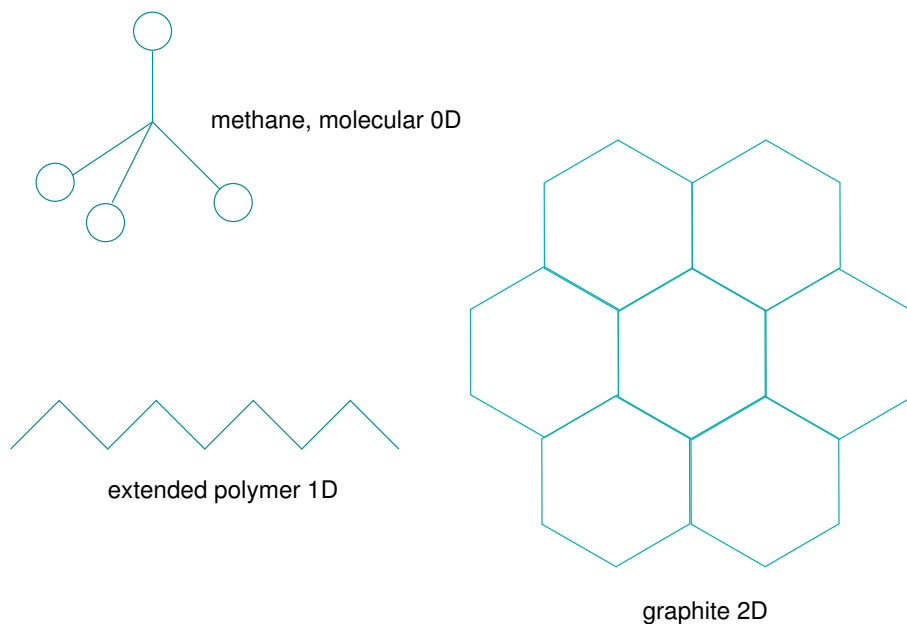# Crystals, packings etc.

Ram Seshadri MRL 2031, x6129, seshadri@mrl.ucsb.edu

These notes complement chapter 6 of Anderson, Leaver, Leevers and Rawlings
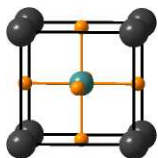
The unit cell and its propagation

Materials usually possess **extended** (in 1, 2 or 3 D) rather than molecular structures (0 D):

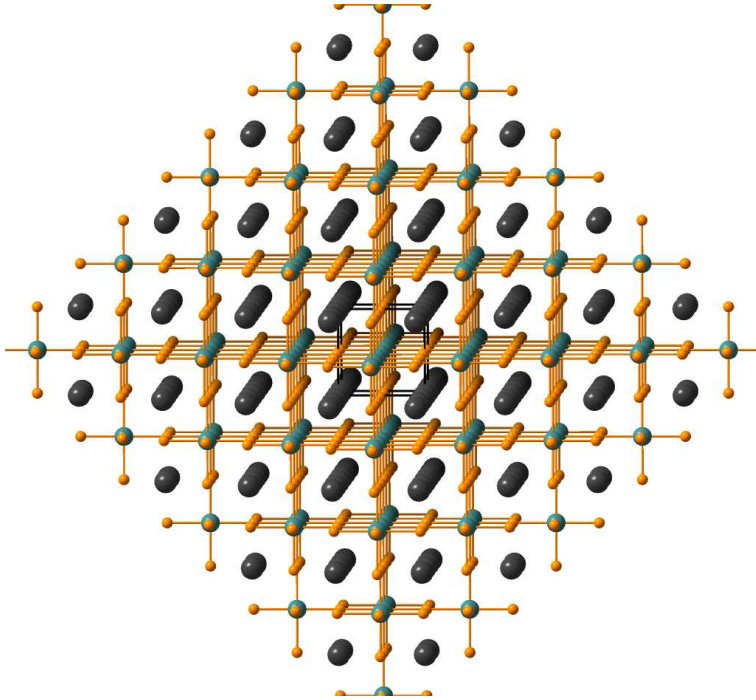

methane, molecular 0D

extended polymer 1D

graphite 2D

Crystal structures (extended structures in 1, 2 or 3D) are built up from a *unit cell* by tiling (repeating) the cell in 1, 2 or 3D as required.
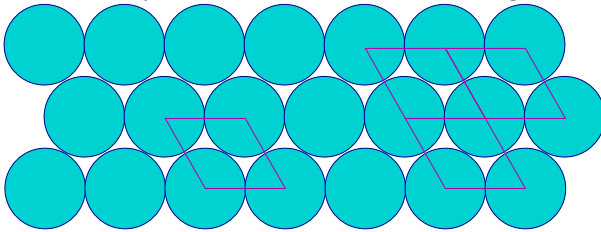
The unit cell of a perovskite:

## The structure on tiling in 3D:

The packing of disks (2D):

In 2D, we can close-pack disks. The unit cell (a rhombus) is indicated. The angle within the rhombus is 120°. To the right, three unit cells are packed together. Such packing is called hexagonal packing, because each disk is surrounded by 6 disks and this forms a hexagon.

Note that there is one disk per unit cell. Calculate the packing efficiency (the ratio of area taken up by the disks to the area of the unit cell) of this structure, and verify that it is:

$$\text{P.E.} = \frac{\pi r^2}{2r \times 2r \sin 60} = \frac{\pi}{2\sqrt{3}} 90.69\%$$

We can also place disks on a square array. The structure is then:
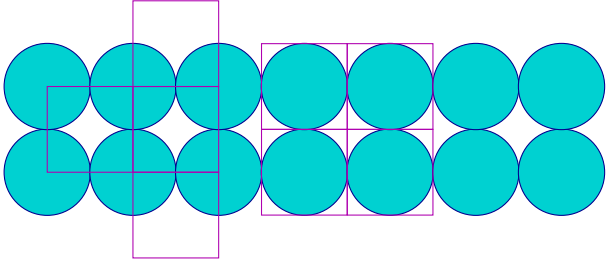
Note that there is again one disk per unit cell. The packing efficiency is now:

$$\text{P.E.} = \frac{\pi \times r^2}{4 \times r^2} = 78.54\%$$

and is much reduced from what we obtained for hexagonal packing. Because it is highly efficient, hexagonal packing is called close-packing.

Note that for the square lattice example, we have shown that the unit cell can be drawn in two different ways !

The packing of spheres (3D):

Simple cubic structure (P = primitive cubic):   The simplest crystal structure that we can think of in 3D is called the simple cubic structure. It is adopted by the element Po in the α modification. It is formed by placing atoms (spheres) at the corners of a cube.
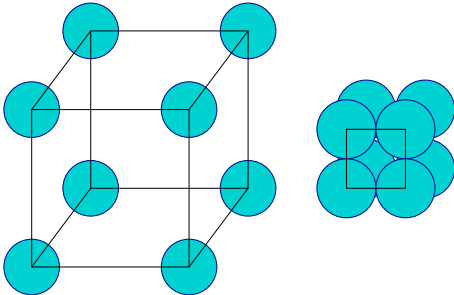

Two views of the simple cubic structure. In the second view, on the right, the atomic spheres are shown touching each other. Verify that there is only one atom per unit cell by noting that the 8 atoms at corners are all only 1/8th within the cell. In other words, the 8 atoms are each shared between 8 cells.

The cell is cubic, all the edges are of the same length $a = 2r$ where r is the radius of the atom. The volume of an atom is $(4/3)\pi r^3$ and the volume of the unit cell is $a^3 = (2r)^3$ so the packing efficiency is

$$\text{P.E.} = \frac{(4/3) \times \pi}{8} = 52.36\%$$

This is not very efficient packing — almost half the volume of the cell is wasted. This explains why so few elements (in fact, only one) adopts this structure. For α-Po, the unit cell parameter $a = 3.359$ Å.

The body centered cubic structure (I-cubic):   We obtain this structure by taking the simple cubic one and placing another atom in the center of the cell.

3
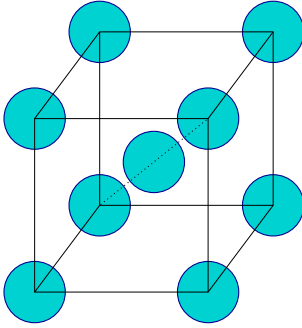
There are now two atoms in the unit cell. The one in the center is not shared with other cells, while the 8 in the corner are each shared with 8 other cells; the total is 1 (center) + 8×$\frac{1}{8}$ (corners) = 2. If the atomic spheres touch each other, we observe that the body diagonal of the cell (shown using a dotted line) = 4r. But the body diagonal (from the Pythagoras' theorem) is $\sqrt{3}a$. Therefore, $a = (4/\sqrt{3})r$.
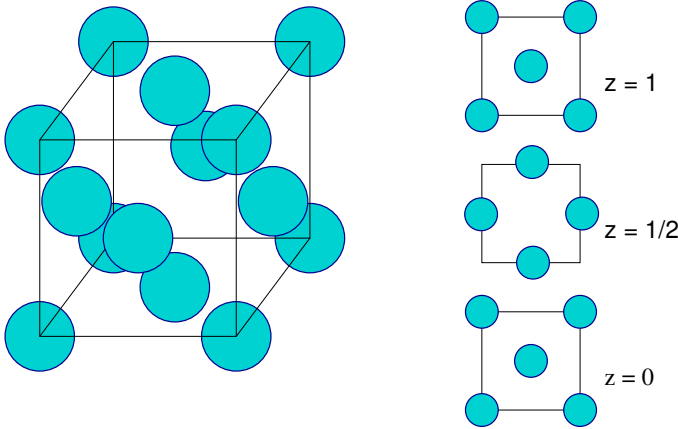
The packing efficiency is given by:

$$\text{P.E.} = \left(2 \times \frac{4}{3}\pi r^3\right) / \left((4/\sqrt{3})^3 r^3\right) = 68.02\%$$

The packing efficiency for the bcc (I-cubic) structure is higher than for the sc (P-cubic) structure. Many elements crystallize in this structure. Some examples are (cell parameters in parentheses):

Na ($a = 4.2906$ Å), K ($a = 5.328$ Å) Rb ($a = 5.585$ Å) V ($a = 3.03$ Å), Nb ($a = 3.3004$ Å), Ta ($a = 3.3013$ Å), Cr ($a = 2.91$ Å), Mo ($a = 3.147$ Å), W ($a = 3.1652$ Å), Fe ($a = 2.8665$ Å)

Face-centered cubic structure (F-cubic): This structure consists of a cubic cell with atoms at all the corners (as in P-cubic) as well as atoms in the centers of all the cube faces.


The structure is a bit crowded so we also draw it as sections along the z axis. Note that the cell parameter a is given by $\sqrt{2}a = 4r$, and that there are four atoms per unit cell. The packing efficiency

$$\text{P.E.} = \left(4 \times \frac{4}{3}\pi r^3\right) / \left(2\sqrt{2}r\right)^3 = 74.05\%$$

This is the most efficient packing in 3D, and many elements take on such a crystal structure: Ca ($a = 5.5884$ Å), Sr ($a = 6.0849$ Å), Ni ($a = 3.524$ Å), Pd ($a = 3.8907$ Å), Pt ($a = 3.9242$ Å), Cu ($a = 3.6149$ Å), Ag ($a = 4.0853$ Å), Au ($a = 4.0782$ Å)

Close packing: Consider two spheres. If there is an attractive interaction between them, they will touch.
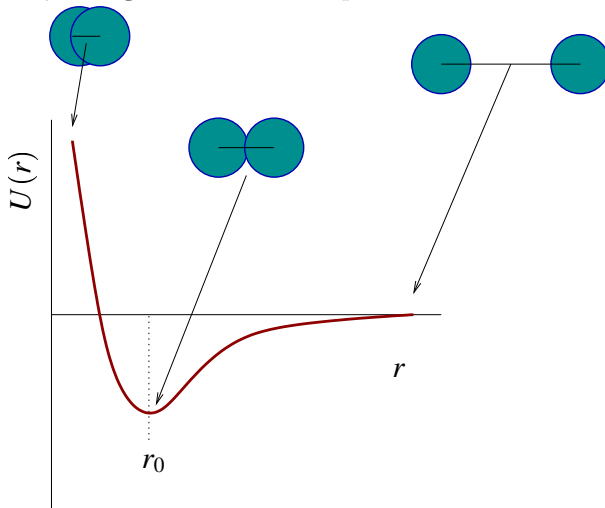
A third sphere that is brought close to the first two will form a triangle in order to maximize contact. A fourth sphere would come on top of the first three to form a tetrahedron, *etc.*
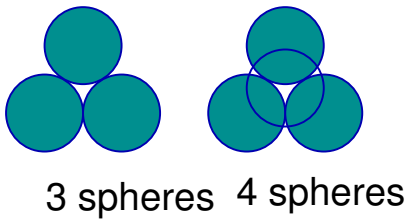
3 spheres 4 spheres

Close packing in three dimensions is obtained by continuing on this theme. Two kinds of packings result, hexagonal close packing (hcp) and cubic close packing (ccp).
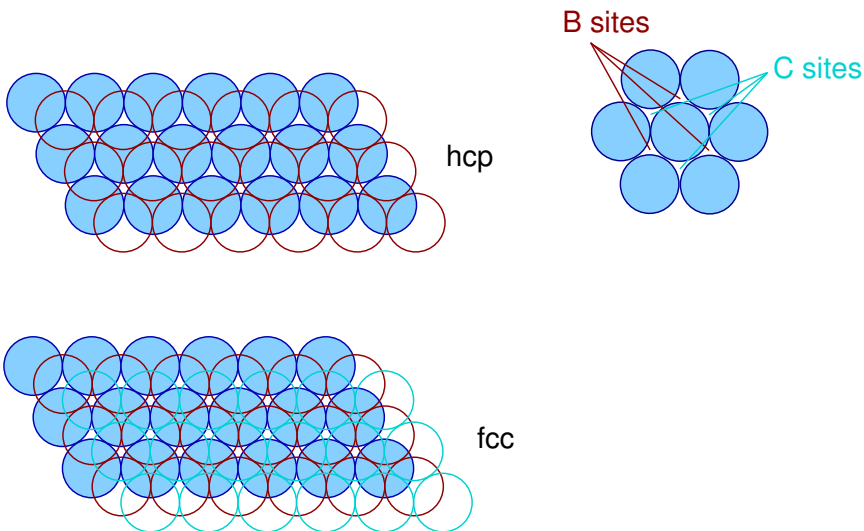
Consider a set of close packed spheres forming a 2D lattice. These are the filled, light blue spheres. The next layer can be formed of red open spheres. Now if the third layer sits exactly on top of the first one, the packing is called hcp. If the third layer (cyan) occupies a new set of positions, the packing is ccp. The figure on the right shows that the close packing of spheres (say on sites that are called A sites) results in two sets of positions for the next layer, we call one of them B and the other C. Then hcp follows the sequence ABABAB and ccp follows the sequence ABCABCABC.