I) Unit Cells and Crystalline Solids: Some Definitions and examples in two dimensions

Unit Cell: a repeating unit of an extended structure. In two dimensions this is a parallelogram and in three dimensions this is a parallelepiped. Translation along each of the edges of the unit cell by the length of the edge allows the entire structure to be generated.

Consider the three two dimensional patterns shown below:

Although the patterns appear to be different, each has a square repeating unit that can generate the rest of the pattern by simple translation of the solid square shown below:

Similarly, the full wallpaper patterns shown below, like all wallpaper patterns, can be generated by repetition of a unit cell. Note that the unit cell may be expressed as a parallelogram and that the unit cell is not necessarily unique.
1) Which of the following parallelograms are valid unit cells? (Hint: there are three)

2) If each circle represents an atom, how many atoms are in the unit cell?

Coordination Number: the number of nearest neighbors to an atom, ion, or molecule in a crystalline solid.

3) In the two dimensional array shown below, what is the coordination number of the central atom?

Packing Efficiency: The % of total area occupied by objects in an extended array.
For the packing arrangement shown in question 3 the packing efficiency is given by the area occupied by the spheres divided by the area of a unit cell. Ignoring any difference in atom colors we see that there the square unit cell is defined by the centers of four spheres. If the radius of each sphere is $r$ then the length of one side of the unit cell is $2r$. Thus

\[
\text{Area of unit cell} = 2r \times 2r = 4r^2
\]

Each unit cell has one sphere, so the area occupied by “objects” is

\[
\text{Area of one sphere} = \pi r^2
\]

Thus the packing efficiency is

\[
\frac{\pi r^2}{4r^2} = \frac{\pi}{4} = 0.785398163
\]

4) Now consider the so-called hexagonal array of steel balls in two dimensions shown below. What is the coordination number of a steel ball? Draw valid unit cell on the picture shown below. Do you think that the packing efficiency is greater or less than 79%? Why? (You do not have to do a calculation for this)

II) Layer diagrams and some examples in three dimensions
A) Primitive Cubic Cell. Some repeating patterns in three dimensions are based on cubic unit cells. The simplest of these is the primitive cubic cell (sometimes called the simple cubic cell), shown below.

Some data concerning the primitive cubic cell shown above:

- Length of unit cell edge = $2r$
- Volume of unit cell = $8r^3$
- Number of atoms per unit cell = $8 \text{ corners} \times \frac{1}{8} \text{ of atom/corner} = 1 \text{ atom}$
- Volume of unit cell occupied by atoms = $4\pi r^3/3$
Packing efficiency = \((\frac{4\pi r^3}{3})/8r^3 = 52\%

Coordination number = 6

It is cumbersome to draw this unit cell. A convenient method is to use layer diagrams. Let's give the unit cell an axis system. Each layer is a slice along the z-axis.

The layer diagram representation is shown below, where z=0 represents the plane that contains the centers of the lower plane of spheres and z=1 represents the upper plane of spheres.

B) Body-Centered Cubic Cell (BCC)
Note that only the upper \((z=1)\) and lower \((z=0)\) planes are shown.

5) Draw the atoms for the middle \((z=1/2)\) layer below.

6) Fill in the missing data for the BCC cell.

Length of unit cell edge = \(4r/sqrt(3)\)  \textit{where sqrt(3) means the square root of 3 = 1.732}
Volume of unit cell =
Number of atoms per unit cell =
Volume of unit cell occupied by atoms =
Packing efficiency =
Coordination number =

C) Face-Centered Cubic Cell (FCC)
7) Draw the $Z=1/2$ and $Z=1$ parts of the layer diagram for the FCC unit cell.

8) Fill in the missing data for the FCC cell.
   
   Length of unit cell edge = $2r*\sqrt{2}=2.82r$  where $\sqrt{2}$ means the square root of 2 = 1.414
   
   Volume of unit cell =
   
   Number of atoms per unit cell =
   
   Volume of unit cell occupied by atoms =
   
   Packing efficiency =
   
   Coordination number =

III) Holes in the PC and FCC structures

The spaces between atoms in the cubic unit cells create holes where other atoms can fit. Holes, and their identification, play a particularly important role in two instances:

a) describing the structures of ionic compounds and

b) describing more complex structures that can be derived from cubic structures.

In many ionic compounds the cations are much smaller than the anions. Therefore the solid state packing is often viewed as a close-packing of anions with cations filling in some or all of the holes. Recall that the negative charge of an anion means that there are more electrons than protons in the ion. Therefore an anion is larger than a neutral atom. Conversely, a cation has more protons in the nucleus than electrons and is smaller than a neutral atom.

Definitions:

- **Tetrahedral Hole**
  
  ![Tetrahedral Hole](image)
  
  CN 4

- **Octahedral Hole**
  
  ![Octahedral Hole](image)
  
  CN 6

- **Cubic Hole**
  
  ![Cubic Hole](image)
  
  CN 8

CN = coordination number of the hole

a) Primitive Cubic Structure and Holes

The PC structure has a cubic hole with coordination number of 8. The hole is located between the upper ($Z=1$) and lower ($Z=0$) layers. Thus, a layer diagram for the cubic hole in the PC unit.
A cell can be drawn in the \( Z=1/2 \) layer as:

\[ \text{Z=1/2} \]

b) Face-Centered Cubic Structure and Holes

The FCC structure has both octahedral and tetrahedral holes. The octahedral holes have the layer diagram shown below:

**Atom Positions for FCC**

**Layer Diagram for Octhedral Holes**

\[ \text{Z}=0 \quad \text{Z}=1/2 \quad \text{Z}=1 \]

9) How many octahedral holes does the FCC structure have per unit cell?

The tetrahedral holes of the FCC structure are located at the positions indicated in the following layer diagram.

\[ \text{Z}=1/4 \quad \text{Z}=3/4 \]

10) How many tetrahedral holes does the FCC unit cell have?

11) Which is larger, the tetrahedral or the octahedral holes of the FCC structure?

12) The ionic compound \( \text{Li}_2\text{O} \) consists of a FCC array of \( \text{O}^2- \) ions with \( \text{Li}^+ \) cations filling some of the holes. Which of the following arrangements of \( \text{Li}^+ \) ions is consistent with the stoichiometry?

   * All Oh holes filled  Yes  No
   * 1/2 Oh holes filled  Yes  No
   * All Td holes filled  Yes  No
13) The BCC structure has octahedral holes. Give a layer diagram illustrating the positions of the octahedral holes in the $Z=0, \frac{1}{2},$ and 1 layers.