Polymer Crystallinity

• Atomic arrangement in polymers is more complex than it is in metals (atoms) and ceramics (ions), since there are molecules involved.
• Polymer crystallinity is thought of as the packing of molecular chains to produce an ordered atomic array.

Ex: polyethylene orthorhombic unit cell (on right):
  • Crystals must contain the polymer chains in some way.
  • HDPE is Space group 62 (Pnma) - last class.
  • PE can also exist in less stable monoclinic form; Cubic forms do not appear in polymers, thus crystalline polymers exhibit high degree of anisotropy. PP is monoclinic.

• Polymers are rarely 100% crystalline, it's too difficult to get all the chains aligned.
• Partial crystalline regions (longer range order) dispersed inside a amorphous (short range order) matrix.
• Any chain disorder or misalignment will result in an amorphous region, which is common due to twisting, kinking and coiling of chains, this prevents ordering.

More info http://www.eng.uc.edu/~gbeaucag/Classes/XRD.html
Brief Summary of Crystallography

• 7 Crystal Systems
  • Based on the number of self consistent combinations of rotation axis in 3D-defines basic Primitive (P) units cells.

• 14 Bravais Lattices
  • Arrangements of lattice points consistent with the above combinations of rotation axes i.e. some unit cells can also be F, I or C centered (translation symmetry).

• 32 Point Groups
  • Combinations of symmetry elements acting through a point - each belongs to a crystal class.
  • Describes macroscopic shape of ideal crystals.
  • Describes symmetry of properties such as thermal expansion, elastic modulus, refractive index, conductivity, etc.

• 230 Space Groups
  • Point group symmetry plus translational symmetry of Bravais lattice and screw axes and glide planes – each belongs to a crystal structure.
  • Not all of the space groups are of equal importance and many of them have few examples of real crystals.
  • About 70% of the elements belong to the space groups Fm\bar{3}m, Im\bar{3}m, Fd\bar{3}m, F\bar{4}3m and 6\bar{3}/mmc. Over 60% of organic and inorganic crystals belong to space groups P2_1/c, C2/c, P2_1, PT, Pbca, P2_12_12_1.
Review of Crystallography
*(what you need to know at a minimum)*

1. **Four 2-D (primitive) crystal systems** → **Seven 3-D (primitive) crystal systems** *(know their lattice parameters)*

2. Types of lattices; Number of lattice points: tells you number of atoms needed to define your basis.

3. Lattice points are categorized based on the 3 possible centering operations (base, face and body) + primitive (simple) arrangements.

4. Can we add additional lattice points to the primitive lattices (or nets), in such a way that we still have a lattice (net) belonging to the same crystal system? **Answer:** in 2-D we can only add one more lattice point to rectangular to get centered rectangular lattice *(Five 2-D Bravais lattices)*.
   1. Remember that since the surroundings of every lattice point must be identical, we can only add new lattice points at centered positions.

5. By repeating this procedure in 3-D, where there are now 3 possible ways to add lattice points at the center between existing lattice points - base (A, B and/or C), face (F) and body (I),

6. We can now apply these 5 forms of centering (I, F, A, B, C) to all seven 3-D (primitive) crystal systems: 5x7=35 possibilities.
   1. In several cases we do generate a new lattice, in other cases we can redefine the unit cell and reduce the cell to another type. Also, must maintain minimum symmetry requirements for that crystal system *(know the minimum symmetry requirements for the 7 crystal systems)*.
   2. Reducing from 35 to **Fourteen 3-D (7 primitive and 7 non-primitive) Bravais lattices** means either the unit cell is not unique (choose one that is easier to work with) or symmetry is lost.
   3. Repeating this exercise for all types of lattice centering, we end up with 7 additional **non-primitive** lattice types that cannot be reduced to primitive ones of the same crystal system: mC, oC, oI, oF, tI, cI, cF. *(know these):*
7. One of the 14 Bravais lattices + basis positions (vectors) = crystal structure (we went over many examples in class 13 as well as other classes).

8. Basis positions can be overwhelming for complex crystal structures, thus we rely on symmetry operations (reflection, rotation, inversion, rotoinversion, translation) to reduce complexity, while satisfying the minimum symmetry criteria:
9. Based on these symmetry operations, the minimal requirements for 7 crystal systems in 3-D become:

1. **Triclinic**, all cases not satisfying the requirements of any other system; thus there is no other symmetry than translational symmetry, or the only extra kind is inversion (3-D). (1 and bar1)

2. **Monoclinic**, requires either 1 two-fold axis of rotation (2) or 1 mirror plane (m). Can also have a combination of these (2/m).

3. **Orthorhombic**, requires either 3 two-fold axes of rotation (222), 1 two fold axis of rotation and two mirror planes (2mm) or combo of two-fold and mirror planes (mmm).

4. **Tetragonal**, requires 1 four-fold axis of rotation. (4, bar4, 4/m, 422, 4mm, bar42m, 4/mmm).

5. **Trigonal** (rhombohedral), requires 1 three-fold axis of rotation (3, bar3, 32, 3m, bar3m).

6. **Hexagonal**, requires 1 six-fold axis of rotation (6, bar6, 6/m, 622, 6mm, bar6m2, 6/mmm).

7. **Cubic**, requires 4 three-fold axes of rotation (23, mbar3, 432, bar43m, mbar3m).

We can thus describe the basis down to a small number of parameters.

• I do not expect you to memorize all 32 point groups; however, if you see objects, molecules, atoms, ions, (e.g. in unit cell), you should be able to determine which symmetry operations you can perform for them to remain invariant.
10. From the symmetry operations you determined, you should be able to determine point group symmetry and equipoints (for simple objects, crystal structures, many we went over in class, HW, old tests) based on:

**Table 9.1. Primary, secondary, and tertiary symmetry directions in each of the seven crystal systems. For the tetragonal system, the symbol \( \langle uvw \rangle \) refers to the fact that equivalent directions are obtained from permutations of the first two indices only.**

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Primary ( \langle uvw \rangle )</th>
<th>Secondary ( \langle uvw \rangle )</th>
<th>Tertiary ( \langle uvw \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>( \langle 100 \rangle )</td>
<td>( \langle 111 \rangle )</td>
<td>( \langle 110 \rangle )</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>( [00.1] )</td>
<td>( [10.0] )</td>
<td>( [12.0] )</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>( [001] )</td>
<td>( [100] )</td>
<td>( [110] )</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>( [100] )</td>
<td>( [010] )</td>
<td>( [001] )</td>
</tr>
<tr>
<td>Trigonal</td>
<td>( [111] )</td>
<td>( [010] )</td>
<td>( [1\bar{1}0] )</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>( [010] )</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Triclinic</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Space groups are representations of the ways that the macroscopic and microscopic symmetry operations (elements) can be self-consistently arranged in space.

There are 230 of them!
11. You should be able to look at any one of the 230 3-D Space groups and identify its 3-D Bravais lattice and 3-D Point group

12. **Space group** (contains Bravais lattice + symmetry requirements), basis positions and lattice constants are what you need to know in defining crystal structures.

13. Consult the course notes, information went over on the board, all HW, Tests, handouts and problems went over in class.

14. Don’t panic!
Quantitative calculations involving the geometry of the lattice

- When computing distances, angles and interplanar spacings in lattices, it is important to remember that Bravais lattice basis vectors are not always mutually orthogonal.
- There are generalized rules for computing the geometric characteristics of lattices, applicable to all 7 crystal systems.
- They can be determined by careful visualization and trigonometric calculation.
- On the right are the interplanar $d$-spacings for the 7 crystal systems. We will return to these when we discuss X-ray diffraction.

The value of $d$, the distance between adjacent planes in the set $(hkl)$, may be found from the following equations.

**Cubic:**
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

**Tetragonal:**
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} + \frac{l^2}{c^2}$$

**Hexagonal:**
$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

**Rhombohedral:**
$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + hl)(\cos^2 \alpha - \cos \alpha)}{a^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}$$

**Orthorhombic:**
$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

**Monoclinic:**
$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$$

**Triclinic:**
$$\frac{1}{d^2} = \frac{1}{V^2} \left( S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl \right)$$

In the equation for triclinic crystals,

- $V =$ volume of unit cell (see below),
- $S_{11} = b^2c^2 \sin^2 \alpha,$
- $S_{22} = a^2c^2 \sin^2 \beta,$
- $S_{33} = a^2b^2 \sin^2 \gamma,$
- $S_{12} = abc^2(\cos \alpha \cos \beta - \cos \gamma),$
- $S_{23} = a^2bc(\cos \beta \cos \gamma - \cos \alpha),$
- $S_{13} = ab^2c(\cos \gamma \cos \alpha - \cos \beta).$
Vegard’s Law – Application of lattice constant for alloys

• Empirical law based on a linear relationship.

• Works for substitutional solid solution alloys that obey the Hume-Rothery Rules.

• **Example**: consider a Nickel coin composed of 75% Cu \((a)\) and 25% Ni \((b)\) which are two FCC metals with lattice constant \((a)\) that obey H-R rules. Pure Cu \(a=0.3608\) nm and Pure Ni \(a=0.3524\) nm

\[
a_{\text{alloy}} = X_a a_a + X_b a_b \quad \text{(Vegard’s Law)}
\]

\[
a_{\text{alloy}} = 0.75(0.3608) + 0.25(0.3524)
\]

\[
a_{\text{alloy}} = 0.3587 \text{ nm}
\]
Angle between Crystallographic Directions (or Planes)

• The angle can be determined from the dot product of two vectors.
• Taking directions \([uvw]\) and \([u'v'w']\) as vectors \(\vec{R}_1 = u\hat{a} + v\hat{b} + w\hat{c}\) and \(\vec{R}_2 = u'\hat{a} + v'\hat{b} + w'\hat{c}\) we can determine the angle, \(\phi\), between these two directions; for cubic system:

\[
\vec{R}_1 \cdot \vec{R}_2 = \left| \vec{R}_1 \right| \left| \vec{R}_2 \right| \cos \phi \quad \text{or} \quad \cos \phi = \frac{\vec{R}_1 \cdot \vec{R}_2}{\left| \vec{R}_1 \right| \left| \vec{R}_2 \right|} = \frac{uu' + vv' + ww'}{\sqrt{u^2 + v^2 + w^2} \sqrt{u'^2 + v'^2 + w'^2}}
\]

Ex. 1: What’s the angle between the [110] and [111] directions in cubic system?

\[
\phi = \arccos \frac{uu' + vv' + ww'}{\sqrt{u^2 + v^2 + w^2} \sqrt{u'^2 + v'^2 + w'^2}}
\]

\[
= \arccos \frac{1 + 1 + 0}{\sqrt{2} \sqrt{3}}
\]

\[
= 35.3^\circ
\]

Ex. 2: What’s the angle between the [100] and [110] directions in cubic system?

Ex. 3: What’s the angle between the [100] and [111] directions in cubic system?

Ex. 4: What’s the angle between the [011] and [121] directions in cubic system?
The angle $\phi$ between the plane $(h_1k_1l_1)$, of spacing $d_1$, and the plane $(h_2k_2l_2)$, of spacing $d_2$, may be found from the following equations. ($V$ is the volume of the unit cell.)

**Cubic:**
\[
\cos \phi = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)}}
\]

**Tetragonal:**
\[
\cos \phi = \frac{h_1h_2 + k_1k_2}{a^2} + \frac{l_1l_2}{c^2}
\]

\[
\sqrt{\left(\frac{h_1^2}{a^2} + \frac{k_1^2}{c^2}\right)\left(\frac{h_2^2}{a^2} + \frac{k_2^2}{c^2}\right)}
\]

**Hexagonal:**
\[
\cos \phi = \frac{h_1h_2 + k_1k_2 + \frac{1}{2}(h_1k_2 + h_2k_1)}{\sqrt{\left(\frac{h_1^2}{a^2} + h_1k_1 + \frac{3a^2}{4c^2}l_1l_2\right)\left(h_2^2 + k_2^2 + h_2k_2 + \frac{3a^2}{4c^2}l_2^2\right)}}
\]

**Rhomboedral:**
\[
\cos \phi = \frac{a^4d_1d_2}{V^2} \left[ \sin^2 \alpha (h_1h_2 + k_1k_2 + l_1l_2) \right.
\]
\[
+ (\cos^2 \alpha - \cos \alpha)(k_1l_2 + k_2l_1 + h_1h_2 + l_2h_1 + h_1k_2 + h_2k_1) \right]
\]

**Orthorhombic:**
\[
\cos \phi = \frac{h_1h_2}{a^2} + \frac{k_1k_2}{b^2} + \frac{l_1l_2}{c^2}
\]

\[
\sqrt{\left(\frac{h_1^2}{a^2} + \frac{k_1^2}{b^2} + \frac{l_1^2}{c^2}\right)\left(\frac{h_2^2}{a^2} + \frac{k_2^2}{b^2} + \frac{l_2^2}{c^2}\right)}
\]

**Monoclinic:**
\[
\cos \phi = \frac{d_1d_2}{\sin^2 \beta} \left[ \frac{h_1h_2}{a^2} + \frac{k_1k_2 \sin^2 \beta}{b^2} + \frac{l_1l_2}{c^2} - \frac{(l_1h_2 + l_2h_1) \cos \beta}{ac} \right]
\]

**Triclinic:**
\[
\cos \phi = \frac{d_1d_2}{V^2} \left[ S_{11}h_1h_2 + S_{12}k_1k_2 + S_{13}l_1l_2 \right.
\]
\[
+ S_{22}(k_1l_2 + k_2l_1) + S_{13}(l_1h_2 + l_2h_1) + S_{12}(h_1k_2 + h_2k_1) \right]
\]

The following equations give the volume $V$ of the unit cell.

**Cubic:**
\[ V = a^3 \]

**Tetragonal:**
\[ V = a^2c \]

**Hexagonal:**
\[ V = \frac{\sqrt{3}a^2c}{2} = 0.866a^2c \]

**Rhomboedral:**
\[ V = a^3\sqrt{1 - 3\cos^2 \alpha + 2\cos^3 \alpha} \]

**Orthorhombic:**
\[ V = abc \]

**Monoclinic:**
\[ V = abc \sin \beta \]

**Triclinic:**
\[ V = abc\sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma} \]
Important Relationships Between Directions <uvw> and Planes {hkl}

1. **Perpendicular** - cannot assume [uvw] is perpendicular to (hkl). This is always true for the cubic system, but not necessarily true for the other 6 systems……

2. **Parallel** - use the Weiss zone law to determine if [uvw] is parallel to, or lies in, (hkl).
   
   **Zone Law (dot product):** \( hu + kv + lw = 0 \), or \( hu + kv + it + lw = 0 \) (hexagonal), if the zone law is satisfied then they are parallel.

   Ex: Is [002] parallel to, or lies in, (321) ?
   
   \( 0(3) + 0(2) + 2(1) = 2 \) → zone law is not satisfied, so not parallel

   Ex: Is [010] parallel to, or lies in, (201) ?
   
   \( 0(2) + 1(0) + 0(1) = 0 \) → zone law is satisfied, so parallel
Important Relationships Between Directions and Planes (continued)

3. Intersection of two planes:
- 2 planes intersect to form a line. **Criss-cross law** (cross product):

```
\[ \begin{array}{ccc}
  & u & v & w \\
 1 & h_1 & k_1 & l_1 \\
 2 & h_2 & k_2 & l_2 \\
\end{array} \]
```

\[ u = (k_1)(l_2)-(k_2)(l_1) \]
\[ v = (h_2)(l_1)-(h_1)(l_2) \]
\[ w = (h_1)(k_2)-(h_2)(k_1) \]

**Ex:** What is the zone axis of (123) and (210), i.e. what line is formed when they intersect?
If \((h_1k_1l_1) = (123)\) and \((h_2k_2l_2) = (210)\), then

\[ u = 2(0)-1(3) = -3 \]
\[ v = 2(3)-1(0) = 6 \]
\[ w = 1(1)-2(2) = -3 \] \( \rightarrow [uvw] = [\bar{3}6\bar{3}] = [\bar{1}2\bar{1}] \)

**Ex:** Do these planes belong to the same zone: \((1\bar{1}0), (\bar{1}21)\) and \((312)\)? If so, what is the zone axis?

-Determining which planes belong to a given zone is important for interpreting diffraction data (see handout for HCP metals), and determining the line along which planes intersect in the study of extended defects and surfaces (e.g. Burgers vector that lies in slip plane(s)).