SYMMETRY

Finite geometric objects ("molecules") are symmetric with respect to

a) rotations
b) reflections (symmetry planes, symmetry points)
c) combinations of translations and rotations (screw axes)

If an object is symmetric with respect to rotation by angle \( \phi = \frac{2\pi}{n} \), it is said to have an "n-fold rotational axis"

n=1 is a trivial case: every object is symmetric about a full revolution. Non-trivial axes have n>1.
Symmetries of an equilateral triangle
180-rotations (flips)

\[
\begin{array}{c}
1' \\
3'
\end{array}
\Rightarrow \text{about 22'} \\
\begin{array}{c}
1 \\
2 \\
3
\end{array}
\Rightarrow \text{about 33'} \\
\begin{array}{c}
1 \\
2 \\
3
\end{array}
\Rightarrow \text{about 11'}
\]
120 degree = $\frac{2\pi}{3}$ rotations
An equilateral triangle is not symmetric with respect to inversion about its center. But a square is.
Gliding (screw) axis

Rotate by 180 degrees about the axis

Slide by a half-period
2-fold rotations can be viewed as reflections in a plane which contains a 2-fold rotation axis.
Crystal Structure

Crystal structure can be obtained by attaching atoms or groups of atoms --basis-- to lattice sites.

Crystal Structure = Crystal Lattice $\bullet +$ Basis $\bullet$

Partially from Prof. C. W. Myles (Texas Tech) course presentation
Building blocks of lattices are geometric figures with certain symmetries: rotational, reflectional, etc.

Lattice must obey all these symmetries but, in addition, it also must obey

**TRANSLATIONAL symmetry**

Which geometric figures can be used to build a lattice?
Crystallographic Restriction Theorem:

Crystal lattices have only 2-, 3-, 4-, and 6-fold rotational symmetries.
1. Suppose that an $n$-fold rotational axis is going through $A$. Another $n$-fold axis is going through $B$.
2. Rotate the lattice about $A$ by $\varphi = 2\pi/n$: $B \rightarrow B'$.
3. Rotate the lattice about $B$ by $\varphi = 2\pi/n$: $A \rightarrow A'$.
4. Distance $A'B'$ must be an integer multiple of $a$. 
\[ ma = a + 2a \sin(\varphi - \pi / 2) = a - 2a \cos \varphi \]

\[-1 \leq \cos \varphi = \frac{1-m}{2} \leq 1; \quad m \geq 0 \Rightarrow 0 \leq m \leq 3\]

\[m = 0 \Rightarrow \cos \varphi = 1/2 \Rightarrow \varphi = \pi / 3 \Rightarrow n = 6\]

\[m = 1 \Rightarrow \cos \varphi = 0 \Rightarrow \varphi = \pi / 2 \Rightarrow n = 4\]

\[m = 2 \Rightarrow \cos \varphi = -1/2 \Rightarrow \varphi = 2\pi / 3 \Rightarrow n = 3\]

\[m = 3 \Rightarrow \cos \varphi = -1 \Rightarrow \varphi = \pi \Rightarrow n = 2\]
Penrose tiling

Icosahedron
Quasicrystals

- Discovered in 1984 in Al-Mn submicron granules
- Have long-range five-fold orientational but no translational long-range order
- Exhibit sharp diffraction patterns
- Hard metals with low heat conductivity
- A commercially produced Al–Cu–Fe–Cr thermal spray cookware coating
- Hydrogen storage?
Metallic Phase with Long-Range Orientational Order and No Translational Symmetry

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Dan Shechtman
Nobel Prize in Chemistry 2011

2 mkm grains

Al-Mn, Fe, Cr
(10-14%)
Fig. 4 The fivefold (A), threefold (B), and twofold (C) diffraction patterns obtained from a region (red dashed circle) of the granule in Fig. 

CuAl₂,CuAl

L Bindi et al. Science 2009;324:1306-1309

Published by AAAS
Simplest type of lattices: Bravais lattices

Two equivalent definitions:

A. An infinite array of discrete points with an arrangement and orientation that appear *exactly* the same, from whichever of the points the array is viewed.

B. A lattice consisting of all points with positions vectors \( \mathbf{R} \) of the form

\[
\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3
\]

Collorary to B: every point of a Bravais lattice can be reached from any other point by a finite number of translations.

Non-Bravais lattice contains points which cannot be reached by translations only. Rotations and reflections must be used in addition to translation.

Bravais lattices: basis consists of one element (atom)
Non-Bravais lattices: can be represented as Bravais lattices with a basis consisting of more than one element.
Bravais lattices in 2D (all sites are equivalent)

- **Oblique**
  - $180^\circ = \frac{2\pi}{2} \Rightarrow 2$-fold axis

- **Rhombohedral**
  - $180^\circ = \frac{2\pi}{2}$

- **Orthorhombic (Rectangular)**
  - $180^\circ = \frac{2\pi}{2}$
  - $60^\circ = \frac{2\pi}{6} \Rightarrow 6$-fold axis
  - $120^\circ = \frac{2\pi}{3} \Rightarrow 3$-fold axis

- **Tetragonal (Square)**
  - $90^\circ = \frac{2\pi}{4} \Rightarrow 4$-fold axis

- **Hexagonal (Triangular)**
Is this a Bravais lattice?

Yes, it is orthorhombic (rectangular) Bravais lattice
and the answer is ….

NO!
“body-centered tetragonal” = tetragonal
Bravais lattices in 3D: 14 types, 7 classes

Classes:
1. Cubic $\times 3$
2. Tetragonal $\times 2$
3. Hexagonal $\times 1$
4. Orthorhombic $\times 4$
5. Rhombohedral $\times 1$
6. Monoclinic $\times 2$
7. Triclinic $\times 1$

Ag, Au, Al, Cu, Fe, Cr, Ni, Mb...
Ba, Cs, Fe, Cr, Li, Na, K, U, V...
He, Sc, Zn, Se, Cd...
S, Cl, Br
Sb, Bi, Hg
Is there a two-dimensional body-centered tetragonal lattice?

- A. Yes
- B. No
An example of a non-Bravais lattice

- Even though graphene is a monoatomic compound, the basis consist of two atoms!
- Red (A) and blue (B) sites are not equivalent.
Nobel Prize 2010

Konstantin Novoselov  Andre Geim
Honeycomb lattice: oblique lattice of diatomic molecules

From Ashcroft and Mermin
Unit cell: an element of lattice that fills the space under translations.
**Primitive Cell:**

The smallest component of the crystal (group of atoms, ions or molecules) that, when stacked together with pure translational repetition, reproduces the whole crystal.

*From Prof. C. W. Myles (Texas Tech) course presentation*
Blue square=primitive cell (area=1/2)
Red parallelogram=unit cell (area=3/4)
Green square=unit cell (area=1)
Is the blue triangle a unit cell?
NO. Space must be filled by unit cells using only translations.
The choice even of a primitive cell is not unique

Areas: $S=S'=S''$
2D "NaCl"
Choice of origin is arbitrary - lattice points need not be atoms - **but the primitive cell area should always be the same.**
- or if you don’t start from an atom
This is **NOT** a primitive cell
- empty space is not allowed!
Graphene lattice as a Rhombohedral Bravais lattice with a 2-atom basis
Graphene

One possible choice of unit lattice vectors

Another possible choice of unit lattice vectors shown along with the unit cell

The electronic properties of graphene
A. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim
Rev. Mod. Phys. 81, 109 (2009)
Primitive and conventional cells

**Primitive cell:**
- A smallest volume (area) of space that, when translated through all the vectors of a Bravais lattice, fills all space without either overlapping or leaving voids.
- Symmetry of the primitive cell does not necessarily coincide with that of a Bravais lattice.
  - The choice of a primitive cell is not unique
  - All primitive cells have the same volume (area)

Different choices of a primitive cell for an oblique 2D Bravais lattice (from Ashcroft and Mermin)
Primitive cells of Bravais lattices contain one atom. If this atom has an odd number of electrons, the element is a metal.
Basis vectors for a *bcc* lattice

one possible choice of basis vectors for a *bcc* lattice

\[ \mathbf{a}_1 = a \hat{x}, \quad \mathbf{a}_2 = a \hat{y}, \quad \mathbf{a}_3 = \frac{a}{2}(\hat{x} + \hat{y} + \hat{z}) \]

a more symmetric choice

\[ \mathbf{a}_1 = \frac{a}{2}(\hat{y} + \hat{z} - \hat{x}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{z} + \hat{x} - \hat{y}), \]
\[ \mathbf{a}_3 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z}) \]
$bcc$ lattice as a superposition of two simple cubic lattices
Basis vectors of an fcc lattice

\[ a_1 = \frac{a}{2} (\hat{y} + \hat{z}), \quad a_2 = \frac{a}{2} (\hat{z} + \hat{x}), \quad a_3 = \frac{a}{2} (\hat{x} + \hat{y}) \]
Volume of a primitive cell: *bcc* lattice

\[ V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) \]

\[ \mathbf{a}_1 = \frac{a}{2}(\hat{y} + \hat{z} - \hat{x}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{z} + \hat{x} - \hat{y}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z}) \]

\[ V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = \left( \frac{a}{2} \right)^2 \mathbf{a}_1 \cdot \begin{bmatrix} \hat{x} & \hat{y} & \hat{z} \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix} = \left( \frac{a}{2} \right)^2 \mathbf{a}_1 \cdot 2(\hat{y} + \hat{z}) \]

\[ = \left( \frac{a}{2} \right)^3 2(\hat{y} + \hat{z} - \hat{x}) \cdot (\hat{y} + \hat{z}) = \frac{a^3}{2} \]
(conventional) unit cell:

- A volume (area) that fills all space, when translated by some lattice vectors.
- Larger than a primitive cell
- Allows to “see” the lattice better

3D face-centered cubic (fcc) lattice

From Prof. C. W. Myles (Texas Tech) course presentation
The most important primitive cell: the Wigner-Seitz cell

**WS cell** about a lattice point:
a region of space that is closer to a given lattice point than to any other point.

**WS cell** has the same symmetry as the lattice itself.

Simple construction method: connect the lattice points by line, choose the middle points, and draw lines normal to the connecting lines. The enclosed volume (area) is the **WS cell**.

The method of construction is the same as for the Brillouin zone in the wavenumber (reciprocal) space.
WS cell for a tetragonal (square) Bravais lattice
Construction of a WS cell for a rectangular lattice

What about next-to-next-to-nearest neighbors?

Adding n.n.n.n. does not change the WS cell for a rectangular lattice

n.n.=nearest neighbor
n.n.n.=next-to-nearest neighbor
WS cell for a hexagonal 2D lattice

NB: In 2D, WS cells are either hexagons or rectangulars
Depending on the shape of the parallelogram, either A or B can be n.n.n.

If $\alpha + \beta < \pi / 2$, $a > b$

If $\alpha + \beta > \pi / 2$, $a < b$

Rectangular:

$\alpha = \pi / 2; \beta = \pi / 4; \alpha + \beta > \pi / 2 \Rightarrow a < b$
Wigner-Seitz Cell - 3D

f.c.c Wigner-Seitz cell

b.c.c Wigner-Seitz cell
Some common non-Bravais lattices
C (diamond), Si, Ge

Zincblende (ZnS): GaAs, GaP, InAs, InSb, ZnSe, CdTe …

Number of atoms
4 atom inside
Each of 8 corner atoms is shared among 8 cell: count as one atom.
Each of 6 face atoms is shared among 2 cells: count as 3 atoms.
4+1+3=8
Hexagonal Close-Packed (HCP)

Be, Cd, Ce, Gd, Ho, Mg, Ni, Zr…

6 atoms per unit cell
“NaCl”: AgBr, AgCl, MnO, LiF…
Lattice Sites in Cubic Unit Cell
Reciprocal lattice to \textit{bcc}?

\[a_1 = \frac{a}{2}(\hat{y} + \hat{z} - \hat{x}), \quad a_2 = \frac{a}{2}(\hat{z} + \hat{x} - \hat{y}), \quad a_3 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z})\]

\[b_1 = \frac{2\pi}{V} a_2 \times a_3, \quad b_2 = \frac{2\pi}{V} a_3 \times a_1, \quad b_3 = \frac{2\pi}{V} a_1 \times a_2\]

\[V = a_1 \cdot (a_2 \times a_3) = \left(\frac{a}{2}\right)^2 \begin{bmatrix} \hat{x} & \hat{y} & \hat{z} \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix} = \left(\frac{a}{2}\right)^2 a_1 \cdot 2(\hat{y} + \hat{z})\]

\[= \left(\frac{a}{2}\right)^3 2(\hat{y} + \hat{z} - \hat{x}) \cdot (\hat{y} + \hat{z}) = \frac{a^3}{2}\]

\[b_1 = \frac{2\pi}{V} a_2 \times a_3 = \frac{4\pi}{V} (\hat{y} + \hat{z}) = \frac{2\pi}{a} (\hat{y} + \hat{z})\]

\[b_2 = \ldots = \frac{2\pi}{a} (\hat{x} + \hat{z})\]

\[b_2 = \ldots = \frac{2\pi}{a} (\hat{x} + \hat{y})\]

Direct \textit{fcc} lattice:

\[a_1 = \frac{a}{2}(\hat{y} + \hat{z})\]

\[a_2 = \frac{a}{2}(\hat{z} + \hat{x})\]

\[a_3 = \frac{a}{2}(\hat{x} + \hat{y})\]
Crystal Directions

• Choose one lattice point on the line as the origin: point O. Choice of origin is completely arbitrary, since every lattice point is identical.

• Choose the lattice vector joining O to any point on the line: point T. This vector can be written as:

\[ R = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} \]

• To distinguish a lattice direction from a lattice point, the triad is enclosed in square brackets \([ \ldots ]\): \([n_1 n_2 n_3]\)

• \([n_1 n_2 n_3]\) is the smallest integer of the same quotient.

[111] direction
Examples

\[ X = 1, \ Y = \frac{1}{2}, \ Z = 0 \]
\[ [1 \ \frac{1}{2} \ 0] \rightarrow [2 \ 1 \ 0] \]

\[ X = \frac{1}{2}, \ Y = \frac{1}{2}, \ Z = 1 \]
\[ [\frac{1}{2} \ \frac{1}{2} \ 1] \rightarrow [1 \ 1 \ 2] \]
Negative directions

Negative directions are written as $[\bar{n}_1 \bar{n}_2 \bar{n}_3]$
Examples of crystal directions

\[ X = 1, Y = 0, Z = 0 \rightarrow [100] \]

\[ X = -1, Y = -1, Z = 0 \rightarrow [\overline{1}10] \]

From Prof. C. W. Myles (Texas Tech) course presentation
Miller indices

\((hkl)\)

\(1/h,1/k,1/l = \) coordinates of intersection points between the \((hkl)\) plane and coordinate axes
$x = 1; y = \infty; z = \infty \implies \frac{1}{x} = 1/1 = 1; \frac{1}{y} = 0; \frac{1}{z} = 0$

$(100)\ (110)\ (111)\ (210)$
Brillouin zones for a square lattice
1st BZ=Wigner-Seitz cell in the reciprocal space
1st BZ for *bcc* lattice

1st BZ for *fcc* lattice