

## **STATE PHYSICS**

### **Study Unit 1 – Solids**

#### **I. Introduction**

Solids are characterized by an orderly arrangement of their particles. If the order is over short distances only (local order), the solid is an *amorphous solid*. Charcoal and glass are amorphous solids. If the order exists throughout the entire solid (long range order), the solid is said to be a *crystalline solid*. Table salt and sugar are two common examples of crystalline solids. This chapter is devoted to the study of crystalline solids. Even a small crystal contains millions and millions of particles. Thus, studying the solid state could be a formidable task.

#### **II. Learning outcomes**

By the end of this unit, you should be able to:

1. Define *unit cell* and *lattice*.
2. Distinguish between simple, body-centered, face-centered cubic unit cells.
3. Determine atomic radii from the unit cell edge length or the edge length from the atomic radii.
4. Determine the fraction of an atom that lies in a unit cell given the lattice site occupied by the atom.
5. Determine the number of atoms, molecules, or ions in a unit cell.
6. Define the term coordination number.
7. Determine the coordination number of an atom or ion in a unit cell
8. Determine relative packing efficiencies of cubic unit cells.
9. Determine the density of a solid from its crystal structure.

#### **III. Unit Cells**

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### **Introduction**

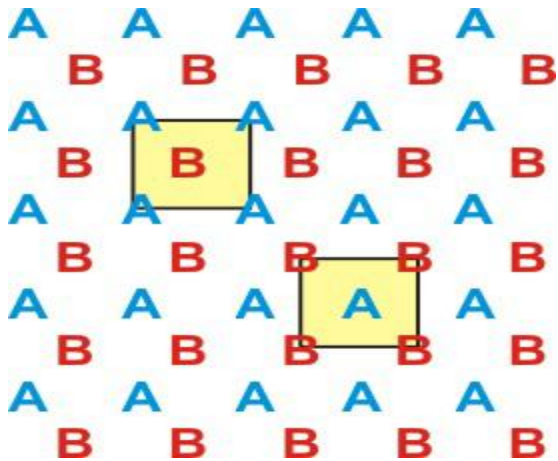
The long range order that characterizes crystalline solids means that there is a small repeat unit, called the unit cell that can be used to generate the entire crystal. Our study is simplified because, instead of studying the positions of the enormous number of particles that constitute the entire crystal, we need study only the small number of particles that comprise a unit cell. In this section, we define the unit cell and discuss how it is packed with atoms.

#### **Box 1.1**

Definition: The unit cell is the smallest repeat unit of the crystalline lattice that generates the entire lattice with translation.

Crystalline solids are orderly, repeating, 3-D arrays of particles, which can be atoms, ions, or groups of atoms, such as polyatomic ions or molecules. The pattern of the array is called the crystal *lattice*, and the individual positions are called **lattice sites**. The simplest portion of the lattice that makes up the repeating unit is called the *unit cell*. When the unit cell is repeated in all three directions, it generates the entire crystalline lattice. The figure shows two different but equivalent unit cells in a two-dimensional array. One unit cell consists of four A's on the corners and a B in the face center, while the other has B's on the corners with an A in the center. Translation by the length of one of the cell edges of either cell in any of the four directions produces an adjacent cell. Continued operations of translation generate the complete crystalline lattice. A three-dimensional lattice is formed by translation of a three-dimensional unit cell in three directions.

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**Figure 1.1:** Definitions of Lattice and Unit Cell

The unit cell is the smallest repeat unit of the crystalline lattice that generates the entire lattice with translation. The figure shows two different but equivalent unit cells highlighted in yellow.

## IV. Unit Cell Parameters

All unit cells can be uniquely characterized by their three edge lengths, ( $a$ ,  $b$ , and  $c$ ) and the angles ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) defined in Figure 1.2. They must be six-sided polygons that completely fill space; that is, no holes are present when the unit cell polygons are packed in three dimensions. As a result, there are only seven different types of unit cells. We limit our discussion to the simplest type of unit cell, the cubic unit cell. The cubic unit cell is one in which

$$a = b = c$$

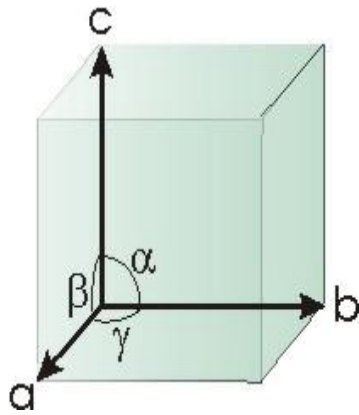
and

$$\alpha = \beta = \gamma = 90^\circ.$$

There are three types of cubic unit cells that differ only in the manner in which the particles fill the cell.

- simple cubic (sc)
- body-centered cubic (bcc)
- face-centered cubic (fcc)

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**Figure 1.2:** Parameters that Define the Unit Cell Type

**V. Cubic Unit Cells and Metallic Radii**  
**VI. Introduction**

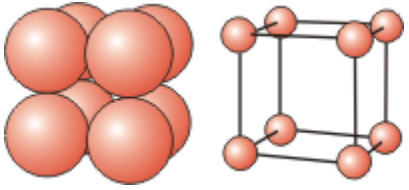
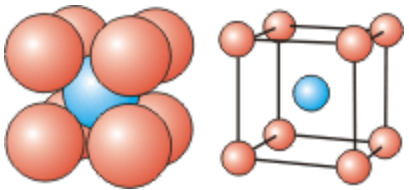
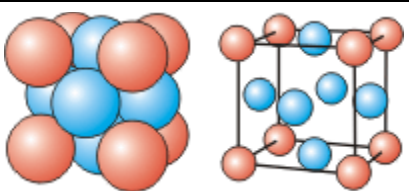
Unit cells must be six-sided polygons that completely fill space (no space between unit cells), and there are only seven types of unit cells that fulfill this requirement. However, our discussion is limited to only one type, the cubic unit cell.

**VII. The Cubic Unit Cells**

There are three cubic unit cells that differ in how the particles fill the cube. In each cubic unit cell, the same atom-type occupies each of the eight corners of the cube. The unit cell type is then dictated by where else in the unit cell that atom-type is found. Note that in the images below, all spheres represent the same atom type—the color differences are used only to distinguish different positions in the cell. There are three different types of cubic unit cells.

Type of Cubic Unit Cell	Location of Identical Particles	Image

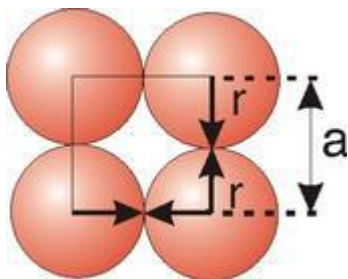
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simple cubic (sc)	on the corners but nowhere else in the cell	
body-centered cubic (bcc)	on the corners and in the center of the cell	
face-centered cubic (fcc)	on the corners and in the centers of the six faces of the cell	

**Table 1.1: Cubic Unit Cells**

## VIII. Metallic or Atomic Radii

Atoms are not hard spheres with distinct boundaries, so their sizes are not determined directly. However, the positions of the atoms in a solid can be determined by x-ray diffraction, and the sizes of the atoms are inferred from those distances. In this method, the radius of an atom is determined from the unit cell edge length ( $a$ ), which is determined from the location of the atoms, and the assumption that the atoms touch as shown in Figures 1.3a, 1.3b, and 1.3c.

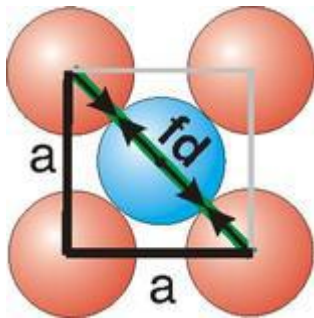


**Figure 1.3a: Atom Contact in Simple Cubic Unit Cells**

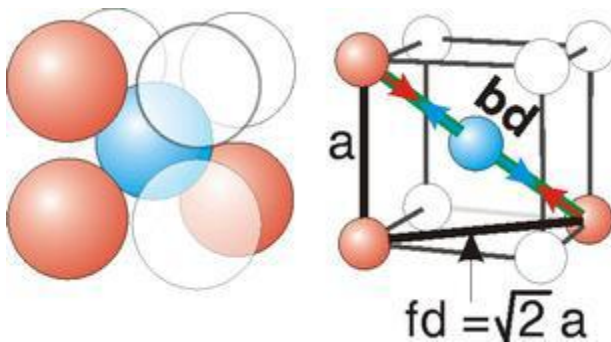
$$2r = a$$

sc

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**Figure 1.3b:** Atom Contact in Face-Centered Cubic Unit Cells



**Figure 1.3c:** Atom Contact in Body-Centered Cubic Unit Cells

Setting the edge length equal to  $2r$  in the sc unit cell, and applying the Pythagorean theorem to the triangles shown in Figures 1.3a, 1.3b, 1.3c, we obtain the relationships between the atomic radius ( $r$ ) of the atom and the edge length of the unit cell ( $a$ ) given in Equation 1.1.

The radius obtained from the structure of a metallic solid is referred to as either the *metallic radius* or the *atomic radius*.

## **IX. Unit Cell Stoichiometry**

### **Introduction**

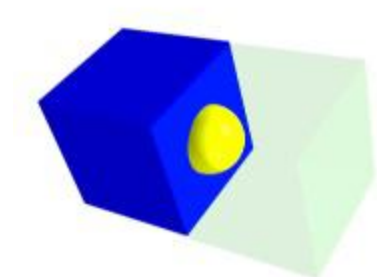
The number of atoms or ions in a unit cell of a compound does not have to be the same as the number of atoms in the formula of the compound, but the stoichiometry of the unit cell must be the same as the stoichiometry of the compound. Thus, a unit cell of NaCl may have many

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sodium and chloride ions, but the number of each ion must be the same because their stoichiometric ratio is 1:1 in the compound. However, when determining the unit cell stoichiometry, you cannot simply count all of the atoms or ions that form the unit because many of the particles may be part of more than one unit cell. In this section, we explain how to determine the stoichiometry of a unit cell.

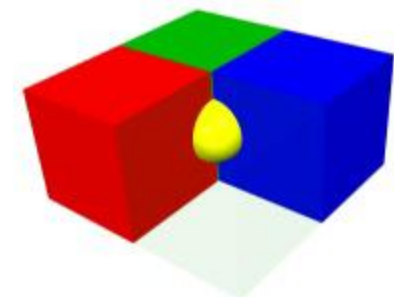
A particle in a face contributes  $1/2$  particle to each unit cell, one on an edge contributes  $1/4$  to a unit cell, and one on a corner contributes  $1/8$  per cell.

The structure of the unit cell is useful for understanding the stoichiometry of the compound. The stoichiometry of a compound can be determined by considering the number of particles (atoms, molecules, or ions) that make up the unit cell. However, most atoms in a unit cell are shared by several unit cells, so the contribution of a particle to any one unit cell is usually less than one.



**Figure 1.4a:** Particle Contributions to Unit Cell Stoichiometry

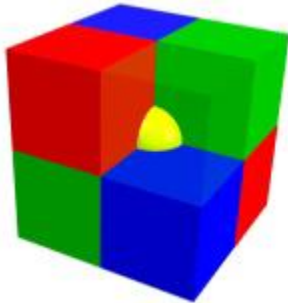
A particle on a **face center** is shared by two unit cells, so it contributes  $1/2$  particle to each.



**Figure 1.4b:** Particle Contributions to Unit Cell Stoichiometry

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A particle on an **edge** is shared by four unit cells, so it contributes  $1/4$  particle to each.



**Figure 1.4c:** Particle Contributions to Unit Cell Stoichiometry

A particle on a **corner** is shared by eight unit cells, so it contributes  $1/8$  particle to each.

## X. Contributions per Unit Cell

The particles on the eight corners combine to contribute 1 particle to a unit cell. Particles in the six face centers combine to contribute 3 particles to a unit cell. Those on twelve edges combine to contribute 3 particles per unit cell.

Atoms that are entirely within a unit cell each contribute a full atom to the cell stoichiometry, but the atoms in the faces, corners, and edges are shared by more than one unit cell.

Atoms located on the *corners* of the unit cell contribute 1 atom per unit cell.

Atoms located on the *edges* of the unit cell contribute 3 atoms per unit cell.

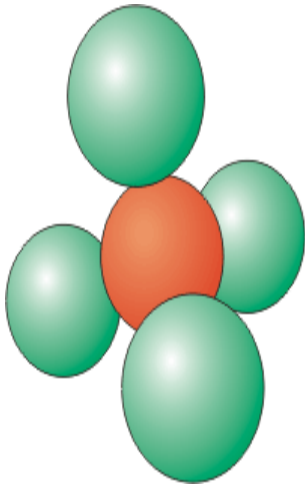
## XI. Coordination Number and Geometry

Definition: The **coordination number** (CN) is the number of nearest neighbors of a given particle in the crystal lattice. It determines the nature of the bonding in a crystal. The most

### Common Coordination Numbers and their Geometries

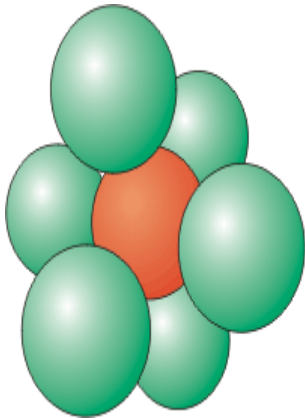


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**Figure 1.5a:** Coordination Number of 4

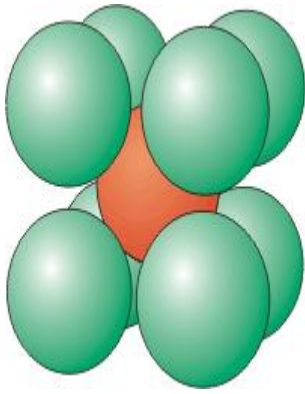
Four atoms around a central atom are located at the corners of a tetrahedron.



**Figure 1.5b:** Coordination Number of 6

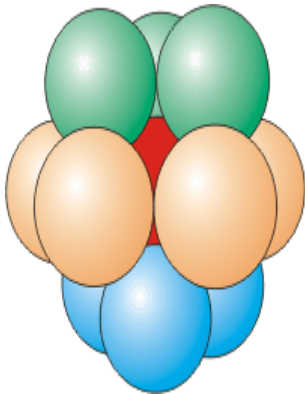
Six atoms around a central atom are located at the corners of an octahedron. An atom on the corner of a simple cubic unit cell has a coordination number of six.

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**Figure 1.5c:** Coordination Number of 8

Eight atoms around a central atom are located at the corners of a cube. The atom in the center of a body-centered unit cell has a coordination number of eight.



**Figure 1.5d:** Coordination Number of 12

Each atom in a face-centered cubic unit cell has a coordination number of 12. The 12 particles, which make up the *coordination sphere* of the red particle lie in three planes. The three planes can be seen in either of two ways:

The top and bottom planes each have three particles, while the plane in the middle contains the central particle and six others forming a belt around it.

The top and bottom planes each have four particles, while the plane in the middle contains the central particle and four others. The central plane is the face of a face-centered cube.

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The packing of equal sized particles shown for the coordination number of twelve represents the tightest possible packing arrangement and is frequently described as the *closest packed* geometry.

## XII. Density and Packing Efficiency

### Introduction

It is impossible to pack spheres without introducing some *void space* (space that is not occupied). How well the atoms pack a unit cell depends upon the unit cell type and is given by the packing efficiency of the unit cell. Solids with tightly packed unit cells are more dense than those with low packing efficiencies. In this section, we examine the packing efficiencies of the cubic unit cells and show how to determine the density of a solid from its crystal structure.

*Density* is the mass-to-volume ratio of a substance.

## XIII. Packing Efficiency

Packing efficiency is the fraction of the unit cell that is occupied by particles. Closest packed spheres pack with a packing efficiency of 74%.

Spheres cannot be packed without creating some void space, but the amount of void space depends upon how well they are packed. *Packing efficiency* (PE) is that fraction of the unit cell volume that is actually occupied by particles, not void space. Thus, the packing efficiency of a unit cell is

( 8.3 )

$$\text{Packing Efficiency} = \frac{\text{Volume of atoms}}{\text{volume of unit cell}} \times 100\%$$

$$PE = \frac{N \times \frac{4}{3} \pi r^3}{a^3} \times 100\%$$

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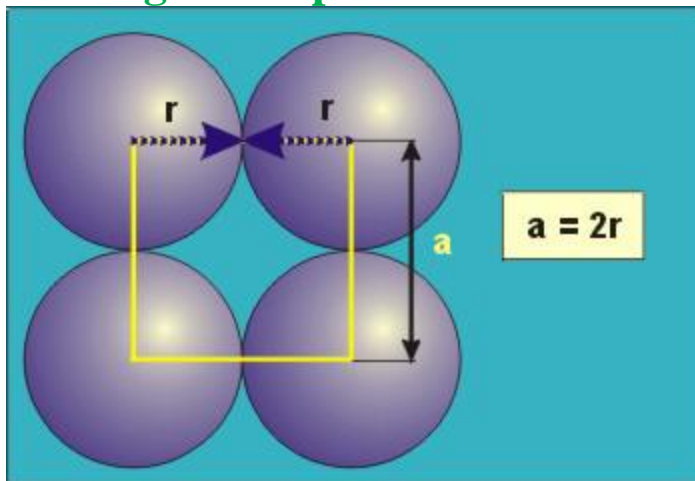
$a$  = the length of a side of the unit cell, so  $a^3$  is the volume of the unit cell.

$r$  = the radius of the atoms that occupy the unit cell, so  $(4/3)\pi r^3$  is the volume of a single atom in the unit cell.

$N$  = the number of atoms in the unit cell, so  $N(4/3)\pi r^3$  is the volume occupied by all of the atoms in the unit cell.

The unit cell size ( $a$ ) is directly proportional to the atom size ( $r$ ), so one can be defined in terms of the other and then canceled in the above expression. Consequently, the packing efficiency depends only upon the cell type, not its size. As shown in the next sections, the relationship between  $a$  and  $r$  depends only upon the unit cell type.

**XIV. Packing in Simple Cubes**



**XV.**

**Figure 1.6**

In the *simple cubic unit cell*, the spheres touch along the cell edge. Consequently, the edge length is two atomic radii

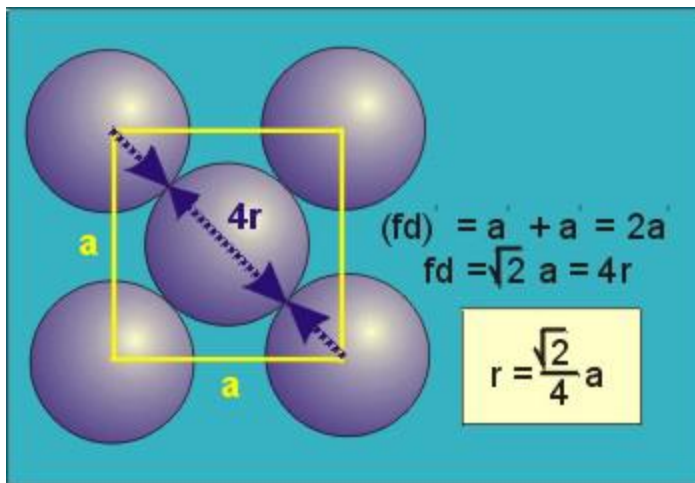
$(a = 2r)$ .

The properties of the simple cubic unit cell:

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- $r = 0.5a$
- $N = 1$  atom/unit cell  $\left(\frac{1}{8} \times 8(\text{corner atoms}) = 1\right)$
- packing efficiency =  $\frac{4/3\pi r^3}{(2r)^3} \times 100\% = 52\%$
- coordination number = 6

**XVI. Packing in Face-Centered Cubes**



**Figure 1.7**

Particle contact in the *face-centered cubic unit cell* is along the face diagonal ( $fd$ ). The face diagonal is four atomic radii

$$(fd = 4r)$$

and is related to the unit cell edge length ( $a$ ) by the Pythagorean theorem.

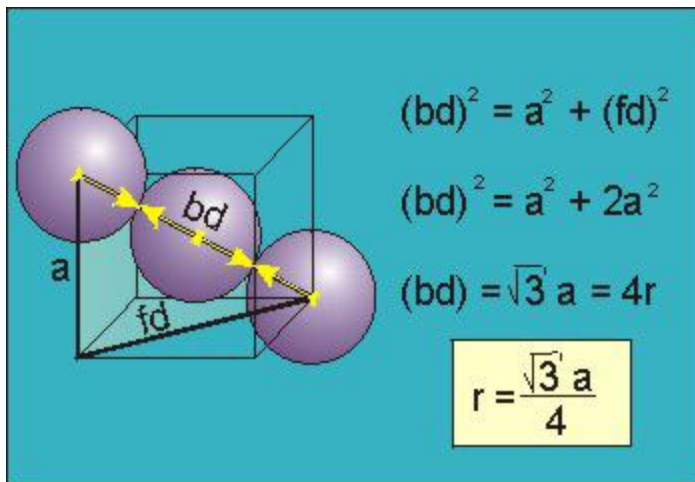
$$N = \frac{1}{8} \times 8(\text{corner atoms}) + \frac{1}{2} \times 6(\text{atoms at face}) = 4$$

$$\text{Packing efficiency} = \frac{N \times \frac{4}{3} \pi r^3}{a^3} \times 100\%$$

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$$PE = \frac{4 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} \times 100\% = 74\%$$

**XVII. Packing in Body-Centered Cubes**



**Figure 1.8**

For the *body-centered cubic unit cell*, the spheres make contact along the body diagonal ( $bd$ ), which is four atomic radii (each yellow arrow is one atomic radius), i.e.,

$$bd = 4r.$$

The body diagonal is related to the face diagonal ( $fd$ ) and the cell edge ( $a$ ) by the Pythagorean theorem. The relationship between the cell edge and the face diagonal was derived in the discussion of the fcc unit cell.

$$N = \frac{1}{8} \times 8(\text{corner atoms}) + 1(\text{body center}) = 2$$

$$\text{Packing efficiency} = \frac{N \times \frac{4}{3} \pi r^3}{a^3} \times 100\%$$

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$$PE = \frac{2 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} \times 100\% = 68\%$$