How do atoms arrange themselves to form solids?

- Fundamental concepts and language
- Unit cells
- Crystal structures
  - Simple cubic
  - Face-centered cubic
  - Body-centered cubic
  - Hexagonal close-packed
- Close packed crystal structures
- Density computations
- Types of solids
  - Single crystal
  - Polycrystalline
  - Amorphous

Types of Solids

Crystalline material: atoms self-organize in a periodic array

Single crystal: atoms are in a repeating or periodic array over the entire extent of the material

Polycrystalline material: comprised of many small crystals or grains

Amorphous: lacks a systematic atomic arrangement
Crystal structure

To discuss crystalline structures it is useful to consider atoms as being hard spheres with well-defined radii. In this hard-sphere model, the shortest distance between two like atoms is one diameter.

We can also consider crystalline structure as a lattice of points at atom/sphere centers.

Unit Cell

The unit cell is the smallest structural unit or building block that can describe the crystal structure. Repetition of the unit cell generates the entire crystal.

Example: 2D honeycomb net can be represented by translation of two adjacent atoms that form a unit cell for this 2D crystalline structure.

Example of 3D crystalline structure:

Different choices of unit cells possible, generally choose parallelepiped unit cell with highest level of symmetry.
Metallic Crystal Structures

- Metals are usually (poly)crystalline; although formation of amorphous metals is possible by rapid cooling

- As we learned in Chapter 2, the atomic bonding in metals is non-directional ⇒ no restriction on numbers or positions of nearest-neighbor atoms ⇒ large number of nearest neighbors and dense atomic packing

- Atom (hard sphere) radius, $R$, defined by ion core radius - typically 0.1 - 0.2 nm

- The most common types of unit cells are the face-centered cubic (FCC), the body-centered cubic (BCC) and the hexagonal close-packed (HCP).
Miller indices - $h,k,l$ - for naming points in the crystal lattice. The origin has been arbitrarily selected as the bottom left-back corner of the unit cell.

<table>
<thead>
<tr>
<th>Position</th>
<th>Coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O$</td>
<td>0, 0, 0 (Origin)</td>
</tr>
<tr>
<td>$A$</td>
<td>1, 0, 0</td>
</tr>
<tr>
<td>$B$</td>
<td>0, 1, 0</td>
</tr>
<tr>
<td>$C$</td>
<td>0, 0, 1</td>
</tr>
<tr>
<td>$D$</td>
<td>1, 1, 0</td>
</tr>
<tr>
<td>$E$</td>
<td>1, 1, 1</td>
</tr>
<tr>
<td>$F$</td>
<td>0, 1, 1</td>
</tr>
<tr>
<td>$G$</td>
<td>1, 0, 1</td>
</tr>
<tr>
<td>$H$</td>
<td>1/2, 1/2, 1/2</td>
</tr>
</tbody>
</table>

(a) the coordinates of the six face centers and the center of the cube, (b) the location of the point $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ which is found by starting at the origin and moving a distance $\frac{a}{4}$ in the x-direction, then $3\frac{a}{4}$ in the y-direction, and finally $\frac{a}{4}$ in the z-direction.
Positions, Directions, and Planes

Lattice Positions and Directions:
1) Always establish an origin
2) Determine the coordinates of the lattice points of interest
3) Translate the vector to the origin if required by drawing a parallel line or move the origin.
4) Subtract the second point from the first: \(u_2-u_1,v_2-v_1,w_2-w_1\)
5) Clear fractions and reduce to lowest terms
6) Write direction with square brackets \([uvw]\)
7) Negative directions get a hat.

Indices of Planes:
1) Identify the locations where the plane intercepts the x, y, z axes as the fractions of the unit cell edge lengths a, b, c.
2) Infinity if the plane is parallel.
3) Take the reciprocal of the intercepts.
4) Clear any fraction but do not reduce to lowest terms.
5) Example: 1/3,1/3,1/3 is (333) not (111)!!!
6) Use parentheses to indicate planes (hkl) again with a hat over the negative indices.
7) Families are indicated by \([hkl]\)

Remember Terminology:
Defined coordinate system: x, y, z
Respective unit cell edge lengths: a, b, c
Direction: Denoted by \([uvw]\)
Family of direction(s): Denoted by: \(<uvw>\)
Plane: Denoted by: \((hkl)\)
Family of Plane(s): Denoted by: \{hkl\}
• Directions are always perp. to their respective planes, i.e. [111] perp. (111) (for cubic systems)
• Families of equivalent planes are equal with respect to symmetrical structures, they do not have to be parallel. Equivalent planes must be translated to the correct atomic positions in order to maintain the proper crystal symmetry.
• Families of directions are equivalent in absolute magnitude.
• (222) planes are parallel to the (111) planes but not equal.
• Intercepts for the (222) planes are ±1/2,±1/2,±1/2
• Intercepts for the (333) planes are ±1/3,±1/3,±1/3, remember this is in what we call “reciprocal space”. If you draw out the (333) plane it is parallel to the (111) plane but not equivalent.

Representation of a series each of (a) (001), (b) (110), and (c) (111) crystallographic planes.
Notation for lattice positions.

Lattice translations connect structurally. Equivalent positions (example shown is body centered) in various unit cells.
Family of directions, <111>, representing all body diagonals for adjacent unit cells in the cubic system.
Miller-Bravais indicies \((hkl1)\): \(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\) \(\rightarrow (010)\)

Note: \(h + k = l\)

Miller-Bravais indicies, \((hkl)\) for the hexagonal System.

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**Simple Cubic**

- Rare due to poor packing (only Po has this structure)
- Close-packed directions are cube edges.

**Coordination # = 6**

\((# \text{ nearest neighbors})\)

**APF** = \(\frac{\text{Volume of atoms in unit cell}^*}{\text{Volume of unit cell}}\)

\(^*\text{assume hard spheres}\)

\(\text{atoms} \quad \text{unit cell}^3\)

\(\frac{4}{3} \pi (0.5a)^3\)

\(a^3 \quad \text{volume} \quad \text{unit cell}\)
Face-Centered Cubic (FCC) Crystal Structure (I)

- Atoms are located at each of the corners and on the centers of all the faces of cubic unit cell
- Cu, Al, Ag, Au have this crystal structure

Face-Centered Cubic Crystal Structure (II)

- The hard spheres or ion cores touch one another across a face diagonal ⇒ the cube edge length, \( a = 2R\sqrt{2} \)
- The coordination number, \( CN \) = the number of closest neighbors to which an atom is bonded = number of touching atoms, \( CN = 12 \)
- Number of atoms per unit cell, \( n = 4 \). (For an atom that is shared with \( m \) adjacent unit cells, we only count a fraction of the atom, \( 1/m \)). In FCC unit cell we have:
  - 6 face atoms shared by two cells: \( 6 \times \frac{1}{2} = 3 \)
  - 8 corner atoms shared by eight cells: \( 8 \times \frac{1}{8} = 1 \)
- Atomic packing factor, \( APF \) = fraction of volume occupied by hard spheres = \( \frac{\text{Sum of atomic volumes}}{\text{Volume of cell}} = 0.74 \) (maximum possible)
**Face-Centered Cubic Crystal Structure (III)**

- Corner and face atoms in the unit cell are equivalent
- FCC crystal has APF of 0.74, the maximum packing for a system equal-sized spheres ⇒ FCC is a close-packed structure
- FCC can be represented by a stack of close-packed planes (planes with highest density of atoms)

![FCC Crystal Structure Diagram]

**Body-Centered Cubic (BCC) Crystal Structure (I)**

Atom at each corner and at center of cubic unit cell
Cr, α-Fe, Mo have this crystal structure

- The hard spheres touch one another along cube diagonal ⇒ the cube edge length, \( a = \frac{4R}{\sqrt{3}} \)
- The coordination number, \( CN = 8 \)
- Number of atoms per unit cell, \( n = 2 \)
  - Center atom (1) shared by no other cells: \( 1 \times 1 = 1 \)
  - 8 corner atoms shared by eight cells: \( 8 \times 1/8 = 1 \)
- Atomic packing factor, \( APF = 0.68 \)
- Corner and center atoms are equivalent

![BCC Crystal Structure Diagram]
**Hexagonal Close-Packed Crystal Structure (I)**

- HCP is one more common structure of metallic crystals
- Six atoms form regular hexagon, surrounding one atom in center. Another plane is situated halfway up unit cell (c-axis), with 3 additional atoms situated at interstices of hexagonal (close-packed) planes
- Cd, Mg, Zn, Ti have this crystal structure

**Hexagonal Close-Packed Crystal Structure (II)**

- Unit cell has two lattice parameters $a$ and $c$. Ideal ratio $c/a = 1.633$
- The coordination number, $CN = 12$ (same as in FCC)
- Number of atoms per unit cell, $n = 6$.
  
  3 mid-plane atoms shared by no other cells: $3 \times 1 = 3$
  
  12 hexagonal corner atoms shared by 6 cells: $12 \times 1/6 = 2$
  
  2 top/bottom plane center atoms shared by 2 cells: $2 \times 1/2 = 1$
- Atomic packing factor, $APF = 0.74$ (same as in FCC)
- All atoms are equivalent
Comparing HCP and FCC structures. The difference between the two structures lies in the different stacking sequences.

Both FCC and HCP crystal structures have atomic packing factors of 0.74 (maximum possible value).
Both FCC and HCP crystal structures may be generated by the stacking of close-packed planes.
The difference between the two structures is in the stacking sequence.

HCP: ABABAB...
FCC: ABCABCABC…
FCC: Stacking Sequence ABCABCABC...

Third plane is placed above the “holes” of the first plane not covered by the second plane.

HCP: Stacking Sequence ABABAB...

Third plane is placed directly above the first plane of atoms.
Density and Atom Packing

• Bulk Measurements
  – Counting atoms within a unit cell
• Area density in plane
  – # atoms/nm²
• Linear density along direction
  – #atoms/nm

Density Computations

Since the entire crystal can be generated by the repetition of the unit cell, the density of a crystalline material, \( \rho \), is given by the density of the unit cell = (atoms in the unit cell, \( n \)) \times (mass of an atom, \( M \)) / (the volume of the cell, \( V_c \))

Atoms in the unit cell, \( n = 2 \) (BCC); 4 (FCC); 6 (HCP)

Mass of an atom, \( M \) = Atomic weight, \( A \), in amu (or g/mol) is given in the periodic table. To translate mass from amu to grams we have to divide the atomic weight in amu by the Avogadro number \( N_A = 6.023 \times 10^{23} \) atoms/mol

The volume of the cell, \( V_c = a^3 \) (FCC and BCC)
  \( a = 2R\sqrt{2} \) (FCC);  \( a = 4R/\sqrt{3} \) (BCC)
where \( R \) is the atomic radius

Thus, the formula for the density is:
\[
\rho = \frac{nA}{V_c N_A}
\]

Atomic weight and atomic radius of many elements you can find in the table at the back of the textbook front cover.
Polycrystalline Materials

- In polycrystalline materials, grain orientations are random, so bulk material properties are isotropic.

- Some polycrystalline materials have grains with preferred orientations (texture), so properties are dominated by those relevant to the texture orientation.

Polymorphism and Allotropy

Some materials may exist in more than one crystal structure, this is called polymorphism. If the material is an elemental solid, it is called allotropy.

An example of allotropy is carbon, which can exist as diamond, graphite, and amorphous carbon.

Pure, solid carbon occurs in three crystalline forms – diamond, graphite; and large, hollow fullerenes. Two kinds of fullerenes are shown here: buckminsterfullerene (buckyball) and carbon nanotube.
Single Crystals and Polycrystalline Materials

**Single crystal:** atoms are in a repeating or periodic array over the entire extent of the material.

**Polycrystalline material:** comprised of many small crystals or grains. The grains have different crystallographic orientation. There exist atomic mismatch within the regions where grains meet. These regions are called **grain boundaries**.

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Polycrystalline Materials

Atomistic model of a nanocrystalline solid by Mo Li, JHU
Polycrystalline Materials

Simulation of annealing of a polycrystalline grain structure

Polycrystalline Materials

Anisotropy

Different directions in a crystal have different packing. For instance, atoms along the edge of FCC unit cell are more separated than along the face diagonal. This causes anisotropy in the properties of crystals, for instance, the deformation depends on the direction in which a stress is applied.

In some polycrystalline materials, grain orientations are random, so bulk material properties are isotropic.

Some polycrystalline materials have grains with preferred orientations (texture), so properties are dominated by those relevant to the texture orientation and the material exhibits anisotropic properties.

- Polycrystals
  - Properties may/may not vary with direction.
  - If grains are randomly oriented: isotropic.
  - If grains are textured, anisotropic.
Anisotropy

- Properties of crystals may be different along different directions, because atomic periodicities are different. E.g. in single crystal cubic system:
  - \(<100>\) Cube edges
  - \(<110>\) Face diagonals
  - \(<111>\) Body diagonals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Modulus of Elasticity (GPa)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Aluminum</td>
<td>63.7</td>
</tr>
<tr>
<td>Copper</td>
<td>66.7</td>
</tr>
<tr>
<td>Iron</td>
<td>125.0</td>
</tr>
</tbody>
</table>

Non-Crystalline (Amorphous) Solids

In amorphous solids, there is no long-range order. But amorphous does not mean random, in many cases there is some form of short-range order.
Summary

Make sure you understand language and concepts:

- Allotropy
- Amorphous
- Anisotropy
- Atomic packing factor (APF)
- Body-centered cubic (BCC)
- Coordination number
- Crystal structure
- Crystalline
- Face-centered cubic (FCC)
- Grain
- Grain boundary
- Hexagonal close-packed (HCP)
- Isotropic
- Lattice parameter
- Non-crystalline
- Polycrystalline
- Polymorphism
- Single crystal
- Unit cell