CH 3: Structure of Solids (Main ideas)

Solids have definite shape. The table salt, sodium chloride, is a crystalline solid. The arrangement of atoms in crystals of sodium chloride salt appear to be cubic when examined under microscope. That is, if we could draw imaginary lines adding the centers of a group of sodium atoms, we could form a cube, and these cubes are repeating to make the whole structure.

We are interested to know how the atoms/molecules are arranged in some crystalline solids. We will represent the locations of atoms (atom-centers) by geometric points. A lattice is a three-dimensional array of geometric points (called lattice points). When we place atoms (or molecules) at the points, we get crystals.

Let's build few crystal structures. Imagine we have a number of atoms (or spheres) and we would like to arrange them in space. We will consider atoms (or molecules) to be spherical. This problem is similar to how you arrange oranges in a box. To do this, we have to make few decisions:

First, **where** do you place the first sphere? The second sphere? We may use a XYZ coordinate system to identify a location (point) and place the sphere there. However, we will do it in a more interesting manner. We will use an imaginary object to keep track of location. That object will be a VIRTUAL CUBE. Then, we can say, for example, place a sphere at the corner of the cube, and so on.

Once we decide on the locations of atomic spheres, next question is **how** do we exactly place the sphere at the designated location (point)? The answer is we will place the atom-**center** at the designated point. To accommodate more than one sphere, if necessary, we will ADJUST the SIZE of the cube, not spheres. We will consider our atomic-spheres HARD, but the length of our cube is adjustable (HARD-SPHERE, FLEXIBLE CUBE).

The third question is **how many** atomic spheres will be associated with a cube? The number is not fixed, and choice of different number and variety of locations gives different structure.

In summary, we need to consider *where, how, and how many*. Based on these considerations, we will build different STRUCTURE.

SIMPLE CUBE:

Step 1: Let us place atom-centers at the corners of the CUBE. There are 8 corners of a cube. We need 8 spheres. To be specific, place spheres at points A, B, C, D, E, F, G, and H of the cube in Fig. 1(a).

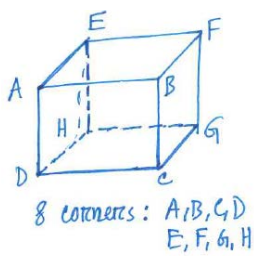

Fig. 1(a). Imaginary cube to locate points for placing spheres. 8 corner points are labelled.

Step 2: Adjust the size of the cube, so that the spheres touch nearest neighboring atoms. For example, if the four atoms at the four points A, B, C, and D are separated as in Fig. 1(b), shrink the cube so that the atomic spheres TOUCH as shown in Fig 1(c).

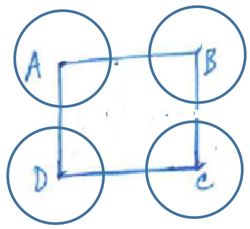

Fig. 1(b). If the sides of the cube are larger than the diameter, spheres do not touch.

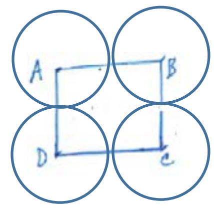

Fig. 1(c). Cube lengths are shortened so that neighboring spheres touch.

Properties of simple cubic unit cell:

Step 3: At the two ends of a side, say AB in Fig 2 below, there are two atom-centers, and these two atoms just touch. Therefore, the length AB = d/2 + d/2 =d, where d/2 is the radius of atoms.

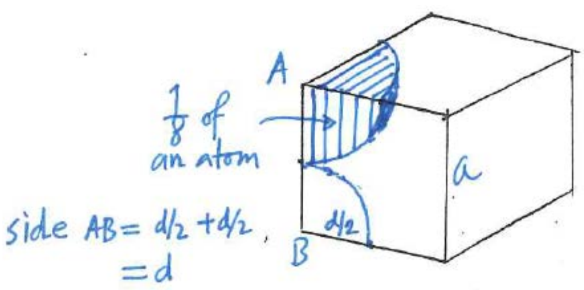

Fig. 2. The two spheres at points A and B are touching. One-eighth of a sphere is inside the cube.

Step 4: Since the side of a cube is equal to d, then its volume = d^3

Step 5: We would like to count the number of atoms in the cube. Note that not all of a corner atom is INSIDE the cube. Only one-eighth of its volume is inside the cube (see Fig. 2). The remaining seven-eighth is outside the cube.

Number of atoms inside the cube, n = (1/8 of an atom at one corner) * 8 corners = 1 atom

Step 6: Density of simple cube

$$\rho = \frac{mass}{volume} = \frac{mass\ of\ one\ atom}{volume\ of\ cube} = \frac{m}{d^3}$$

We can use the above equation to calculate the density of solid metal (pure) which has simple cubic structure. We simply have to divide the mass of one atom divided by d^3. Note that m is equal to molecular weight divided by Avogadro's number.

$$m = \frac{M}{N_A}$$

Step 7: Void fraction

$$void\ fraction, \theta = \frac{volume\ of\ empty\ space\ in\ the\ cube}{total\ volume}$$
$$= \frac{total\ volume\ of\ cube - occupied\ volume}{volume\ of\ cube}$$
$$= 1 - \frac{volume\ occupied\ by\ one\ atom}{volume\ of\ cube} = 1 - \frac{\frac{\pi}{6}d^3}{d^3} = 1 - \frac{\pi}{6} = 0.4764$$
$$= 47.64\%$$

Therefore, if a solid metal has simple cubic crystal structure, then 47.64% of its total volume is empty space, and the remaining 52.36% space is occupied by atoms.

FACE-CENTERED CUBE:

Step 1: We will place atoms at the cube corners as before. We need 8 spheres to place at 8 corners. The cube has 6 faces (wall). Each face is a SQUARE. In addition to corners, we will also place atoms at the CENTER/middle of each face. Center of a square is where the two diagonals intersect. We need 6 more atoms for that.

Step 2: Focus for a moment on just a face, say face ABCD in Fig. 3 and related atoms. There are four atoms at four corners (only two are shown in Fig. 3) of this face and one atom at the center of this face. Adjust the size of the cube so that the FACE-ATOM touch the atoms at the face corners, as in Fig. 3.

We have got a face-centered cubic unit cell.

Properties of FCC unit cell:

Step 3: Focus on a DIAGONAL on a face. In Fig. 3, AC is a face-diagonal on face ABCD. AC joins three atom-centers.

Length of the face-diagonal AC = d/2 + d + d/2 = 2d

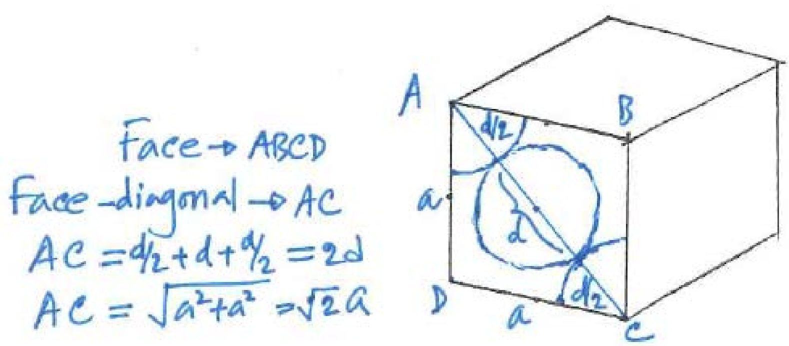

Fig. 3. Face-diagonal AC extends from point A (center of a corner atom), passes through the center of face-atom, ends at point C (another corner atom). Half of the face-atom is inside the cube.

Step 4: volume of cube

We know from geometry that the face-diagonal of a cube is equal to $\sqrt{2}a$ where a is its side (see Fig. 3).

Therefore, using results from step 3, $\sqrt{2}a = 2d$

$$a = \sqrt{2}d = side\ of\ FCC\ cube$$

Volume of cube = $\left(\sqrt{2}d\right)^3 = 2\sqrt{2}d^3$ (bigger than simple cubic cell)

Step 5: Only half of each face-atom is inside the cube. So, number of atoms in the cube = (1/8 of an atom at one corner) * 8 corners + (1/2 of an atom at one face) * 6 faces = 1+3 = 4 atoms [To remember: FCC, F for four]

Step 6: Density of face-centered cube (FCC)

$$\rho = \frac{mass\ of\ 4\ atoms}{volume\ of\ cube} = \frac{4m}{2\sqrt{2}d^3} = \frac{\sqrt{2}m}{d^3}$$

We can use this formula to calculate the bulk density of solid which have FCC crystal structure.

Step 6: Void fraction

$$void\ fraction, \theta = 1 - \frac{volume\ occupied\ by\ one\ atom}{volume\ of\ cube} = 1 - \frac{4 * \frac{\pi}{6} d^3}{2\sqrt{2}d^3} = 1 - \frac{\sqrt{2}\pi}{6} = 0.2595$$
$$= 25.95\%$$

Therefore, solid with FCC structure is 25.95% empty.

BODY-CENTERED CUBE:

Step 1: We will place atoms at the corners as before. In addition, we will also place a sphere at the CENTER of the CUBE (at the midpoint of a SPACE-DIAGONAL). This sphere is completely inside the cube (see Fig. 4).

Step 2: Adjust the size of the cube so that the 8 corner spheres touch the sphere that is totally inside (the space-sphere).

We have got a body-centered cubic unit cell.

Properties:

Step 3: Focus on a SPACE-DIAGONAL (diagonal that connects the opposite corners, diagonal AB in Fig. 4). There are three TOUCHING SPHERES associated with it. The SPACE-DIAGONAL just pass through the centers of the three spheres.

Length of the space-diagonal = d/2 + d + d/2 = 2d

Step 4: volume of cube

We know from geometry that if a cube has side a, then its space-diagonal is equal to $\sqrt{3}a$

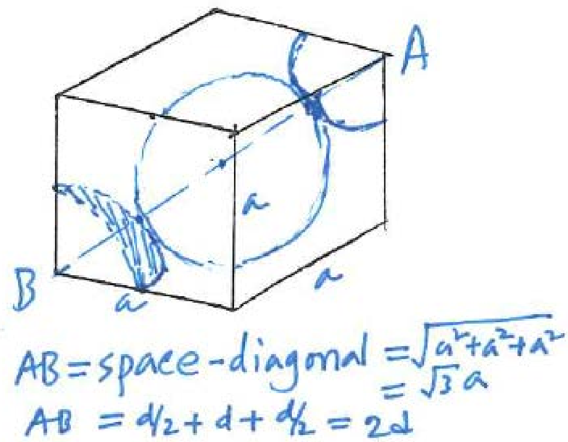

Fig. 4. Space-diagonal AB extends from point A (center of a corner atom), passes through the center of space-atom, ends at point B (another corner atom). All of the space-atom is inside the cube.

Therefore, using results from step 3, $\sqrt{3}a = 2d$

$$a = 2d/\sqrt{3} = side\ of\ BCC\ cube$$

Volume of cube = $\left(\sqrt{3}d\right)^3 = 8d^3/3\sqrt{3}$

Step 5: Effective number of atoms in the cube = (1/8 of an atom at one corner) * 8 corners + 1 full space atom = 1+1 = 2 atoms [To remember: B for Bi =2]

Step 6: Density of body-centered cube (BCC)

$$\rho = \frac{mass\ of\ 2\ atoms}{volume\ of\ cube} = \frac{2m}{8d^3/3\sqrt{3}} = \frac{3\sqrt{3}m}{4d^3} = 1.299\frac{m}{d^3}$$

This unit cell density will also be the bulk density of solid which have BCC crystal structure.

Step 6: Void fraction

$$void\ fraction, \theta = 1 - \frac{volume\ occupied\ by\ one\ atom}{volume\ of\ cube} = 1 - \frac{2 * \frac{\pi}{6}d^3}{\frac{8d^3}{3\sqrt{3}}} = 1 - \frac{\sqrt{3}\pi}{8}$$

$$= 0.3198 = 31.98\%$$

Therefore, 31.98% of BCC crystal is empty.

SUMMARY

Diameter of spherical atom = d
Mass of spherical atom = m

$$m = \frac{M}{N_A}$$

Unit Cell	**Number of atom**	**Mass**	**Length of a side**	**Volume**	**Density**	**Void fraction**
Simple Cube	1	m	d	d^3	$\frac{m}{d^3}$	47.64%
FCC	4 (F=four)	4m	$\sqrt{2}d$	$2\sqrt{2}d^3 = 2.828d^3$	$1.414\frac{m}{d^3}$	25.95%
BCC	2 (B=Bi=2)	2m	$2d/\sqrt{3}$	$\frac{8d^3}{3\sqrt{3}} = 1.54d^3$	$1.299\frac{m}{d^3}$	31.98%