Discussion Questions

• What is a crystal and what is the meaning of crystal structure?
• What are X-rays and how do they help us investigate crystals?
• What are closest packed structures?

You all know that solid, liquid, and gas are the three states of matter. These states are also known as phases, and often a substance may exist in a few forms of solid, and each form is also a phase. As the temperature increases, a solid usually melts at some temperature. During the melting process, the temperature does not change as long as there are liquid and solid present. The energy absorbed by a solid during the melting process is called enthalpy of fusion. When all solid is melted, the liquid temperature will increase as it absorbs heat. Of course, vapour pressure of the liquid increases with temperature. When the vapour pressure is the same as the atmosphere, the liquid boils. The temperature at which the liquid and gas phases are in equilibrium is called the boiling point. A solid also sublimes into a vapour. The changes among vapour, liquid, and solid are called phase transitions.

A glass state is also seen as a solid, but from a structural point of view, a glass is really a frozen liquid, because the molecules do not have long range regular and periodic arrangement. On this web page, we concentrate on crystalline solids. We encounter solids all the time, and solids are used both in everyday life as well as technology. Metals, oxides, cement (concrete), diamond, minerals, and silicon devices are some of the important materials, and we must equip ourselves to deal with and understand them.

What is a crystal and what is the meaning of crystal structure?

At sufficiently low temperature, a material usually becomes a solid or crystal, in which the arrangement of atoms are periodic over a very large range. All solids occupy a volume, and the arrangement of atoms, chemical bonds, or molecules in them are in a 3-dimensional space. These arrangements are called their crystal structures. A portion of such an arrangement is animated here to show various orientations of this pattern.

Representation of 3-dimensional structures should usually be made using models, and their representation on a flat surface is difficult. For simplicity, we use a 2-dimensional pattern (plane) to illustrate a 2-dimensional (planar) crystal structure.
This pattern or crystal structure is generated by using a unit marked by the centers of any four @ or # signs. The choice is up to you in this case. Such a unit is called a primitive unit. The pattern has a square (or rectangular on some screens) appearance, and to preserve the square, we may use a square unit of

```
@ # @ | @ # @
@ # @ | @ # @
```

or

```
@ # | @ #
@ # | @ #
```

as our unit cell. Such choices result in having two @ and # per unit cell, and these are called centered cells.

Thus, if we know the arrangement of a unit cell, we can use our imagination to build a crystal structure, or use symbols or models to represent a crystal structure. Since each pattern has features shared by many structures, often such a pattern is called a lattice. For example, the diamond, zinc blende, wurtzite, and \(\text{NaCl}\) structures have been called lattices; however, the word lattice has a more formal definition by crystal physics and chemists. The above site gives a gallery of lattices.

**Definition: Crystals**

Inorganic Chemistry by Swaddle defined crystals as packed regular arrays of atoms, ions, or molecules in a pattern repeated periodically ad infinitum.

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**What are X-rays and how do they help us investigate crystals?**

Like light, X-rays are electromagnetic radiation with wavelengths in the order of inter atomic distances. Thus X-rays are diffracted by crystals. The diffraction patterns of a crystal reveal the symmetry, geometry, and the measures of unit cell parameters. The details are rather complicated to learn, and we leave them out at this point.

However, it is important to understand what X-rays are by working on a problem related to X-rays. You are asked to calculate the frequencies and photon energies of X-rays of certain wavelengths. These are compared to photons of ordinary light. The equation required for this comes from Max Planck's postulates that lights are emitted one bundle of energy at a time. The energy \(E\) of the photon is proportional to the frequency \(\nu\) of the photon, and the proportional constant is \(h\), now known as the Planck constant.

\[E = h \nu\]

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**What are closest packed structures?**

We do not know what the shape of an atom is, but we often use a sphere to represent an atom. For example, the common crystal structures of metals can be represented by packing of spheres. These models illustrate not only the lattice types, but also explain the properties. When you put spheres on a flat surface, you have got a layer as shown on the right here. Note that an atom is surrounded by six atoms on the same layer.
On top of this layer, you can pack a second layer. As you do so, please note that you have created two typical sites or holes called **octahedral** and **tetrahedral** sites. These sites accommodates spheres up to 0.414 and 0.225 times the radii of the sphere or atom, $r_{\text{atom}}$.

![Diagram showing 1 layer and 2 layers](image)

A side view showing the spheres (P), tetrahedral sites (T) and octahedral sites (O) is also shown here.

When you put the third layers on, there are two possible options. The 3rd layer can go directly on top of the first layer. In such an arrangement, you produce an ABAB... type of sequence. Such a sequence is called a **hexagonal closest packing (hcp)**. A second option is to place a layer that is not directly on top of A nor on top of B. We call such a location C. Thus, we produce an ABCABC... sequence. Such a sequence belongs to the cubic type, and is usually called **face-centered closest packing (fcc)**.
We demonstrated these types of packing in lectures, and asked you to evaluate the radii of the small balls that fit tightly in the octahedral and tetrahedral sites respectively in terms of \( r_{\text{atom}} \).

If you do not have a set of models, take a good look at a pile of oranges in a super market on your next shopping trip. Dr. Heyes has an illustration shown here. This pile is the cubic arrangement.

The Crystal Lattice and Structures gives a dynamic view on these structures.
Example 1

Assume the radius of the ball used for closest packing as \( R \) and the radius of a small ball that just fits in the octahedral site as \( r \). What is the relationship between \( R \) and \( r \)?

**SOLUTION**

If we assume the 6 balls forming the octahedral site to be located on the two directions of a set of Cartesian coordinates in such a manner that each ball touches four others, the coordinates will be \((r+R, 0, 0), (-r-R, 0, 0), (0, r+R, 0), (0, -r-R, 0), (0, 0, r+R), \text{ and } (0, 0, -r-R)\).

The ball touches along the edges. Therefore, we have

\[
2(r+R)^2 = (2R)^2
\]

**DISCUSSION**

Show that \( r = 0.414 \) \( R \)

Example 2

Assume the radius of the ball used for closest packing as \( R \) and the radius of a small ball that just fits in the tetrahedral site as \( r \). What is the relationship between \( R \) and \( r \)?

**SOLUTION**

A tetrahedral site can be modeled by having the four balls of radius \( R \) located at alternate corners of a cube. The balls touch each other along the faces of the cube, whose edges have a length of \( a \). Thus,

\[
2a^2 = (2R)^2
\]

The body diagonal of the cube \( = 2 (r + R) \). Thus, we have

\[
3a^2 = (2(r+R))^2
\]

and therefore

\[
a = 2^{1/2} \frac{2(r+R)}{3^{1/2}}
\]

**DISCUSSION**

Show that \( r = 0.215 \) \( R \)

Example 3

What fraction of the volume is occupied by spheres in an fcc type closest packing of spheres?

**SOLUTION**

Let the edge of a unit cell of the fcc closest packing be \( a \), and the radius of the spheres be \( R \). Then \( a = 8^{1/2} R \). There are four spheres per unit cell, and the volume occupied by each sphere is \( V_{\text{sphere}} \). The volume of the unit cell is \( V_{\text{cell}} \). We have these relationships
\( a = 8^{1/2} R \)

\[
\text{V}_{\text{sphere}} = \frac{4}{3} \pi R^3
\]

\[
\text{V}_{\text{cell}} = a^3 = 16 \times 2^{1/2} R^3
\]

Fraction of volume occupied by spheres

\[
= \frac{2 \times \text{V}_{\text{sphere}}}{\text{V}_{\text{cell}}}
\]

\[
= \frac{\pi}{3 \times 2^{1/2}}
\]

\[
= 0.7405 \text{ or } 74\%
\]

Please work out these relationships with a diagram. There is no point remembering these formulas, except the formula for the volume of a sphere.

**DISCUSSION**

Show that the fraction of volume occupied by spheres in an hcp arrangement is 0.74.

Example 4

What is a unit cell of hcp structure? What are the relationships of the unit cell parameters and the atomic radii? What is the fraction of volume occupied by spheres?

**SOLUTION**

The hcp unit cell is outlined by the two top diagrams of the figure below.

A unit cell can be constructed in such a way that it has two base vectors of \( a = 2R \), extended by 120 degrees \((2\pi/3)\), \( R \) being the radii of the spheres. The third \( c \) axis is perpendicular to both \( a \)'s. It can be shown that for ideal hcp structures, \( c = a \sqrt{8/3} \). The volume of the unit cell:

\[
\begin{align*}
\text{V}_{\text{cell}} &= a \times a \times \sin \left(\frac{2\pi}{3}\right) \times c \\
&= (2R)^2 \times \frac{\sqrt{3}}{2} \times \sqrt{\frac{8}{3}} \times 2R \\
&= 8 \times 2^{1/2} \times R^3
\end{align*}
\]

\[
\text{V}_{\text{sphere}} = \frac{4}{3} \pi R^3
\]

Fraction of volume occupied by spheres

\[
= \frac{2 \times \text{V}_{\text{sphere}}}{\text{V}_{\text{cell}}}
\]

\[
= \frac{\pi}{3 \times 2^{1/2}}
\]

\[
= 0.74 \text{ or } 74\%
\]

Note that there are two spheres per unit cell, and the volume occupied by the spheres is \( \frac{8}{3} \pi R^3 \).
Types of structures

One of the most common structure classifications is the Strukturbericht Types. Since the study of crystal began a long time ago, various notations have been used to represent types of crystal structures. This link provides a detailed index.

Questions

1. **How many spheres are in contact with a sphere deep in a pile of closest packed spheres?**

   Hint: 12

   **Skill** -
   Be able to construct a closest packed array of spheres and answer some specific questions. There are 12 neighbours in both the fcc and the hcp types of packing.

2. **What is the ratio** $O$

   $O = \frac{\text{number of octahedral sites}}{\text{number of spheres}}$

   in an infinite array of closest packed spheres?

   Hint: 1

   **Skill** -
   Realize that a structure with closest packed of anion $\ce{X}$ with all the octahedral sites occupied by $\ce{A}$ has a stoichiometry of $\ce{AX}$.

3. **What is the ratio** $T$

   $T = \frac{\text{number of tetrahedral sites}}{\text{number of spheres}}$

   in an infinite array of closest packed spheres?

   Hint: 2

   **Skill** -
Realize that a structure with closest packed of anion $\text{X}^-$ with all the tetrahedral sites occupied by $\text{A}^+$ has a stoichiometry of $\text{A}_2\text{X}$.

Contributors

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