Precession photograph

Note symmetrical pattern. Crystal symmetry leads to diffraction pattern symmetry.

Spacing of spots is used to get unit cell dimensions.
Groups

Total 230 space groups (Table 1.9 Giacovazzo)
For proteins 65 groups (due to asymmetry of objects)
Laue group 11 space groups (reduction from 230 to 11 due to redundancy)

32 crystallographic point groups (PGs) [leave one point fixed; i.e. no translation] (Hessel 1830) – shown in Table 1.6 (Giacovazzo)
11 Laue classes (LCs) from the 32 PGs. These LCs are observable through diffraction; PGs that differ only by presence/absence of an inversion center are not differentiated by diffraction (Neumann principle).

Lattices

Consider geometry of the repetition (rather than motif – molecule or crystal) itself. This leads to a lattice (generated through translation)

7 crystal systems (discussed previously)

Including non-primitive cells one arrives at
14 Bravais lattices in 3d (5 in 2d) see Figure 1.19 (Giacovazzo)
Crystal Lattice

- A crystal has translational symmetry by definition.
  - If $\rho (r)$ is the electron density within a crystal at $r$ then there exist vectors $a$, $b$ and $c$ such that:
    $$\rho (r) = \rho (r + u \cdot a + v \cdot b + w \cdot c)$$
    where $u$, $v$ and $w$ are integers.
- Each identical copy (the repeating unit) is called a unit cell.
- $a$, $b$ and $c$ are called unit cell vectors.
- Unit cell vector lengths are $a = |a|$, $b = |b|$, $c = |c|$.
- $\alpha$, $\beta$ and $\gamma$ describe the angles between unit cell vectors.
- Use a right handed (counterclockwise) coordinate system.
Fractional coordinates.

- Any position within the crystal can be described by
  \[ r = (u + x)\cdot \mathbf{a} + (v + y)\cdot \mathbf{b} + (w + z)\cdot \mathbf{c} \]
  where \( u, v \) and \( w \) are integers and \( 0 < x, y, z < 1 \).
- \( x, y \) and \( z \) are called “fractional coordinates” and describe a position within the unit cell.
Lattice Planes

- Lattice planes are planes which pass through the lattice points.
- Labeled after the fractional position where they first cross the \( \mathbf{a}, \mathbf{b} \) and \( \mathbf{c} \) axes.
- If a lattice plane crosses the axes at the fractional coordinates \( (x, y, z) \) then the lattice plane is given the Miller indices \( (h, k, l) \) equal to \( (1/x, 1/y, 1/z) \).

Lattice plane given indices \( (1, 3) \).
Lattice plane given indices \( (2, 1) \).
Unit Cells

Dimensions designated by 6 numbers
Three unique axes \((a, b, c)\)
Three angles \((\alpha, \beta, \gamma)\)

Lowest symmetry unit cell
triclinic \((a \neq b \neq c; \alpha \neq \beta \neq \gamma)\)

Highest symmetry unit cell
cubic \((a = b = c; \alpha = \beta = \gamma = 90^\circ)\)

Planes are sources of diffractions. Most apparent planes are faces of unit cells. Crystal is \textbf{ordered} structure of “scatterers” which define a \textbf{lattice}. Planes through these lattice points are also sources of diffractions. Planes are designated by \textbf{lattice indices} (Miller indices) \((hkl)\) which identify particular set of equivalent, parallel planes:

\[
\begin{align*}
    h &\leftrightarrow x \\
    k &\leftrightarrow y \\
    l &\leftrightarrow z
\end{align*}
\]

Miller indices are assigned as follows: If the first plane encountered cuts the \(a\) edge at some fraction \(1/n_a\) the \(h\) index is \(n_a\). The \((100)\) plane corresponds to the \(yz\)-plane.
Miller indices can also be negative – designated by bars (“minus sign”) above the numerals.
Unit cells (contd.)

“Bragg Model”

Diffraction = Reflection from sets of planes which act as independent diffractor and produce a single reflection.

This model is useful to determine the geometry of data collection. “Where to look for data”

“Fourier Model”

Each atom is independent diffractor. Corresponds to one term in a Fourier expansion that describes each reflexion. “What does data say about molecular structure – where are atoms located in unit cell”
Symmetry, point-groups & space groups

- Crystallography is based upon the idea of translational, rotational and inversion (or mirror), symmetry.
**Crystal definition**

A crystal is an object with translational symmetry:

\[ \rho(r) = \rho(r) + u \cdot a + v \cdot b + w \cdot c \]
**Other crystallographic symmetry**

- In addition to translational symmetry there is frequently other symmetry within the crystal lattice:
  - Rotational symmetry.
  - Mirror plans.
  - Inversion.
  - Combinations of rotation or mirror planes plus translation.
An object or function is symmetrical if a spatial transformation of it looks identical to the original.

This is the original

This is rotated by 180°
Symmetry operators

A spatial transformation can be expressed as an operator that changes the coordinates of every point in the object the same way. Symmetry operators do not distort the object. In other words, the distance between any two points is the same before and after being moved by the symmetry operation.

Here is the operator for a 180° rotation around Z.

\[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
=
\begin{pmatrix}
-x \\
y \\
z
\end{pmatrix}
\]

equivalent positions
3x3 Matrix multiplication

\[
\begin{pmatrix}
a & b & c \\
d & e & f \\
g & h & i \\
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z \\
\end{pmatrix}
= 
\begin{pmatrix}
ax + by + cz \\
dx + ey + fz \\
gx + hy + iz \\
\end{pmatrix}
\]
Types of symmetry operations

- Point of inversion
- Mirror plane
- Glide plane
- Rotation (2, 3, 4 or 6-fold)
- Screw axis
- Lattice symmetry
Fractional coordinates

The crystallographic coordinate system is defined by the unit cell. The location of a point is defined by fraction of traveled (from 0 to 1) along each unit cell axis.

Fractional coordinates are always measured parallel to each axis. The axes are not necessarily 90° apart!
**Point of Inversion**

\[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1 \\
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z \\
\end{pmatrix} =
\begin{pmatrix}
-x \\
-y \\
-z \\
\end{pmatrix}
\]
mirror plane
\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
=
\begin{pmatrix}
x \\
y \\
-z
\end{pmatrix}
\]
$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} 1/2 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} x + 1/2 \\ y \\ -z \end{pmatrix}$
rotation
\[
\begin{pmatrix}
\cos \theta & -\sin \theta & 0 \\
\sin \theta & \cos \theta & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
=
\begin{pmatrix}
x' \\
y' \\
z
\end{pmatrix}
\]

Object

non-centric symmetry
**Screw Rotation**

\[
\begin{pmatrix}
\cos \theta & -\sin \theta & 0 \\
\sin \theta & \cos \theta & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
+
\begin{pmatrix}
0 \\
0 \\
1/3
\end{pmatrix}
=
\begin{pmatrix}
x' \\
y' \\
z + 1/3
\end{pmatrix}
\]
Why proteins cannot have centric symmetry

Mirror images and points of inversion cannot be re-created by pure rotations.

Centric operations would change the chirality of chiral centers such as the alpha-carbon of amino acids or the ribosomal carbons of RNA or DNA.
Rotational symmetry

A 2-fold (180°) rotation around the Z-axis

\[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix} =
\begin{pmatrix}
-x \\
-y \\
z
\end{pmatrix}
\]
rotation
Rotation matrices

...the mathematical description of a rotation.

In polar coordinates, a rotation is the addition of angles.

atom starts here...

..rotates by $\beta$..

...goes here

axis of rotation

In polar coordinates, a rotation is the addition of angles.
REMINDER: sum of angles rules

\[
\cos (\alpha+\beta) = \cos \alpha \cos \beta - \sin \alpha \sin \beta
\]

\[
\sin (\alpha+\beta) = \sin \alpha \cos \beta + \sin \beta \cos \alpha
\]
Adding angles in Cartesian space
converting internal motion to Cartesian motion

\[ x = |r| \cos \alpha \]
\[ y = |r| \sin \alpha \]

\[ x' = |r| \cos (\alpha + \beta) \]
\[ = |r| (\cos \alpha \cos \beta - \sin \alpha \sin \beta) \]
\[ = (|r| \cos \alpha) \cos \beta - (|r| \sin \alpha) \sin \beta \]
\[ = x \cos \beta - y \sin \beta \]

\[ y' = |r| \sin (\alpha + \beta) \]
\[ = |r| (\sin \alpha \cos \beta + \sin \beta \cos \alpha) \]
\[ = (|r| \sin \alpha) \cos \beta + (|r| \cos \alpha) \sin \beta \]
\[ = y \cos \beta + x \sin \beta \]

in matrix notation...

\[
\begin{pmatrix}
x' \\
y'
\end{pmatrix}
= \begin{pmatrix}
\cos \beta & -\sin \beta \\
\sin \beta & \cos \beta
\end{pmatrix}
\begin{pmatrix}
x \\
y
\end{pmatrix}
\]

rotation matrix
2D rotation using matrix notation

\[
\begin{pmatrix}
    x' \\
    y'
\end{pmatrix}
= \begin{pmatrix}
    \cos \beta & -\sin \beta \\
    \sin \beta & \cos \beta
\end{pmatrix}
\begin{pmatrix}
    x \\
    y
\end{pmatrix}
\]

“row times column”

\[
x' = x \cos \beta - y \sin \beta =
= \left| x \right| \cos \alpha \cos \beta - \left| x \right| \sin \alpha \sin \beta
= \left| x \right| \cos (\alpha + \beta)
\]

\[
y' = y \cos \beta + x \sin \beta
= \left| x \right| \sin \alpha \cos \beta + \left| x \right| \cos \alpha \sin \beta
= \left| x \right| \sin (\alpha + \beta)
\]
Transposing the matrix reverses the rotation

To rotate the opposite direction, flip the matrix about the diagonal.

the “transpose”

\[
\begin{pmatrix} A & B \\ C & D \end{pmatrix}^T = \begin{pmatrix} A & C \\ B & D \end{pmatrix}
\]

\[
\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos \beta & \sin \beta \\ -\sin \beta & \cos \beta \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}
\]

inverse rotation matrix = transposed rotation matrix.

\[
\begin{pmatrix} \cos \beta & \sin \beta \\ -\sin \beta & \cos \beta \end{pmatrix} \begin{pmatrix} \cos \beta & -\sin \beta \\ \sin \beta & \cos \beta \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\]

...because \( \cos \beta \cos \beta + \sin \beta \sin \beta = 1 \)
A 3D rotation matrix

Is the product of 2D rotation matrices.

\[
\begin{pmatrix}
\cos \beta & -\sin \beta & 0 \\
\sin \beta & \cos \beta & 0 \\
0 & 0 & 1 \\
\end{pmatrix}
\begin{pmatrix}
\cos \gamma & 0 & -\sin \gamma \\
0 & 1 & 0 \\
\sin \gamma & 0 & \cos \gamma \\
\end{pmatrix}
= 
\begin{pmatrix}
\cos \beta \cos \gamma & -\sin \beta & \cos \beta \\
\sin \beta \cos \gamma & \cos \beta & -\sin \beta \sin \gamma \\
\sin \gamma & 0 & \cos \gamma \\
\end{pmatrix}
\]

Rotation around z-axis

Rotation around y-axis

3D rotation
Example:

Rotate \( v=(1.,2.,3.) \) around \( Z \) by 60°, then rotate around \( Y \) by -60°.

\[
\begin{bmatrix}
\cos 60° & -\sin 60° & 0 \\
\sin 60° & \cos 60° & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
1 \\
2 \\
3
\end{bmatrix}
= \begin{bmatrix}
1(0.5) - 2(0.866) + 3(0) \\
1(0.866) + 2(0.5) + 3(0) \\
0 + 0 + 3(1)
\end{bmatrix}
= \begin{bmatrix}
-1.232 \\
1.866 \\
3
\end{bmatrix}
\]

\[
\begin{bmatrix}
\cos 60° & 0 & -\sin 60° \\
0 & 1 & 0 \\
\sin 60° & 0 & \cos 60°
\end{bmatrix}
\begin{bmatrix}
-1.232 \\
1.866 \\
3
\end{bmatrix}
= \begin{bmatrix}
-1.232(0.5) + 1.866(0) - 3(0.866) \\
-1.232(0) + 1.866(1) + 3(0) \\
-1.232(0.866) + 1.866(0) + 3(0.5)
\end{bmatrix}
= \begin{bmatrix}
-3.214 \\
1.866 \\
0.433
\end{bmatrix}
\]
90° rotation around X

\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 0 & -1 \\
0 & 1 & 0
\end{pmatrix}
\]

Helpful hint:
For a R-handed rotation, the minus sine is the one on the “Right.”
### Euler angles, $\alpha \beta \gamma$

**Axis of rotation:**

<table>
<thead>
<tr>
<th>$z''$</th>
<th>$x'$</th>
<th>$z$</th>
</tr>
</thead>
</table>
| \[
\begin{pmatrix}
\cos \gamma & -\sin \gamma & 0 \\
\sin \gamma & \cos \gamma & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
1 & 0 & 0 \\
0 & \cos \beta & \sin \beta \\
0 & \sin \beta & \cos \beta
\end{pmatrix}
\begin{pmatrix}
\cos \alpha & -\sin \alpha & 0 \\
\sin \alpha & \cos \alpha & 0
\end{pmatrix}
\] |

**Order of rotations:**

3 2 1

---

### Polar angles, $\phi \psi \kappa$

**Axis of rotation:**

<table>
<thead>
<tr>
<th>$z'''$</th>
<th>$y'''$</th>
<th>$z''$</th>
<th>$-y'$</th>
<th>$-z$</th>
</tr>
</thead>
</table>
| \[
\begin{pmatrix}
\cos \phi & -\sin \phi & 0 \\
\sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\cos \varphi & 0 & -\sin \varphi \\
0 & 1 & 0 \\
\sin \varphi & 0 & \cos \varphi
\end{pmatrix}
\begin{pmatrix}
\cos \kappa & -\sin \kappa & 0 \\
\sin \kappa & \cos \kappa & 0
\end{pmatrix}
\begin{pmatrix}
\cos \varphi & 0 & \sin \varphi \\
0 & 1 & 0 \\
\sin \varphi & 0 & \cos \varphi
\end{pmatrix}
\begin{pmatrix}
\cos \phi & \sin \phi & 0 \\
-sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{pmatrix}
\] |

**Order of rotations:**

5 4 3 2 1

**Net rotation** $= \kappa$
Properties of rotation matrices

• Square, 2x2 or 3x3
• The product of any two rotation matrices is a rotation matrix
• The inverse equals the transpose, $R^{-1} = R^T$

orthogonality

• The dot-product of any row or column with itself is one.
• The dot-product of any row or column with a different row or column is zero.
• $|x|$ equals $|Rx|$, for any rotation $R$. 

180° rotation. Called a 2-fold because doing it twice brings you back to where you started.

Equivalent positions in fractional coordinates:

\( x, y, z \quad -x, -y, z \)
3-fold rotation

In fractional coordinates:

\[
\begin{pmatrix}
0 & -1 & 0 \\
1 & -1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
= 
\begin{pmatrix}
-x - y \\
x - y \\
z
\end{pmatrix}
\]

Equivalent positions:

\(x,y,z\), \(-y,x-y,z\), \(-x+y,-x,z\)
4-fold rotation

\[
\begin{pmatrix}
\cos90^\circ & -\sin90^\circ & 0 \\
-\sin90^\circ & \cos90^\circ & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
=
\begin{pmatrix}
x \cos90^\circ - y \sin90^\circ \\
x \sin90^\circ + y \cos90^\circ \\
z
\end{pmatrix}
\]

In fractional coordinates (same as orthogonal coords):

\[
\begin{pmatrix}
0 & -1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
=
\begin{pmatrix}
-y \\
x \\
z
\end{pmatrix}
\]

Equivalent positions:

- \(x, y, z\) \quad -x, -y, z
- -y, x, z \quad y, -x, z

P4
6-fold rotation

\[
\begin{pmatrix}
\cos 60^\circ & -\sin 60^\circ & 0 \\
-\sin 60^\circ & \cos 60^\circ & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix} =
\begin{pmatrix}
x \cos 60^\circ - y \sin 60^\circ \\
x \sin 60^\circ + y \cos 60^\circ \\
z
\end{pmatrix}
\]

In fractional coordinates:

\[
\begin{pmatrix}
-1 & 1 & 0 \\
-1 & 0 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix} =
\begin{pmatrix}
-x + y \\
-x \\
z
\end{pmatrix}
\]

Equivalent positions:

\[
\begin{aligned}
x,y,z & \quad -y,x-y,z & \quad -x+y,-x,z \\
-x,-y,z & \quad y,-x+y,z & \quad x-y,x,z
\end{aligned}
\]
In class exercise: rotating a point

(a) Choose a point \( r = (0.1, 0.2, 0.3) \) [orthogonal coordinates]

Rotate the point by 30° in x.
Then rotate it by -90° in y.
What are the new coordinates?

(b) Choose a point \( r = (0.1, 0.2, 0.3) \) [fractional coordinates]

Multiply by the symmetry operator:

\[
\begin{pmatrix}
0 & -1 & 0 \\
1 & -1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

What are the new fractional coordinates?
No 5-fold symmetry in crystals??

A crystal lattice must be space-filling and periodic.

This “Penrose tile pattern” is spacefilling but not periodic.
Which rotations are consistent with a lattice?

• Suppose $\phi = \frac{360^\circ}{n}$ then (from figure)

$$2a \cos \phi = ka$$

since it must be possible to get from one point to the next by the lattice translation symmetry.

• Only possible solutions are $k = -2, -1, 0, 1$ or $2$ only.
<table>
<thead>
<tr>
<th>k</th>
<th>cos φ</th>
<th>φ</th>
<th>symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2</td>
<td>-1</td>
<td>180</td>
<td>2</td>
</tr>
<tr>
<td>-1</td>
<td>-1/2</td>
<td>120</td>
<td>3</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>90</td>
<td>4</td>
</tr>
<tr>
<td>1</td>
<td>1/2</td>
<td>60</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

- Only 1, 2, 3, 4 and 6 rotations consistent with translational symmetry.
- Eg. 5 is never seen as crystal rotational symmetry.
Non-crystallographic symmetry.

- In addition to the crystallographic symmetry, molecules may repeat with non-crystallographic symmetry.
- eg. A virus capsid has 5-fold symmetry, which is not a crystallographic symmetry.
- Two molecules may pack against each other in a slightly skewed manner and fail to give a perfect crystallographic symmetry.
Quasicrystals: 5-fold **point group** symmetry, but no **space group** symmetry
The poliovirus crystal structure has 5-fold, 3-fold, and 2-fold point-group symmetry.
Screw symmetry

Equivalent positions are related by rotation AND translation

Example: 6-fold in the projection. Screw moves up and to the right 4/6 units.

Equivalent positions are related by rotation AND translation
A screw rotation is a rotation of $2\pi/n$ plus a translation along the axis of rotation by $1/n$ (right-handed screw) or $-1/n$ (left-handed screw).
translational symmetry

The crystal lattice is an example of translational symmetry. Equivalent positions are \((x,y,z)\) and \((x+1,y+1,z+1)\), in fractional coordinates.

Space groups that have no other translational symmetry operations are called “primitive”. Space group letter “P”

Space groups have letters indicating the type of translational symmetry:

- C (centered)
- F (face-centered)
- I (body-centered)
Centered lattices

Centered: “C”

Translational symmetry operator \((1/2,1/2,0)\)

This is “face-centered” but only on one face.
Centered lattices

Face-centered: “F”

Translational symmetry operators:
\((1/2,1/2,0),(0,1/2,1/2),(1/2,0,1/2)\)
Centered lattices

Body-centered: “I”

Translational symmetry operator:
(1/2,1/2,1/2)
A symmetry “group” is a set of symmetry operators that is closed, meaning any two operations, applied in succession, create a third operation that is part of the group. A “space group” is a symmetry group that includes lattice symmetry operators.

All space groups implicitly include lattice operators:

$$(\pm 1, \pm 1, \pm 1)$$
The International Tables for Crystallography

$P \ 2_1$

No. 4

$C_2$

$P \ 1 \ 1 \ 2_1$

$2$

Mono

Patterson symmetry

UNIQUE AXIS $c$

Equivalent positions: $(x, y, z), (-x, -y, z+1/2)$
Space groups

- Cell type P, C, I or F
- I = body centered

**I4_122**

- Principle axis of symmetry is 4-fold screw
- Secondary axes of symmetry are proper 2-folds
**Primitive crystal systems**

- 2, 3, 4 and 6 fold rotational symmetry possible.
- At least two axes must be equal for 3, 4 or 6 fold rotational symmetry.
  - These ideas underly the division into seven primitive unit-cells.

**Triclinic:**
contains no extra symmetry.
\[ a \neq b \neq c \text{ } \& \text{ } \alpha \neq \beta \neq \gamma \neq 90^\circ \]

**Monoclinic:**
contains one 2-fold rotation.
\[ a \neq b \neq c \text{ } \& \text{ } \text{two of } \alpha \text{ or } \beta \text{ or } \gamma = 90^\circ \]
**Orthorhombic:**

\[ a \neq b \neq c \& \alpha = \beta = \gamma = 90^\circ \]

Has three 2-fold axes.

**Tetragonal:**

\[ a = b \neq c \& \alpha = \beta = \gamma = 90^\circ \]

Has a 4-fold axes.

**Cubic:**

\[ a = b = c \& \alpha = \beta = \gamma = 90^\circ \]

Has three 4-fold axes.
**Trigonal:**

**Rhombohedral axes:**
\[ a = b = c \text{ and } \alpha = \beta = \gamma \neq 90^\circ \]
Has a 3-fold axis.

**Hexagonal:**
\[ a = b \neq c \text{ and } \alpha = \beta = 90^\circ, \gamma = 120^\circ \]
6-fold axis.

**Trigonal:**

**Hexagonal axes:**
\[ a = b \neq c \text{ and } \alpha = \beta = 90^\circ \text{ and } \gamma = 120^\circ \]
but has only 3-fold axis.
Non-primitive unit cell.

- Four classes:
  - Primitive unit cell (P).
  - Plane centred unit cell (A, B or C).
  - Body centred unit cell (I).
  - Face centred unit cell (F).
- In combination with previous 7 primitive cells leads to 14 Bravais lattices.
**Notation.**

- Space groups are first labelled according to lattice ie. P, A (B or C), F or I.
- Next labelled relative to the highest symmetry axes.
  - P6 means a primitive lattice with one 6-fold axis.
  - P222 means a primitive lattice with three two-fold axes.
  - F means a face-centred lattice with no additional symmetry.
- A subscript then is used to denote screw axes.
  - P6₃ means a six-fold screw axis.
  - P2₁₂₁₂₁ means three two-fold screw axes.
A space group is a **closed set of operators**.

If you apply any two operators in succession, the result is another one of the operators in the group.

Equivs for P2$_1$:
(x, y, z),
(-x, -y, z+1/2)
**Cubic space group P2₁3**

\[ T^4 \]

- **x, y, z**
- \(-x + 1/2, -y, z + 1/2\)
- \(-x, y + 1/2, z + 1/2\)
- \(x + 1/2, -y + 1/2, -z\)
- \(z, x, y\)
- \(z + 1/2, -x + 1/2, -y\)
- \(-z + 1/2, -x, y + 1/2\)
- \(-z, x + 1/2, -y + 1/2\)
- \(y, z, x\)
- \(-y, z + 1/2, -x + 1/2\)
- \(y + 1/2, -z + 1/2, -x\)
- \(-y + 1/2, -z, x + 1/2\)
In class exercise: Use the Escher web sketch applet to find the equivalent positions for \(cm\), \(p4mm\), and \(p6\).

Draw a dot at fractional coordinates (0.1, 0.2, 0.3)
What are the fractional coordinates of the equivalent positions?
Write the 2D symmetry operators (matrix and vector)
Point group symbols, etc.

- Inversion
- Reflection
- Rotatory inversion
- Axial glide
- Diagonal glide
Finding symmetry in an image
Plane groups

space group p1
**Summary**

• To fully describe a crystal packing:
  - Length of unit cell axes, a, b and c.
  - Unit cell angles, $\alpha$, $\beta$, $\delta$, $\gamma$.
  - Crystal packing: Primitive, plane centred, body centred or face centred?
  - Additional symmetry: rotation, screw axes, mirror, inversion and glide symmetries.
  - Must identify the asymmetric unit.
  - Must identify any non-crystallographic symmetry.

• There are 14 possible crystal lattices.
• 230 possible space groups.
• Macromolecules can occupy only 65 space groups due to their chirality.
Unit cell symmetry

Internal symmetry of the unit cell is fundamental. Symmetry of unit cell is determined by space group and a particular symbol \((P2_12_12_1)\)

Letter determines lattice type:
- \(P\) primitive (one lattice point at each corner/vertex of the cell)
- \(I\) internal (body centered)
- \(F\) face centered

Because each lattice point is shared between eight neighboring unit cells, a \(P\) lattice contains 8 times 1/8 (=1) lattice point per unit cell. The \(I\) lattice contains an additional point per cell, i.e. 2 lattice points per unit cell.

Numerals determine symmetry operations.

There are usually more than one way to choose the unit cell. Conventions: unit cell is the one that is most symmetrical. \(I\) and \(F\) are chosen if they have higher symmetry than any of the \(P\) cells.

Symmetry operations:
Proteins are inherently asymmetric (consist of chiral amino acids).
If only one protein molecule occupies a unit cell then cell itself is chiral – thus no further symmetry elements (rare).
Usually, molecules aggregate (oligomers
Unit cell symmetry (contd)

Proteins are inherently asymmetric (consist of chiral amino acids). If only one protein molecule occupies a unit cell then cell itself is chiral – thus no further symmetry elements (rare).

Usually, molecules aggregate (oligomers) or unit cell contains several identical molecules.

Asymmetric unit: largest aggregate of molecules that possesses no symmetry elements.

**Symmetry elements:**
Translation, rotation, reflection, inversion center, screw axis, glide plane

Proteins are asymmetric: mirror planes and elements containing them are absent. Only translation, rotation and screw axis (rotation plus translation). Other compounds: all elements can occur.

Screw axis: symbol $n_m$ represents an $n$-fold screw axis with a translation of $m/n$ of the unit translation.

Symmetry elements are related to certain reflections to be missing (no intensity). Actually: the unit cell space group is determined by absences in the diffraction pattern.
The reciprocal lattice

“Reciprocal space” = “space occupied by Bragg reflections”
To every real lattice there exists a reciprocal lattice.

Origin of lattice (O) is the same for the real and the reciprocal space.

Geometrical construction:
• Start from neighboring lattice point N.
• Draw a crystallographic plane (e.g. (110)) through N.
• Draw a line orthogonal to (110) through O with length $1/d_{110}$ where $d_{110}$ is the lattice spacing of the (110) plane.
• This produces the reciprocal grid point.

Remember: The higher the indices (hkl) the smaller the spacing in the real lattice and the further away the point in the reciprocal space (hence the name).

For a small real unit cell plane spacings are small and lines from origin to the reciprocal lattice points are long. Therefore reciprocal unit cell is large.
Unique reflections

Depending on the lattice type, different numbers of unique reflections (“real data”) can be measured.

Lowest symmetry (P2): 1/4 of all reflections are unique
Highest Symmetry (P432): 1/48 of all reflections are unique

In practice: measure several times the minimum number of reflections.
Reason: Redundancy is used to improve signal/noise ratio.
Packing of protein crystals.

- The asymmetric unit may contain:
  - One molecule.
  - Several molecules with different conformations.
  - Identical domains of one molecule.
- Amino acids are chiral.
  - Inversion & mirror symmetry operations are not allowed.
  - Only 65 of the possible 230 space groups are available.
- Protein crystals are loosely packed.
  - Approximately 50 % to 80 % of a protein crystal is solvent.
  - Crystal conformations well approximate physiological conformations.