Energy and Packing

- Non dense, random packing

- Dense, ordered packing

Dense, ordered packed structures tend to have lower energies.
Crystal Structures

- a ceramic (crystalline) and a glass (non-crystalline)

Crystalline structure - the atoms of the material are arranged in a regular and repeating manner over large atomic distances (long-range order)

Unit cell: is chosen to represent the symmetry of the crystal structure,
- small repeat entity,
- basic structural unit
- building block of crystal structure

Repeating unit cell
**Lattice parameters** a, b, c, α, β, γ
Cubic: a=b=c, α=β=γ=90°

What is the unit cell?
- A parallelepiped
- Cubic, 2-dimensions

SiO₂ 72%
Na₂O and CaO 28%
The seven crystal systems

Table 3.2 P47

- Cubic
- Tetragonal
- Orthorhombic
- Rhombohedral
- Hexagonal
- Monoclinic
- Triclinic

The 14 crystal (Bravais) lattices

- Simple lattice
- Body-centered
- Face-centered
- Base-centered
For the face-centered cubic (fcc) crystal structure: (a) a hard sphere unit cell, (b) a reduced-sphere unit cell, (c) an aggregate of many atoms.

• Coordination number: number of nearest-neighbor atoms
• Close packed directions:
• Unit cell volume: \( V_c \)
• Number of atoms in each unit cell: \( n \)
• Volume of atoms in a unit cell: \( V_s \)
• Atomic packing factor: \( \text{APF} = \frac{V_s}{V_c} \)
• Density computations: \( \rho = \frac{nA}{V_c N_A} \)

\( N_A \): Avogadro’s number

Example problem 3.1 and 3.2 (p44)

For the body-centered cubic crystal structure.

• Coordination number: number of nearest-neighbor atoms
• Close packed directions:
• Unit cell volume \( V_c \)
• Number of atoms in each unit cell: \( n \)
• Volume of atoms in a unit cell \( V_s \)
• Atomic packing factor \( \text{APF} = \frac{V_s}{V_c} \)
• Density computations, \( \rho = \frac{nA}{V_c N_A} \)
example problem 3.3 calculate the density (g/cm\(^3\)) of copper (p45)

Crystal structure: fcc
Atomic mass: 63.5g/mol
Atom radius r: 0.128 nm
*Lattice parameters: a, b, c, α, β, γ
*Atoms/unit cell: n
Avogadro’s number, 0.6023 x 10\(^{24}\) atoms/mole

\[ \rho = \frac{nA_{\text{Cu}}}{V_c N_A} \]

Homework
3.3, 3.7, 3.10 (p.74)

SIMPLE CUBIC STRUCTURE
- Rare due to poor packing (only Po (polonium) has this structure)
- Close-packed directions are cube edges.
- Coordination number = 6
  (nearest neighbors)

<table>
<thead>
<tr>
<th>lattice</th>
<th>SC</th>
<th>BCC</th>
<th>FCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>APF</td>
<td>0.52</td>
<td>0.68</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Homework
Calculate the APF for SC, BCC and FCC respectively.
FACE CENTERED CUBIC STRUCTURE (FCC)

- Close packed directions are face diagonals.
  - Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

- Coordination number = 12

BODY CENTERED CUBIC STRUCTURE (BCC)

- Close packed directions are cube diagonals.
  - Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

- Coordination number = 8

Close-packed directions:
length = 4R = $\sqrt{3} \times a$
How can we stack metal atoms to minimize empty space?

2-dimensions

Now stack these 2-D layers to make 3-D structures.

Close-packed structure hcp

A portion of a close-packed plane of atoms; A, B, and C position are indicated.

The AB stacking sequence: ABABABABABAB……..
Hexagonal close-packed crystal structure

(a) A reduced-sphere unit cell,  (b) an aggregate of many atoms

Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection

- 2D Projection

- Coordination number = 12
- APF = 0.74, \( c/a = 1.633 \)

6 atoms/unit cell
ex: Cd, Mg, Ti, Zn
Close-packed structure fcc

Close-packing stacking for face-centered cubic
**Allotropic transformation** p48

*(allotropy/polymorphism)* Two or more distinct crystal structures for the same material

Body-centered tetragonal

<table>
<thead>
<tr>
<th>Structure</th>
<th>Crystallographic Points</th>
<th>Crystallographic Directions</th>
<th>Crystallographic Planes</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.30 g/cm³</td>
<td>q r s</td>
<td>[uvw]</td>
<td>(hkl)</td>
</tr>
<tr>
<td>cooling</td>
<td></td>
<td>expansion</td>
<td>crumbled</td>
</tr>
<tr>
<td>White tin and grey tin,</td>
<td></td>
<td>expansion</td>
<td>crumbled</td>
</tr>
</tbody>
</table>

**Lattice geometry**

*(Crystallographic points, directions, and planes)*

**Indexing:**
- *point coordinate* q r s
- *crystallographic direction* [uvw]
- *crystallographic plane* (hkl)
Point coordinates (in terms of $a$, $b$, and $c$)

The position of $P$ within a unit cell is designated using coordinates $q \, r \, s$ with values that are less or equal to unity.
Crystallographic directions \([uvw]\)

1. A vector to be positioned such that it passes through the origin of the coordinate system,
2. To obtain the length of the vector projection on each of the three axes in terms of \(a\), \(b\), and \(c\)
3. To reduce them to the smallest integer values
4. The three indices to be enclosed in square brackets, thus \([uvw]\).
5. families of directions \(<uvw>\)

<table>
<thead>
<tr>
<th>Point Number</th>
<th>Fractional Lengths</th>
<th>Point Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(x) axis</td>
<td>(y) axis</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>(\frac{1}{2})</td>
<td>(\frac{1}{2})</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Question 3.30 (p76) Sketch within a cubic unit cell the following directions: [101], [    1     ]; [211]; .......

Question 3.31 (p76) Determine the indices for the directions shown in the following cubic unit cell

The vectors should pass through the origin of the coordinate system, if not:
1. Choose a new origin, or
2. Move the vectors
Crystallographic planes

1. The crystallographic planes are specified by three Miller indices (hkl).
2. Any two crystal planes parallel to each other are equivalent and have identical indices.
3. The plane intercepts or parallels each of the three axes
4. Family of planes (hkl) (enclosed within braces)

Choose a new origin O'

Intercepts
Intercepts (in terms of lattice parameters)
Reciprocals of the numbers, or the inverse intercepts
Reductions (multiplied or divided by a common factor to reduce them to the smallest integers)
Enclosed within parentheses (hkl)

---

Determine the Miller indicis of plane A, B, and C

Plane A:
- Intercepts x = 1, y = 1, z = 1
- 1/x = 1, 1/y = 1, 1/z = 1
- No fractions to clear
- (111)

Plane B:
- Intercepts x = 1, y = 2, z = ∞ (infinity)
- 1/x = 1, 1/y = ½, 1/z = 0
- Clear fractions 1/x = 2, 1/y = 1, 1/z = 0
- (210)

Plane C:
- Move the origin to 010, then
- (0 10)
Any two crystal planes parallel to each other are equivalent and have identical indices.

Hexagonal crystals

Using a four-axis \((a_1, a_2, a_3\) and \(c\), or Miller-Bravais, coordinate system

**HCP Crystallographic Directions**

1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions \(a_1\), \(a_2\), \(a_3\), or \(c\)
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

\([uvtw]\)

ex: \(\frac{1}{2}, \frac{1}{2}, -1, 0\) => \([1\bar{1}20]\)

dashed red lines indicate projections onto \(a_1\) and \(a_2\) axes

Adapted from Fig. 3.9, Callister 7e.
HCP Crystallographic Directions

- 4 parameter Miller-Bravais lattice coordinates are related to the direction indices (i.e., $u'v'w'$) as follows.

\[
[u'v'w'] \rightarrow [uvtw]
\]
\[
u = \frac{1}{3}(2u' - v')
\]
\[
v = \frac{1}{3}(2v' - u')
\]
\[
t = -(u + v)
\]
\[
w = w'
\]

Fig. 3.8(a), Callister 7e.

Crystallographic Planes (HCP)

- In hexagonal unit cells the same idea is used, (hkil)
- $i = -(h+k)$

<table>
<thead>
<tr>
<th>example</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercepts</td>
<td>1</td>
<td>$\infty$</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>Reciprocals</td>
<td>1</td>
<td>$1/\infty$</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>Reduction</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>Miller-Bravais Indices</td>
<td>(10\overline{1}1)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Adapted from Fig. 3.8(a), Callister 7e.

Homework
3.38, 3.39 (b, f, g), 3.40, 3.48*, 3.49* (p76-78)
X-ray Diffraction (XRD)* p66

**Bragg’s law:**
If the path length difference \(2dsin\theta = n\lambda\), the interference will be constructive so as to yield a high-intensity diffracted beam.

**Interplanar spacing:**
Cubic, \(d_{hkl} = a / (h^2 + k^2 + l^2)^{1/2}\)

Fig. 3.18

---

In phase, constructively interfere

Out of phase, destructively interfere
X-ray Diffractometer

Diffraction pattern of aluminium powder

\[
\lambda = 0.1542 \text{ nm (CuK}_{\alpha}\text{-radiation)}
\]
Diffraction pattern of aluminium powder

The red lines give the diffraction angle (2θ) for the first three peaks in the α-Fe pattern.

Crystal defects (Chapter 4)

Types of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms
- Dislocations
- Grain Boundaries

Point defects

Line defects

Area (planar) defects
POINT DEFECTS

- **Vacancies:**
  - vacant atomic sites in a structure.

- **Self-Interstitials:**
  - "extra" atoms positioned between atomic sites.

![Vacancy distortion of planes](image)

![Self-interstitial distortion of planes](image)

Line Defects

**Dislocations:**
- are line defects,
- slip between crystal planes result when dislocations move,
- produce permanent (plastic) deformation.

Schematic of Zinc (HCP):
- before deformation
- after tensile elongation

![Schematic of Zinc (HCP)](image)

Adapted from Fig. 7.8, Callister 7e.
Dislocations

- Linear Defects
  - Are one-dimensional defects around which atoms are misaligned
- Edge dislocation:
  - extra half-plane of atoms inserted in a crystal structure
  - $b \perp$ to dislocation line
- Screw dislocation:
  - spiral planar ramp resulting from shear deformation
  - $b \parallel$ to dislocation line

Burger’s vector, $b$: measure of lattice distortion
(a) A screw dislocation within a crystal,
(b) The screw dislocation in (a) viewed from above.

TEM pictures of dislocations

TEM micrograph of dislocations in an Fe-35%Ni-20%Cr alloy, creep tested at 700°C

Dislocation in Silicon iron. TEM
Dislocations formed in a die cast Mg alloy AE42 (Mg-4Al-2 rare earth) after tensile creep test under 175°C and 60MPa (a) TEM bright field image, (b) the corresponding electron diffraction pattern.

Planar defects

- Twin boundary
- Surface
- Grain-boundary

Optical micrograph, low-carbon steel. The grain boundaries have been lightly etched with a chemical solution from the polished grains.
A garnet single crystal

Various stages in the solidification of a polycrystalline material; the square grids depict unit cells (a) crystallite nuclei in liquid, (b) growth of the crystalite, (c) upon completion of solidification, (d) the grain structure under the microscope

Optical Microscopy

- Useful up to 2000X magnification.
- Polishing removes surface features (e.g., scratches)
- Etching changes reflectance, depending on crystal orientation.

Adapted from Fig. 4.13(b) and (c), Callister 7e. (Fig. 4.13(c) is courtesy of J.E. Burke, General Electric Co.)

0.6 mm
Grain boundary structures

A high-angle ($\theta = 36.9^\circ$) grain boundary

A low-angle grain boundary ($\theta = 7^\circ$)

TEM image of a grain boundary

Electron beam

The parallel lines identify the boundary. A dislocation intersecting the boundary is labeled "D".