Two Important Concepts

1. A **unit cell** is the most basic repeating structure of any solid.

Atoms in a *crystalline solid* form a regular repeating pattern.

2. Crystalline solids have periodic arrays of atoms which forms a grid system that fills all space. We call the grid system a *crystal lattice*. Amorphous solids and glasses are exceptions.
The unit cell can be classified as **primitive** or **conventional**.

- There are **many** ways to define a unit cell.

- **A primitive** unit cell has atoms **only at the corners** of the unit cell. This will be the simplest representation of the crystal structure, but it may not reflect the complete symmetry of the crystal structure.

- **The conventional** unit cell will have atoms at **additional sites** within the unit cell (i.e. on the faces, at the body center, etc.), causing the conventional unit cell to have the same symmetry as the entire crystal structure. Chosen for convenience.

- By **international convention**, a **unit cell** is specified to be right-handed, to have the highest symmetry, and to have the smallest cell volume.

Visualize crystal structures: [http://surfexp.fhi-berlin.mpg.de/SXinput.html](http://surfexp.fhi-berlin.mpg.de/SXinput.html)
Example: There are many possible choices for primitive vectors and primitive unit cells (parallelograms) in two-dimensions.

Area of Primitive cell (in 2D) = $|\vec{a}_1 \times \vec{a}_2| = a_1 a_2 \sin \theta$
Organizing Space

Specify Unit Cell

Identify all Rotations, Reflections and Inversions that transform the cell into itself

Defines one of 32 possible crystallographic Point Groups

Four Lattice Types

Primitive

Body Centered

Face Centered

Base Centered

Add Space Filling Translations to define Space Groups

Find 14 Space Filling Lattices (Bravais Lattices)

Bravais Lattices classified into 7 distinguishable Point Groups

7 Crystal Systems
The 14 Bravais Lattices (A. Bravais, 1848)

All 3d crystalline materials (not including quasicrystals) can be classified into one of 14 Bravais Lattices (space lattices).

A Bravais Lattice is the collection of ALL points from the origin specified by the position vectors

$$\mathbf{L} = \ell_1 \mathbf{a}_1 + \ell_2 \mathbf{a}_2 + \ell_3 \mathbf{a}_3$$

$$\ell_1, \ell_2, \ell_3$$ signed integers

SC=Simple Cubic (P=primitive)
BC=Base-Centered (C)
BC=Body-Centered (I)
FC=Face-Centered (F)

The dots represent lattice points, not atoms! The Bravais lattice forms a “grid system” that fills all space.
A Crystal is a space-filling Lattice - where are the atoms?

2D crystal lattice (example)

Any atom in the lattice is specified by a 2D vector

\[ \vec{L} = \ell_1 \vec{a}_1 + \ell_2 \vec{a}_2 \]

\( \ell_1 \) and \( \ell_2 \) signed integers

Simple cubic lattice in 3D

Any atom in the lattice is specified by a 3D vector

\[ \vec{L} = \ell_1 \vec{a}_1 + \ell_2 \vec{a}_2 + \ell_3 \vec{a}_3 \]

\( \ell_1, \ell_2, \text{ and } \ell_3 \) signed integers
In 3d - use a Crystal Viewer

http://undergrad-ed.chemistry.ohio-state.edu/xtal/xtal.html
The packing fraction is defined as the ratio of the maximum total atomic volume to the volume of the unit cell. The packing fraction measures the space occupied by “spherical” atoms in a unit cell.

<table>
<thead>
<tr>
<th></th>
<th>Simple cubic</th>
<th>Body-centered cubic</th>
<th>Face-centered cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume, Conventional Cell</td>
<td>$a^3$</td>
<td>$a^3$</td>
<td>$a^3$</td>
</tr>
<tr>
<td>Bravais lattice points per cell</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Number primitive cells in a conventional cell</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Volume, Primitive Cell</td>
<td>$a^3$</td>
<td>$a^3/2$</td>
<td>$a^3/4$</td>
</tr>
<tr>
<td>Number nearest neighbors</td>
<td>6</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>Nearest neighbor distance</td>
<td>$a$</td>
<td>$\sqrt{3}a/2 = 0.866a$</td>
<td>$\sqrt{2}a/2 = 0.797a$</td>
</tr>
<tr>
<td>Number next nearest neighbors</td>
<td>12</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Next nearest neighbor distance</td>
<td>$\sqrt{2}a$</td>
<td>$a$</td>
<td>$a$</td>
</tr>
<tr>
<td>Packing fraction</td>
<td>$\pi/6 = 0.524$</td>
<td>$\sqrt{3}\pi/8 = 0.680$</td>
<td>$\sqrt{2}\pi/6 = 0.740$</td>
</tr>
<tr>
<td>Empty space</td>
<td>0.476</td>
<td>0.320</td>
<td>0.260</td>
</tr>
</tbody>
</table>
What Determines the Structure of a Crystalline Solid?

Non-directional bonding between atoms (close packing of atoms)

Highly directional bonding between atoms (electron orbitals and quantum mechanics)

All atoms in the crystal are the same, no directional bonding; dense ordered structures tend to have lower energies

The symmetry of atomic orbitals plays dominant role
Naming Crystal Planes – Miller Indices

The Miller indices of a crystal plane \((h,k,l)\) are defined to be a set of integers with no common factors, inversely proportional to the intercepts of the crystal plane along the crystal axes:

\[
h : k : \ell = \frac{1}{x} : \frac{1}{y} : \frac{1}{z}
\]

Smallest three integers with same ratio:

\[
6 \left( \frac{1}{3} : \frac{1}{2} : \frac{1}{2} \right) = 2 : 3 : 3
\]

Miller indices of plane: \((233)\)

Miller indices of line \(\perp\) plane: \([233]\)

For cubic system:

\[
\frac{1}{a_{hk\ell}^2} = \frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{\ell^2}{a^2}
\]
Miller indices of high symmetry planes in cubic system

\{100\} includes (100), (010), (001)

- If a Miller index is zero, the plane does not intersect that axis.
- Multiplying or dividing a Miller index by a constant has no effect on the orientation of the plane.
- Miller indices are almost always small integers.
Example

Two (110) planes in cubic system where $a_1=a_2=a_3=a_o$. What is distance between the two planes?

$$\frac{1}{d_{hk\ell}^2} = \frac{h^2}{a_1^2} + \frac{k^2}{a_2^2} + \frac{\ell^2}{a_3^2}$$

$$\frac{1}{d_{110}^2} = \frac{h^2}{a_o^2} + \frac{k^2}{a_o^2} + \frac{\ell^2}{a_o^2} = \frac{h^2 + k^2 + \ell^2}{a_o^2}$$

$$d_{110}^2 = \frac{a_o^2}{h^2 + k^2 + \ell^2} = \frac{a_o^2}{1^2 + 1^2 + 0^2}$$

$$d_{110} = \frac{a_o}{\sqrt{2}}$$
Directions in 3-dimensions

Notation:
individual direction (vector) \([hkl]\)
set of directions (vector set) \(<hkl>\)
individual surface (plane) \((hkl)\)
set of planes (family of set) \{hkl\}

Examples: draw
\([102]\) = \(\frac{1}{2}a, 0b, 1c\)
\([1\bar{1}2]\) = \(\frac{1}{2}a, -\frac{1}{2}b, 1c\)

Direction \(OA = [011] = 0a, 1b, 1c\)
Direction \(OB = [110] = 1a, 1b, 0c\)

a, b, c need not be equal
Up Next - Energy States in a Periodic Crystal
APPENDIX A: A brief word about the abstract concept of a “Group”

If you step back from individual problems and look at their underlying structure, you might develop useful insights to comprehend common features of the many different problems that confront us.

The “Group” concept provides a definition that captures common features of many familiar objects in one unifying definition.

Key Insight: instead of numbers, focus on the symmetries.

Traditionally groups were used to identify symmetries of geometric objects.

Today the concept of a group has been extended to include a group of symmetries describing different mathematical objects like matrices.

A connection to the physical world: e.g., a mathematical group called $SU(2)$ is useful for understanding the difference between bosons and fermions.

Check out http://plus.maths.org/content/power-groups
Point Groups

• Identify all symmetry-operations (reflection, rotation, inversion, etc.) that specify the geometric symmetry of a unit cell.

• A unit cell may be rotated around a line as an axis, reflected through a mirror plane, or inverted through a point located in the center. These lines, planes, or points are called symmetry elements.

• Symmetry elements (with defined geometrical relations among themselves) can be found for any given unit cell.

• Surprisingly, there are only a limited number of combinations of symmetry elements and these combinations are called point groups.

• A unit cell is said to have a symmetry described by a given point group.

• Different unit cells with different symmetries will therefore be described by different point groups.

• There are only 32 point groups.

• Animated gif movies at:
  http://materials.cmu.edu/degraef/pg/pg.html#AGM
A point group must fulfil the mathematical requirements of a group:

i) There must be an operation or procedure that combines two elements in the group to form another element of the group

ii) The identity element (I) must be present

iii) An inverse operator must be identified such that RR⁻¹ = I (identity element)

iv) Group operations in sequence must obey the associative law

Example: All positive and negative integers plus zero constitute a group.

i) the required operation is summation (+);

ii) the identity element is I=0, a + 0 = a;

iii) negative integers are the inverse of positive integers, so a + (a)⁻¹ = a + (-a) = I;

and

iv) The addition of integers satisfies the associative law: a+(b+c)=(a+b)+c
These very general considerations lead to four distinct lattice types:

i) Primitive (P),
ii) Body centered (BC),
iii) Face centered at all faces (FC),
iv) Side-centered or Base-centered (C), (face centered on only two opposite faces).

These four different lattice types can be used to specify 14 different translational space-filling lattices known as Bravais lattices.

Bravais lattices can be mathematically classified using a set of well-defined symmetry operations (defined as space groups = point group elements PLUS translational elements) which take the lattice into itself.

The 14 Bravais lattices fall into seven different point group elements (symmetry under reflection and rotation operations), leading to seven different crystal systems: cubic, tetragonal, orthorhombic, hexagonal, rhombohedral (trigonal), monoclinic, and triclinic.
APPENDIX B: Why the Miller notation works
(consider 2D case for simplicity: plane → line)

Any line $AB$ is defined by an equation based on its intercepts ($a$ and $b$). From plane geometry, a second line $OP$ through the origin $O$ and perpendicular to the original line is also defined by an equation that must contain the intercepts of the original line.

1. Eq. for original line $AB$:
\[
y = -\left(\frac{b}{a}\right)x + b
\]
\[
\left(\frac{x}{a}\right) + \left(\frac{y}{b}\right) = 1
\]

2. Eq. for line $OP$:
\[
y = x \tan(p) = x \cdot \frac{a}{b}
\]
or
\[
yb = xa
\]

- form the Miller Indices of line $AB$: $h : k = \frac{1}{a} : \frac{1}{b}
- find Least Common Denominator: $ab\left(\frac{1}{a} : \frac{1}{b}\right) = (b : a)$
- perpendicular line $OP$ given by notation $[ba] \Leftrightarrow b \hat{i} + a \hat{j}$