

Module 4 : Solid State Chemistry

Lecture 17 : Closed Packed Structures

Objectives

In this lecture, you will learn the following

- The packing fraction.
- Evaluation of the packing fractions in simple cubic, FCC and BCC lattices.
- Estimate of the critical radius ratios for spherical particles that can be inserted in the holes of the lattice structures.
- Examples to illustrate radius ratios.

17.1 Introduction

We are all too familiar with the ideas of packing, whether we go on a trip or when we move from one house to another. Nature too uses the principles of efficiency and economy in its myriad forms of close packed structures. We will illustrate these principles with spherical objects for simplicity. For non spherical objects too, packing is governed by the "sizes" of objects and the intermolecular forces.

Close packed Structures

Consider a single horizontal line of touching hard spheres. When we want to place the next layer below it, the second layer has to be shifted by one radius so that it can closely fit into the "gaps" provided between every two adjacent spheres of the first layer. The next lower layer, i.e., the third layer is now parallel to the first layer and uses the gaps below the second layer. This is the closed packed arrangement in a plane. (If all the three layers were exactly parallel to one another without a lateral shift, the packing would have been short of closest packing, and this would correspond to a simple cubic lattice).

To get three dimensional structures, we need to place a plane of spheres (similar to the original plane) such that each sphere rests on the cavities formed in the first plane of spheres (this is to ensure closest packing; you may convince yourself of this by using marbles or ping pong balls). Let us label the second layer as the b layer and the first as the a layer. The third layer of atoms can now be exactly on top of the first layer giving an arrangement like ababab-----or it can be placed at cavities labeled c, giving an arrangement abcabcabc..... the first arrangement (abab...) is the hexagonal closest packed (HCP) structure and the second arrangement is the cubic closest packed structure (CCP) which is identical to a face centered cubic (FCC) Lattice. This is illustrated in the picture below (figures 17.1 and 17.2).

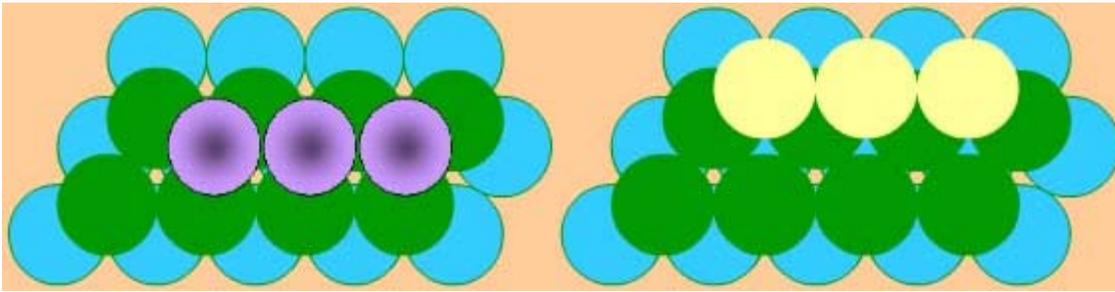
Figure 17.1 Packing arrangements in a plane.

The location of sites a, b, and c is shown in Fig 17.1 and the packing according to HCP mode is shown in Fig 17.2.

a)

ababab (HCP)

abcabc (CCP)



b)

c)

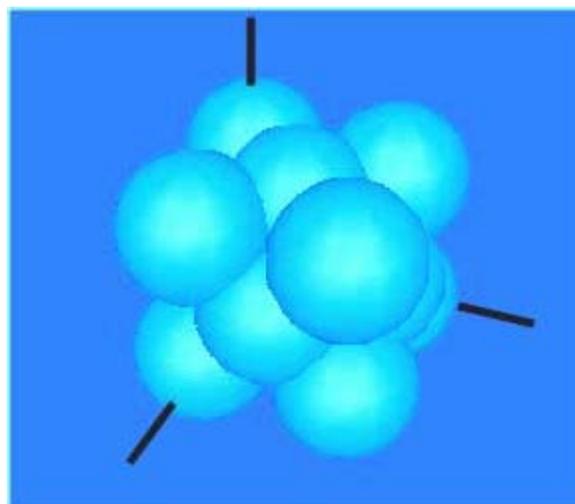


Figure 17.2 (a) Three layers of spheres showing HCP (i.e., abab layers) arrangement. Notice that the C layers are not occupied here. This figure is shown in flash mode and static mode. (b) Three layers of spheres showing FCC (CCP) (i.e., abcabc layers) arrangement. Notice that the C layers are occupied here, (c) FCC (abc layers) arrangement.

The abc packing is identical to FCC packing and we have already seen FCC structures in the previous lecture. You should actually use ping pong balls to construct abcabc layer structures and convince yourself that this is

FCC. No amount of explanation or visualization on the screen is equal or equivalent to a hands on experience.

Before we consider the calculation of packing fractions in these structures, let us consider what kind of voids or holes can be created in the above packing process. On the first layer of (three) spheres, when a single sphere is placed, it creates a tetrahedral hole near the location of the base of this (fourth) sphere. The center of the tetrahedral hole is midway between the two layers a and b and the tetrahedral hole is equidistant from these four spheres.

The tetrahedral hole is shown in Figure 17.3.

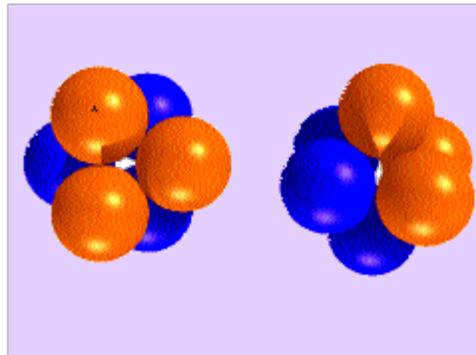
a)

b)

Figure 17.3(a) Tetrahedral and octahedral sites (holes). b) Tetrahedral holes.

When two more spheres are placed adjacent to the single sphere placed in layer b, the central point between these six spheres (3 from layer a and 3 from layer b) is referred to as an octahedral hole and is shown in figure 17.4

a)



b)

Figure 17.4 Octarahedral holes.

There is an upper limit to the size of the sphere that can be placed in these holes and we will take this up after calculating the packing fraction.

17.2 Packing Fraction

When spheres are placed in any kind of arrangement, they can not occupy the whole space because some voids such as the one created between three spheres touching one another are unavoidable. The ratio of the volume occupied by the spheres to the total volume available is called the packing fraction. The highest packing fraction possible is for the ababab or the abcabc packing described earlier.

Let us consider the packing fraction of a simple cubic lattice first. In this structure, the packing is neither ababab nor abcabc but it is aaaaaa. Eight spheres at the corners of a cube constitute the unit cell whose edge length is equal to the diameter of the sphere.

Figure 17.5 Packing fraction in a) simple cubic lattice, b) BCC lattice and c) FCC lattice.

If r is the radius of each sphere, the volume of each sphere is $\frac{4}{3} \pi r^3$. Since $\frac{1}{8}$ th volume of each of the eight spheres is inside the cube of edge length $2r$, the packing fraction, η is

$$\eta = \frac{\text{volume occupied by the spheres}}{\text{volume of the space containing the spheres}} = \frac{4 \pi r^3 / 3}{(2r)^3} = 4 \pi / 24 = \pi / 6 = 0.5236 \quad (17.1)$$

This means that in a simple cubic lattice, 52.36 % volume is occupied by the spheres. In the void space available, other spheres of smaller radii can easily be fitted, resulting in a much higher packing fraction.

Consider the packing fraction in a body centered cubic lattice. In this lattice, if the radius of the spheres is r , then the body diagonal of the BCC unit cell is $4r$ and therefore the edge length l is

$$(4r)^2 = l^2 + l^2 + l^2 \text{ or } l = (4 / \sqrt{3}) r = 2.309 r$$

$$\eta = \frac{(8/3) \pi r^3}{(2.309 r)^3} = 0.6806 \quad (17.3)$$

In the case of an FCC lattice, the face diagonal = $4r$ (See Fig 17.5 (c)), and therefore, the edge length $l = 4r / \sqrt{2}$. The number of spheres in the FCC unit cell is 4 and hence the packing fraction in the FCC lattice (closest packed) is

$$\eta = \frac{4 * 4/3 \pi r^3}{(4r / \sqrt{2})^3} = \sqrt{2} \pi / 6 = 0.7404 \quad (17.4)$$

The highest packing fraction possible is 74.04 % and this is for the FCC lattice. The same value of packing fraction is for the HCP structure as well, which only differs from FCC in that the location of the third layer is different (ababab), but the number of atoms in a given volume is identical in FCC and HCP.

17.3 Critical Radius Ratios:

We have made a passing mention in the earlier section by placing atoms or ions in the voids or holes generated during triangular, tetrahedral, octahedral or cubic as shown in Fig 17.6. We shall now calculate the critical radius ratios (i.e., the ratio of the radius of the largest sphere that can be fitted in the holes to the radius of the spheres that have generated the hole) for the various coordinations that are possible.

The case of triangular coordination is shown in Fig 17.6(a)

Figure 17.6 (a) Triangular Coordination , b) Tetrahedral coordination and c) Cubic coordination.

Let r be the radius of the smaller inner sphere and let R be the radius of the outer sphere. Then,

$$R / (R + r) = \cos (30^\circ) = 0.866 \quad (17.5)$$

and the critical radius ratio $r / R = 0.155$ (17.6)

For tetrahedral coordination, two spheres of radius R and the smaller one of radius r are shown in fig 17.6 (b). The other two spheres of radius R lie above and below the plane of the figure, with the four spheres of radius R equidistant from the central point O .

The tetrahedral angle is $109^\circ 28'$ and is indicated in Fig 17.6 (b)

$$\theta = 90 - (109^\circ 28')/2 = 35^\circ 16' \quad (17.7)$$

$$\text{and } \cos (35^\circ 16') = R / (R + r) \quad (17.8)$$

$$r / R = 0.255 \quad (17.9)$$

The case of octahedral coordination is shown in Fig 17.6 (c). In this case,

$$\cos 45^\circ = R / (r + R) \text{ and } r / R = 0.414 \quad (17.10)$$

In this manner, we can evaluate the critical radius ratios for all other coordinations. In Table 17.1, examples for different radius ratios have been given. In ionic crystals cations and anions pack as closely as possible to maximize the Coulombic interaction. Anions always remain farther than what their ionic radii would permit and the cations try to be surrounded by as many anions as possible around them within the permitted radius ratios. For example, if the radius ratio is 0.35, octahedral coordination is ruled out, because, for closest packing, the anions have to be closer than that permitted by the sum of their radii and hence tetrahedral coordination prevails.

Range of Radius Ratios	Geometries	Coordination numbers	Examples of solids	Central Cation
0 → 0.155	linear	2	HF	H ⁺
0.155 → 0.225	triangular	3	BO ₃	B ³⁺
0.225 → 0.414	tetrahedral	4	SiO ₂	Si ⁴⁺
0.414 → 0.712	octahedral	6	MgO ₂	Mg ²⁺
0.712 → 1	cubic	8	CsCl	Cs ⁺

Table 17.1 Radius ratios, geometries and coordination numbers.

17.4 Defects in Solids:

At non-zero temperatures, there is hardly a perfect solid and imperfections or defects in solids not only exist, but also play a crucial role in the dynamics of atoms in crystals as well as catalysis. The defects include vacancies, substitutional impurities, interstitial impurities, self interstitial dislocation, edge dislocations and grain boundaries. Some of these examples are shown in Fig 17.7. If ΔE is the energy required to create one impurity or vacancy, then the fraction of vacancies or impurities (f) is given by

$$f = N_v / N = e^{-\Delta E / RT} \quad (17.11)$$

Among point defects we have vacancies (atom or ion missing from the site), substitutional impurities (one site in the lattice substituted by a "foreign" site, which is not a part of the crystal), self interstitial site (a particle moving to a site which is not the usual site of particle in the lattice) and an interstitial impurity (a foreign particle sitting in an interstitial position). All these defects are shown in Fig 17.7(a). In ionic lattices, the above imperfections can be reclassified as a Frenkel defect (an ion moving from a regular site to an alternative site), a Schottky defect (a missing anion - cation pair) and an F - center (an electron in place of a negative charge). These are shown in Fig 17.7(b). Other more complex defects are edge dislocations (rows of atoms missing from a layer) and grain boundaries (boundaries along which there are a collection of defects). When a crystal is placed under a shearing stress, the motion is around the dislocations. When a lattice dissolves, the "dissolution" starts near dislocations or grain boundaries. Defects play major role in conductivity, reactivity and catalysis by permitting greater mobility and reactivity at these active sites.

Figure 17.7 (a)

Figure 17.7 (b)

Figure 17.7 (c)

17.5 Problems

- 17.1) For the tetragonal (four spheres whose centers coincide with the corners of a square and which are such that each sphere is touching two adjacent spheres) and pentagonal coordination, estimate the critical radius ratios for the spheres that can be accommodated in the void space available. Treat the problem as a planar problem as this is much simpler .
- 17.2) We have given a few examples of triangular, cubic and other coordinations. From web-sites / literature, give another distinct example for each one of these coordinations.
- 17.3) When we go from planar to non - planar coordination in exercise 17.1 above, does the critical radius ratio increase or decrease ?
- 17.4) Find the critical radius ratio for cubic coordination.

Recap

In this lecture you have learnt the following

Summary

In this lecture, we have studied the closest packing of spheres. Layerwise packing of ababab type gives the hexagonal close packing (HCP) arrangement, while abcabc type of layerwise packing gives the cubic closest packing which is equivalent to the face centered cubic (FCC) packing. In both these arrangements, the packing fraction is 74 % and is the highest possible value for spheres. For body centered cubic and simple cubic packing, the packing fraction is smaller. We have also estimated the sizes of the largest spheres (critical radius ratios) that can be accommodated in the various coordination schemes that can be generated with spheres and given examples for systems that fall in each one of these categories. Towards the end of the lecture we have also described in brief the nature of impurities and imperfections in solids and also their role in catalysis and the dynamics of particles in lattices. At high temperatures the lattice develops defects or impurities and the fraction of the defect sites can be calculated using the Boltzmann distribution.