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1  Frieze patterns and frieze groups

Friezes are two dimensional patterns that are repetitive in one dimension. They have been employed by essentially all human cultures to create ornamentations on buildings, textiles, metalwork, ceramics, etc. (see examples below). Depending on the nature of the object, these decorative motifs can be linear, circular (as on the neck of a vase) or follow the contour of a polygon. Here, we will imagine that the pattern is unwrapped to a linear strip and is infinite. In addition, we will only consider monochrome patterns Although the design can comprise a variety of naturalistic or geometrical elements, as far as the symmetry is concerned frieze patterns follow a very simple classification. There are only five types of symmetries, three of them already known to us:

1. **Rotations** through an axis perpendicular to the viewing plane. Only the 2-fold rotation, as for the symmetry of the letter “S”, is allowed.

2. **Reflections** through lines in the plane of the pattern, **perpendicular to the translations**, as for the symmetry of the letter “V”. Again, we will liberally use the term “mirror plane” instead of the more rigorous ”mirror line”, to be consistent later on with the space group definitions.

3. **Reflections** through a line in the plane of the pattern, **parallel to the translations**, as for the symmetry of the letter “K”.

4. **Translations**. This is a new symmetry that we did not encounter for point groups, since, by definition they had a fixed point, whereas translations leave no point fixed. In all frieze patterns, there exists a fundamental (“primitive”) translation that defines the repeated pattern. Its opposite (say, left instead of right) is also a symmetry element, as are all multiples thereof, clearly an infinite number of symmetry translations (see box here below).

5. **Glides**. This is a composite symmetry, which combines a translation with a **parallel reflection**, neither of which on its own is a symmetry. The primitive translation is always *twice* the glide translation, for a reason that should be immediately clear (see Problem 2.1 below). This symmetry is represented by the repeated fragment ⌈⌋, as in ...⌈⌋⌈⌋⌈⌊....

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**All symmetry translations can be generated as linear combinations of “primitive” translation. This is a general result valid in all dimensions**

These elements can be combined in 7 different ways, the so-called ”7 frieze patterns” (and corresponding groups). In addition to pure translations or translations combined with one of the other four types, we have two additional frieze Groups, both containing translations and perpendicular reflections, combined either with a parallel reflection or with a glide. In both cases, rotations are always present as well. The 7 frieze groups are illustrated in Fig. 1 to 4.
2 Symbols for frieze groups

The new symmetry elements in Fig. 1 to 4 are shown in a symbolic manner, as in the case of point groups. The symbols for the new symmetry elements are:
Figure 3: Frieze groups $p_{11g}$ and $p_{2mm}$

Figure 4: Frieze group $p_{2mg}$

- **Translations** are shown both with arrows ($\rightarrow$) and by means of a repeated unit. The choice of the latter, however, is arbitrary, in that we could have chosen a shifted repeated unit or even one with a different shape.

- **Glides** are represented by a dashed bold line, always parallel to the periodic direction.

### 2.1 A few new concepts from frieze groups

Here, we introduce a few more formal definitions related to the frieze groups; in some case, they extend analogous concepts already introduced for the point groups.
Figure 5: A detail of the Megalopsychia mosaic (Fifth century AD, Yakto village near Daphne, Turkey). The symmetry is \( p211 \). From [1].

Figure 6: A detail from the border of the Megalopsychia mosaic (Fifth century AD, Yakto village near Daphne, Turkey). The symmetry is \( p11m \). From [1].

- **Repeat unit or unit cell.** A minimal (but never unique, i.e., always conventional) part of the pattern that generates the whole pattern by application of the pure translations.

- **Asymmetric unit.** A minimal (but never unique) part of the pattern that generates the whole pattern by application of all the operators. It can be shown that there is always a simply
Figure 7: A mosaic from the “Tomb of Amerimnia” (Calmness), fourth century Antioch, Turkey, showing different types of frieze symmetry. From the center outwards: \( p2mm \), \( p1m1 \), \( p2mg \), \( p1m1 \). From [1].

connected choice of asymmetric unit.

- **Multiplicity.** It is the number of equivalent points in the unit cell.

- **Points of special symmetry.** These are points that are invariant by application of one or more operator, and have therefore reduced multiplicity with respect to “general positions”. This is analogous to the case of the point groups. They are essentially the graphs of generalized rotations and their intersections. the generalized rotation operators intersecting in each given point define a point group, known as the local symmetry group for that point.

2.2 Frieze groups in the ITC

The 7 frieze groups are listed in ITC-Volume E ([2]) on pages 30–36. An explanation of all the entries is provided in Appendix III. One item in the IT entries deserves special attention — the crystal class, which we have not introduced before.

**Definition of crystal class**

The crystal class is a point group obtained by combining all the rotational parts of the operators in the frieze group. The same definition is valid for wallpaper and space groups.
Figure 8: Part of a splendid “carpet” mosaic, found in an upper level of the ”House of the Bird Rinceau” in Daphne and dating from 526–40 AD. The mosaic was divided among sponsoring institutions after excavation; this is known as the Worcester fragment. The symmetry of the bottom frieze is $p11g$. The top frieze has symmetry $p1$, but note that introducing color would increase the symmetry of the fragment, since the pattern is symmetric by two-fold rotation combined with black-white interchange. Color symmetry is used in crystallography to describe magnetic structures. From [1].

3 Wallpaper groups

3.1 A few new concepts for Wallpaper Groups

- **Translations.** This is a new symmetry that we did not encounter for point groups, since, by definition they had a fixed point, whereas translations leave no point fixed. In all 2D (Wallpaper) and 3D (Space) group, there exist fundamental (“primitive”) translations that defines the repeated pattern.

- **Repeat unit or unit cell.** A minimal (but never unique, i.e., always conventional) part of the pattern that generates the whole pattern by application of the pure translations.

- **Asymmetric unit.** A minimal (but never unique) part of the pattern that generates the whole pattern by application of all the operators. It can be shown that there is always a simply connected choice of asymmetric unit.

- **Multiplicity.** It is the number of equivalent points in the unit cell.

- **Points of special symmetry.** These are points that are invariant by application of one or more operator, and have therefore reduced multiplicity with respect to “general positions”. This is analogous to the case of the point groups. They are essentially the graphs of generalized rotations and their intersections. the generalized rotation operators intersecting in each given point define a point group, known as the local symmetry group for that point.

- **Crystal class** This is is a point group obtained by combining all the rotational parts of the operators in the group. The same definition is valid for wallpaper and space groups.
• **Glides.** This is a composite symmetry, which combines a translation with a *parallel* reflection, neither of which on its own is a symmetry. In 2D groups, the glide is indicated with the symbol \( g \). *Twice* a glide translation is *always* a symmetry translation: in fact, if one applies the glide operator twice as in \( g \circ g \), one obtains a pure translation (since the two mirrors cancel out), which therefore must be a symmetry translation.

### 3.2 Lattices and the “translation set”

The symmetry of the translation set must be “compatible” with that of the other operators of the group. In other words, if one applies a rotation to one of the primitive translation vectors (remember that this means transforming the translation by *graph symmetry*, one must find another primitive translation. This is best seen by introducing the concept of *lattices*.

Lattices are an alternative representation of the translation set. They are sets of points generated from a single point (*origin*) by applying all the translation operators.

![Portions of the square and hexagonal lattices, with their respective point symmetry groups.](image)

**Figure 9:** Portions of the square and hexagonal lattices, with their respective point symmetry groups. Note that the symmetry or the lattice is *higher* than that of the minimal point group needed to construct them from a single translation (4 and 3, respectively)

The symmetry of the lattice (known as the *holohedry*) must be at least as high as the *crystal class*, supplemented by the inversion (180° rotation in 2 dimensions). This result is also valid in 3 dimensions.

### 3.3 Bravais lattices in 2D

Bravais lattices, named after the French physicist Auguste Bravais (1811–1863), define all the translation sets that are mutually compatible with crystallographic point groups. There are 5 of them: "Oblique", "\( p \)-Rectangular", "\( c \)-Rectangular", "Square" and "Hexagonal". They can all be generated constructively in simple ways.
3.3.1 Oblique system

Here, each translation is symmetry-related to its opposite only, so there is no restriction on the length or orientation of the translations. The resulting lattice is a tiling of parallelograms.

3.3.2 Rectangular system

Here we have two cases (Fig. 10):

- A simple tiling of rectangles, known as a "p-Rectangular" (primitive rectangular) lattice.
- A rectangular lattice with nodes at the centers of the rectangles, known as a "c-Rectangular" (centered rectangular) lattice.

![Diagram of p and c rectangular lattices](image)

Figure 10: The two types of rectangular lattices ("p" and "c") and their construction.

3.3.3 Square system

There are two point groups in this system: \(4\) and \(4mm\). They both generate simple square lattices. In the latter case, as we have already shown, the nodes must lie on the mirror planes (Fig. 9).
3.3.4 Hexagonal system

There are four point groups in this system: \(3, 3m1\) (or \(31m\)), \(6\) and \(6mm\). They all generate simple hexagonal lattices. In the case of \(6mm\), the nodes must lie on the mirror planes (Fig. 9), whereas in the case of \(31m\) they must lie either on the mirror planes (setting \(31m\)) or exactly in between (setting \(3m1\)). Note that here the distinction is real, and will give rise to two different wallpaper groups.

3.4 Primitive, asymmetric and conventional Unit cells in 2D

![Possible choices for the primitive unit cell on a square lattice.](image)

**Figure 11**: Possible choices for the primitive unit cell on a square lattice.

**Primitive unit cells** Minimal units that can generate the whole pattern by translation.

**Asymmetric unit cells** Minimal units that can generate the whole pattern by application of all symmetry operators.

**Conventional unit cells** In the case of the \(c\)-rectangular lattice, the primitive unit cell is either a rhombus or a parallelogram and does not possess the full symmetry of the lattice. It is therefore customary to introduce a so-called *conventional centered* rectangular unit cell, which has double the area of the primitive unit cell (i.e., it always contains two lattice points), but has the full symmetry of the lattice and is defined by orthogonal translation vectors, known as *conventional translations* (Fig. 12).
Figure 12: Two primitive cells and the conventional unit cell on a $c$-centered rectangular lattice.

Table 1: The 17 wallpaper groups. The symbols are obtained by combining the 5 Bravais lattices with the 10 2D point groups, and replacing $g$ with $m$ systematically. Strikeout symbols are duplicate of other symbols.

<table>
<thead>
<tr>
<th>crystal system</th>
<th>crystal class</th>
<th>wallpaper groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>oblique</td>
<td>1</td>
<td>$p1$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>$p2$</td>
</tr>
<tr>
<td>rectangular</td>
<td>$m$</td>
<td>$pm, cm, pg, m$</td>
</tr>
<tr>
<td></td>
<td>$2mm$</td>
<td>$p2mm, p2mg (=p2gm), p2gg, c2mm, c2mg, c2gg$</td>
</tr>
<tr>
<td>square</td>
<td>4</td>
<td>$p4$</td>
</tr>
<tr>
<td></td>
<td>$4mm$</td>
<td>$p4mm, p4gm, p4mg$</td>
</tr>
<tr>
<td>hexagonal</td>
<td>$3$</td>
<td>$p3$</td>
</tr>
<tr>
<td></td>
<td>$3m1-31m$</td>
<td>$p3m1, p31m, p31g$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>$p6$</td>
</tr>
<tr>
<td></td>
<td>$6mm$</td>
<td>$p6mm, p6mg, p6mm, p6gg$</td>
</tr>
</tbody>
</table>

3.5 The 17 wallpaper groups

3.6 Analyzing wallpaper and other 2D art using wallpaper groups

The symmetry of a given 2D pattern can be readily analyzed and assigned to one of the wallpaper groups, using one of several schemes. One should be careful in relying too much on the lattice symmetry, since it can be often higher than the underlying pattern (especially for true wallpapers). Mirrors and axes are quite easily identified, although, once again, one should be careful with pseudo-symmetries. Fig. 14 shows a decision-making diagram that can assist in the identification of the wallpaper group. Here, no reliance is made on the lattice, although sometimes centering is easier to identify than glides.
4 Fourier transform of lattice functions

In this section, we will consider a generic real or complex function $f(r)$ defined over the real space, $r$ being a position vector from an appropriately defined origin. We assume that $f(r)$ has the symmetry properties defined by one of the 230 space groups. We will calculate the Fourier transform of this function, $F(q)$, over the whole space. As we shall see in the next lectures, $F(q)$ corresponds to the diffraction structure factor. We have:

$$F(q) = \frac{1}{(2\pi)^{3/2}} \int d^3r f(r) e^{-i\mathbf{q}\cdot\mathbf{r}} \quad (1)$$

where the integral extends to the whole space. We now exploit the lattice periodicity of the function $f(r)$, which we can express by writing $r = r_0 + x$ and

$$f(r_0 + x) = f(x) \quad (2)$$

The $r_0$ are the symmetry translation vectors, and $x$ is a position vector within the first unit cell, i.e., $x, y, z < 1$. We can also decompose the integral in Eq. 1 in integrals over the unit cells:

$$F(q) = \frac{1}{(2\pi)^{3/2}} \sum_{r_0} \int_{\text{u.c.}} d^3x f(x) e^{-i\mathbf{q}\cdot(r_0 + x)} \quad (3)$$

where the integral is now over a single unit cell. We now introduce a set of coordinates that are appropriate for the symmetry\(^1\) and recall that in these coordinates the symmetry translation vectors are expressed as $[n^i]$, i.e., a set of three integers. By using the relation $dx = dx dy dz (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c} = v_0 dx dy dz$, $v_0$ being the volume of the unit cell, eq. 3 becomes:

$$F(q) = \frac{v_0}{(2\pi)^{3/2}} \sum_{n^i} e^{-2\pi i \sum_i q_i n^i} \int_{\text{u.c.}} d^3x f(x) e^{-2\pi i \sum_i q_i x^i} \quad (4)$$

The sum is now over all the symmetry translations, i.e., over all the positive and negative values of the $[n^i]$. The $[n^i]$ are integers or simple fractions (for centering translations). We will perform the infinite summation by summing over a finite number $N$ real-lattice vectors first, and then letting $N \to \infty$. The following statements is now clear by inspecting Eq. 4:

\(^1\)In this section, it should become absolutely clear why we do not use Cartesian coordinates.
In fact, if $\mathbf{q}$ belongs to the *primitive* reciprocal lattice, then by definition its dot product to the symmetry lattice translation is a multiple of $2\pi$, the exponential factor is 1 and the *finite* summation yields $N$ (i.e., the number of unit cells). Conversely, if $\mathbf{q}$ does not belong to the *primitive* reciprocal lattice, the exponential factor will vary over the unit circle in complex number space and will always average to zero. In particular, $F(q)$ is zero for the conventional $RLV$ that are **extinct by centering** (as we anticipated — this explains the terminology "extinction" we just introduced). For non-extinct $RL$ vectors, the infinite summation yields $\infty$. In lecture 5, we shall see that that $F(q)$ is actually a series of $\delta$ **functions**, centered at the $RL$ nodes.

### 4.1 Supplementary extinction conditions due to roto-translations

> When the symmetry of the crystal contains roto-translation operators, *supplementary extinction conditions are present*. Unlike centering extinctions, roto-translation extinctions only apply to certain $hkl$’s within *planes* (glides) or *lines* (screws) in reciprocal space.

Roto-translation extinctions are listed in the International Tables vol A [4] for each space group, and are discussed in [3].

### 5 Point groups in 3D

Having discussed in great detail the 2D point groups, we now move to analyze the 3D point groups, which represent the rotations of a 3D object around a fixed point that are mutually compatible with a system of 3D translations. **There are 32 point groups of this kind in 3D.** As we shall see, we can easily obtain 27 of them by “extruding” (so to speak), the 10 2D point groups. The remaining 3D point groups cannot be obtained in this way, and correspond to the 5 **cubic groups**. We will not insist on notation issues in this lecture, but some guiding notes are provided in Appendix I.
5.1 The new generalized (proper & improper) rotations in 3D

The inversion. We indicate it with the symbol $I$, and represent it graphically by a small circle ($\circ$), which can be combined with other symbols, if required (see for instance the roto-inversion $\bar{3}$ below).

The roto-inversions obtained by composition of an axis $r$ of order higher than two with the inversion, as $I \circ r$. These operators are $3$ ($\Delta$), $4$ ($\mathcal{V}$) and $6$ ($\Delta$), and their action is summarized in Fig. 13. The symbols are chosen to emphasize the existence of another operator inside the "belly" of each new operator. Note that $\bar{3} \circ \bar{3} \circ \bar{3} = I$, and $\bar{3}^3 = 3$, i.e., symmetries containing $\bar{3}$ also contain the inversion and the 3-fold rotation. Conversely, $\bar{4}$ and $\bar{6}$ do not automatically contain the inversion. In addition, symmetries containing both $\bar{4}$ (or $\bar{6}$) and $I$ also contain $4$ (or $6$).

![Figure 13: Action of the $\bar{3}$, $\bar{4}$ and $\bar{6}$ operators and their powers. The set of equivalent points forms a trigonal antiprism, a tetragonally-distorted tetrahedron and a trigonal prism, respectively. Points marked with "+" and "-" are above or below the projection plane, respectively. Positions marked with "+/−" correspond to pairs of equivalent points above and below the plane.](image)

Clearly, more orientations of all the allowed axes are possible than in the 2D case, so some kind of convention has to be established to draw the stereographic projections. Generally, the axis of highest order is chosen to be perpendicular to the projection plane (other rules are described in Appendix I).

5.2 The 3D point groups with a 2D projection

As we mentioned before, we can derive 27 of the 32 3D point groups directly from the 10 2D point groups by a process of “extrusion”. The limited amount of space does not allow us here to go into any detail (for a complete description, see [3]). However, the procedure is outlined with an example in fig. 15. Basically, one looks for possible 3D groups that have a 2D point group as a “projection” onto a plane perpendicular to the highest-order axis. As shown in fig. 15, different 3D groups with the same projection will differ by the different “heights” of the equivalent points above and below the plane. There are three ways of doing this: point only "above" the plane
Figure 14: Decision-making tree to identify wallpaper patterns. The first step (bottom) is to identify the axis of highest order. Continuous and dotted lines are “Yes” and “No” branches, respectively. Diamonds are branching points.
would correspond to the same symmetry elements as the 2D group, without additional symmetry. Points both above and below the plane would correspond to an additional mirror plane perpendicular to the highest-order axis. Points alternating above and below the plane will correspond to replacing the rotation with a roto-inversion. Using this method, and considering that the 2D “mirror lines” can in 3D be considered either “lines” or “planes”, one generates 27 groups (and several duplicate entries).

![Figure 15: Schematic representation of the method employed to generate, from 2D point groups, 3D groups that have that 2D group as a projection.](image)

### 5.3 The other 3D point groups: the 5 cubic groups

At this point, we may legitimately ask which other 3D point groups can exist, beside the ones we just derived. In order to answer this question, we should observe that in-plane operators of these groups are proper or improper 2-fold rotation, all forming angles of 90° with the highest-order axis. The missing groups will therefore involve at least two higher-order axes, either at 90° with each other or set at different angles. It can be shown that only two such rotations can exist, both related to the symmetry of the cube.

1. 3-fold axes set at 70.53° ($\cos \gamma = \frac{1}{\sqrt{3}}$), as the diagonals of a cube. Composition of two such rotations in the same direction gives a 2-fold axis through one of the cube faces. Composition in opposite direction yields another 3-fold axis. By subsequent composition and graph symmetry, one retrieves all the four 3-fold axes and three 2-fold axes through faces and diagonals of a cube.

2. 4-fold axes set at 90°, as through the faces of a cube. Compositions in any direction gives a 3-fold axis through the cube diagonals. By subsequent composition and graph symmetry,
one retrieves all the four 3-fold axes and three 4-fold axes, plus six 2-fold axes through the cube edges.

From these two groups, composed with proper rotation only, plus compositions with the inversion, one can obtain the 5 cubic point groups. Their Hermann-Mauguin symbols are similar to those of the other groups, with the **cube faces as primary symmetry direction** (first symbol), the **cube diagonal as secondary** and the **cube edges as tertiary**. The cubic symmetry directions are shown in fig. 16. The Schoenflies symbol (see Appendix I) is \( T \) (for tetrahedral) or \( O \) (for octahedral) depending on the absence or presence of proper 4-fold rotations.

![Figure 16: The symmetry directions of a cube](image)

**Figure 16**: The symmetry directions of a cube: **primary** (I) - three 4-fold axes through the faces; **secondary** (II) four 3-fold axes through the corners and **tertiary** (III) six 2-fold axes through the edges.

23 (Schoenflies notation \( T \)). Corresponds to the group described in item 1 above, and is the symmetry of a "chiral" tetrahedron (e.g., with faces marked with a 3-fold propeller).

2/\( m\bar{3} \) (\( m\bar{3} \) in short, Schoenflies notation \( T_h \)). The same generators as 32 plus the inversion. It is the symmetry of a double tetrahedron yielding a centrosymmetric solid.
432 (Schoenflies notation $O$). Corresponds to the group described in item 2 above, and is the symmetry of a "chiral" cube, for example, with faces marked with a 4-fold propeller. Note that the 2-fold axis along the tertiary direction is obtained by composition of the 4-fold axis (say along the $z$ direction) with a $4^2$ 2-fold axis (say, along the $x$ direction).

$\bar{4}3m$ (Schoenflies notation $T_d$). This is the full symmetry of the tetrahedron. It is obtained from the previous group by replacing the 4-fold axis with $\bar{4}$. By the previous argument, the tertiary 2-fold axes are now replaced by mirrors.

$4/m\bar{3}2/m$ ($m\bar{3}m$ in short, Schoenflies notation $O_h$). It represents the full symmetry of a cube or octahedron.

6 The 14 Bravais lattices in 3D

The procedure followed to derive the 14 Bravais lattices in 3D is closely related to the one used for the 2D case. However, there are many more possibilities to obtain “centered” lattices, i.e., lattices in which the primitive translations are not orthogonal. For example, fig. 17 shows the three lattices with cubic symmetry: Primitive, Face Centred Cubic (BCC) and Body-Centred Cubic (BCC) (you have probably encountered these lattices already). Here, we simply list the 14 Bravais lattices with their symmetry (holohedry) and the crystal classes they support.

Figure 17: Primitive and conventional cells for the three cubic lattices - Primitive - $P$ (left), Body-centered-$I$ (middle) and Face-centered-$F$ (right).

Triclinic system (Classes 1 and $\bar{1}$, holohedry $\bar{1}$, lattice $P$). There is no symmetry restriction on the basis vectors, which are therefore allowed to be at any angle with each other. There is a single primitive lattice and its symbol is $P$.

Monoclinic system (Classes 2, $m$ and $2/m$, holohedry $2/m$, lattices $P$ and $C$)
- No face is centred: the lattice is **monoclinic primitive** (symbol $P$).
- One of the faces containing the “unique” 2-fold axis is centred: the lattice is **monoclinic face-centred** (symbol $C$).

**Orthorhombic system** (Classes $222$, $mm2$ and $mmm$, holohedry $mmm$, lattices $P$, $C$, $F$ and $I$).

- No face is centred: the lattice is **orthorhombic primitive** (symbol $P$).
- One of the faces is centred: the lattice is orthorhombic $A$-, $B$- or $C$-centred, depending on which face is centered (this is to some extent arbitrary — the ITC convention is normally $C$). The symbols are $A$, $B$ or $C$.
- All of the faces are centred: the lattice is **orthorhombic face-centred**, symbol $F$.
- The body (middle) of the cell is centred: the lattice is **body-centered orthorhombic** (symbol $I$).

**Tetragonal system** (Classes $4$, $422$, $4/m$, $4mm$, $4m2$, $4/mmm$, holohedry $4/mmm$, lattices $P$ and $I$).

- No face is centred: the lattice is **primitive tetragonal** (symbol $P$).
- The body (middle) of the cell is centred (face-centering can be reduced to body-centering by a cell transformation): the lattice is **body-centred tetragonal** (symbol "$I$").

**Trigonal system** (Classes $3$, $3m1$, $321$, $3m1$, lattices $P$ and $R$). This system is peculiar, in that each class can be supported by two lattices, $P$ and $R$, with different holohedries.

- The **trigonal primitive** $P$ lattice is simply the 3D extension of the 2D hexagonal lattice by a translation along the $z$ axis, and has holohedry $P6/mmm$. Here, the unit cell is a hexagonal prism.
- In the **trigonal rhombohedral** $R$ lattice, the primitive cell is a **rhombohedron**, i.e., a cube "stretched" along one of the body diagonals (it is easy to see that a rhombohedron has 3-fold symmetry). A conventional larger hexagonal cell (3 times the volume) can be constructed ("hexagonal" setting; both cells are shown in fig. 18). Both rhombohedral and hexagonal settings are used and are listed in the ITC.

**Hexagonal system** (Classes $6$, $6/m$, $622$, $6m2$, $6mm$, $6/mmm$, holohedry $6/mmm$, lattice $P$). This system supports a single lattice, the **primitive hexagonal lattice** (symbol $P$); the unit cell is a hexagonal prism.

**Cubic system** (Classes $23$, $m3$, $432$, $43m$ and $43m$, holohedry $43m$, lattices $P$, $I$ and $F$). See (Fig. 17).

- No face is centred: the lattice is **primitive cubic** ($P$), and the primitive unit cell is a cube.
- The body of the cubic cell is centred: the primitive cell is a rhombohedron with angles between edges $\alpha = 109.3^\circ$ ($\cos \alpha = -\frac{1}{3}$). The lattice is **body-centered cubic (BCC)** — symbol $I$.

- All of the faces are centred: The primitive cell is a rhombohedron with angles between edges $\alpha = 60^\circ$. The lattice is **face-centered cubic (FCC)** — symbol $F$.

### 7 Notation for 3D point groups

#### 7.0.1 Notation for "projective" 3D point groups

The notation we will employ is largely the same as that for 2D point groups. The only significant difference is that the presence the mirror plane $m_z$ orthogonal to a symmetry axis is denoted with the symbol "/m" right after the axis itself. There is also a new "rule of priority", stating that "un-barred" axes take precedence over "barred" ones, except for $m$ that takes precedence over $2$. There are two forms of the point-group Hermann-Mauguin symbol: the "short form", in which only the highest-order axis is indicated (as in 4/mmm and the "long form", in which all axes are indicated explicitly (as in $\frac{4}{m} \frac{2}{m} \frac{2}{m}$).

The Schoenflies notation for 3D point groups is still widely used, and its knowledge is indispensable to understand older literature. In this notation, rotation and roto-inversion axes of order $n$ are indicated with the symbols $C_n$ and $S_n$, respectively ("C" for cyclic, "S" from the German word for mirror, "Spiegel"). The symbol $D_n$ (from "Dihedron") indicate a cyclic axis with $n$ 2-fold axes.
orthogonal to it. The subscripts $h$ (horizontal) and $v$ (vertical) stand for mirror planes orthogonal and parallel, respectively to the highest-order axis, whereas the subscript $i$ stands for the inversion. Special symbols are used for point group $\bar{1}$ (consisting of the identity and the inversion, symbol $C_1$ instead of $C_{1i}$) and point group $m$ (consisting of the identity and a mirror plane, symbol $C_s$ instead of $S_2$). Sometimes, more than one notation can be found for the same point group; the convention is to use $C$ and $D$ whenever possible in preference to $S$ (which is in fact only used for point group $S_4$).

Axes conventions are significantly more intricate than in the case of 2D point groups, where the first symbol always referred to the rotation axis, chosen to coincide with the $z$-axis. For 3D groups, the same convention applies to tetragonal (4-fold axis), trigonal (3-fold axis) and hexagonal (6-fold) point groups: the highest-order axis is listed first and is oriented in the $c$-direction. For monoclinic (2-fold), the 2-fold axis (proper or improper) can coincide with the $b$ direction (standard setting) or the $c$ direction (alternate setting). For orthorhombic groups, the symbol refers to directions $x$, $y$ and $z$ in this order.

A full presentation of the 3D point groups is given in the ITC-Volume A [4], pp. 770-790. The groups are arranged in crystal systems, based on the symmetry of the lattices they support (see below). The following points summarize the few symbols and conventions used in these tables that have not been previously introduced.

- In all cases, the projection axis is the $z$ axis, regardless of the group setting (see below).

- In the left-handed projection, dots refer to general position (or face poles) above the projection plane, whereas open circles are below the projection planes.

- **Monoclinic** groups ($2$, $m$ and $2/m$) are presented in two different setting, with the "unique" axis (i.e., the direction of the proper or improper rotation) along either $b$ or $c$.

- **Trigonal** groups ($3$, $\bar{3}$, $321$, $3m1$, and $\bar{3}m1$) are each presented in 3 different settings. In addition to the two settings already present in the 2D case (i.e., with the hexagonal axes either parallel or perpendicular to the secondary symmetry direction, there is a third setting, labeled "Rhombohedral". Here, only three semi-axes are shown, meaning that the 3 basis vectors are coming out of the projection planes in the direction shown (see below for the definition of rhombohedral lattice).

- **Rule of priority.** When more than one kind of symmetry operator occurs for a given symmetry direction, the priority rule states which operator takes precedence in the Hermann-Mauguin symbols. The choice for reflections is made in order of descending priority:

  $m, e, a, b, c, n, d$

  Rotation axes take priority over screw axes, which take priority over roto-inversions (with the exception of $3$, which takes priority over $\bar{3}$).
8 Glide planes in 3D

\(a, b, \text{ or } c\)  The glide translation is parallel to one of the in-plane basis vectors of the conventional cell, and \(\frac{1}{2}\) of their length.

\(n\)  The "diagonal" glide translation is half the sum of in-plane basis vectors (e.g. \(\frac{1}{2}a + \frac{1}{2}b\)).

\(e\)  This symbol for "double" glide planes stands for the graph of two distinct glide planes, each with glide translations parallel to an in-plane basis vector and \(\frac{1}{2}\) of it in length. These operators only occur in centered cells, because the composition of the two operators gives a pure translation \(\frac{1}{2}a + \frac{1}{2}b\), i.e., a centering translation. The symbol "\(e\)" is new to the fifth edition of the ITC [4]. In previous editions, only one of the glides was indicated ("\(a\)" or "\(b\)" in the standard setting).

\(d\)  For this so-called "diamond glide", the glide translation is half of a centering translation. Because the projections of the diamond glide translations along the symmetry directions is \(\frac{1}{4}\) of a lattice translations, diamond glides are especially restricted, and occur in very few space groups. Naturally they only occur in centered cells, but, for example, they can never be orthogonal to mirror planes.

9 “Real” crystal structures

Having discussed at length the symmetries of periodic “patterns” in 2 and 3 dimensions, we will devote the last part of this lecture to looking at “real” crystal structures. This is in itself a vast subject that cannot be exhausted in such a short space. An interesting set of lectures devoted to the subject can be found in [5]. It is also worth pointing out to the interested student the existence of several very useful Crystal Structure Databases. The Inorganic Crystal Structures Database (ICSD), freely accessible on-line from the UK [6], can be searched for names, chemical formulas, crystallographic data and more, to display the resulting crystal structures in 3D and even to plot their powder diffraction patterns. The Cambridge Structural Database is the corresponding source for small-molecule structures. Here, we will outline a few basic principles that should provide a starting point to understand “real” crystal structures.

9.1 Cohesive forces in crystals — atomic radii

A number of different forces contribute to the cohesion of crystals, including:

- The **Coulomb interaction** between charged ions.
- **Chemical bonding** and **metallic bonding**.
• The Van der Waals (dipole-dipole) interaction.
• Hydrogen bonding.

These forces, which often coexist within the same crystal structure, are of very different strength. Another crucial difference is the directionality of these forces. Chemical bonding (both ionic and covalent) is usually strongly directional, and leads to the formation of specific coordination polyhedra (e.g., octahedra, tetrahedra) within the crystals. Conversely, most other interactions are poorly directional.

One useful way to understand many crystal structures, particularly those of inorganic compounds of greater interest for physicists, is that of considering them as packings of spheres of different sizes. Within this very simplistic picture, each ion is characterised by a radius. Atomic radii are not completely unique to each species, but vary depending on several factors:

• The valence state of the ion.
• The spin state of the ion.
• The number of neighbours (coordination number).
• Whether the bonding is ionic or covalent.

The standard reference for covalent and ionic radii was compiled by R.D. Shannon and can be found in [7]. Several versions of this table can be found on line.

Over most of the periodic tables, ionic and covalent radii vary between 0.5 Å and 2 Å. Typical interatomic distances are therefore of the order of 1.5–2.5 Å. This sets the length-scale of the probes (X-rays, neutrons, electrons) that can be most profitably used to study these structures.

9.2 Close-packed structures

When all the “spheres” are of equal size and the interactions between them are not strongly directional, the most common arrangement is one of the close packed structures (fig. 19):

CCP i.e., Cubic Close-Packed, which has a face-centered cubic (FCC) lattice (space group Fm3m). Many metals, including all those of the Cu and Ni groups, adopt this structure.

HCP Hexagonal Close-Packed, which has a hexagonal lattice with two atoms per unit cell (space group P63/mmc). Metals such as Co, Zn, Cd, Hg, Mg and others adopt this structure.
Several metals, including Fe, Cr and its group, V and its group and all the alkaline metals adopt the **BCC (Body Centered Cubic) structure** — space group $Im\bar{3}m$, which is **not close-packed**.

Close-packed and BCC structures are also adopted by much more complex systems — for instance C$_{60}$ (“Buckyballs”) and even viruses (fig. 20) — clearly with much larger inter-sphere distances. Here we have roughly spherical objects with strong internal bonding, which are weakly bonded among themselves.

### 9.3 Packing spheres of different radii

Many simple binary or ternary compounds are made of ionic species with different radii. In these cases, their crystal structures can often be thought of as being close-packed arrangements of the larger spheres, with the smaller spheres located in the “interstices” or “vacancies” between the larger spheres. Both CCP and HCP structures have vacancies of this type, surrounded by four spheres (tetrahedral vacancies) or six spheres (octahedral vacancies). Because of the geometry of the vacancies, this structural arrangement is suitable for ions with **strongly directional bonding**. When strong directional bonding is present, compounds with ions with similar radii and even mono-atomic compounds can adopt these structure. Among the structures that can be described in this way are:

**The NaCl structure** (space group $Fm\bar{3}m$) where Na fills all the octahedral holes of the CCP structure.

**The fluorite structure** (prototype compound CaF$_2$, space group $Fm\bar{3}m$), where the F atoms fill all the tetrahedral holes of the CCP structure (fig. 21).

**The zinc blende structure** (prototype compound ZnS, space group $F4\bar{3}m$), where the Zn ions fill half of the tetrahedral holes of the CCP structure.

**The perovskite structure** (prototype compound CaTiO$_3$, space group $Pm\bar{3}m$). In this interesting ternary example, the CCP array is formed by both Ca$^{2+}$ (positively charged) and O$^{2-}$...
(negatively charged). The smaller Ti ion fills a quarter of the octahedral vacancies.

**The corundum structure** (Al$_2$O$_3$, space group $R3c$). Here, the oxygen ions form a HCP structure, and the much smaller Al ions fit into 2/3 of the octahedral vacancies (1/3 of the vacancies are empty). The *ilmenite* (FeTiO$_3$, space group $R3$) is a variant with two metal ions instead of one.

**The diamond structure** is adopted, among others, by C and Si. It is identical to the zinc blende structure but with two identical, strongly-bonded atoms.

![Figure 21: Three cubic structures obtaining by inserting ions in the “interstices” of the CCP structure. Left the fluorite structure; center the zinc blende structure; right the perovskite structure.](image)

9.4 Framework structures

Many crystal structures cannot be simply thought of in terms of close packing. One notable example is given by framework structures — structures built out of very rigid polyhedra (most often tetrahedra) with rather “flexible” connections to each other. Framework structures are low-density structures, and can often collapse rather easily to higher-density forms upon application of pressure.

The structure of *quartz* (SiO$_2$) consists of corner-sharing SiO$_4$ tetrahedra so that each Si is bonded to four oxygens, and each oxygen is bonded to two silicon atoms. The resulting structure forms an open three-dimensional framework, and it is quite flexible, so that different crystal variants exist (α- and β-quartz, cristobalite, tridymite etc.) When cooled rapidly, the quartz structure is unable to “choose” between these variants and forms a **glass**. An even more extreme example of silicate framework structure is provided by *zeolite* (SiO$_2$, fig. 22), where the tetrahedral framework encompasses large cavities. Zeolite is the prototype of a large family of silicates and alumino-silicates, collectively known as “zeolites”, which have wide-ranging applications in catalysis.
9.5 Layered structures

Many crystal structures have a pronounced 2-dimensional character, with strong covalent or ionic bonding in 2 dimensions and weaker (typically Van der Waals) bonding in the third. A well known example of this is graphite (space group $P6_3/mmc$ with two atoms per unit cell). Due to the weak inter-layer forces, the layers can “slip” onto each other, so that structures of this types are often employed as lubricants. Other examples of this kind are provided by the clays, such as vermiculite (fig. 23), and by the delafossite family (prototype CuFeO$_2$, space group $R\bar{3}m$ or $P6_3/mmc$). Less extreme examples of 2D structures are provided by the high- $T_c$ superconducting cuprates (fig 24).

Figure 23: The structure of the vermiculite clay (chemical formula $A_3B_4O_{10}\cdot(H_2O)_n$, with $A=$Mg, Fe, Al, $B=$Al, Si; space group $C2/m$) is highly 2-dimensional. The $A$ site forms triangular layers with formula $AO_2$, connected to “rings” of $BO_2$ tetrahedra. These layers are widely separated and weakly interacting, and, as typical of clays, can accommodate large amounts of rather disordered water molecules.

Figure 22: The structure of zeolite $\beta$ (space group $P4_2/mmc$). Note the complex framework of SiO$_4$ tetrahedra, defining a large cavity in the middle of the unit cell. Many silicate and alumino-silicate zeolites exist, both natural and synthetic.
Figure 24: The structure of the 90 K-high-$T_c$ superconductor YBa$_2$Cu$_3$O$_7$ or YBCO is also 2-dimensional, but with a less pronounced 2D structural character compared to clays. The central ion, Y, is  ionically bonded to oxygen, so the structure does not exfoliate like that of graphite. Nevertheless, the electronic structure is highly 2D. Note that Cu exists both in square-pyramidal (“planes”) and in square-planar (“chains”) coordinations.

Figure 25: The molecular crystal structure of aspirin. The individual molecules are easily identifiable, and are linked to each other by hydrogen bonds (dotted lines).

9.6 Molecular structures

All the structures we have defined up to this point are built of infinite “networks” of atoms, either in 3D or in 2D. By contrast, molecular structures are built out of well defined “molecules”, with strong internal covalent bonding but weakly interacting with each other. A simple example is the structure of ice, with covalent bonding within the H$_2$O molecule and weak hydrogen bonding between molecules. Ordinary ice is known as “ice 1h”, and has space group $P6_3/mmc$. However, due to the particular geometry of the molecules, ice is highly polymorphic as a function of temperature and pressure, with 15 known different crystallographic structures being known to date. Molecular structures are adopted by most small molecules (such as drugs) and macromolecules (such as proteins). The molecule itself has rigid components (such as benzene rings) connected to each other by “joints” having some degree of flexibility. Therefore, the same molecule can often adopt different crystal structures (polymorphism), having different molecular configurations and packing of different molecules within the unit cell.
10 Symmetry in Reciprocal Space — the Wigner-Seitz construction and the Brillouin zones

Non-periodic phenomena in the crystal (elastic or inelastic) are described in terms of generic (non-RL) reciprocal-space vectors and give rise to scattering outside the RL nodes.

In describing these phenomena, however, one encounters a problem: as one moves away from the RL origin, symmetry-related “portions” of reciprocal space will become very distant from each other. In order to take full advantage of the reciprocal-space symmetry, it is therefore advantageous to bring symmetry-related parts of the reciprocal space together in a compact form. This is exactly what the Wigner-Seitz (W-S) constructions accomplish very cleverly. “Brillouin zones” is the name that is given to the portions of the extended W-S contructions that are “brought back together”. A very good description of the Wigner-Seitz and Brillouin constructions can be found in [8].

10.1 The Wigner-Seitz construction

The W-S construction is essentially a method to construct, for every Bravais lattice, a fully-symmetric unit cell that has the same volume of a primitive cell. As such, it can be applied to both real and reciprocal spaces, but it is essentially employed only for the latter.

For a given lattice node \( \tau \), the W-S unit cell containing \( \tau \) is the set of points that are closer to \( \tau \) than to any other lattice node.

It is quite apparent that:

- Each W-S unit cell contains one and only one lattice node.
- Every point in space belongs to at least one W-S unit cell. Points belonging to more than one cell are boundary points between cells.
- From the previous two points, it is clear that the W-S unit cell has the same volume of a primitive unit cell. In fact, it “tiles” the whole space completely with identical cells, each containing only one lattice node.
- The W-S unit cell containing the origin has the full point-group symmetry of the lattice (holohedry). In real space, the origin is arbitrary, and all the W-S unit cells are the same. In the “weighed” reciprocal space the W-S at \( q = 0 \) is unique in having the full point-group symmetry. As we shall see shortly, the Brillouin zone scheme is used to project fully-symmetric portions of reciprocal space away from the origin into the first W-S unit cell.
Figure 26: Construction of the W-S unit cell for the case of a $C$-centered rectangular lattice in 2D. A: bisecting lines are drawn to the segments connecting the origin with the neighbouring points (marked “1”. B: these lines define a polygon — the W-S unit cell. C: the W-S unit cell is shown together with lines bisecting segments to more distant lattice points.

**A dummies’ guide to the W-S construction (fig. 26)**

- Draw segments connecting the origin with the neighbouring points. The first “ring” of points (marked with “1” in fig. 26 A) should be sufficient, although these points may not all be symmetry-equivalent.
• Draw orthogonal lines bisecting the segments you just drew. These lines define a polygon containing the origin (fig. 26 B)—this is the W-S unit cell. In 3D, one would need to draw orthogonal bisecting planes, yielding W-S polyhedra.

• Fig. 26 C shows an extended construction (to be used later) including lines bisecting the segments to the second and third “rings”. As you can see, the new lines do not intersect the original W-S unit cell.

• The whole space can be “tiled” with W-S cells (fig. 27).

10.2 “Reduction” to the first Wigner-Seitz unit cell (first Brillouin zone).

As anticipated, the main use of the W-S unit cell is in reciprocal space:

\[ \mathbf{q} = \mathbf{k} + \mathbf{\tau} \]  

(5)

where \( \mathbf{\tau} \) is a \( RL \) vector and \( \mathbf{k} \) is within the first W-S unit cell. (i.e., the one containing the origin). We more often say that \( \mathbf{k} \) is the “equivalent” of \( \mathbf{q} \) reduced to the first Brillouin zone (see here below).

The repeated W-S scheme shown in fig. 27 is used to determine which \( \mathbf{\tau} \) should be used for a given \( \mathbf{q} \) — clearly, the one corresponding to the lattice node closer to it.

10.3 The extended W-S construction: higher Brillouin zones

We have just learned how to “reduce” every reciprocal-space point to the first W-S unit cell (or first Brillouin zone). But the question is: which “bits” of reciprocal space should be “reduced” together? One may be tempted to think that an entire W-S unit cell around a \( RL \) point should be “reduced” together — after all, one would only need a single \( RL \) vector to accomplish this.

It is readily seen, however, that this is not a good idea. As we mentioned before, higher W-S unit cells (i.e., other than the first) do not possess any symmetry, and we are specifically interested in “reducing” together symmetry-related parts of reciprocal space. Therefore, a different construction, known as the extended W-S construction—is required to reduce symmetry-related portions of reciprocal space simultaneously.

The first Brillouin zone coincides with the first W-S unit cell. Higher W-S unit cells are emphatically not Brillouin zones.
A dummies’ guide to the extended W-S construction (fig. 28)

- Start off in the same way as for the “normal” W-S construction, but with lines bisecting the segments to higher-order “rings” of points, as per fig. 26 C.

- Many polygons of different shapes (polyhedra in 3D) will be obtained. Each of these will be given a number according to how many lines (planes in 3D) are crossed to reach the origin with a straight path. If $m$ lines (planes) are crossed, the order of the Brillouin zone will be $m + 1$.

- A Brillouin zone is formed by polygons (polyhedra) having the same number (fig. 28 A).

- As anticipated, the first Brillouin zone is also the first W-S cell (no line is crossed).

- The different portions of a Brillouin zone are “reduced” to the first Brillouin zone in the normal way, i.e., using the repeated W-S construction (fig. 28 B).

- All the portions of a higher Brillouin zone will tile perfectly within the first Brillouin zone (fig. 28 C).
Figure 28: The extended W-S construction. The starting point is fig. 26 C. A A number is given to each polygon, according to how many lines are crossed to reach the origin. Polygons with the same number belong to the same Brillouin zone. The figure shows the scheme for the first three Brillouin zones. B Portions of a higher Brillouin zone can be reduced to the first Brillouin zone in the normal way, i.e., by using the repeated W-S construction (here, the reduction procedure is shown for the third zone). C When reduced, higher zones “tile” perfectly within the first W-S cell.
References


[6] Online access on http://icsd.cds.rsc.org/icsd/
