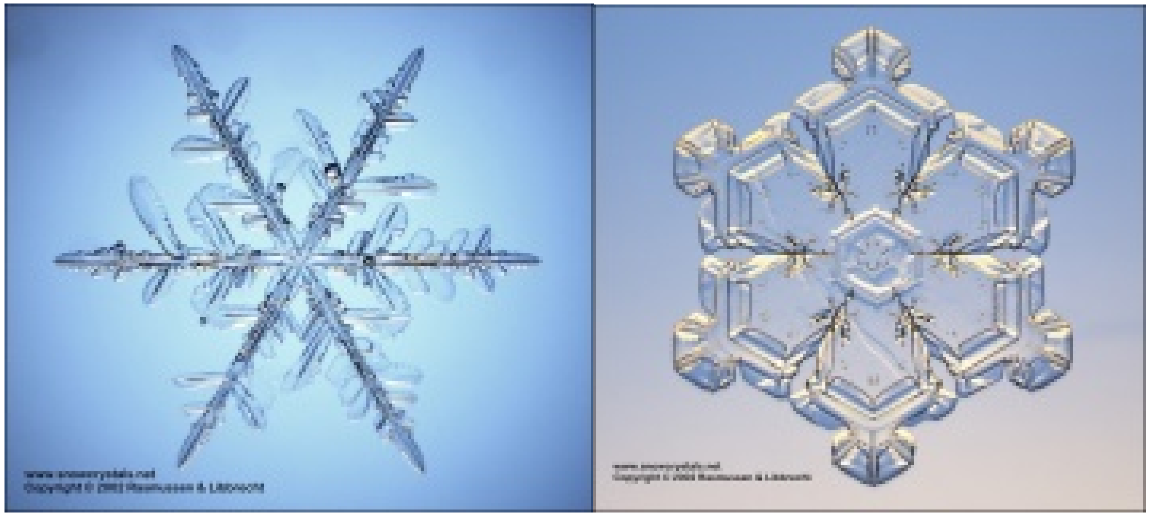


FIGURE 4: Snow crystals.

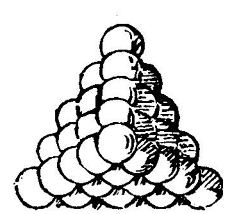
FIGURE 5: Crystals of stibnite (Sb_2S_3).

1.1 What is special about crystals?

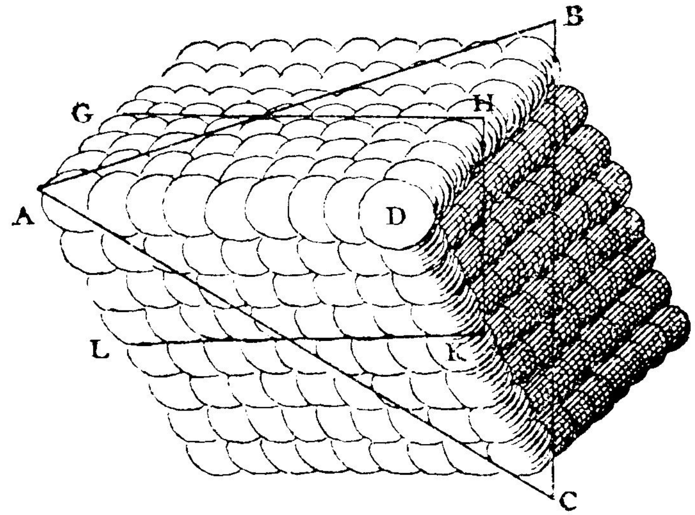
- **precise symmetries**
- **flat surfaces**
- **straight edges**
- **Haüy's "Tout est trouvé!" on dropping iceland spar**

1.2 What does this suggest about their structure?

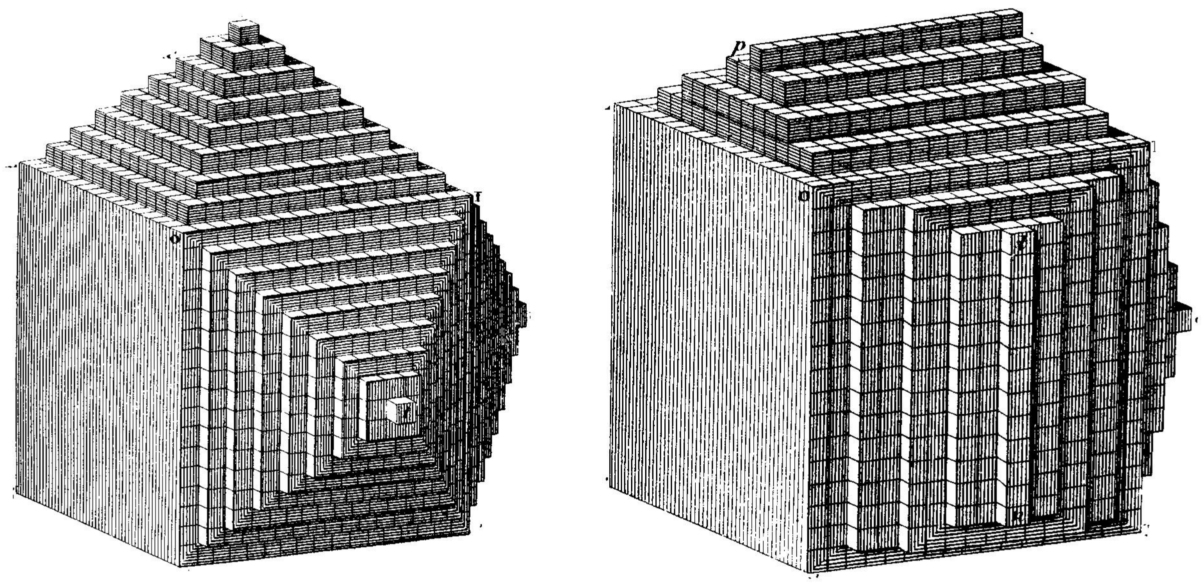
Regular pattern of simple building blocks (Kepler, Robert Hooke, Huygens, Descartes).



A crystal made from spherical particles, according to Robert Hooke (*Micrographia Restaurata*, London 1745).



Christiaan Huygens's picture of a calcite ($\mathrm{CaCO_3}$) crystal made from spherical particles (*Traité de la Lumière*, Leiden 1690).



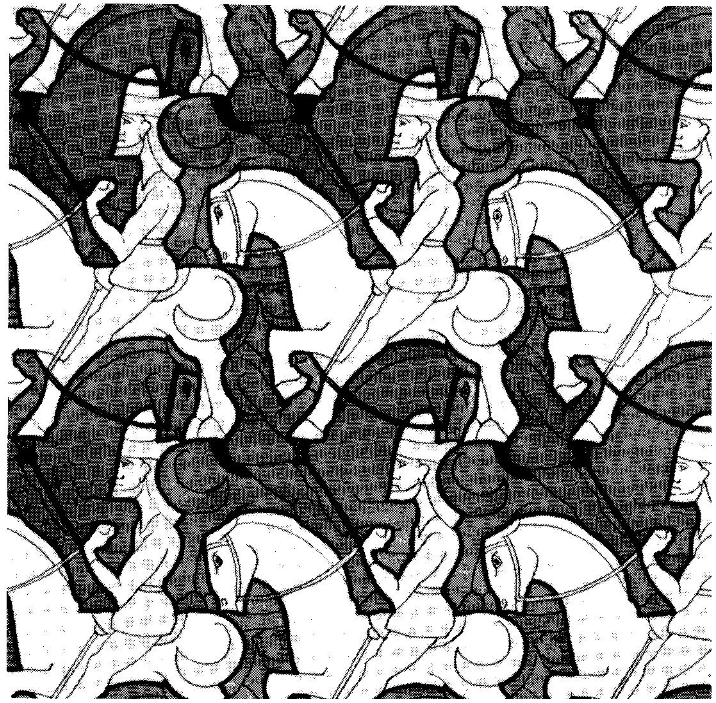
A crystal structure as depicted by René Haüy (*Traité de Cristallographie*, Paris 1822).

1.3 Artistic Example

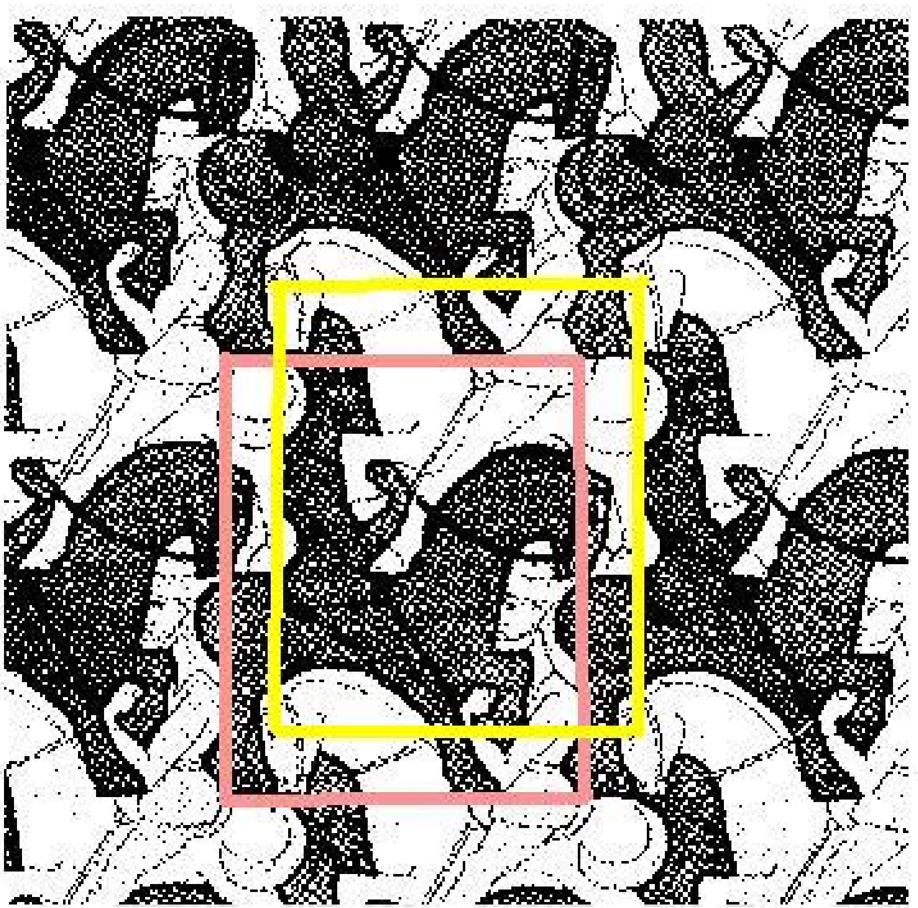
The key points about building this pattern are that

***motifs* are assembled *periodically* the motifs are all in the same orientation note that the motif contains *two* knights**

Figure shows engravings by M.C. Escher



The plane is completely filled.



We can pick a unit cell: but note

- **the unit cell is not unique. For example, we could pick a cell with a white knight in the middle**
- **or we could pick a larger cell which could be a bigger square or a rectangle or other shape**

1.4 Formal description

Separate the motif from the repetition pattern.

1.4.1 The Lattice

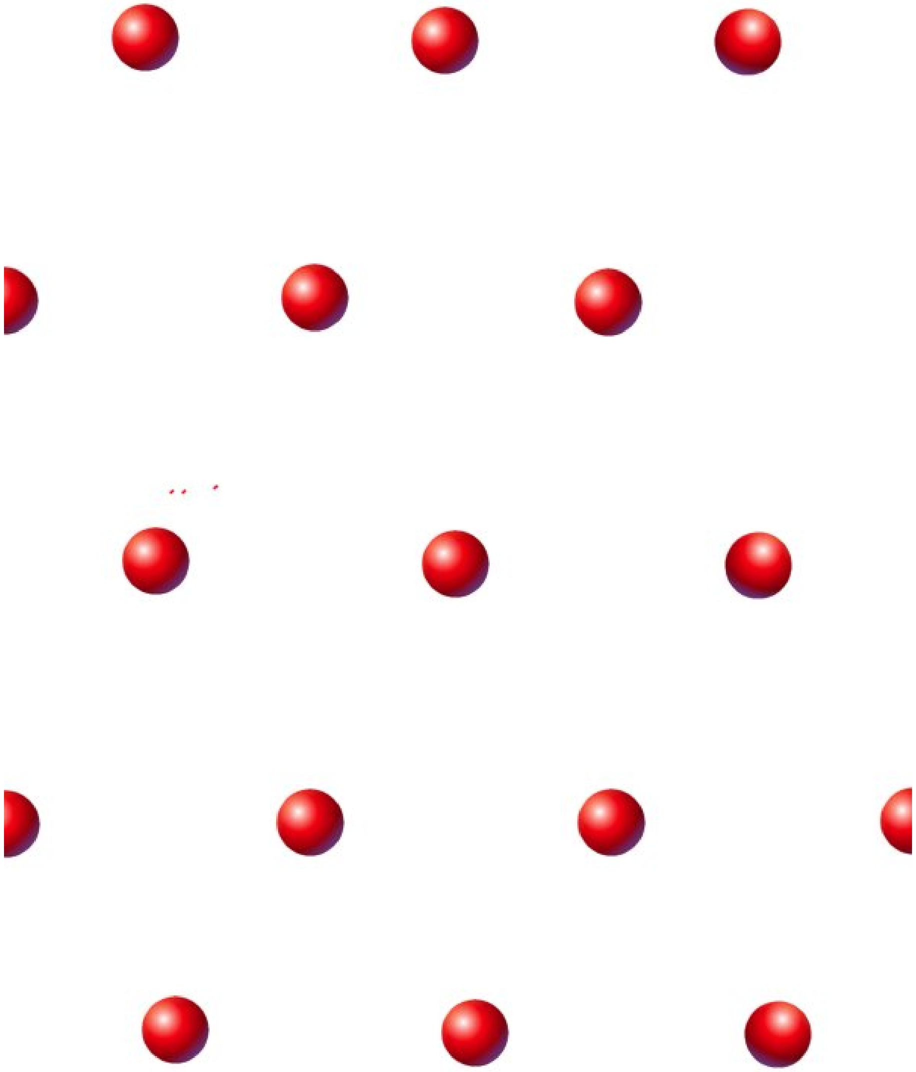
A *lattice* is an arrangement of points in space such that the environment of any point is identical to that of any other point.
Note: points, space – this is now a *mathematical problem*.
The mathematicians tell us how many different lattice types there are in spaces of 2, 3,... dimensions. These are the *Bravais lattices*. Lattices have symmetries, more fully *point group symmetries*, described in terms of rotations and reflections.
Remember: the lattice is *not* the crystal – it's the collection of points in space on which the crystal is hung (but people often use the word lattice when they mean crystal).

1.4.2 Lattice vectors

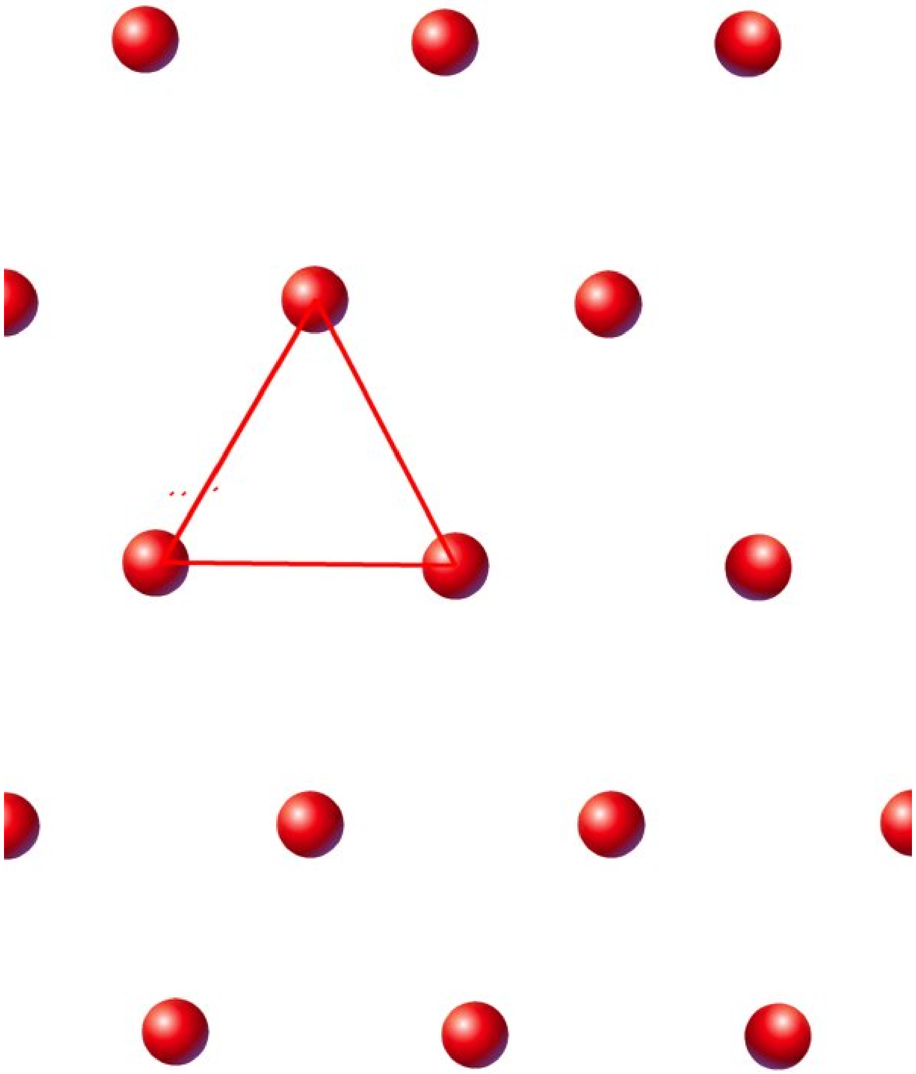
A *lattice vector* is any vector joining two lattice points. It is convenient to define a set of *primitive lattice vectors*: this is the set of the shortest linearly independent lattice vectors. Linear independence ensures that they can span all dimensions of the space - for example, in 2D they must not be parallel, and in 3D in addition they must not lie in the same plane. These vectors, conventionally referred to as a, b and c, allow us to start from any point on the lattice and generate the rest of the lattice points at $n_1\mathrm{a} + n_2\mathrm{b} + n_3\mathrm{c}$ where n_1, n_2 and n_3 are integers, running in principle from $-\infty$ to $+\infty$.

1.4.3 The Unit Cell

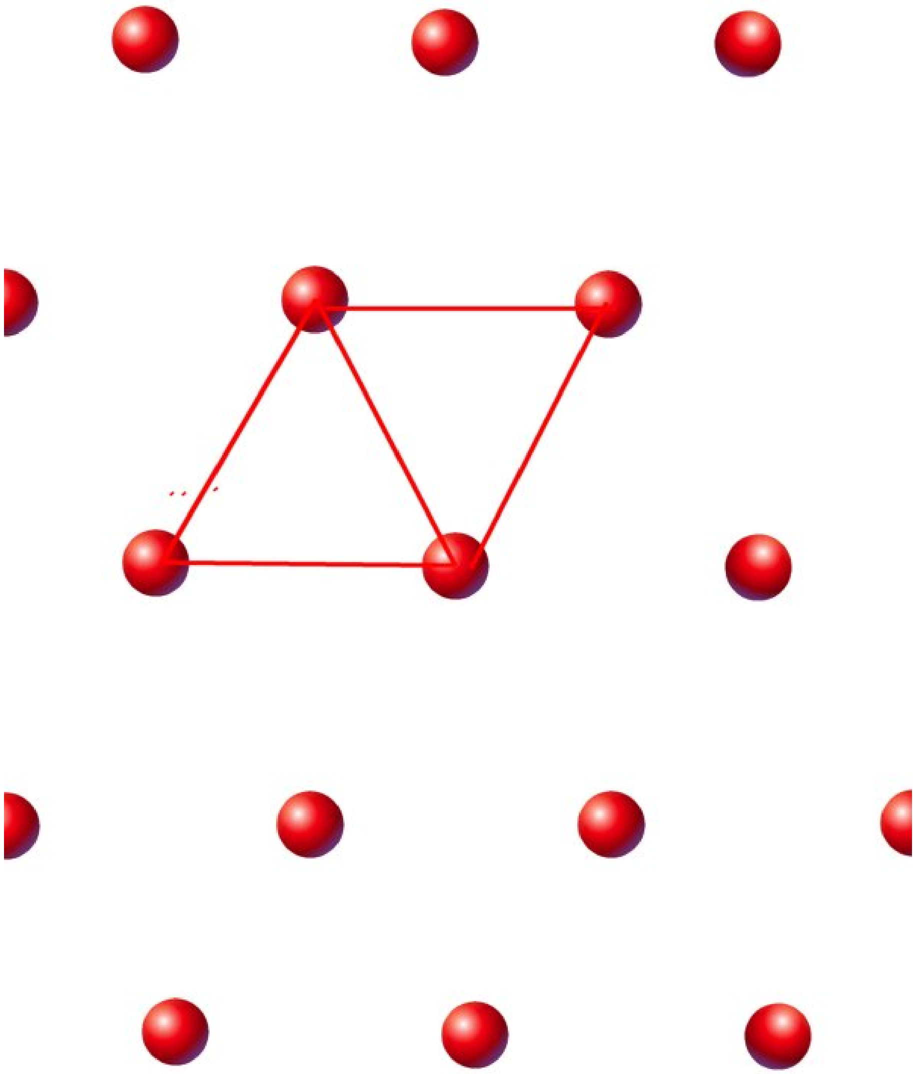
A *unit cell* is a volume (area in 2D) which, when repeated by being translated by the lattice vectors, will fill all space. N.B. *translated*, without rotation or change of shape.



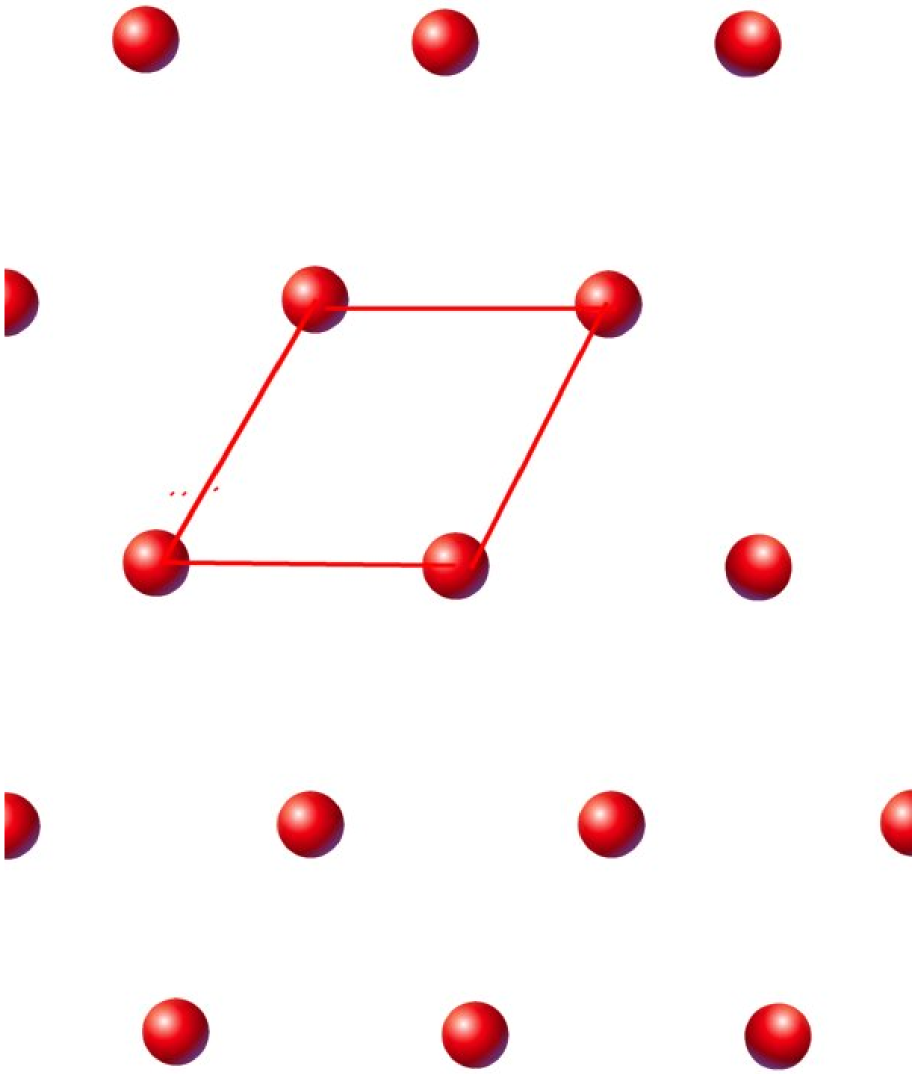
The triangular lattice - the dots represent *points, not atoms*.



The triangle is not a suitable unit cell,



because we cannot fill space just by replicating it – we have to invert it.



The rhombus is a suitable unit cell, the triangle is not.

1.4.4 Number of lattice points in cell

Two approaches:

Count points, sharing face, edge and corner points

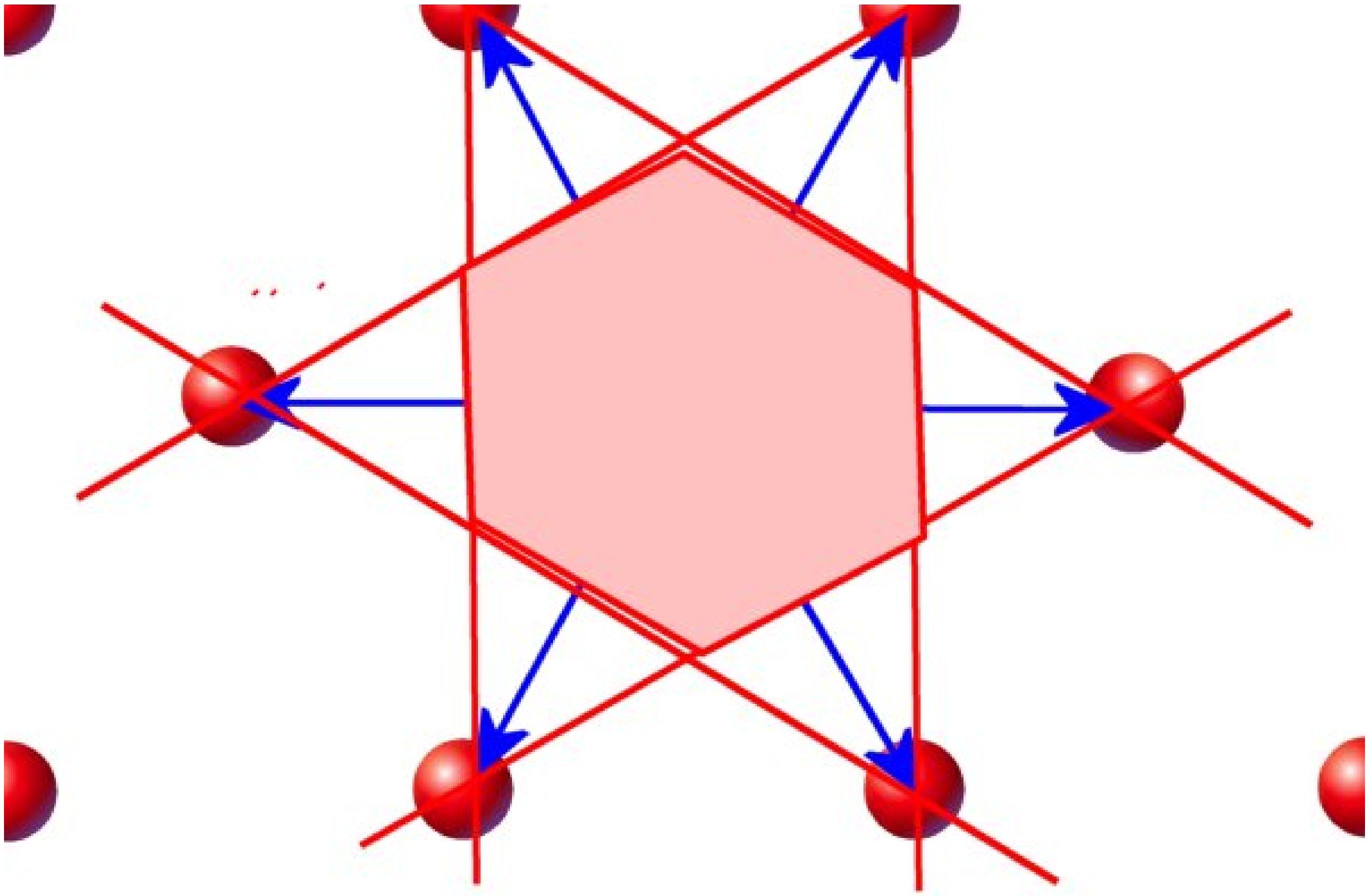
Shift the cell so that all points are internal, then count

Rectangular lattice (points have been given size to allow us to subdivide them)
Here, each point is shared with *four* neighbouring cells, so the cell contains $4 \times \frac{1}{4} = 1$ point.
Alternatively, we can take advantage of the fact that the unit cell is not uniquely defined, so we can shift it.
This is a *primitive* unit cell.

1.4.5 Wigner-Seitz cell

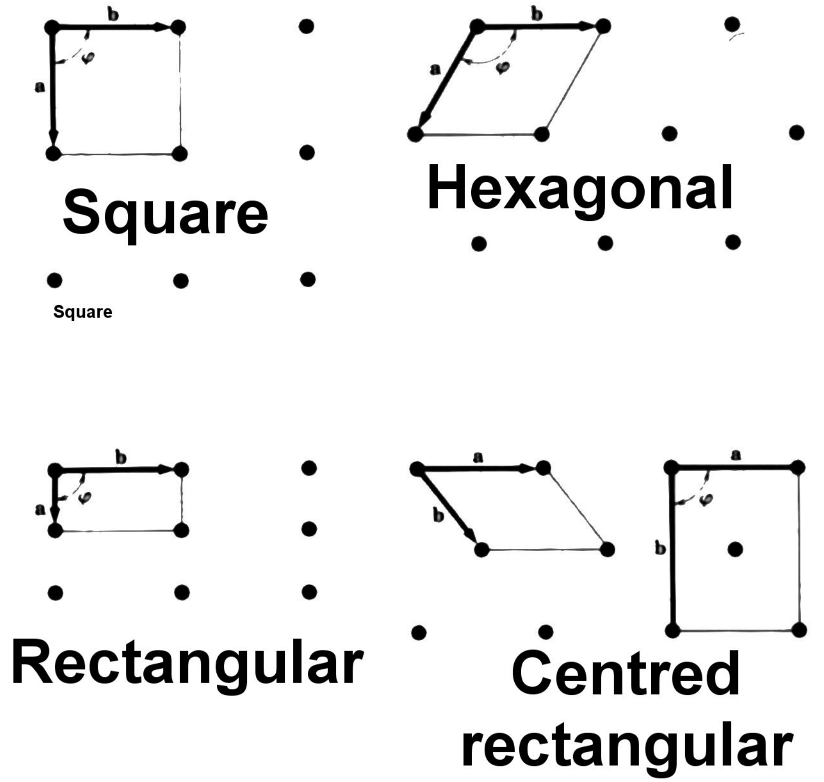
Construction

- **select a lattice point**
- **draw lines joining it to its neighbours**
- **draw perpendicular bisectors (planes in 3D, lines in 2D) of those lines**
- **the Wigner-Seitz cell is the volume (area in 2D) is the area within the bisectors.**



The Wigner-Seitz cell tends to show the symmetry of the lattice.

1.4.6 Five Lattices in Two Dimensions



Lattice	Unit Cell	Restrictions	Symmetry
Oblique	**Parallelogram**	$a \neq b, \quad \phi \neq 90^\circ$	**2**
Square	**Square**	$a = b, \quad \phi = 90^\circ$	**4mm**
Hexagonal	60° **Rhombus**	$a = b, \quad \phi = 120^\circ$	**6mm**
Primitive Rectangular	**Rectangle**	$a \neq b, \quad \phi = 90^\circ$	**2mm**
Centred Rectangular	**Rectangle**	$a \neq b, \quad \phi = 90^\circ$	**2mm**

Summary

Definitions
Analysis of structure
Beginning on real structures