MSE-238
Structure of Materials

Week 13 – composites and wrap –up

Spring 2025

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General Outline

- introduction and reminder of atomic bonds, crystals – week 1

Part I: crystallography - weeks 2-6

- packing of spheres, constructing crystal structure week 2
- crystal lattice and symmetry operations week 3
- mathematical description of the lattice, Miller indices week 4
- reciprocal space (&diffraction) week 6
- characterization I: diffraction week 7
- diffraction & recap of crystallography week 8

BREAK 18.4. & 25.4.

Part III: amorphous & hierarchical structures – week 9-13

- glasses
- polymers
- Characterization II: scattering
- biological and **hybrid materials week** 12 & 13

Recap – week 13

Hybrid materials/Composite materials

mud bricks with straw, photo Leon Mauldin

Ancient Egypt: improved mechanical properties of bricks by adding short straw to clay

natural composites:
bone: collagen (protein) and calcium-phosphate (ceramic)
wood: cellulose (polysacharide) in Lignin (polysacharide)

composite materials: mixture on the microscopic scale of several phases

hybrid materials are composites consiting of two consituents at the nanometer or molecuar level

not a strict separation between composite and hybrid material. Both combine properties from from than one material with distinct structure and chemocal composition, contributing synergistically to the physical, chemical or mechanical properties

Application

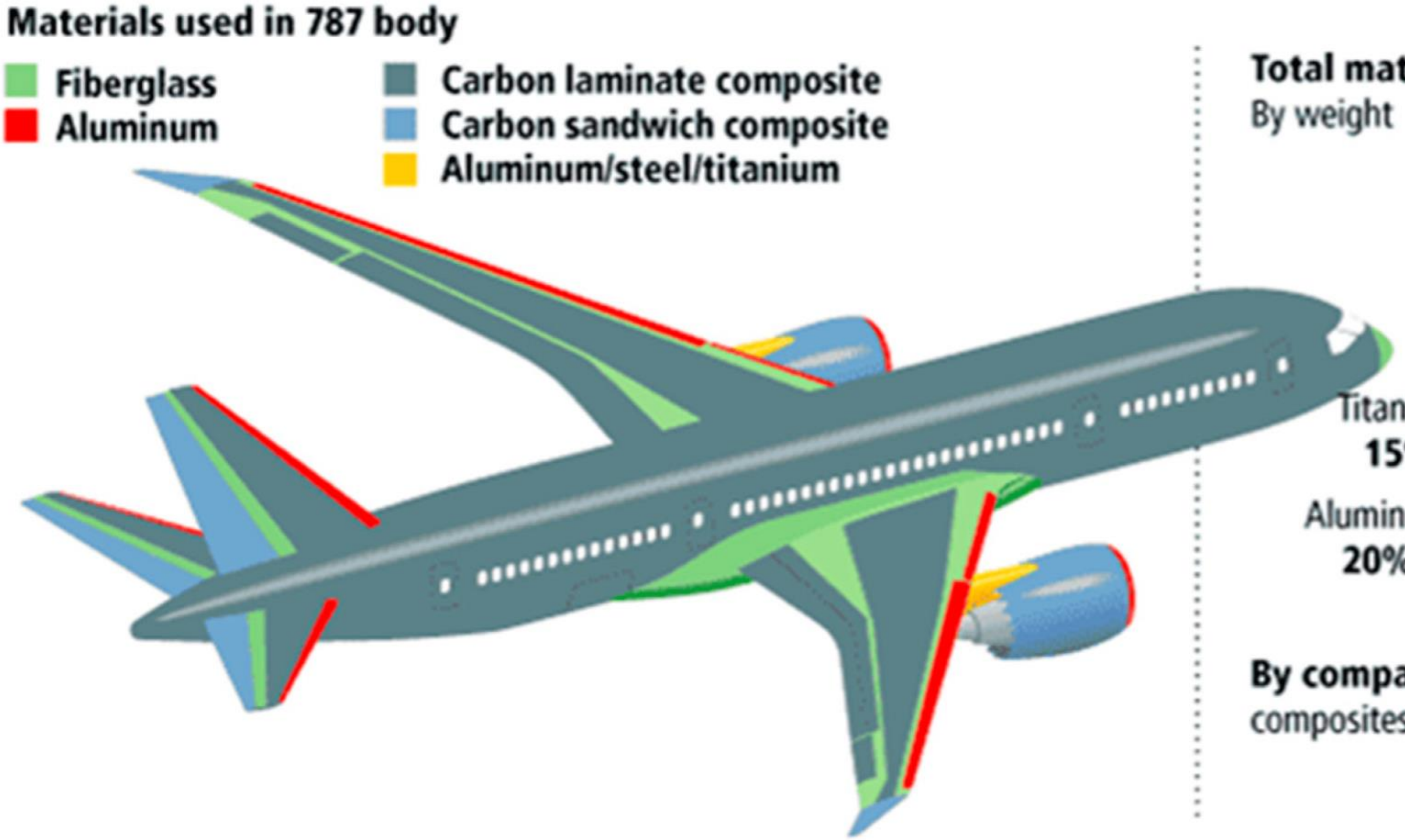
- Mobility (automotive, aeronautics and space)
- Sport (marine, ski, bike, …)
- biomedical (encapsulation, prosthethics)
- electronic devises (encapsulation, flexibel electronics)
- energy (wind turbines, solar panels integration)
- bio-inpired composites
- construction (cement reinforced with steel)

yrs.edu

composite.com.au

sampe.org

Applications: example Boeing 787



By comparison, the 777 uses 12 percent composites and 50 percent aluminum.

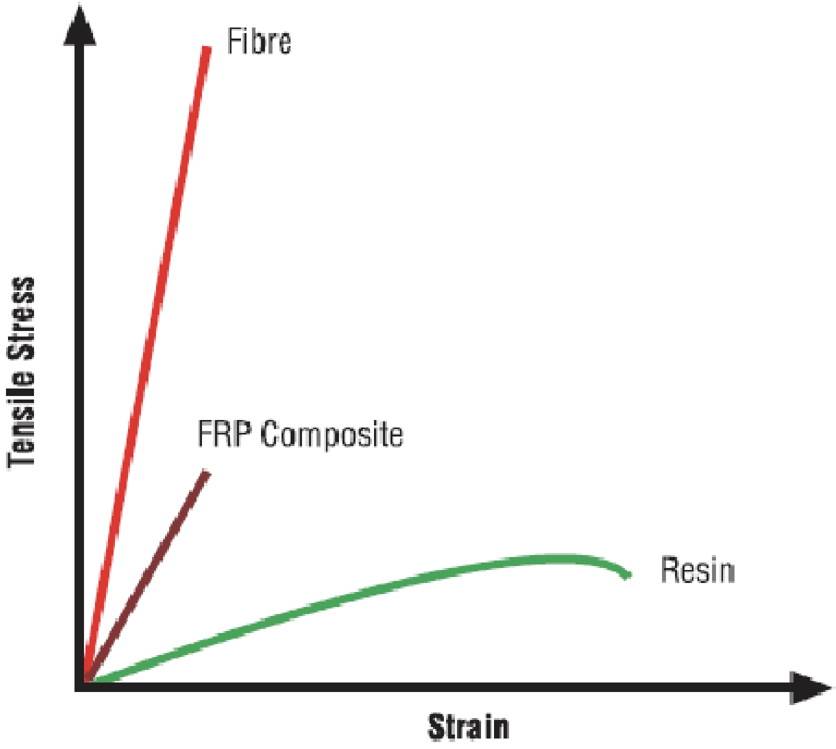
Composite materials

- Reinforced composites:
    - fiber composites: continous matrix reinforced with high strenght fibres
        - short (discontinous) fibers
        - long (continous) fibers
    - particulate composites: (isotropic) particles immersed in a matrix

      examples: Al-particle in rubber, silicon carbide in Al, gravel,sand and cement forming concrete
    - flake composites: flat reinforcements aligned in plane in matrix

    matrix can be for example: polymer (mostly thermoset or thermoplastics (PEEK)), metalceramic, carbon
- sandwich structures: combining various materials used to form functional structures
- functional composites: example composites with sensing functionality

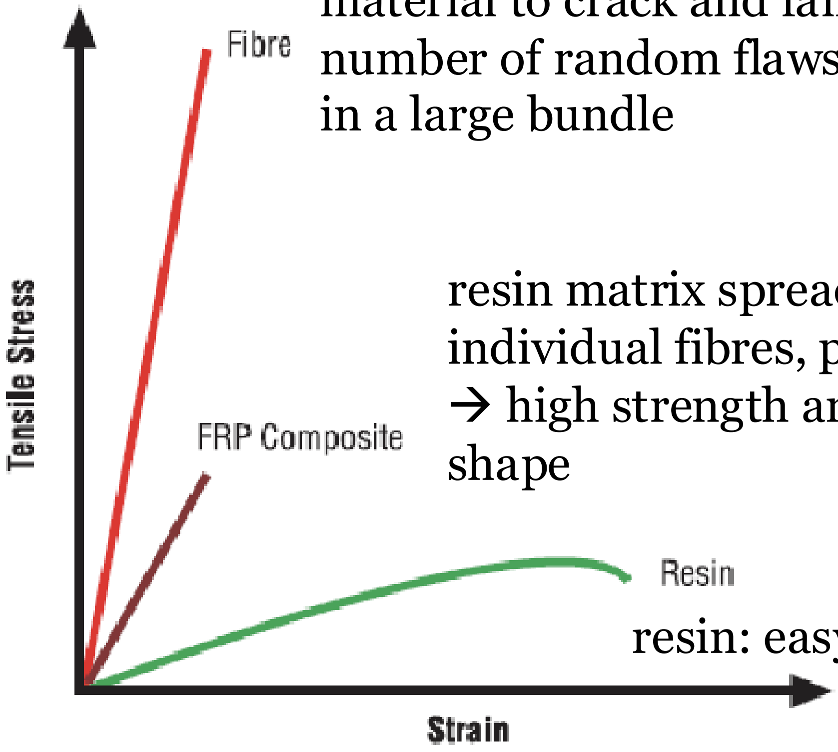
Polymer fiber composites



properties of the composite determined by
- properties of the fibre
- properies of the resin
- the ratio of fibre to resin (Fibre volum fraction)
- the geometry and orientation of the fibres in the composites

Polymer fiber composites

glass or aramid: high tensile and compressive strength but as solids random surface flaws cause material to crack and fail→ in fibre form: same number of random flaws but restricted to some fibres in a large bundle



resin matrix spreads load between each of the individual fibres, protects them from abrasion damage → high strength and stiffness, low density, easy to shape

resin: easy , but not very resisten against tensile stress

Polymer fiber composites

- Tension: tensile stiffness and strength properites of the reinforcement fibres
- compression: adhesive and stiffness of the matrix, maintain fibres as straight columns, prevent buckling
- shear: matrix plays major role, transferring the stressses across the composite, high adhesion between matrix and fibre is improtant
- flexure: combination of tensile, compression, and shear loads

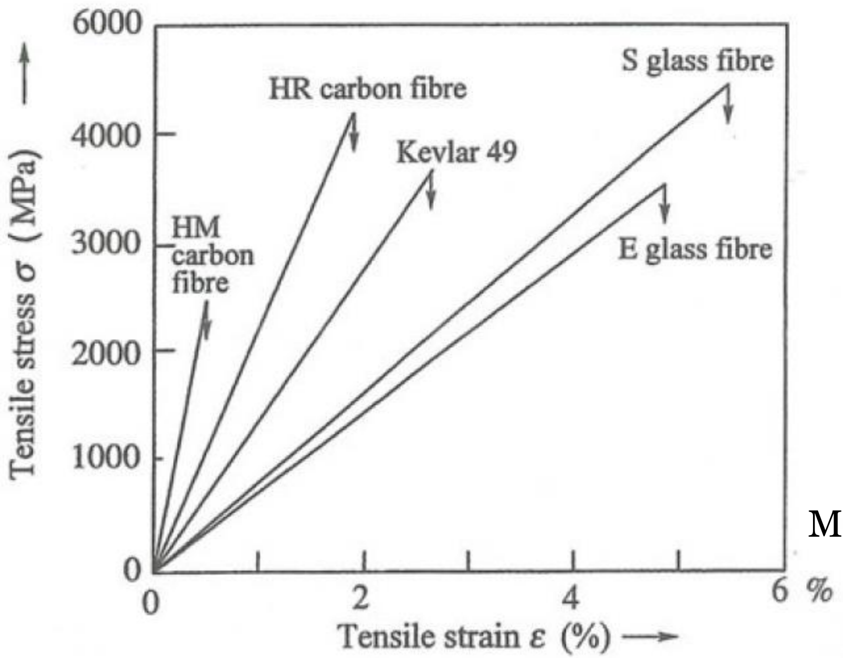
Fiber reinforced composite

- uniaxially oriented fiber, short fiber composites, woven fibers…

→ glass fibers, mainly aluminium borosilicates, S glass fibers high mechanical strength

→ carbon fibers (high modulus fibres HT and high-strength fibres HR)

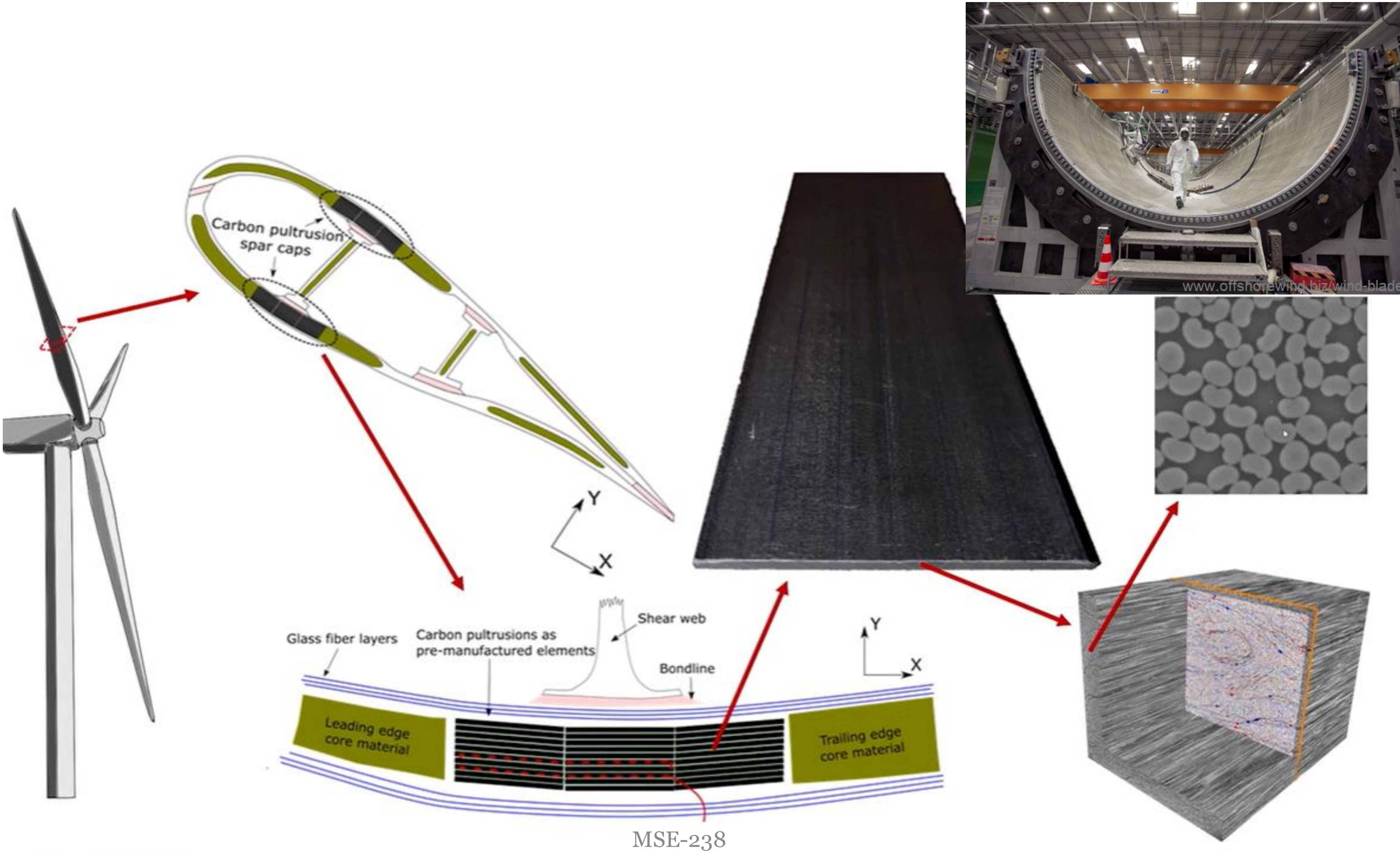
→ aramid (Kevlar)



- flexible and deformable components: glass fibers (ski, pole for pole vault)
- rigid elements with little deformation: carbon fibres (aircrafts)

Mercier, Zambelli, Kurz, “Introduction to Materials Science”, Elsevier

Fiber composites: wind turbine blades



Mikkelsen, L. P. Lecture: Composite materials for wind energy, (2023)

Sandwich structure: laminated sheets and shells

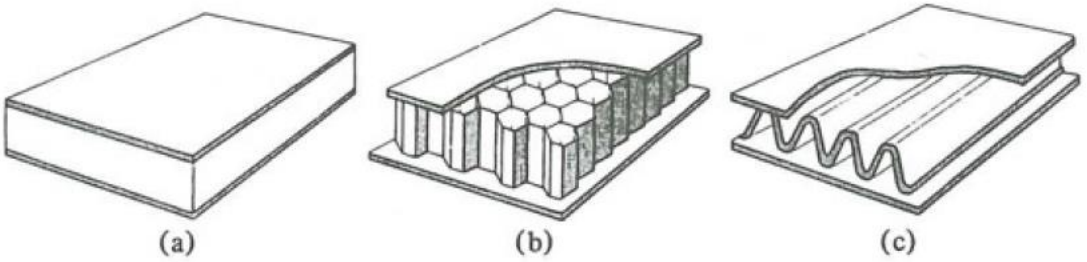


Figure 16.11. Various sandwich structure constructions: (a) solid core (foam-balsa); (b) honeycomb; (c) corrugated core.

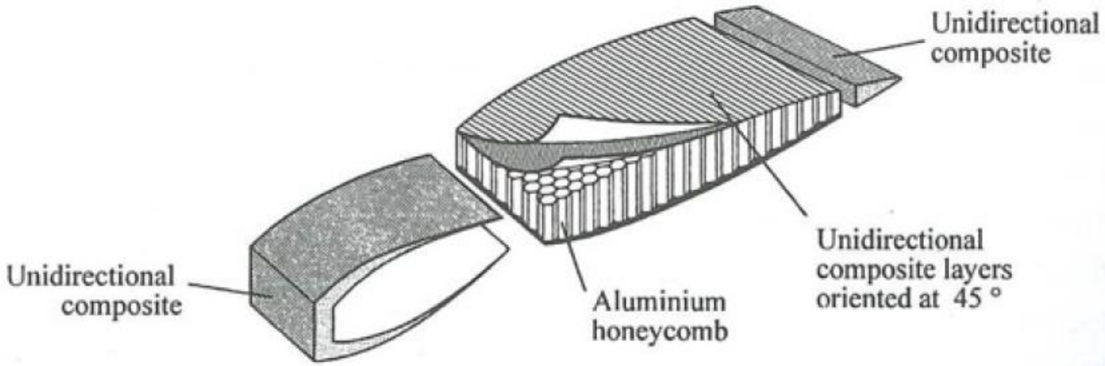
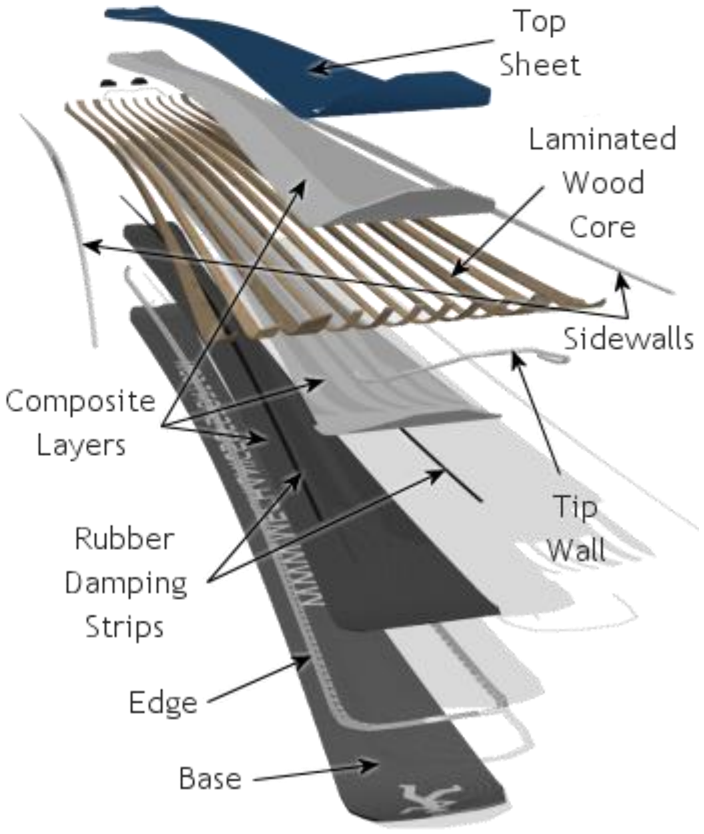


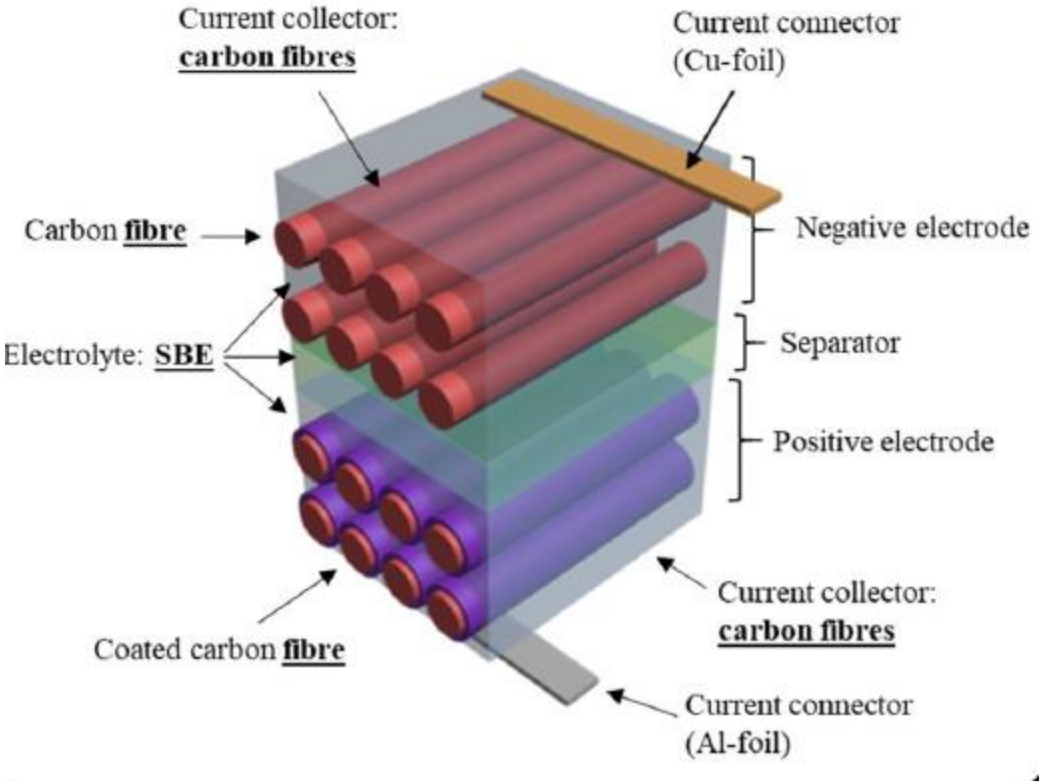
Figure 16.12. Helicopter rotor blade (after Golé, 1979).



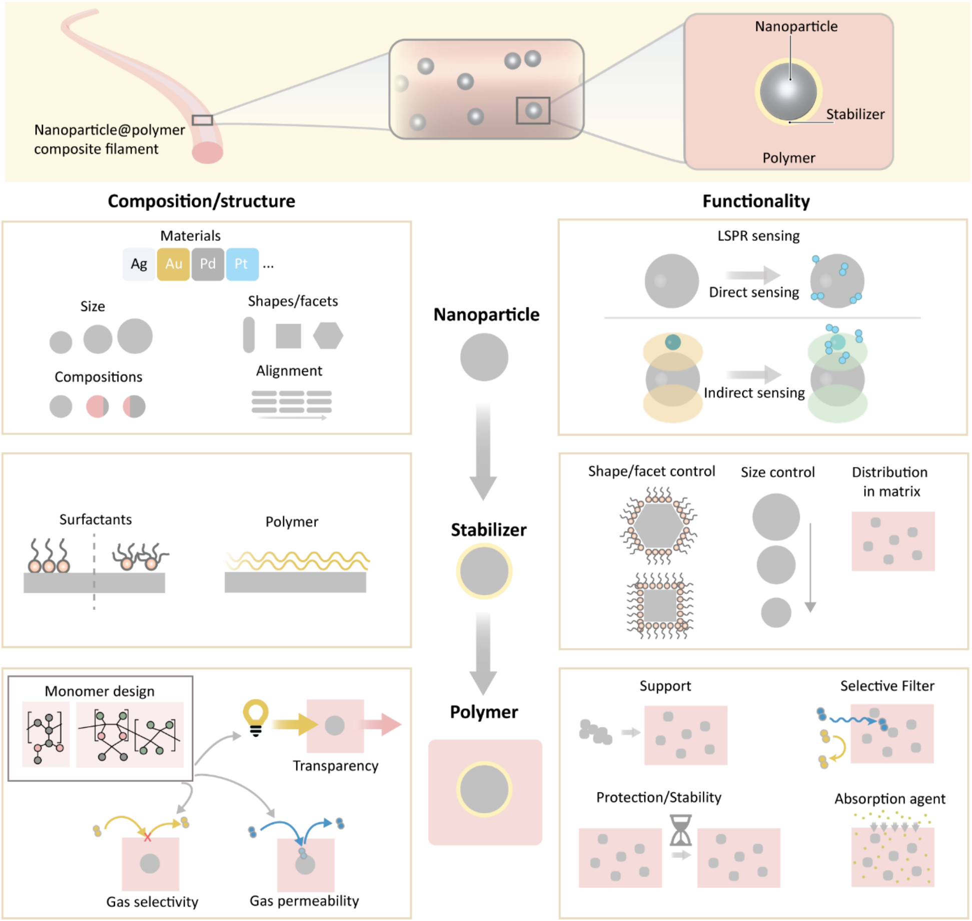
Mercier, Zambelli, Kurz, “Introduction to Materials Science”, Elsevier

Functional composites: structural batteries

coated carbon fibers act as structural reinforcement as well as current collector



Functional composite example: Hydrogen gas sensors



Plasmonic plastics composites comprise three key components:

(i) plasmonic metal nanoparticles → sensing

(ii) surfactant/stabilizer molecules on the nanoparticle surface

(iii) polymer matrix,

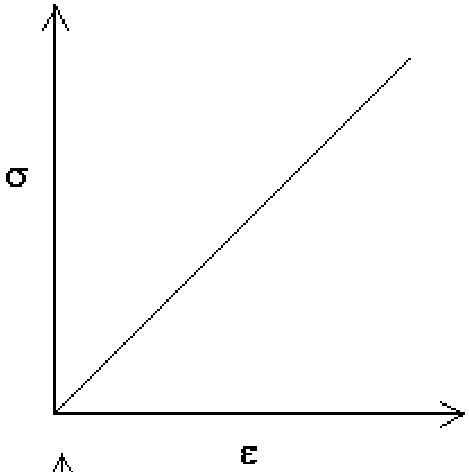
Biocomposites

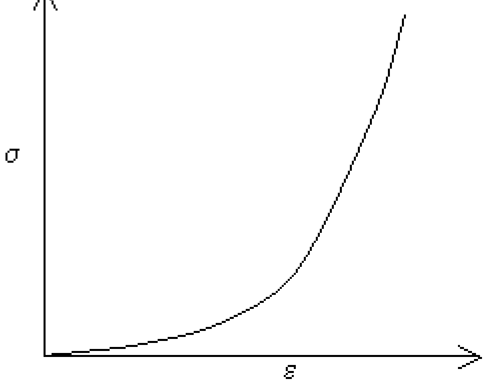
Biominerals

- Linear elastic stress-strain plot
- In general high stiffness, low toughness

Biopolymers

- Non-linear, tensile curve or a curve with an inflection point
- The distinct properties of biopolymers allow these materials to be strong and highly extensible with distinctive molecular deformation characteristics.
- In general high toughness, low young’s modulus (longitudinal stress divided by the strain)



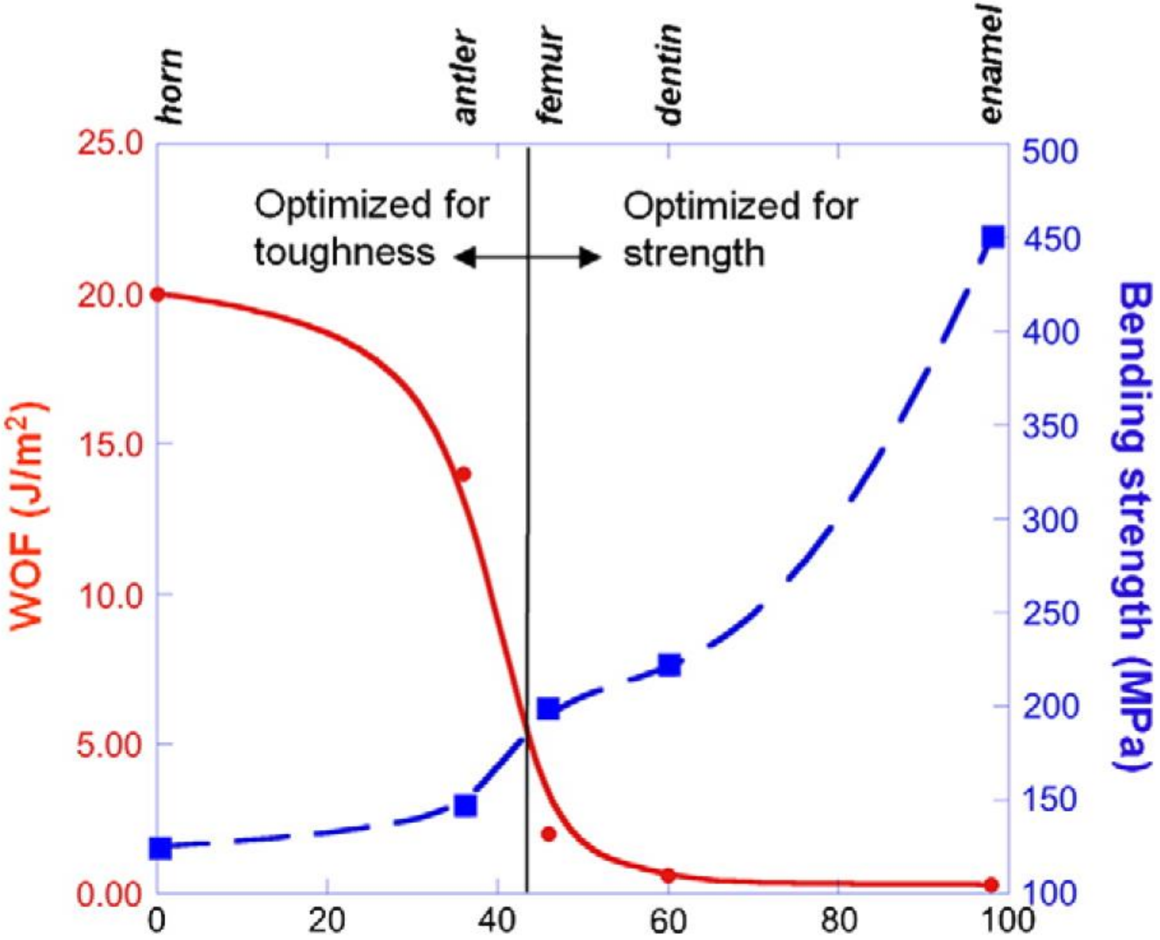


Composites

- Broad variety of constitutive responses
- Many interesting biological materials are composites of flexible biopolymers and stiff minerals. The combination of these two constituents leads to the creation of a tough material.

Biocomposite: toughness and strength

work of fracture

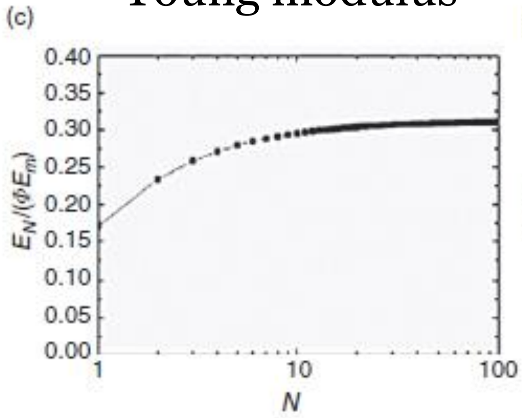


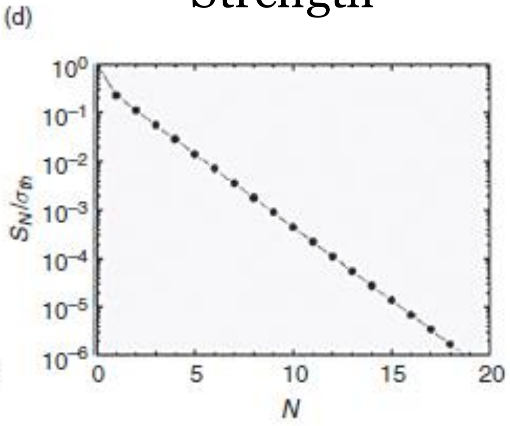
mineral fraction

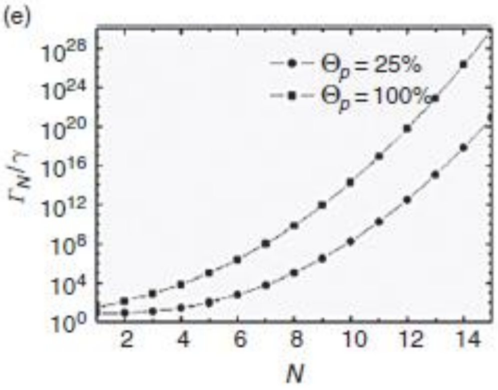
McKittrick et al. 2010 Materials Science and Engineering C

Hierarchical materials

Stiffness, strength and toughness depend on the level in the hierarchy

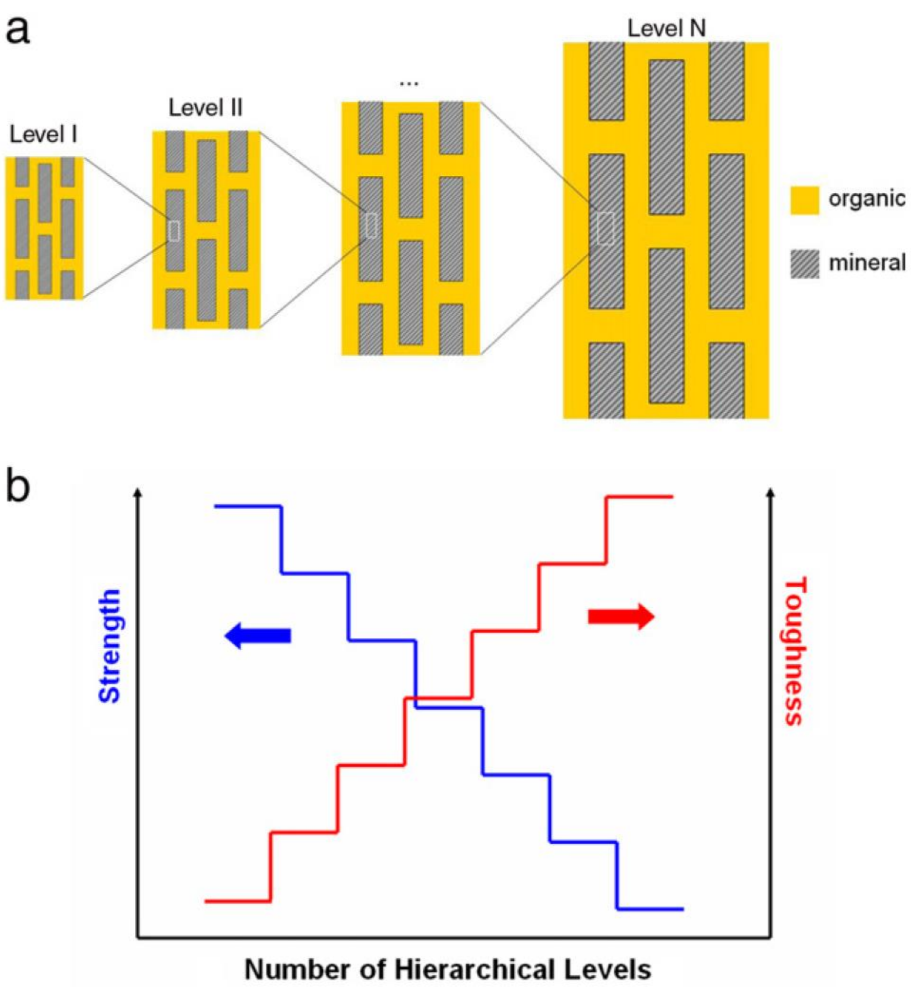

Young modulus


Strength


Toughness

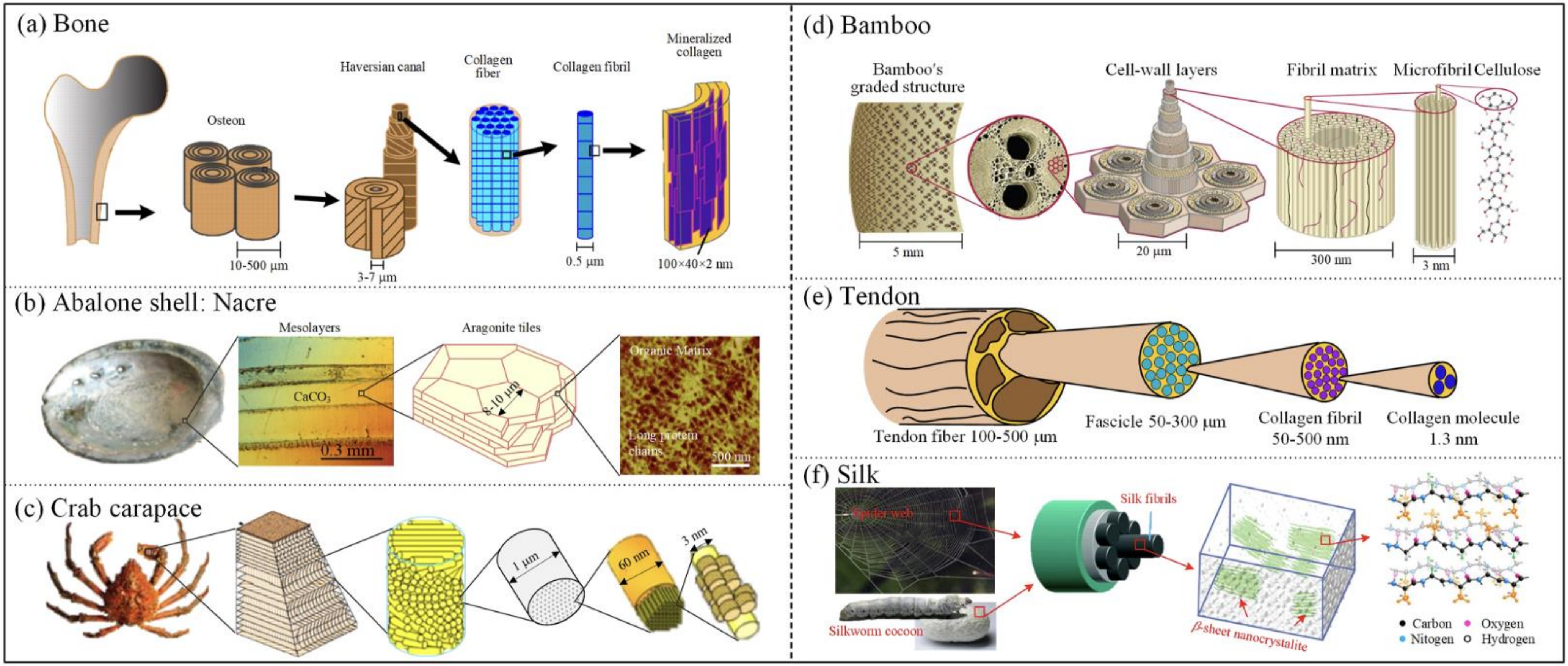
Φ= aspect ratio
Θ= strain
σ_{th}= strength at th hierarchical level
N= number of hierarchical levels
Γ= Fracture energy
γ= surface energy

Hierarchical materials



- Strength decreases due to existence of flaws
- The increase in toughness counteracts this: A growing crack will encounter barriers as it propagates

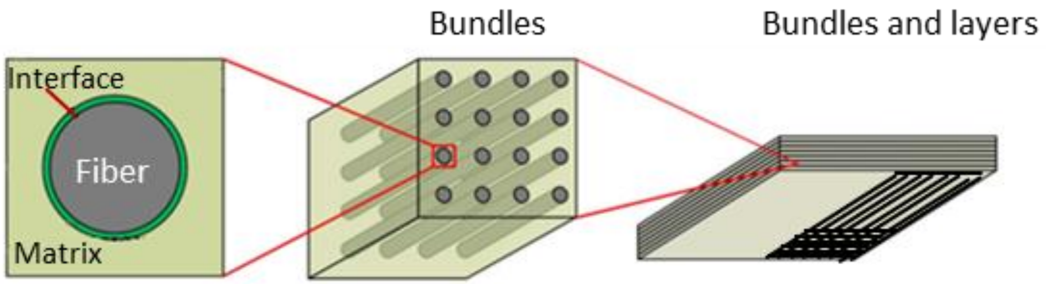
Bio-composites: hierarchical structure



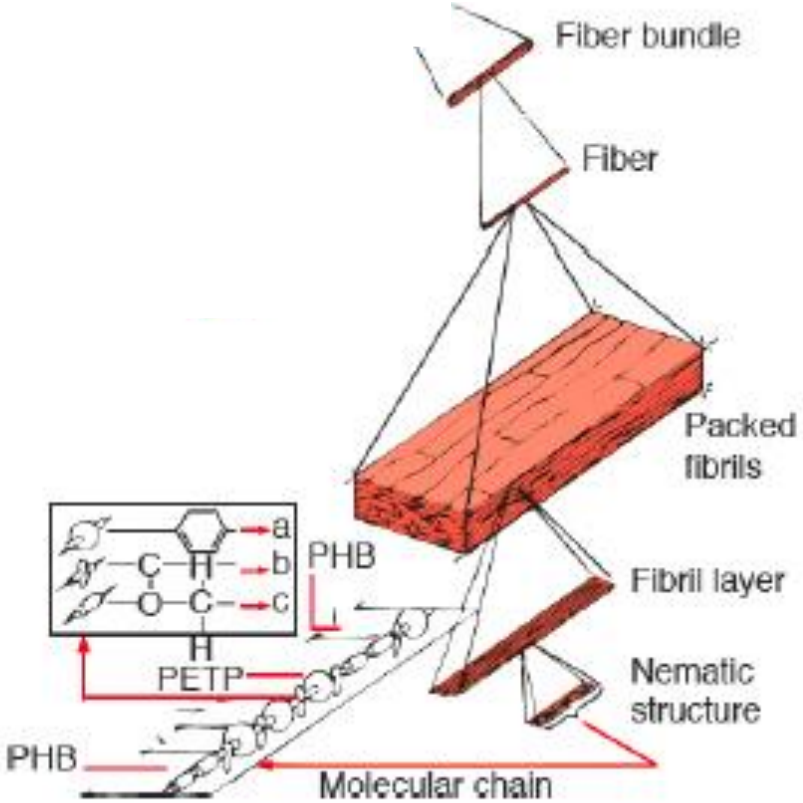
Chen, Y., et al. (2021). Advances in mechanics of hierarchical composite materials. *Composites Science and Technology*, *214*, 108970.

Fiber composite: hierarchical structure

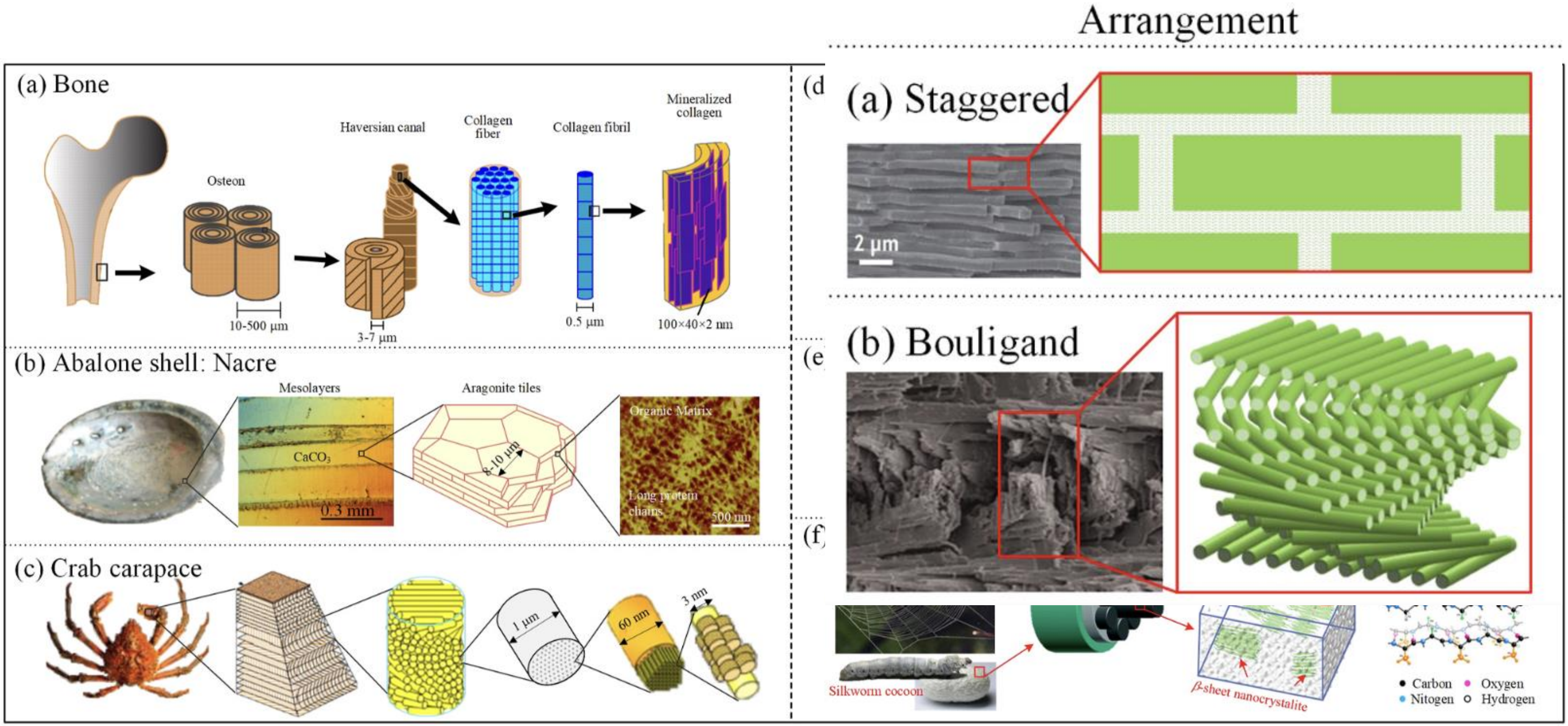
example: Aramid (Kevlar) fiber composite



unidirectional or woven structures



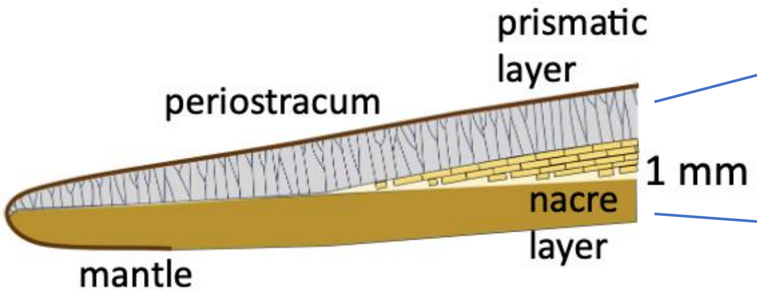
Bio-composites: hierarchical structure



Chen, Y., et al. (2021). Advances in mechanics of hierarchical composite materials. *Composites Science and Technology*, *214*, 108970.

Example: Mollusk shell

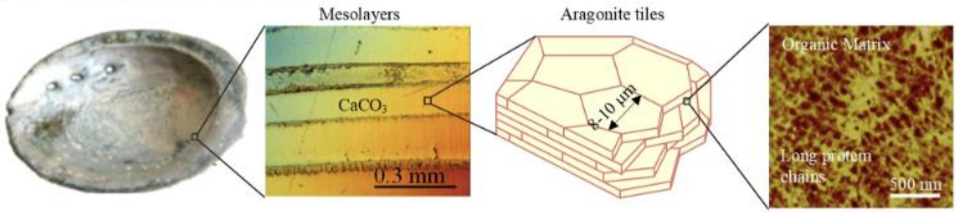
The crystalline structure of Calcium carbonate: Polymorph



prismatic layer: mainly calcite

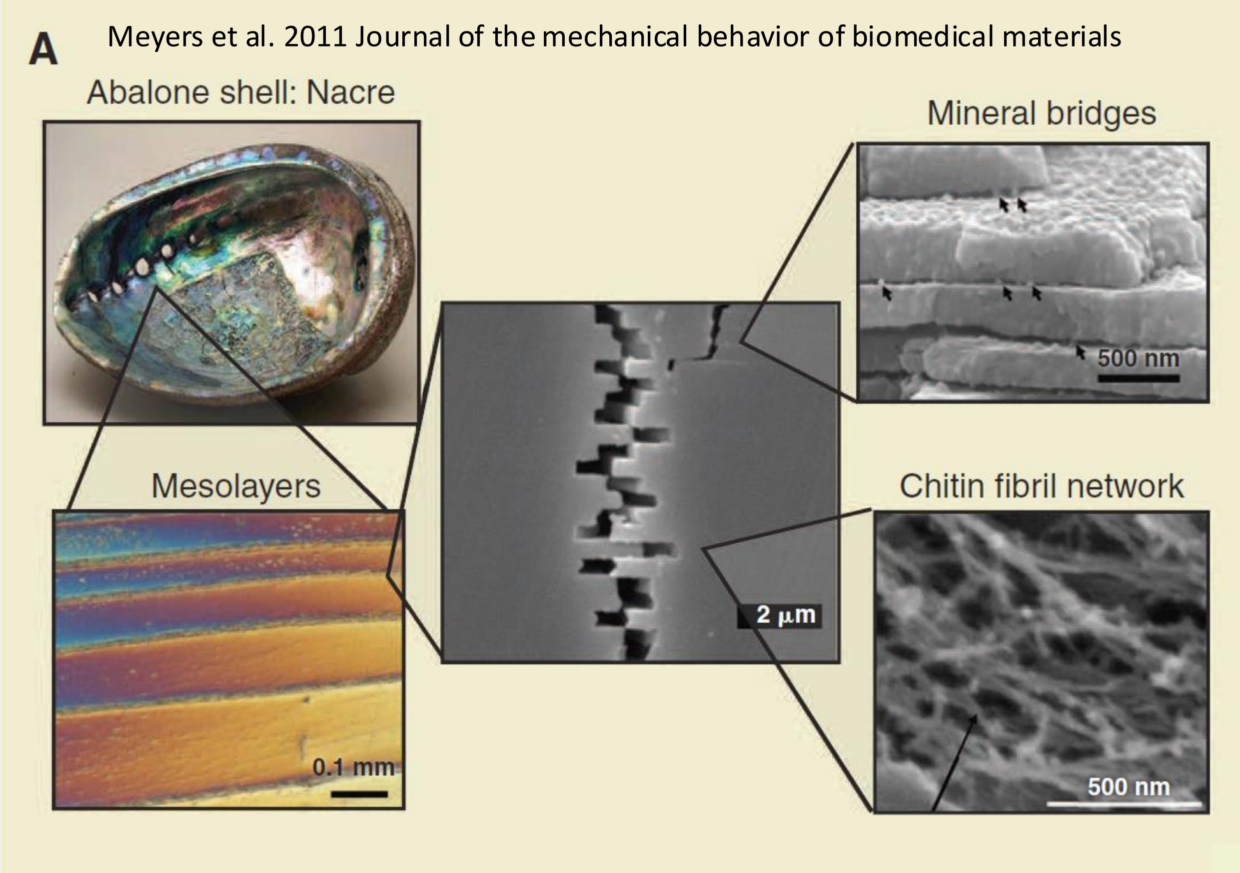
nacre layer: mainly aragonite

(b) Abalone shell: Nacre



Chen, Y., et al. (2021). Advances in mechanics of hierarchical composite materials. *Composites Science and Technology*, *214*, 108970.

Abalone nacre: a superior fracture toughness



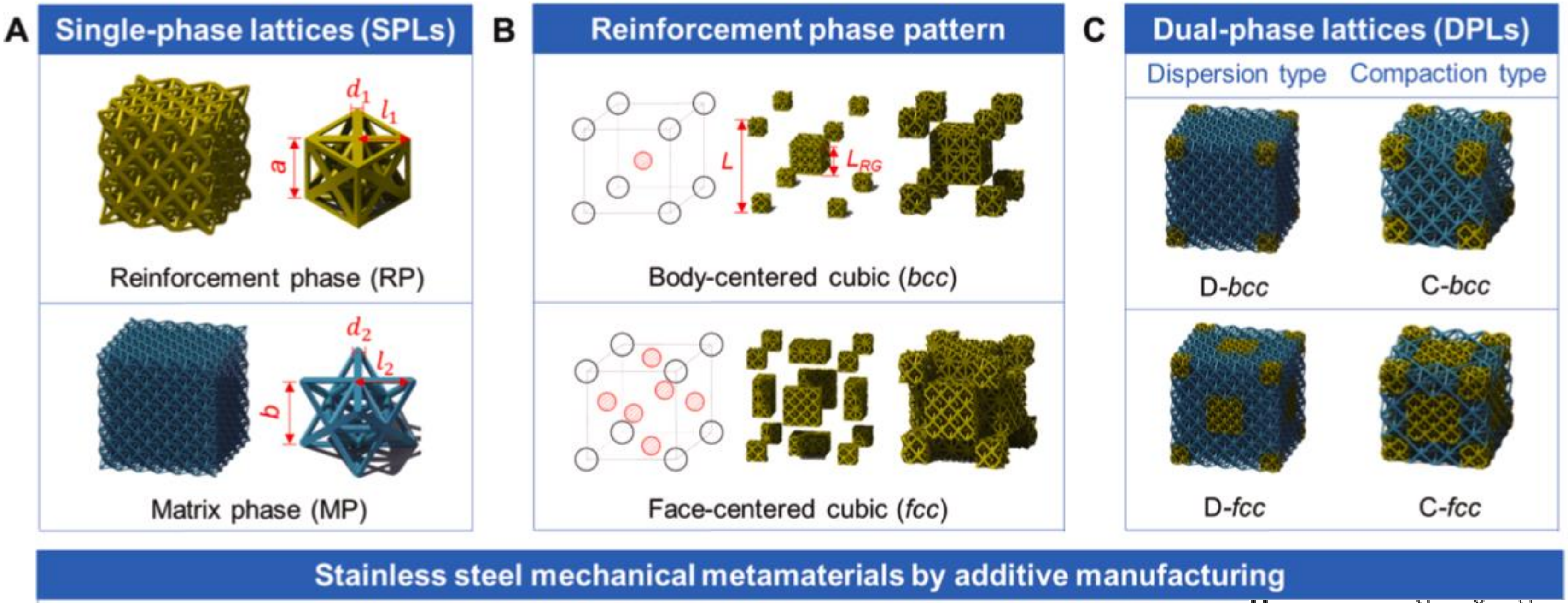
Meyers et al. 2011 Journal of the mechanical behavior of biomedical materials

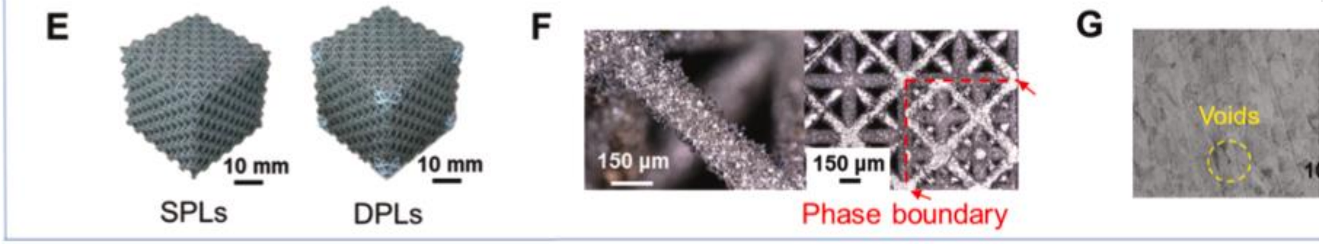
Three contributions to the mechanical performance

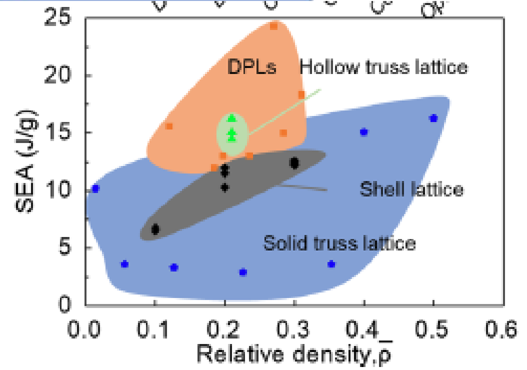
- Mineral bridges attach the tiles together
- Tile surfaces have asperities and produce frictional resistance and strain hardening
- Energy is required for stretching and shearing of the organic layer

Bioinspired materials

Strong and Tough Bioinspired Additive-Manufactured Dual-Phase Mechanical Metamaterial Composites







Yin, S.; Guo, W.; Wang, H.; Huang, Y.; Yang, R.; Hu, Z.; Chen, D.; Xu, J.; Ritchie, R. O.,. *Journal of the Mechanics and Physics of Solids* **2021,** *149.*

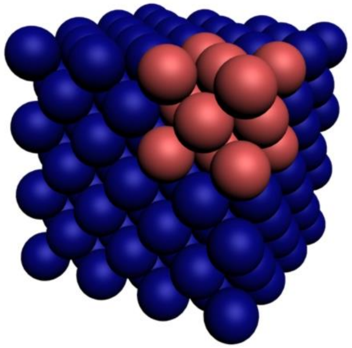
Recap

The hard sphere model

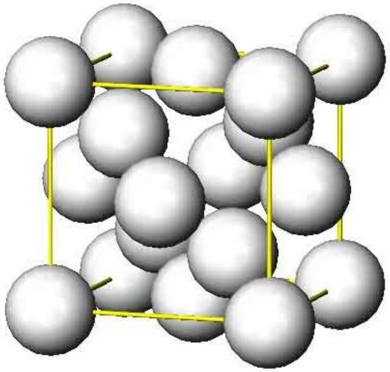
- A first intuitive representation of crystals can be obtained by considering atoms as hard spheres packed into 3D geometrical forms.

- Metals have loose requirement on the number of first neighbor . Intuitively, the closer the ions from one another, the higher the electrostatic potential they will create in the material, resulting in a lower energy for electrons. So **metals will tend to form dense packing**, up to 12 nearest neighbors !

- Semiconductors or dielectrics like C or Si that are **covalently bounded** will **need to respect the Octet rule** and to have 4 closest neighbor.



Face-centered Cubic structure typical of many metals: Al, Cu, Ag, Au, Ni..



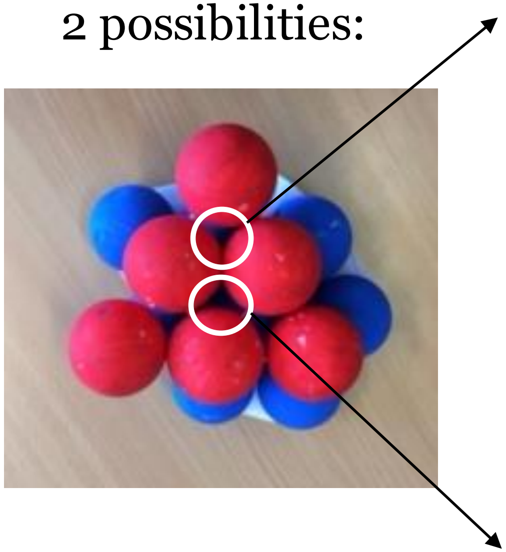
Diamond structure for C or Si: it looks more dense but actually is not !

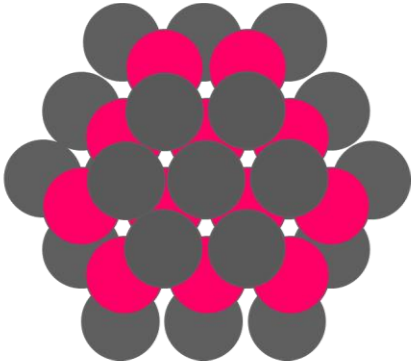
The hard sphere model

- 2D configuration:

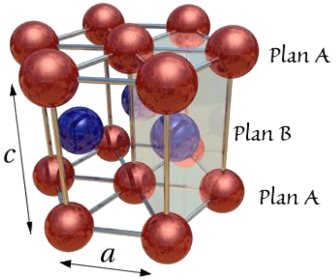
- 3D configuration:

2 possibilities:

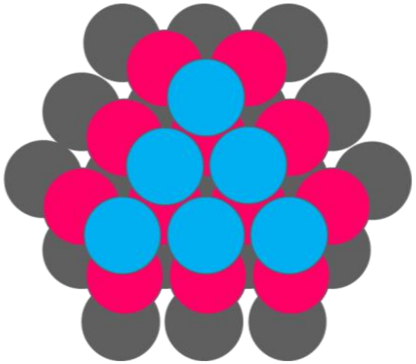




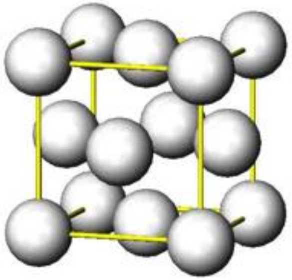
A-B-A



Hexagonal Compact



A-B-C



Face-centered Cubic

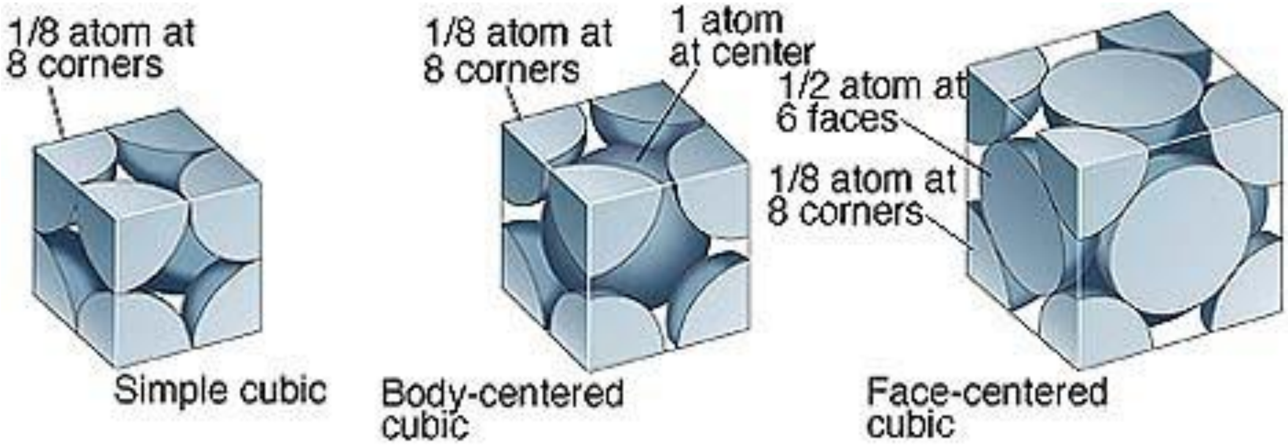
(= cubic-closed packed)

Packing density

- Represent motif as rigid spheres (hard sphere model) to give insight about the atomic arrangement and resulting properties
  - Packing factor/packing fraction $p = \frac{N_{atoms\ per\ unit\ cell} \times V_{atoms}}{V_{unit\ cell}}$

  also called compacity *c*

  - Density: $\rho = \frac{N_{atoms\ per\ unit\ cell} \times m_{atoms}}{V_{unit\ cell}}$

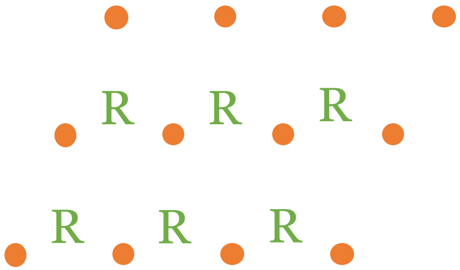


Crystalline material

- Definition: A **crystalline material** is a material characterized by a **regular arrangement of atoms** or group of atoms over "large" distances, i.e. a crystal displays translational symmetry over a long range.
  In a crystal it is always possible to **identify a group of atoms or molecules** (can be also one atom) that **repeats** itself periodically **on a grid** in space.

Crystal = Motif + Lattice

- in 2D



Motif: repeating "unit of pattern"
here represented by R
atom, group of atoms, molecules → chemical composition

Lattice: (imaginary) grid, intersections
→ lattice points ●
can be placed anywhere, but always in the same position with respect to the motif
in each point of the lattice, the crystal appears identical, **translational symmetry** in between

Crystalline material

- recap Definition: A **crystalline material** is a material characterized by a **regular arrangement of atoms** or group of atoms over "large" distances, i.e. a crystal displays translational symmetry over a long range.
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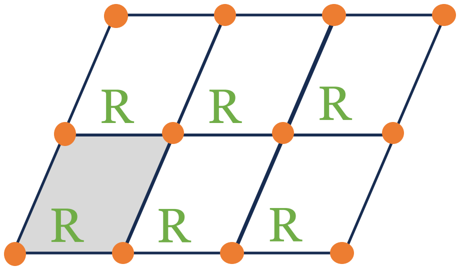
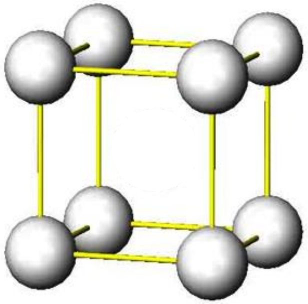


unit cell: arbitrary ways of joining up the lattice points.
primitive unit cell: smallest possible unit, contains one lattice point (here 4 times 1/4th)
conventional unit cell: larger unit cell, chose to reflect the crystal's symmetry better
contain more than one lattice points
makes visualization and classification of crystal structure easier

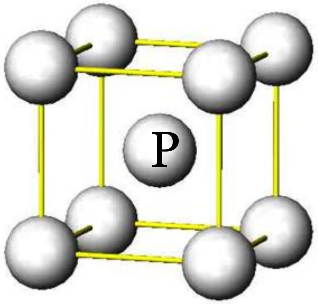
The cubic system: unit cells

primitive unit cell: smallest possible unit, contains one lattice point
conventional unit cell: larger unit cell, chose to reflect the crystal’s symmetry
contain more than one lattice points (and motifs)
makes visualization and classification of crystal structure easier

(**a**,**b**,**c**) is not a basis for BCC, P has the coordinates (1/2, 1/2, 1/2)



Primitive cubic
basis: (**a**,**b**,**c**)

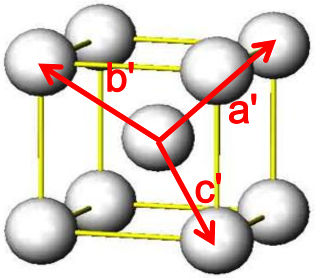


$$\vec{a}' = \frac{1}{2}(-\vec{a} + \vec{b} + \vec{c})$$

$$\vec{b}' = \frac{1}{2}(\vec{a} - \vec{b} + \vec{c})$$

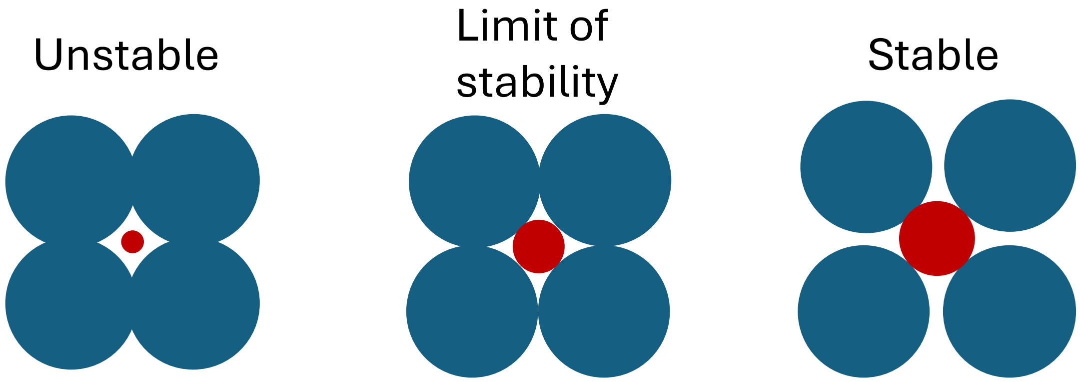
$$\vec{c}' = \frac{1}{2}(\vec{a} + \vec{b} - \vec{c})$$

Body-centered cubic
basis: (**a’**,**b’**,**c’**)



Interstitial Sites: Ionic crystals

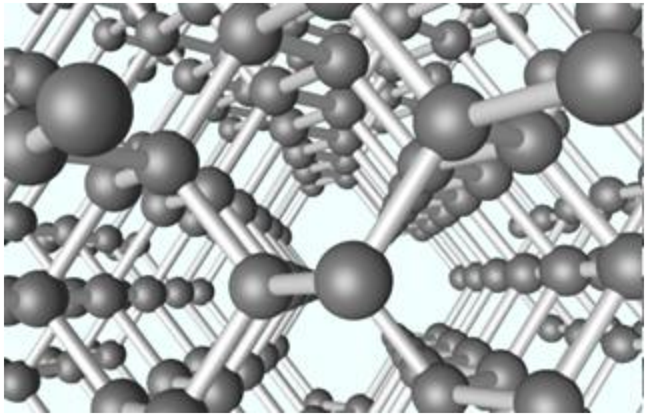
- Crystal structures have a certain packing density, and hence also a free volume where voids exist called interstitial sites.
- Different rules exist regarding the relative size of the Anions and the Cations in the molecules and their charges (take valence into account).
- For two atoms (NaCl, ClCs, ZnS etc…), a first rule called the Radius Ratio rule, or first Pauling rule, establishes a formula that defines the coordination number depending on the ratio of the radius of the cation to the one of the anion:
- $\rho = \frac{r_+}{r_-} = \sqrt{\frac{12}{12-CN}} - 1$, where CN = coordination number
- Based on the hard sphere model, it predicts that if the cation is too small, anions get too close to each other which lead to an unstable structure due to repulsive forces.



Covalent crystals and covalent/ionic crystals

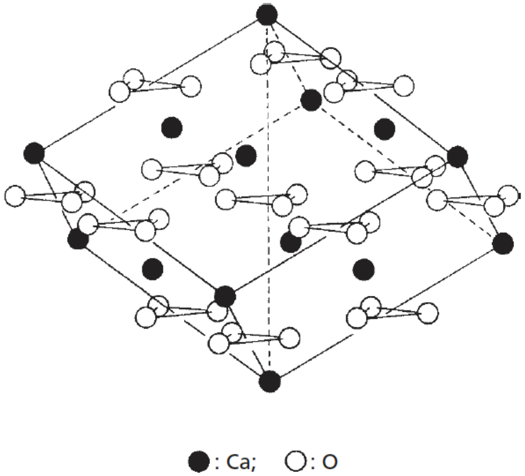
- While ionic crystals and crystals with metallic bonds usually take closed packed forms, the structure of covalent crystals is dictated by the directional covalent bond and the configuration of the atomic orbitals
- high strength of covalent and ionic bonds: high hardness

“pure” covalent crystals:
Diamond, Silicon
sp^3 orbitals → tetrahedrally
coordination number: 4



packing fraction only 34%

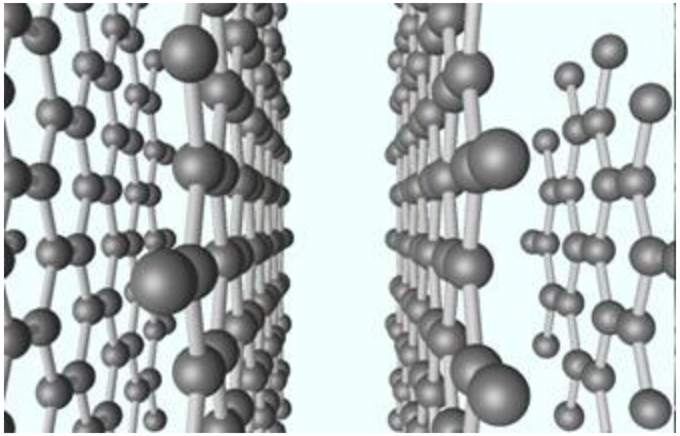
many inorganic crystals
mixture of covalent and ionic bonds
$Ca^{+} (CO_3)^{-}$



Covalent and VDW crystals

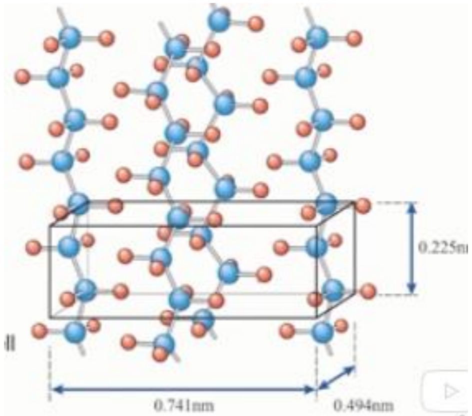
- Layered inorganic structures: covalently bond within a layer, van der Waal bonds between the layers: graphite, talc, mica
- Organic crystal: covalent bonds within molecule, van der Waal (and H-bonds) in between

covalent bond
sp_2 orbital → planar
in between Van der Waal bonds



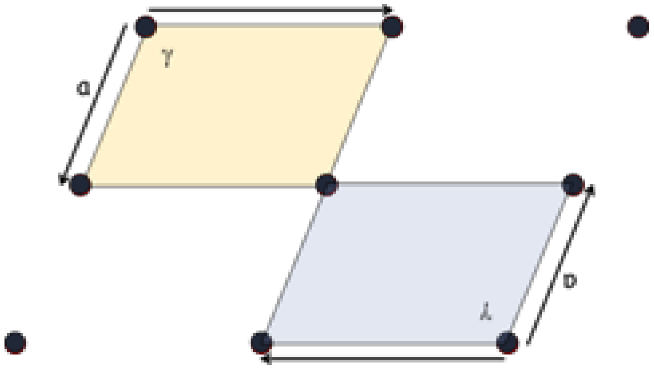
graphite
→ anisotropic mechanical properties

organic crystals
molecules strongly bond
if they can be arranged regularly form crystal



Polyethylene crystal
→ soft materials

Symmetries in lattice

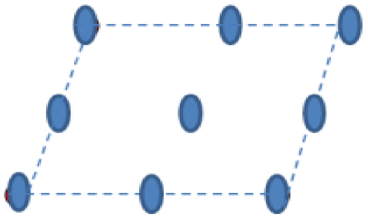


Unit cell with

- The two shortest vectors, a≠b
- Both angles are "closest" to 90°
- Primitive "P"

→ oblique lattice

180° rotational symmetry → 2-fold axis ⬮ "2"

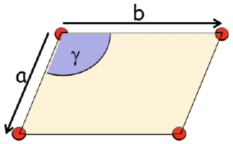
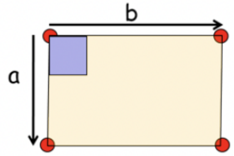
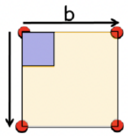
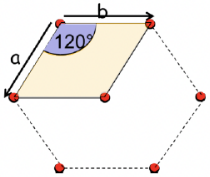
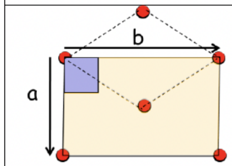


- **A symmetry operation** is an action that leaves an object unchanged.
- **A symmetry element** is a part of the object that doesn't move during the operation: a point, a line, a plane, an entire object.

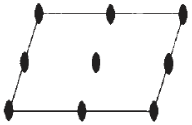
rotational symmetry is a point symmetry
(at least one point remains unchanged)

5 plane lattices → classification according to symmetry

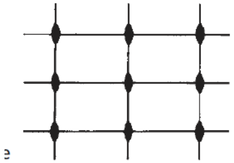
- lattice: how translation is done, classified according to symmetry in a plane

2D lattice	Maximal symmetry of 2D lattice
 **oblique P** a ≠ b ; γ ≠ 90, 120°	2-fold axis
 **rectangular P** a ≠ b ; γ = 90°	2-fold axis with two reflection lines
 **square P** a = b ; γ = 90°	4-fold axis with two reflection lines
 **Hexagonal P** a = b ; γ = 120°	6-fold axis with three reflection lines
 **rectangular C** a ≠ b ; γ = 90° When a primitive lattice is taken, it is called Rhombic	2-fold axis with 2 reflection lines

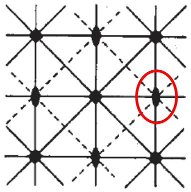
notation according to Hermann–Mauguin



p2

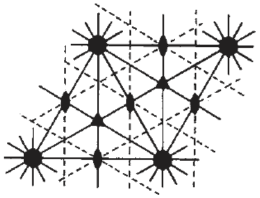


p2mm

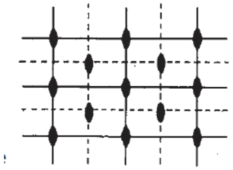


p4mm

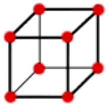
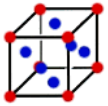
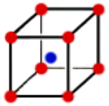
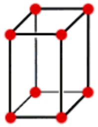
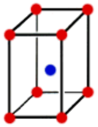
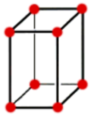
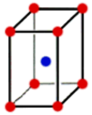
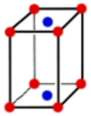
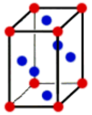
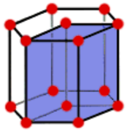
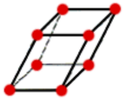
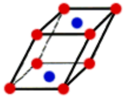
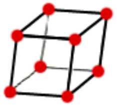
→ additional symmetries, such as 2-fold axis, the highest symmetry is given



p6mm



c2mm

in 3D: 7 crystal system		14 Bravais lattices	defining symmetry
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	 Simple cubic  Face-centered cubic  Body-centered cubic	4x 3-fold axis 3x 4-fold axis
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	 Simple tetragonal  Body-centered tetragonal	4-fold axis
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	 Simple orthorhombic  Body-centered orthorhombic  Base-centered orthorhombic  Face-centered orthorhombic	3x 2-fold axis
Trigonal or rhombohedric	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	 Rhombohedral	3-fold axis
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ; \ \gamma = 120^\circ$	 Hexagonal	6-fold axis
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	 Simple Monoclinic  Base-centered monoclinic	2-fold axis
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	 Triclinic	1-fold axis

Point groups

- Point groups are mathematical constructs that capture all the non-translation symmetry options that can be performed on an object: reflection, rotation, (rotoinversion in 3D)

- From mathematical group theory
  - Closure: The combination of symmetry operators is a symmetry operator in the group.
  - All symmetry operators have an inverse, some are their own inverse.
  - Identity is part of all the Point group symmetry.
  - Associativity is respected

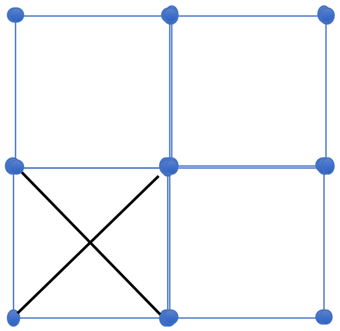
- A Point Group describes all the symmetry operations that can be performed on a motif that result in a conformation indistinguishable from the original.
- all symmetry operations of a point group must pass through the center of the object (point symmetry)

Symmetry operations in 2D

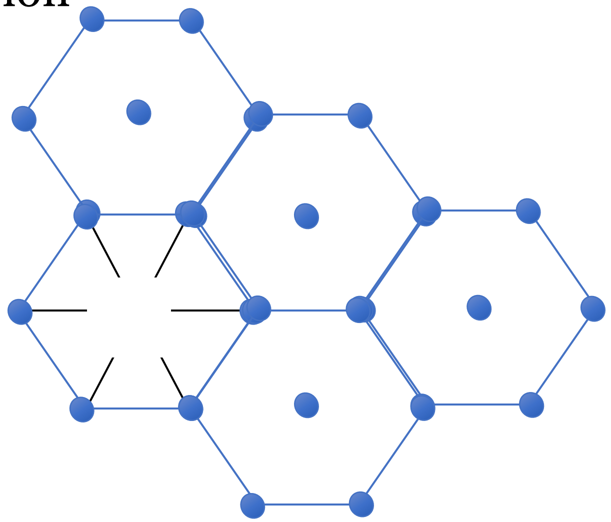
For discrete objects, rotational symmetries can only be discrete: $\frac{2\pi}{n}$

rotational symmetry must be compatible with a translational symmetry!

n=1 → 1-fold, no symmetry
n=2 → 2-fold, 180° rotation
n=3 → 3 fold, 120° rotation
n=4 → 4 fold, 90° rotation
n=6 → 6 fold, 60° rotation

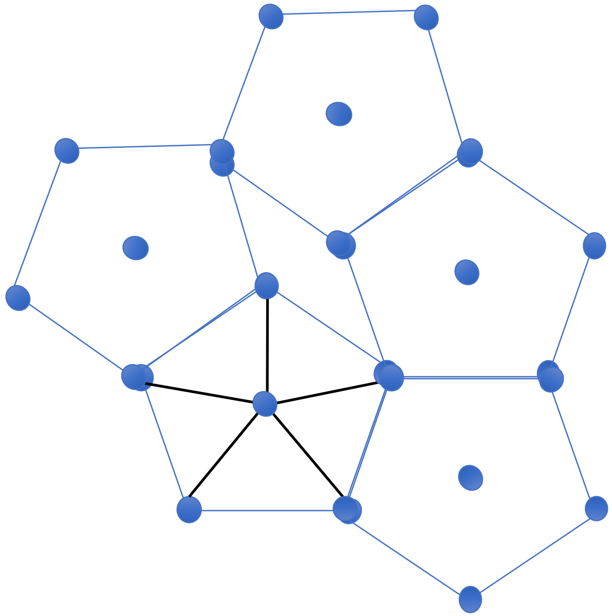


4-fold



6-fold

no 5-fold!



and mirror symmetry (m)

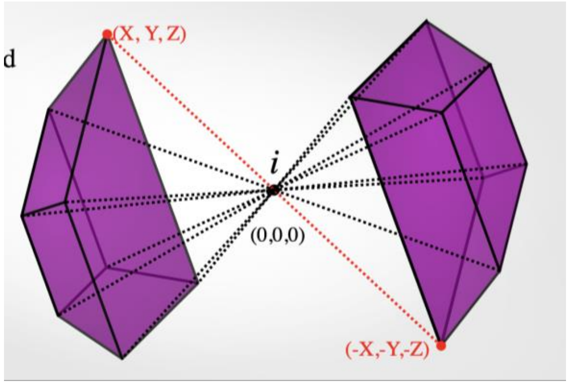
Point Symmetry operations in 3D

- **Rotation axis**
  1-fold (no symmetry)
  2-fold (180° rotation)
  3-fold (120° rotation)
  4-fold (90° rotation)
  6-fold (60° rotation)

→ in 2D rotation axis perpendicular to the plane
→ in 3D there can be several axes in idfferent directions
(but always through the center of the object)

- **Reflection or mirror plane**

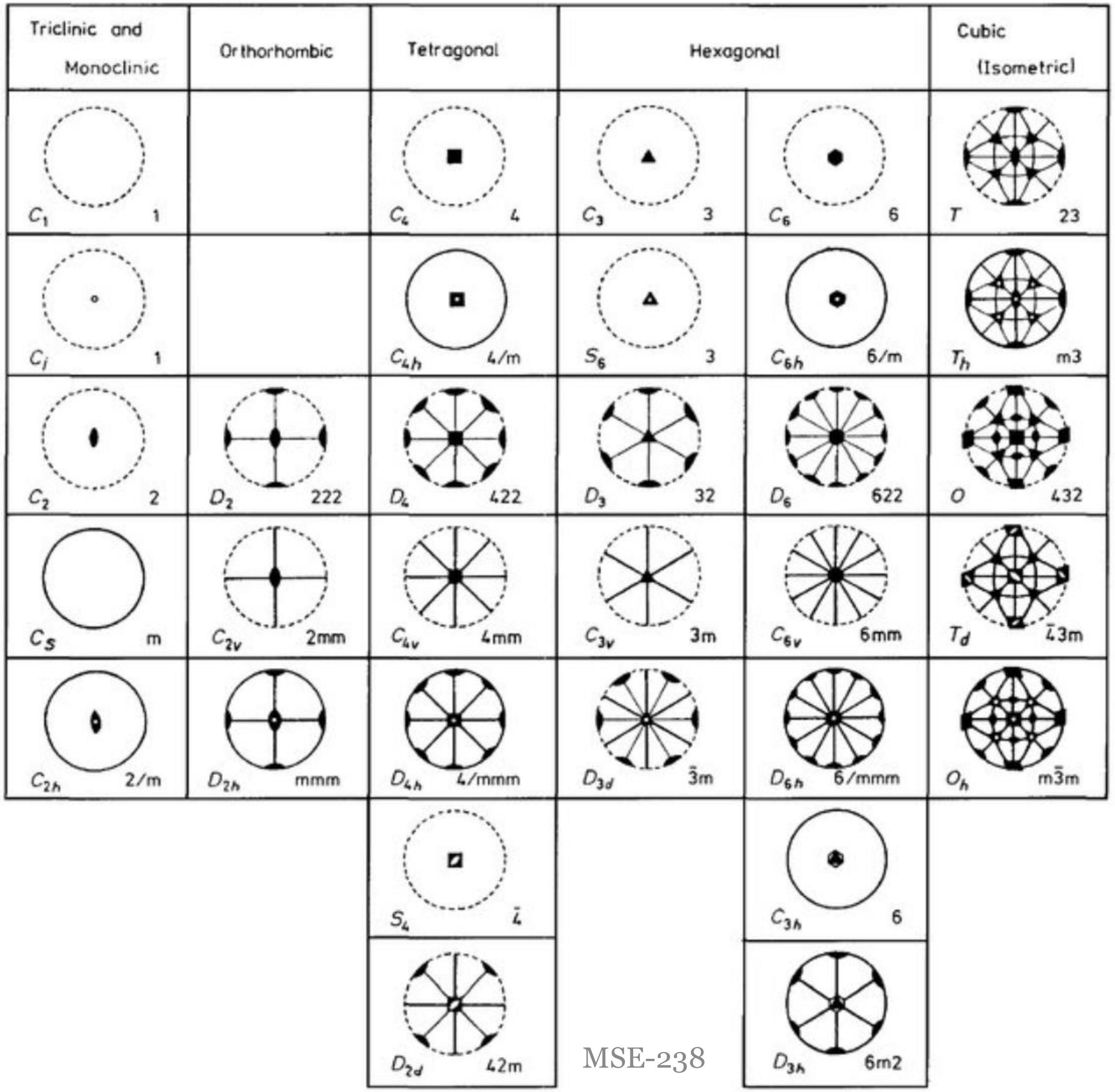
- **the inversion center and the roto-inversion axis**



every point pulled through center of inversion *I*

rotation and inversion combined → roto-inversion

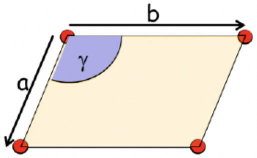
32 Point groups in 3D



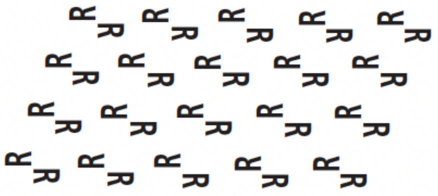
2D Plane groups

crystal = lattice + motif

combine the 10 2D point groups with the appropriate 5 lattice
→ total number of 2D pattern, the so called plane groups

2D lattice	Maximal symmetry of 2D lattice
 **oblique P** $a \neq b$; $\gamma \neq 90, 120°$	2-fold axis

p1 (1)



p2 (2)

For the oblique lattice, a motif with no symmetry would match.
A motif with a 2-fold symmetry also

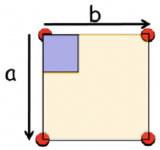
we could put the point group 2 on a square lattice

But it does not bring new symmetry, no 4-fold symmetry, but the 2-fold symmetry is maintained: so it is the same group symmetry as the oblique p2.
→ no new plane group

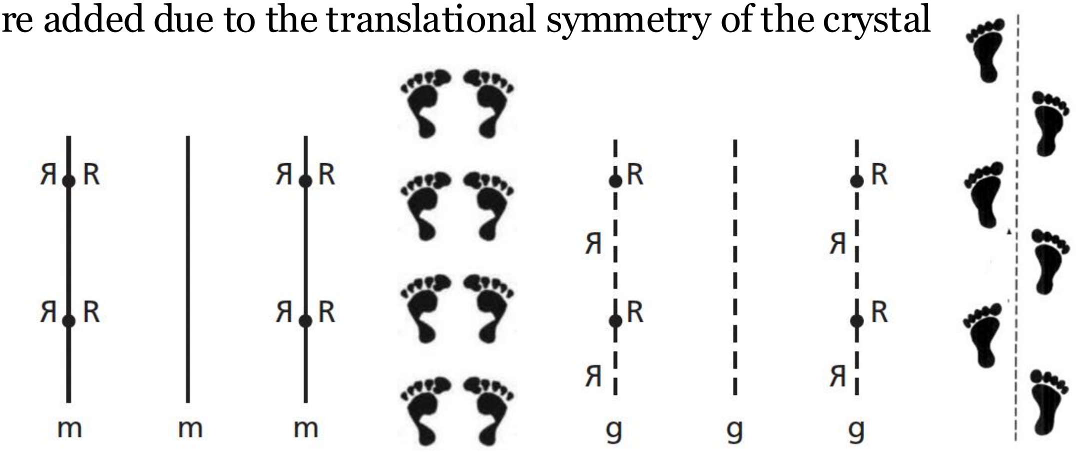
Travel symmetry operations 2D

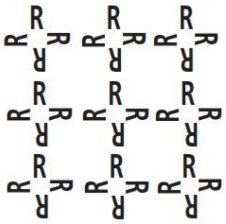
Point symmetries combined with the lattice of matching symmetry:

4 fold symmetry will only be associated to the square lattice.

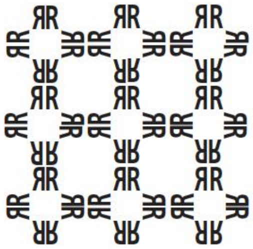
	***square P*** a = b ; γ = 90°	4-fold axis with two reflection lines

- One could think that there is only 2 plane groups associated with the 2 point groups noted 4 and 4mm.
- There is however a third one
  Associated to a glide plane symmetry noted g.
- Glide planes are added due to the translational symmetry of the crystal

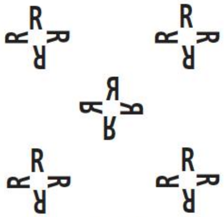




p4 (10)



p4mm (11)



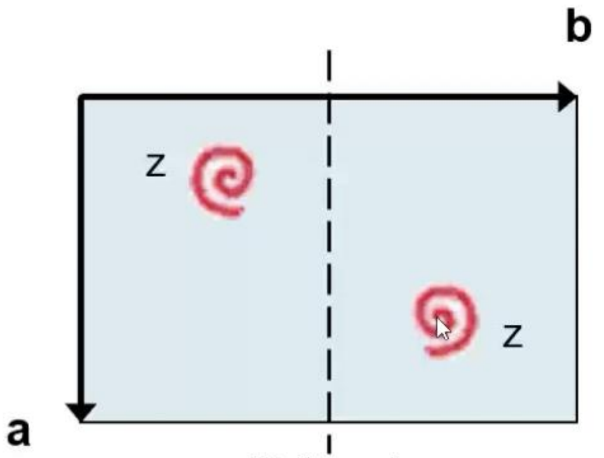
p4gm (12)

90° symmetry

Travel symmetry operations in 3D

Glide plane:

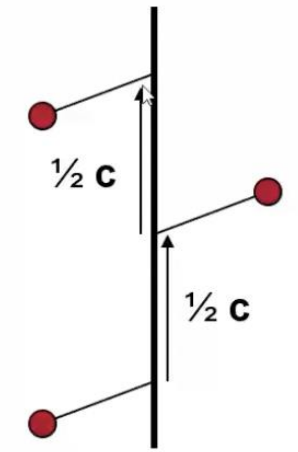
Reflect through a plane then translate parallel to it



a glide plane
translate by ½ **a**

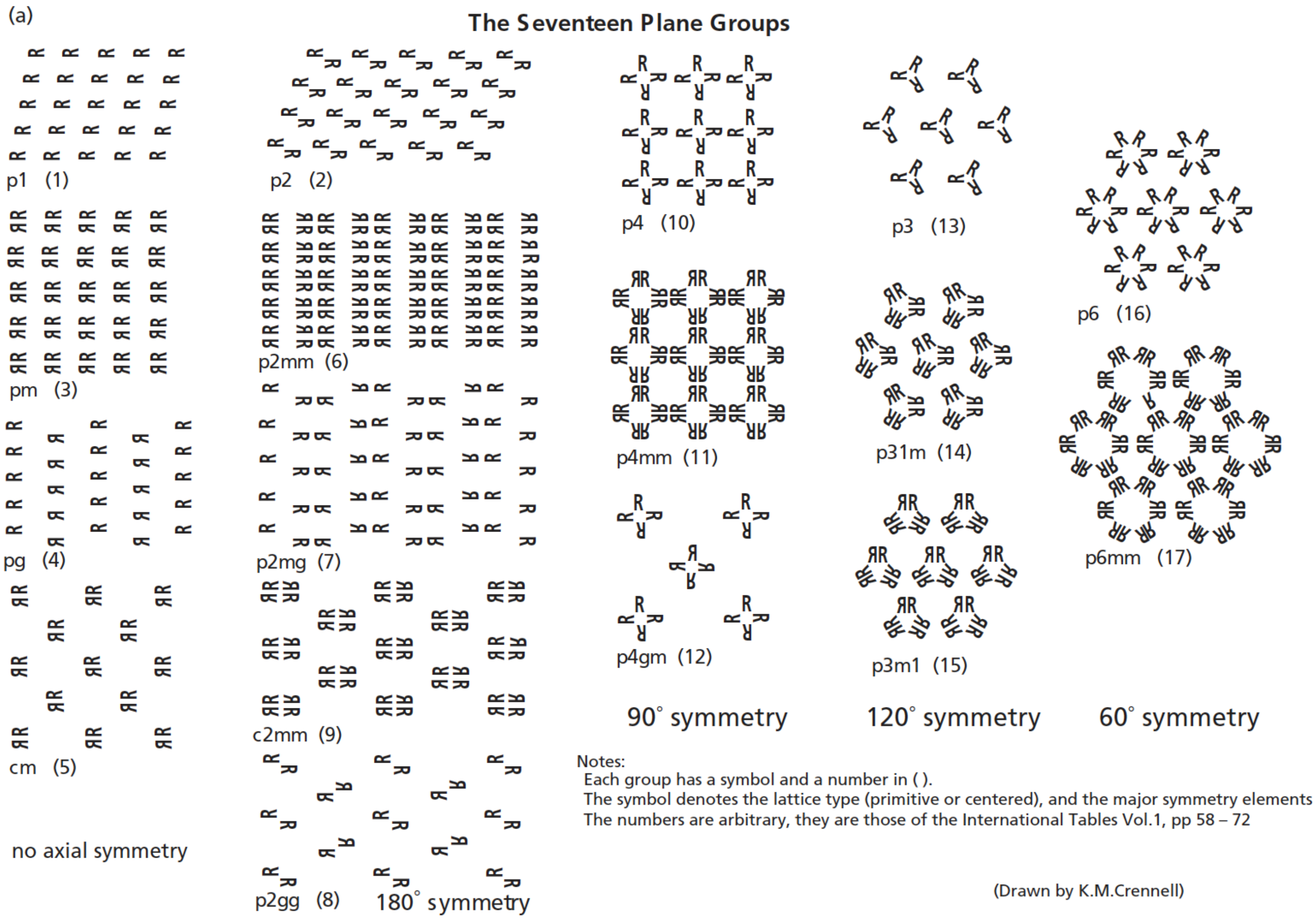
Screw axis

Rotation by 360/N around an axis and translation along the axis



2_1 screw axis
Rotate by 180°
Translate by ½ **c**

17 plane groups in 2D



The Seventeen Plane Groups

Notes:
Each group has a symbol and a number in ( ).
The symbol denotes the lattice type (primitive or centered), and the major symmetry elements
The numbers are arbitrary, they are those of the International Tables Vol.1, pp 58 – 72

(Drawn by K.M.Crennell)

230 The Space Group List Project

by Frank Hoffmann

More information at
crystalsymmetry.wordpress.com

Crystal structures drawn with VESTA
K. Momma and F. Izumi, J. Appl. Crystallogr. 2011, 44, 1272-1276.

230 space groups in 3D

- The construction of the space groups associated to the 3D 14 Bravais lattices, from the 32 3D point groups, proceed similarly than in 2D, but:
    - 3D has 32 point groups and not 10, because of extra possible symmetry operations: inversion and roto-inversion.
    - For glide planes, the glide can happens along different directions in 3D;
    - Screw axis operations also occur: n_m is a n-fold rotation followed by a translation

- The first letter is a capital letter indicating the Bravais lattice, and many different types occur: P, I, F, C

- Glides bring several new types of symmetries and notations:
    - a,b,c: glide translation along half the lattice vector of this face;
    - N,d: glide translation along half and a quarter respectively, along the face diagonal
    - e: two glides with the same glide plane and translation along two half-lattice vectors.

- There are 230 space groups that can be built from the 32 point group in 3D.

- A list of all the space groups can be found here: https://en.wikipedia.org/wiki/List_of_space_groups

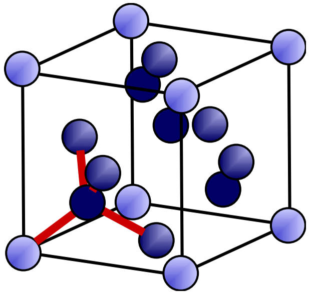
- A more concise one: https://en.wikipedia.org/wiki/Space_group

- You can find them all here: https://onlinelibrary.wiley.com/iucr/itc/Ac/contents/

Symmetry in 3D: Space groups

- For the cubic Bravais Lattice, the BCC and FCC structures add atoms that do not change the symmetry operations !
- Space groups are then $P4/m\bar{3}2/m$, I$4/m\bar{3}2/m$ and F$4/m\bar{3}2/m$ respectively.
    - Example: let's look at F$4/m\bar{3}2/m$ (#225)

for example Aluminium



- What happens when we change the motif ? Diamond structure:
    - The extra atom in this case changes the possible symmetries
    - Space group: Fd$\bar{3}m$ (#227): → glide symmetry gained, other lost
    - still highly symmetric, order of the group 48

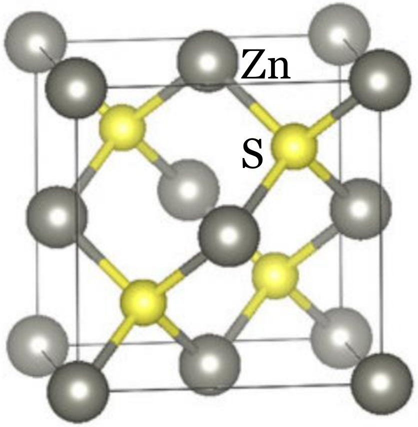
As the motif looses symmetry, the symmetry of the resulting crystal tends to be lower.

Symmetry in 3D: Space groups

What happens when we add atoms of different nature ?

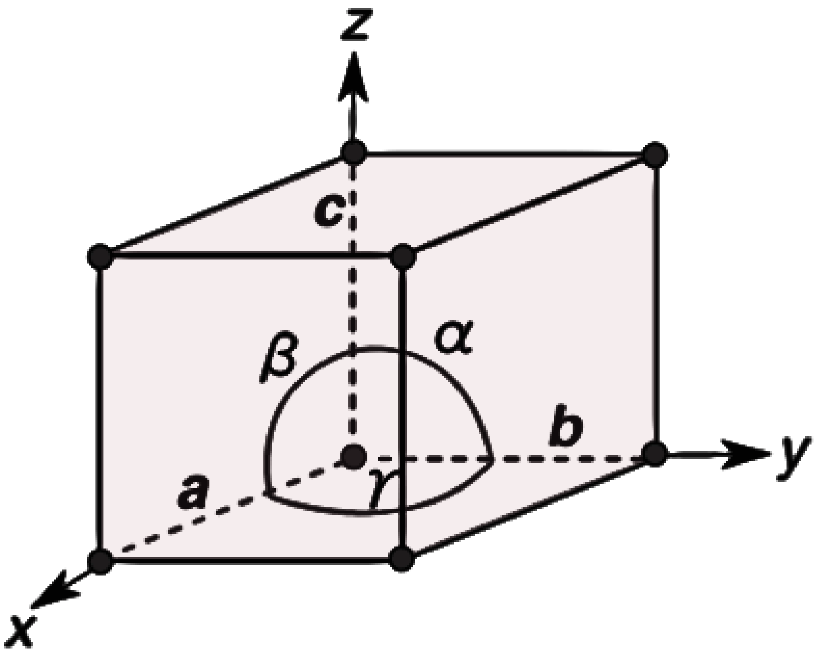
- Diamond structure becomes Zincblende when considering two different atoms

- Example: ZnS
- Space group $F\bar{4}3m$ (#216): less symmetries. Order of the group 24
- No more glide symmetry since the two atoms are of different nature



When adding atoms of different nature, the symmetry also tends to get lower.

Geometry of the unit cell



right-handed set of crystallographic axes, x,y,z which point along the edges of the unit cell. The origin of our coordinate system coincides with one of the lattice points

The length of the unit cell along the x,y and z direction are defined as a,b, and c. The angles between the crystallographic axis are defind by
α = the angle between b and c
β = the angle between a and c
γ = the angle between a and b

a, b, c, α, β, γ are collectively known as the **lattice parameters** (often also called ‘unit cell parameters’, or just ‘cell parameters’).

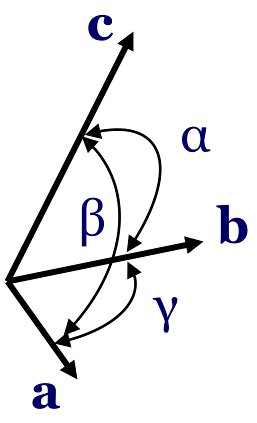
→ Miller indices are a coordinate system!
→ it depends on the unit cell structure, and with that on the crystal system

Crystalline material

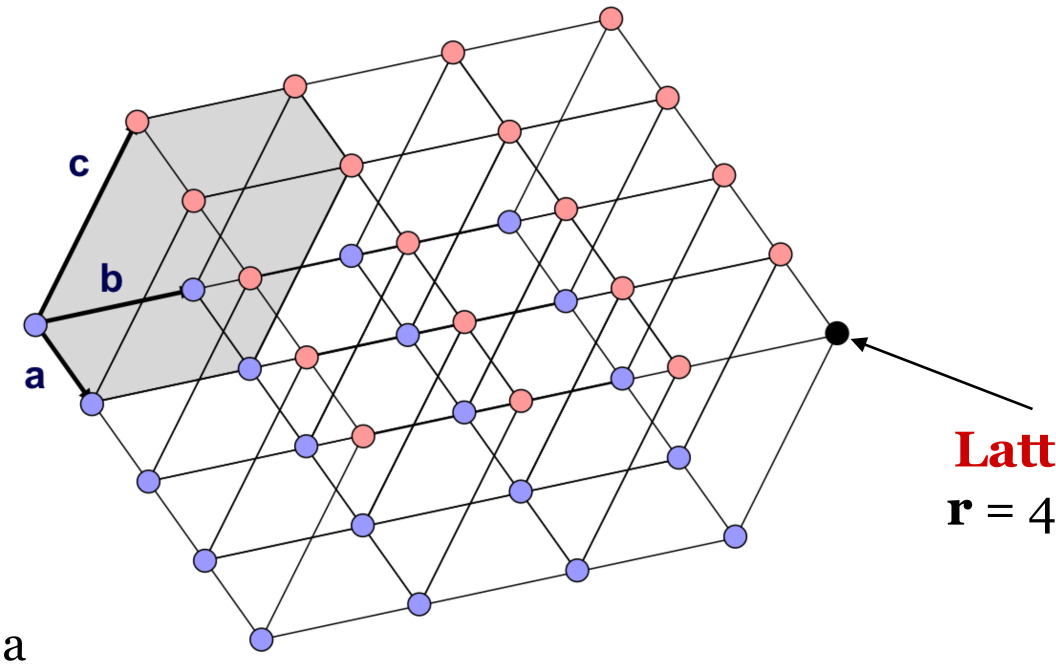
- in 3D: Bravais Lattice

The Bravais lattice is expressed mathematically as an infinite set of points with translational symmetry along three axis that form a vector basis. Choosing an origin O, one can write

$$\mathcal{B} = \{P, \boldsymbol{OP} = n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c}, (n_1,n_2\ n_3) \in \mathbb{Z}^3\}$$



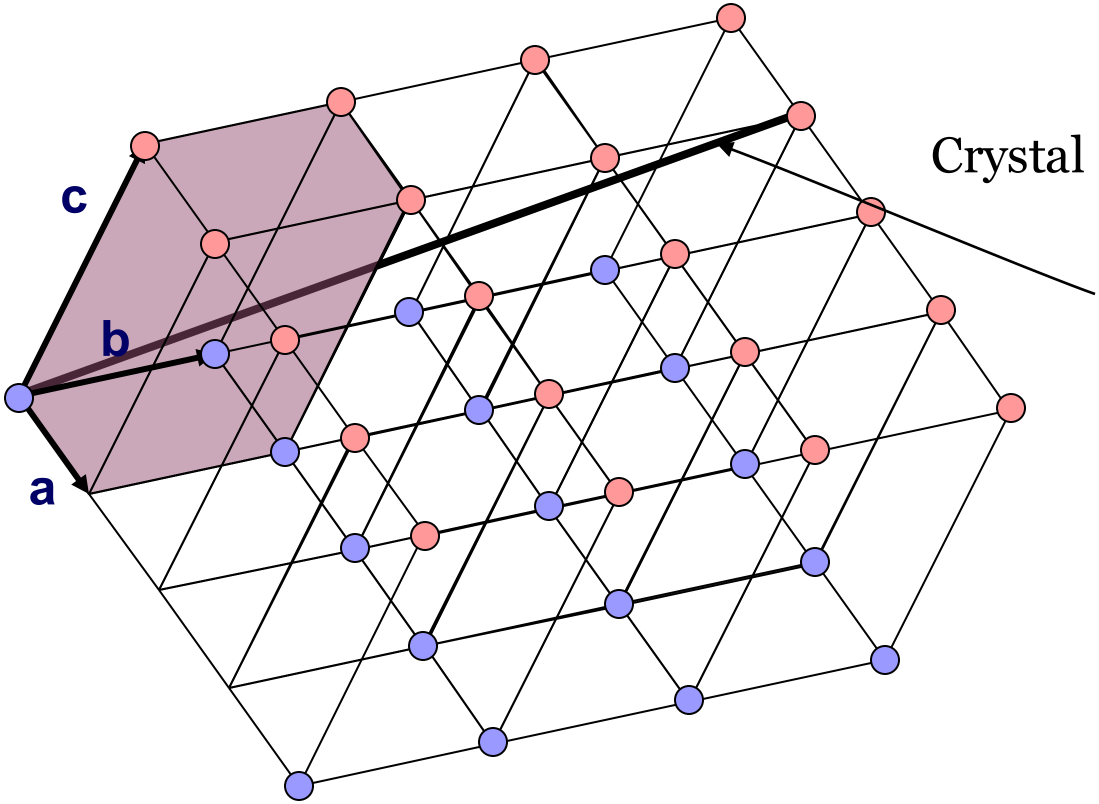
set of 3 vectors
form the basis:
every lattice point is a linear combination with relative integers as coefficients



Lattice point
$\mathbf{r} = 4\mathbf{a} + 3\mathbf{b} + \mathbf{c}$

Crystal directions

- Crystal directions are lines that pass through at least two lattice points.
- The direction can be defined by an origin (all lattice point can be an origin) and the coordinate of the other point in the lattice basis.
- The coordinates, which are relative integers, represent the Miller indices.



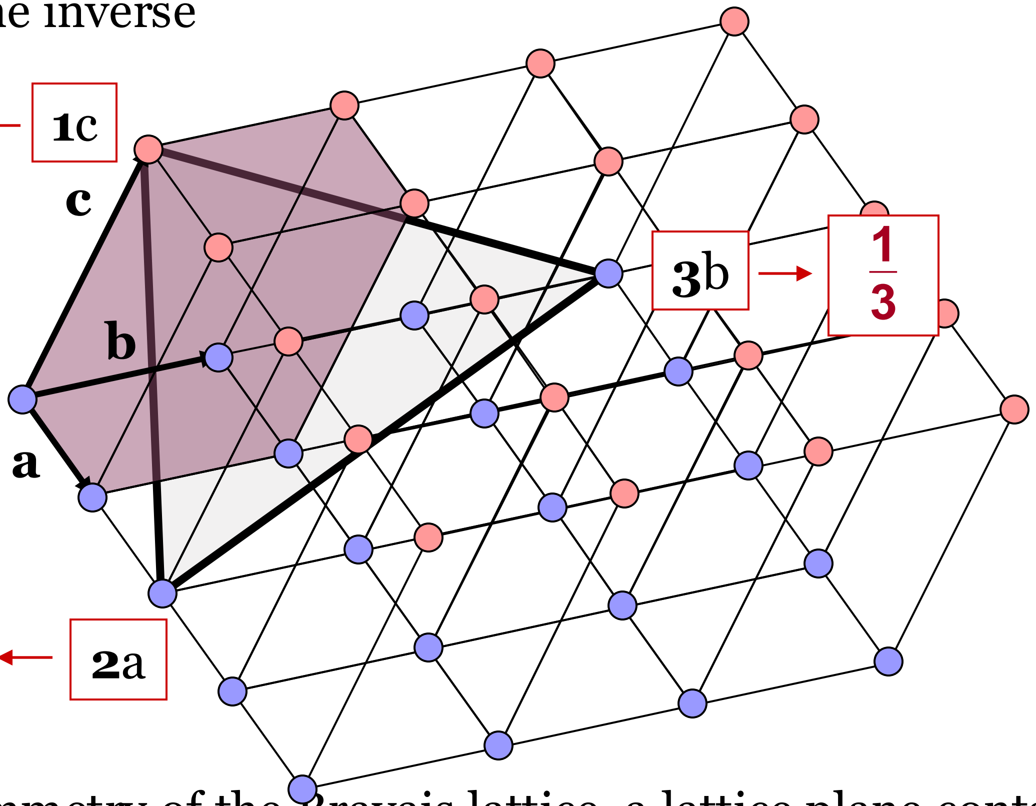
Crystal Direction : **r** = λ(1**a** + 3**b** + 1**c**)

[1 3 1]

if they are not integers, multiply by common denominator to get the Miller index

Crystal planes

- Crystal or lattice planes are planes that pass through at least 3 lattice points.
- They can be defined by the intercept of the plane with the basis axis:



take the inverse

$\frac{1}{1} \leftarrow$ 1c

3b $\rightarrow \frac{1}{3}$

$\frac{1}{2} \leftarrow$ 2a

lowest common multiple

$$\boxed{\left(\frac{1}{2}\quad\frac{1}{3}\quad\frac{1}{1}\right)\times 6 = (3\ 2\ 6)}$$

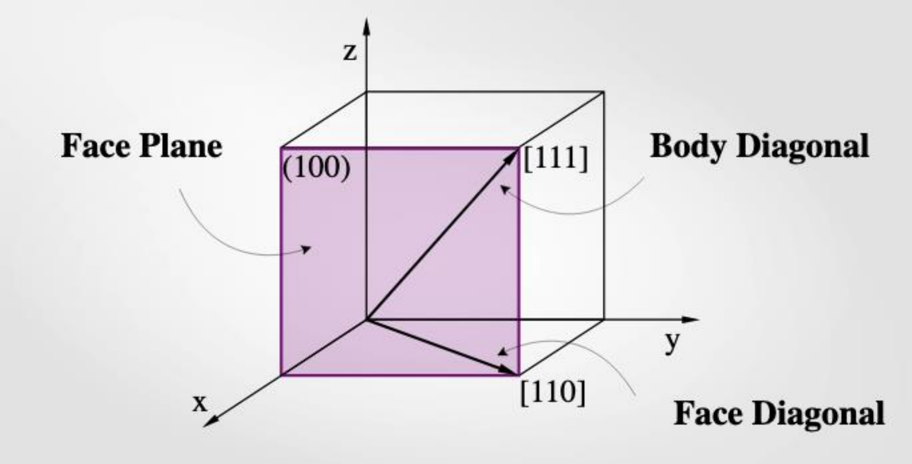
- Because of the translational symmetry of the Bravais lattice, a lattice plane contains an infinite number of lattice points

Summary of notations

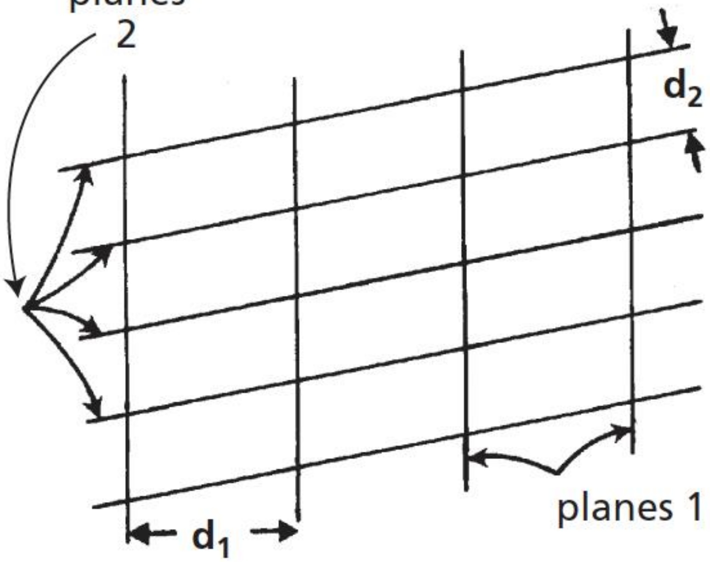
(h, k, l) is for points. Remember to use the negative sign (-*h*) instead of bar sign ($\bar{h}$) and **don't** reduce fractions–these rules apply to directions and planes.

[hkl] is for a specific direction.
<hkl> is for a family of directions.

(hkl) is for a specific plane. Remember about reciprocal (inverse) space in planes!
{hkl} is for a family of planes.



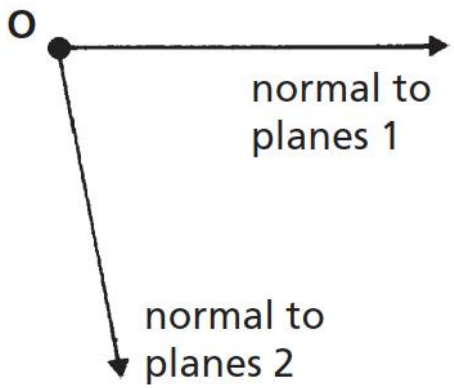
Reciprocal lattice vectors



(a)

two families of planes with d-spacing d_1 and d_2

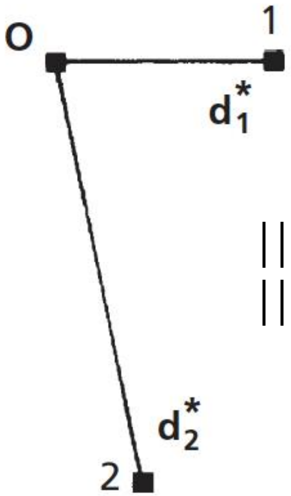
direction normal to plane



(b)

normals to the family of planes from common origin O

length inversely proportional to lattice spacing d



$||\mathbf{d}_1^*|| = C/d_1$

$||\mathbf{d}_2^*|| = C/d_2$

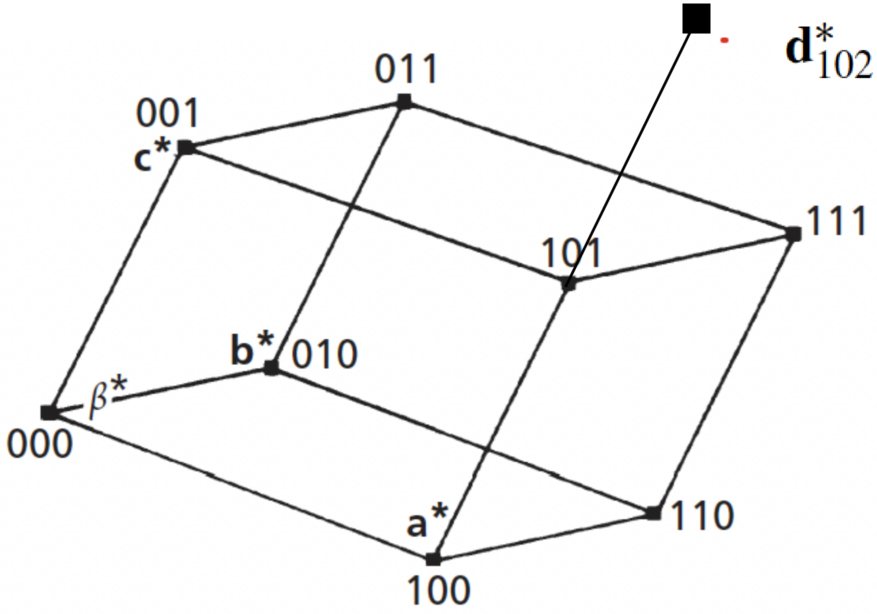
$C = 2\pi$

(c)

reciprocal (lattice) vectors

longer vector for smaller d-spacing

Reciprocal lattice



The reciprocal lattice unit cell of a monoclinic P crystal defined by reciprocal lattice vectors **a***, **b*** and **c***

for the (102) planes:

$$\mathbf{d}^*_{102} = 1\mathbf{a}^* + 0\mathbf{b}^* + 2\mathbf{c}^*$$

for the (hkl) planes:

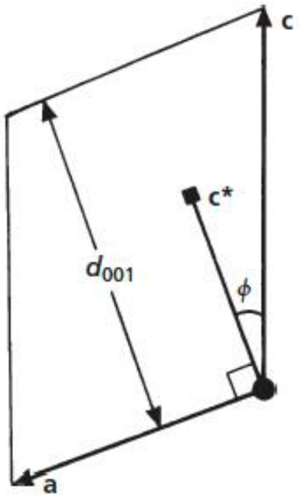
$$\mathbf{d}^*_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*.$$

plane indices are components of the $\mathbf{d}^*_{hkl}$ vector

direct lattice vector: directions are its components

$$\mathbf{r}_{uvw} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

Reciprocal lattice



Plan of a monoclinic unit cell perpendicular to the y-axis

c* is perpendicular to both **a** and **b**, which means their dot products are zero

c* • **a** = 0 and **c*** • **b** = 0

c* • **c** = cc* cos ϕ

with $||\mathbf{c}^*|| = 2\pi/d_{001}$ and from drawing: c cos ϕ = d_{001}

c* • **c** = $2\pi d_{001}/d_{001} = 2\pi$

does we have:

$$\begin{array}{lll}
\vec{a^*}.\ \vec{a} = 2\pi & \vec{b^*}.\ \vec{a} = 0 & \vec{c^*}.\ \vec{a} = 0 \\
\vec{a^*}.\ \vec{b} = 0 & \vec{b^*}.\ \vec{b} = 2\pi & \vec{c^*}.\ \vec{b} = 0 \\
\vec{a^*}.\ \vec{c} = 0 & \vec{b^*}.\ \vec{c} = 0 & \vec{c^*}.\ \vec{c} = 2\pi
\end{array}$$

We have a new basis new basis (O, **a***, **b***, **c***) in which a vector $\mathbf{N}^*_{\mathbf{hkl}}$ = h**a*** + k**b*** + l**c*** is perpendicular to the plane (hkl)

If we consider any vector in the direct space $\boldsymbol{R} = r_1\boldsymbol{a} + r_2\boldsymbol{b} + r_3\boldsymbol{c}$ and one in the reciprocal space $\boldsymbol{N}^* = n_1\boldsymbol{a}^* + n_2\boldsymbol{b}^* + n_3\boldsymbol{c}^*$, we have:

$$\boldsymbol{R}\cdot\boldsymbol{N}^* = r_1n_1\boldsymbol{a}\cdot\boldsymbol{a}^* + r_2n_2\boldsymbol{b}\cdot\boldsymbol{b}^* + r_3n_3\boldsymbol{c}\cdot\boldsymbol{c}^* = 2\pi(r_1n_1 + r_2n_2 + r_3n_3)$$

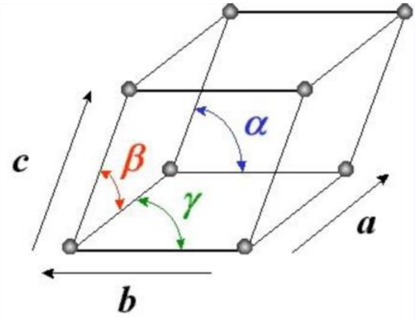
an integer

Find the reciprocal space vectors from direct lattice vectors

find **a*** which is orthogonal to **b** and **c** → cross product!
and fullfills **a** • **a*** = 2π

Reminder Volume:

$$V = (\vec{a}, \vec{b}, \vec{c}) = \vec{a} \cdot (\vec{b} \times \vec{c}) = \vec{b} \cdot (\vec{c} \times \vec{a}) = \vec{c} \cdot (\vec{a} \times \vec{b})$$



$$\mathbf{a}^* = (\boldsymbol{b} \times \boldsymbol{c}) \frac{2\pi}{V}$$

$$\mathbf{a} \cdot \mathbf{a}^* = \mathbf{a} \cdot (\boldsymbol{b} \times \boldsymbol{c}) \frac{2\pi}{V} = 2\pi$$

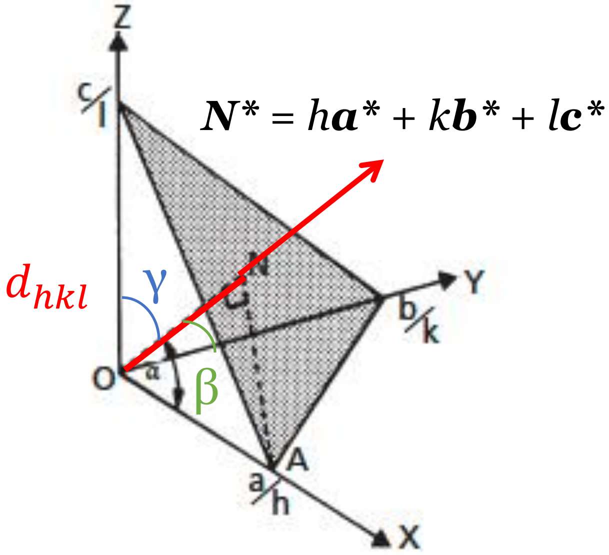
so we can find the reciprocal space vectors by:

$$\vec{a^*} = 2\pi \frac{\vec{b} \times \vec{c}}{V} \qquad \vec{b^*} = 2\pi \frac{\vec{c} \times \vec{a}}{V} \qquad \vec{c^*} = 2\pi \frac{\vec{a} \times \vec{b}}{V}$$

Distances between (hkl) planes

The reciprocal space formalism facilitates the derivation of the interplane distance of parallel (hkl) planes.

$$\boldsymbol{OA} = \frac{1}{h}\boldsymbol{a} \qquad \boldsymbol{OB} = \frac{1}{k}\boldsymbol{b} \qquad \boldsymbol{OC} = \frac{1}{l}\boldsymbol{c}$$



distance $d_{(hkl)}$ is the projection of **OA** (or **OB** or **OC**) onto the normal of the plane → the scalar product

now we have the reciprocal lattice vector $\mathbf{N}^*_{(\mathrm{hkl})}$ which is perpendicular to the (hkl) plane

does we can now calculate the distance by projection of OA onto the unit vector along $\mathbf{N}^*_{(\mathrm{hkl})}$

$$d_{(hkl)} = \boldsymbol{OA} \cdot \frac{\boldsymbol{N}^*_{(\boldsymbol{hkl})}}{\left\|\boldsymbol{N}^*_{(\boldsymbol{hkl})}\right\|}$$

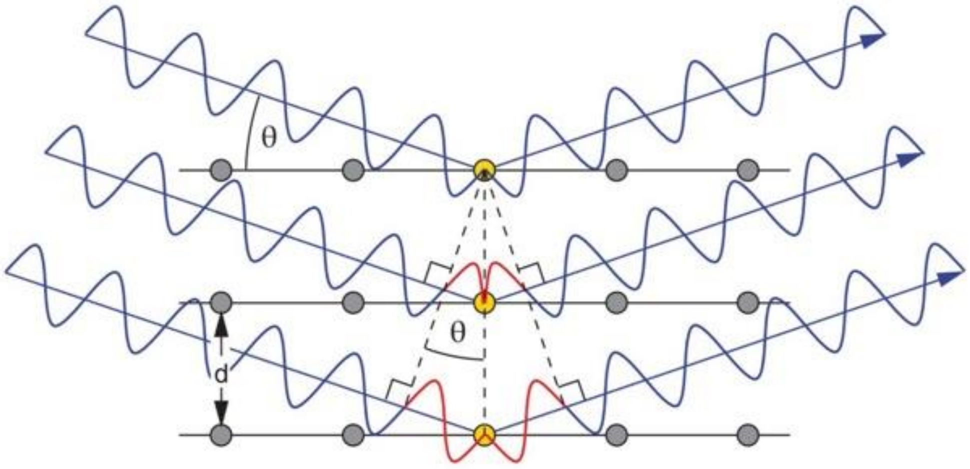
as we have seen before, for any vector (e.g. **OA**) in real space it holds

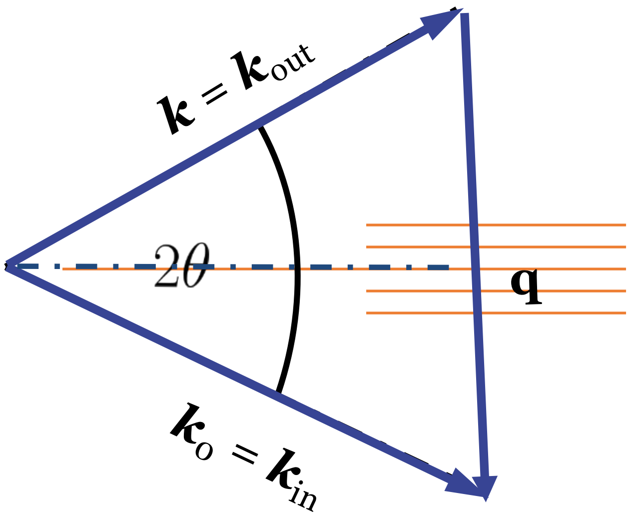
$$\boldsymbol{OA} \cdot \boldsymbol{N}^*_{(\boldsymbol{hkl})} = \boldsymbol{OB} \cdot \boldsymbol{N}^*_{(\boldsymbol{hkl})} = \boldsymbol{OC} \cdot \boldsymbol{N}^*_{(\boldsymbol{hkl})} = 2\pi * \text{integer}$$

$$\boxed{d_{(hkl)} = \frac{2\pi}{\left\|\boldsymbol{N}^*_{(\boldsymbol{hkl})}\right\|}}$$

- Calculate the reciprocal lattice vectors $\boldsymbol{a}^*, \boldsymbol{b}^*, \boldsymbol{c}^*$ and the vector $\boldsymbol{N}^*_{(\boldsymbol{hkl})}$
- Find the norm of $\boldsymbol{N}^*_{(\boldsymbol{hkl})}$ -→ find the distance.

Bragg law





The scattering vector $\boldsymbol{q}$ always lies perpendicular to the scattering planes if the Bragg condition is fullfilled

the angle subtended by $\mathbf{k}_{in} = 2\pi/\lambda$ (or $\mathbf{k}_{out}$) and the scattering planes is θ.

The scattering angle is 2θ

Bragg law: $2d \sin\theta = \mathrm{n}\lambda$

$$|\boldsymbol{q}| = q = \frac{4\pi \sin(\theta)}{\lambda}$$

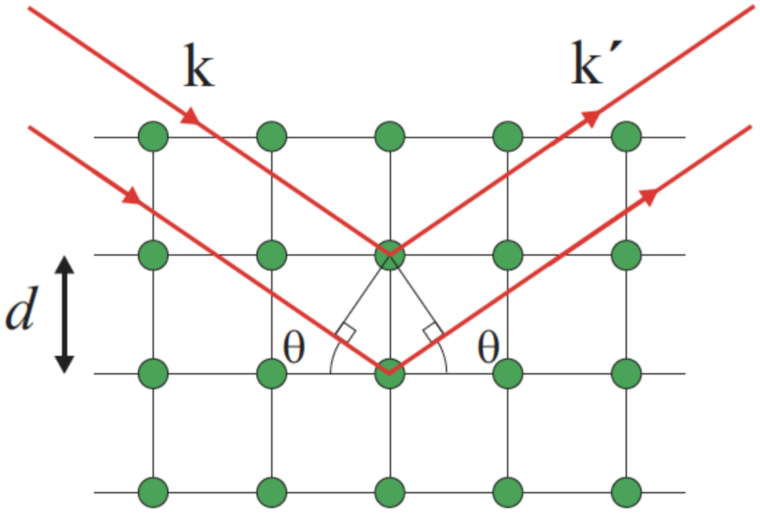
$$d = \mathrm{n}\frac{2\pi}{q}$$

independent of wave length (experimental condition)

Laue's condition and Bragg's law

Bragg

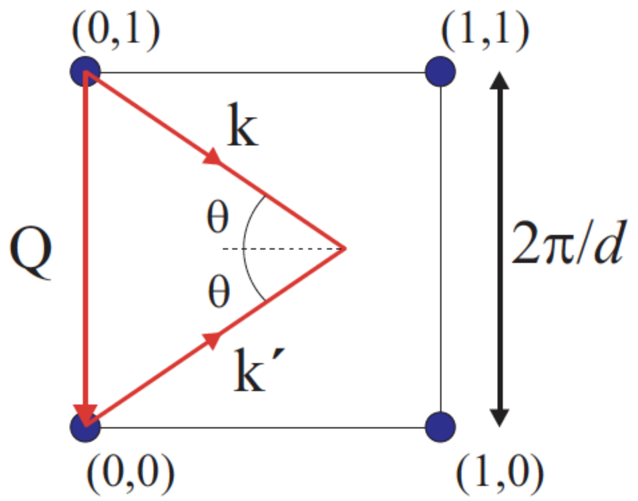
$\lambda=2d\sin\theta$



Real

Laue

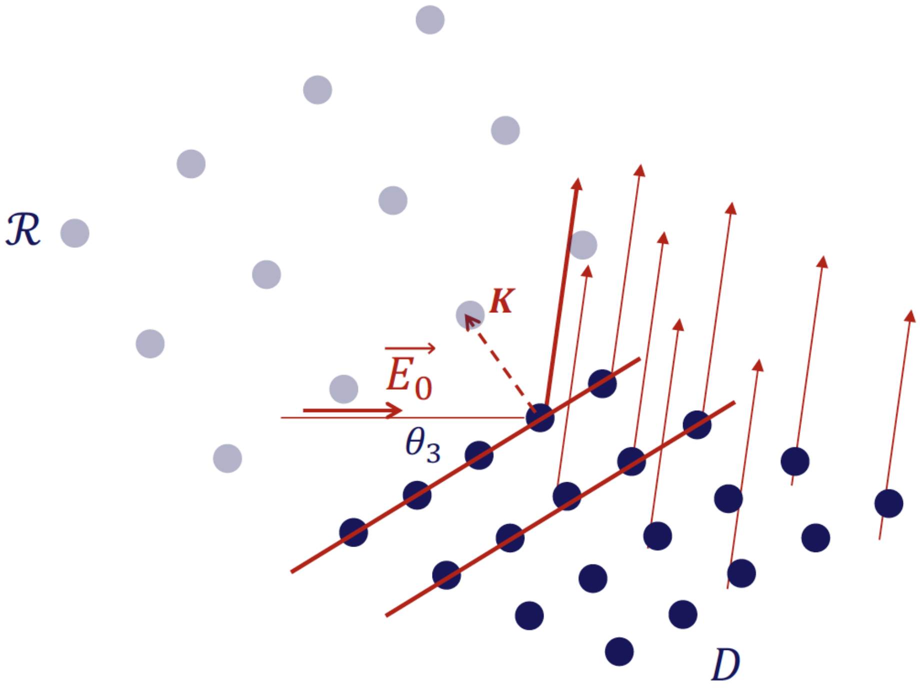
$Q=$ $\mathbf{N}^*$



Reciprocal

Laue condition → The reciprocal space lattice

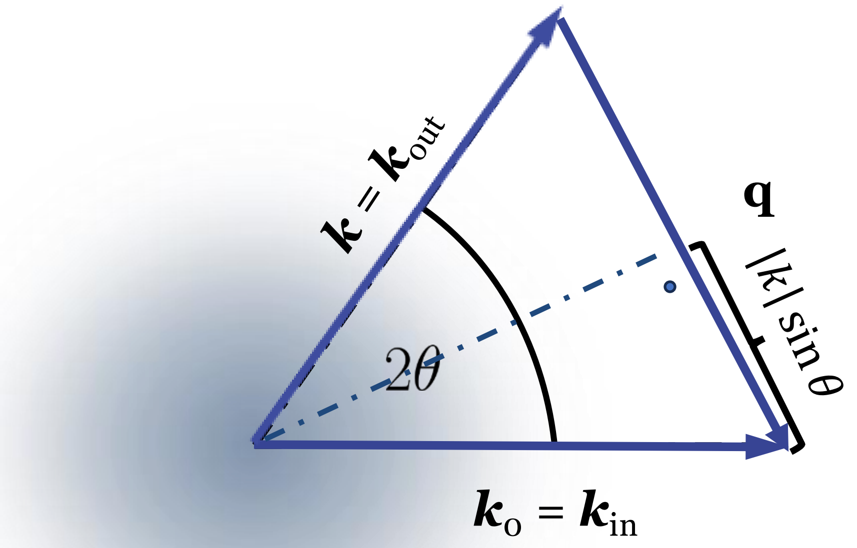
$$2d_{(hkl)}sin(\theta_3) = n\lambda$$



reciprocal lattice vector **N***= $\boldsymbol{K} = \boldsymbol{k} - \boldsymbol{k}_0$

Laue condition

Elastic scattering and scattering vector



wave vector $\boldsymbol{k} = \frac{2\pi}{\lambda}$

elastic scattering: no loss in photon energy but direction of the photon can change with a scattering angle 2θ

$$|\boldsymbol{k}_{in}| = |\boldsymbol{k}_{out}|$$

scattering vector $\boldsymbol{q} = \boldsymbol{k}_0 - \boldsymbol{k}$

$$q = 2|k| \sin\theta = \frac{4\pi \sin\theta}{\lambda}$$

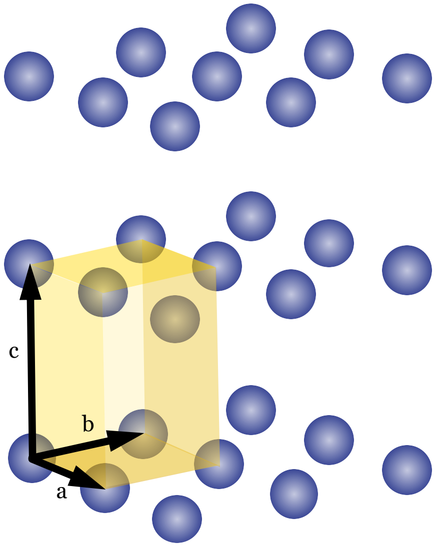
light λ = 400 to 600 nm
X-ray tube λ = 1 to 2 Å
Cu Kα = 1.5406 Å
synchrotron λ = 0.1 to 5 Å
thermal neutrons λ = 1 to 10 Å
electrons λ = 0.025 Å

X-ray energy mostly given in keV

λ [Å] = 12.3984/E [keV]

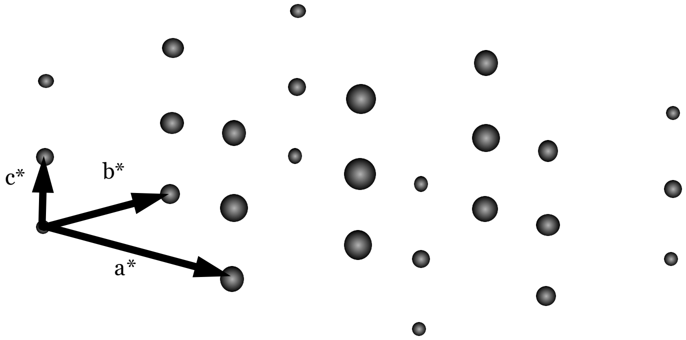
Reciprocal space lattice → diffraction pattern

The reciprocal lattice represents the framework and components of the diffraction pattern



e.g. $a < b < c$

Real space



$a^* > b^* > c^*$

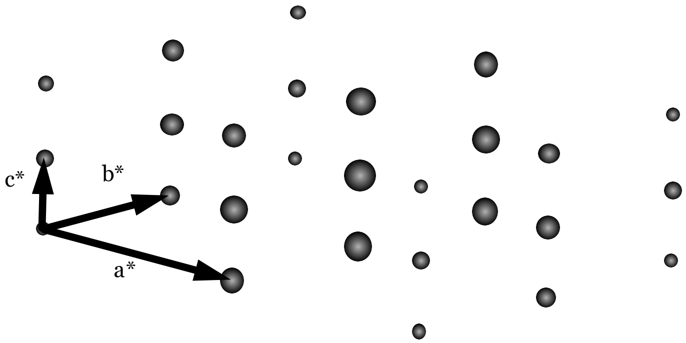
Reciprocal space

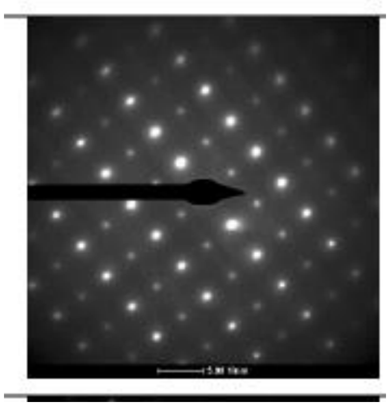
The reciprocal lattice is the Fourier transform of the direct lattice!

The spacings between peaks in reciprocal lattice (a^*, b^*, c^*) are inversely proportional to the corresponding dimensions in real space (a, b, c)

Diffraction

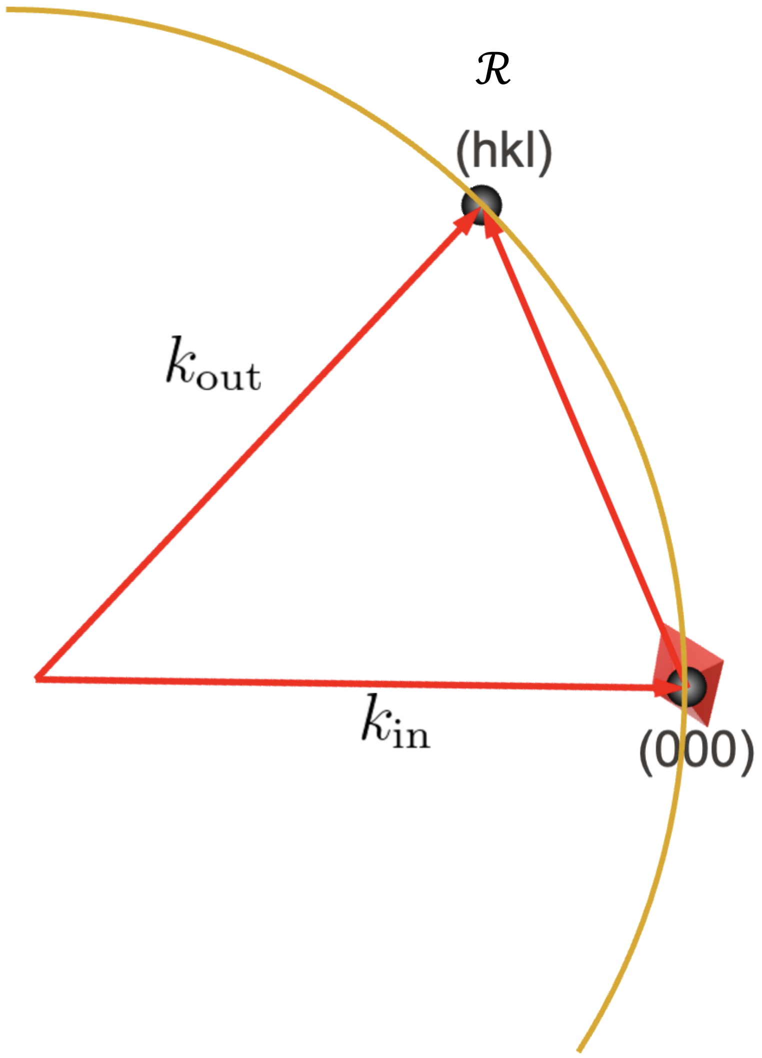
- Bragg’s law: simple geometric consideration if a constructive interference CAN occur
- Crystal is not just the lattice (and lattice planes) but also consists of a motif!
- it is the lattice which determines the geometry of the pattern and the motif which determines the intensities of the X-ray diffracted beams.





- The diffraction pattern is the is the square of the Fourier transform of that system

Bragg condition and the Ewald sphere



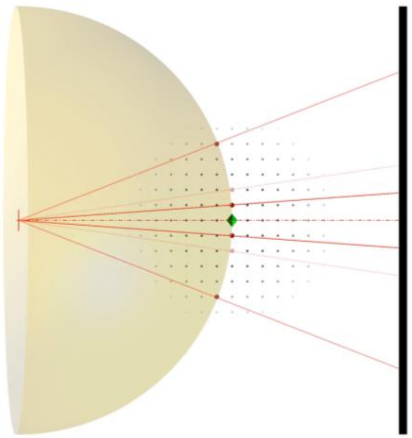
elastic scattering: $|\boldsymbol{k}_{in}| = |\boldsymbol{k}_{out}|$

To see a diffraction peak @ (hkl) :

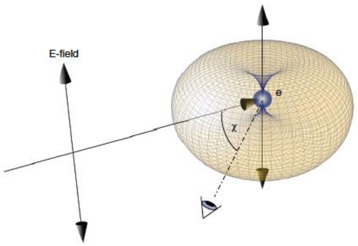
the Bragg points (000), which is at the position of the direct incoming beam

and the Bragg point (hkl) from the reciprocal space lattice

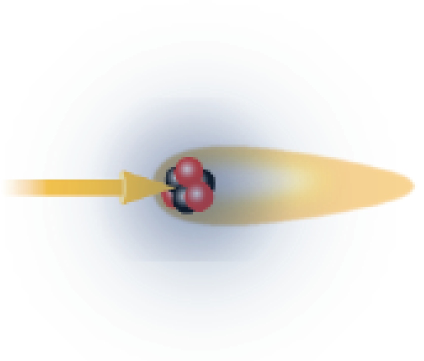
must lie on a sphere of radius equal |k| (the wave vector of the experiment) in reciprocal space $\mathcal{R}$, the so called Ewald sphere



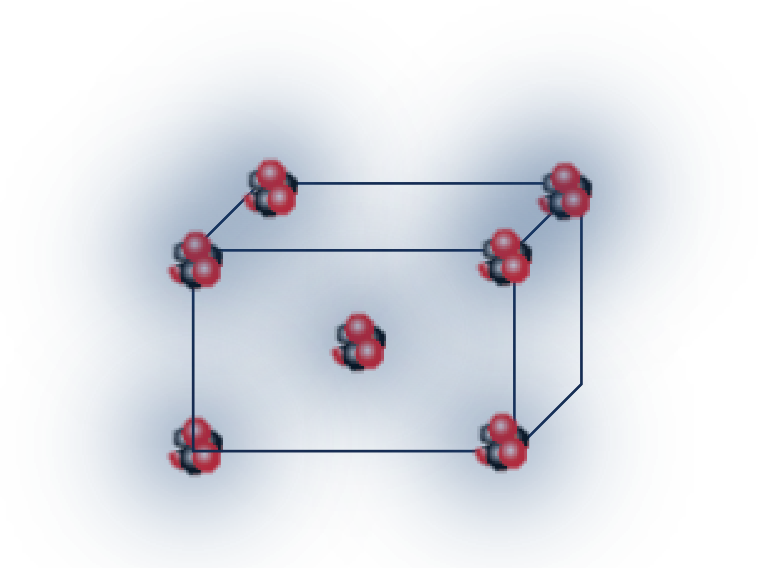
Interaction of X-rays with a crystal



interaction with electron
polarization factor



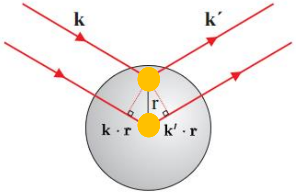
scattering from an atom
atomic form factor f



scattering from unit cell
structure factor F

Scattering and Fourier Transform

2 electrons



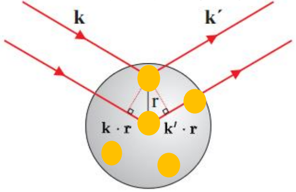
Phase difference of electron placed at position $\vec{r}$:
$\Delta\varphi(\boldsymbol{r}) = (\boldsymbol{k} - \boldsymbol{k}') \cdot \boldsymbol{r} = \boldsymbol{q} \cdot \boldsymbol{r}$

→ Phase *factor* : $e^{\Delta\varphi(\boldsymbol{r})} = e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$

Scattering amplitude: $A(\boldsymbol{q}) = -r_0(1 + e^{i\boldsymbol{q}\cdot\boldsymbol{r}})$

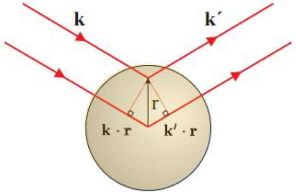
contribution of electron placed at origin $(\boldsymbol{r} = \vec{0})$

N electrons



Scattering amplitude: $A(\boldsymbol{q}) = -r_0 \sum_j e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$

Electron distribution $\rho(\vec{r})$

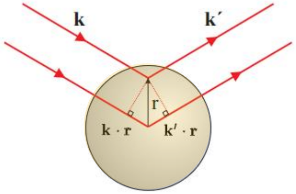


atomic form factor: $f^0(\boldsymbol{q}) = \int \rho(\boldsymbol{r}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}} d\boldsymbol{r}$

Fourier Transform of electron density distribution !

Atomic form factor and structure factor → scattering from unit cell

Electron distribution $\rho(\vec{r})$

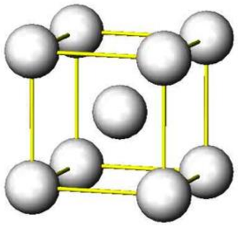


at large **Q**: small structure
atomic scales

Scattering amplitude: $F(\vec{Q}) = -r_0 \boxed{\int \rho(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} d\vec{r}}$

Fourier Transform of electron density distribution !

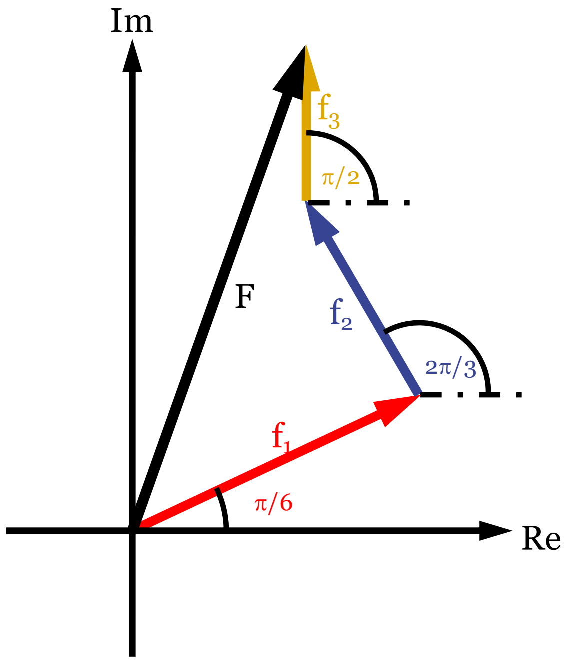
→atomic form factor



scattering from unit cell:
interaction between atoms (constructive and destructive interference)
structure factor

$$S(\boldsymbol{K}) = \sum_{l=1}^{N_a} f_l(\boldsymbol{K})\; e^{-i\boldsymbol{K}.\boldsymbol{r}_l}$$

Interaction with a unit cell: the structor factor



S = vector sum of atomic form factors

as mathematically calculated in the last lecture!

$$S(\boldsymbol{K}) = \sum_{l=1}^{N_a} f_l(\boldsymbol{K})\ e^{-i\underbrace{\boldsymbol{K}.\boldsymbol{r}_l}_{\text{phase } \phi}}$$

$\boldsymbol{K}.\boldsymbol{r} = (\mathrm{h}\boldsymbol{a}{*}+k\boldsymbol{b}{*}+l\boldsymbol{c}{*}).(x_l\boldsymbol{a}+yl\boldsymbol{b}+z_l\mathbf{c})$
$\boldsymbol{a}^*\boldsymbol{a}=\boldsymbol{b}^*\boldsymbol{b}=\mathbf{c}^*\mathbf{c}=\boldsymbol{2\pi}$ and
$\boldsymbol{a}^*\boldsymbol{b}=\boldsymbol{b}^*\boldsymbol{a}=\boldsymbol{c}^*\boldsymbol{a}\ \ldots=0$

$$\phi_l = 2\pi(hx_l + ky_l + lz_l)$$

Intensity of measured Bragg peak (hkl) is proportional to $|S_{\mathrm{hkl}}|^2$

All phase information is lost!

Diffraction and Fourier transform

scattering amplitude from a crystalline material

$$F^{crystal}(\boldsymbol{q}) = \sum_{l}^{all\ atoms} f_l(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}_l} = \sum_{\boldsymbol{R}n+\boldsymbol{r}j}^{all\ atoms} f_j(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot(\boldsymbol{R}n+\boldsymbol{r}j)} = \underbrace{\sum_n e^{i\boldsymbol{q}\cdot\boldsymbol{R}n}}_{\text{lattice}} \underbrace{\sum_j f_j(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}j}}_{\text{unit cell structure factor}}$$

atomic form factor of the atom situated at position $\boldsymbol{r}_l$

$\boldsymbol{r}_l = \boldsymbol{R}_n + \boldsymbol{r}_j$

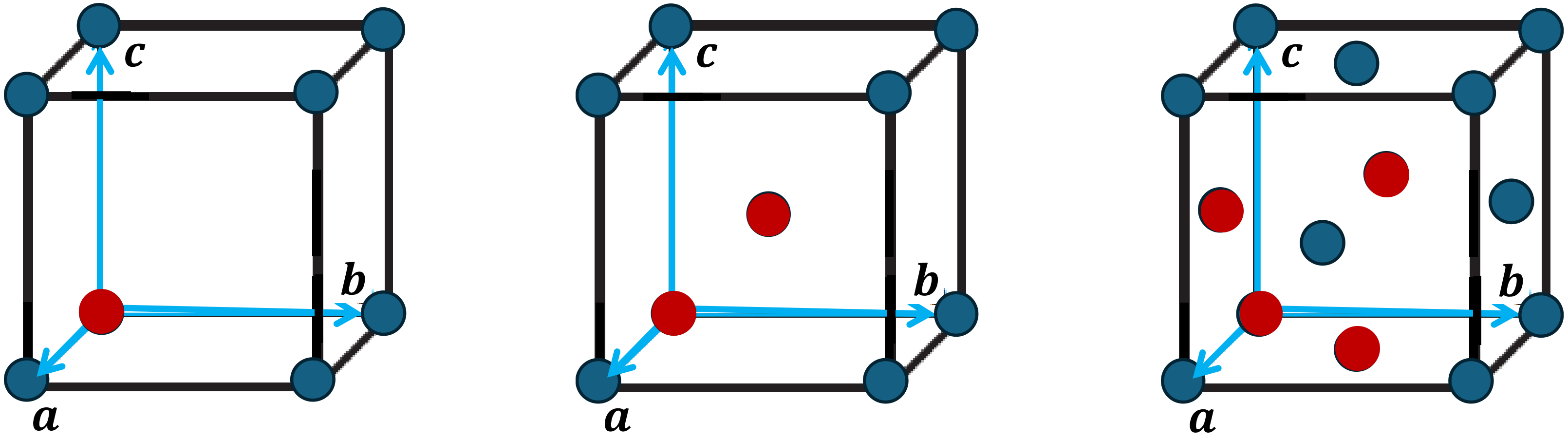
$\boldsymbol{R}_n$ lattice vector
$\boldsymbol{r}_j$ position vector of the atoms in the unit cell (= the motif)

with Laue's condition for constructive interference
$\boldsymbol{q} = \boldsymbol{K}$, with $\boldsymbol{K} \in \mathcal{R}$
at any other scattering vector q, the intensity is zero

$$S(\boldsymbol{K}) = \sum_j f_j(\boldsymbol{K}) e^{i\boldsymbol{K}\cdot\boldsymbol{r}j}$$

X-ray diffraction and systematic absences

We can view non-primitive crystal structures as being defined by the conventional cell, and a motif with a number of atoms equal to the number of atoms per conventional cell.



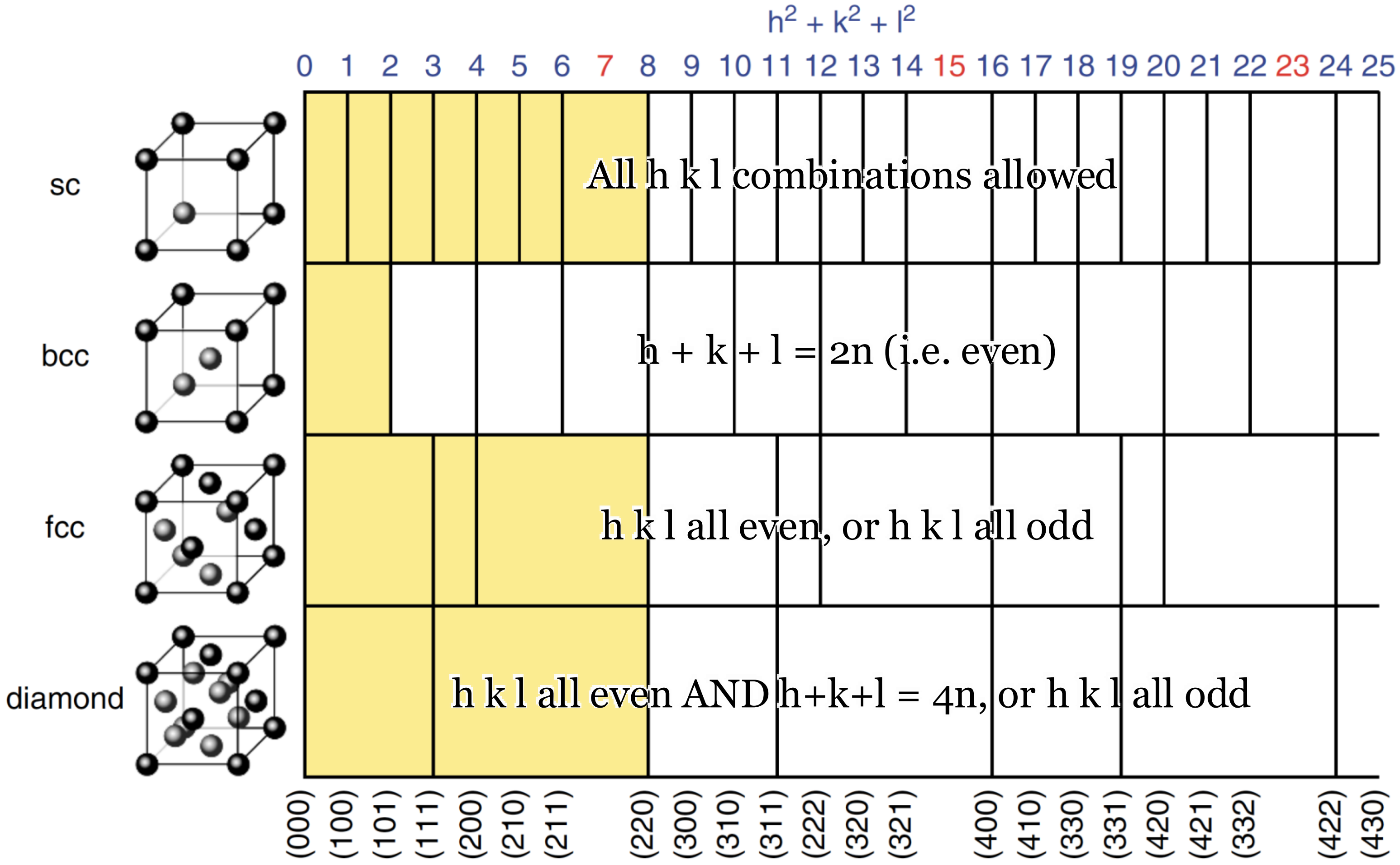
- Be careful: while it describes a similar crystal, it is not a rigorous way to look at crystal structures, as it leads to believe that the BCC and FCC don't have their own Bravais Lattice prime vectors. Also, it leads to believe that planes like the (200) planes are not crystal planes for the BCC and FCC structures !

It is however a good way to treat diffraction and understand systematic absences.

- Indeed, to these multiple atoms motifs, we can now apply the formalism of structure factors $S(\boldsymbol{K}) = f_{Mo}\left(1 + (-1)^{(h+k+l)}\right)$

$$\begin{cases} S(\boldsymbol{K}) = 2f_{Mo} & \text{for } (h+k+l) \text{ even} \\ S(\boldsymbol{K}) = 0 & \text{for } (h+k+l) \text{ odd} \end{cases}$$

Interaction with a unit cell: systematic absences



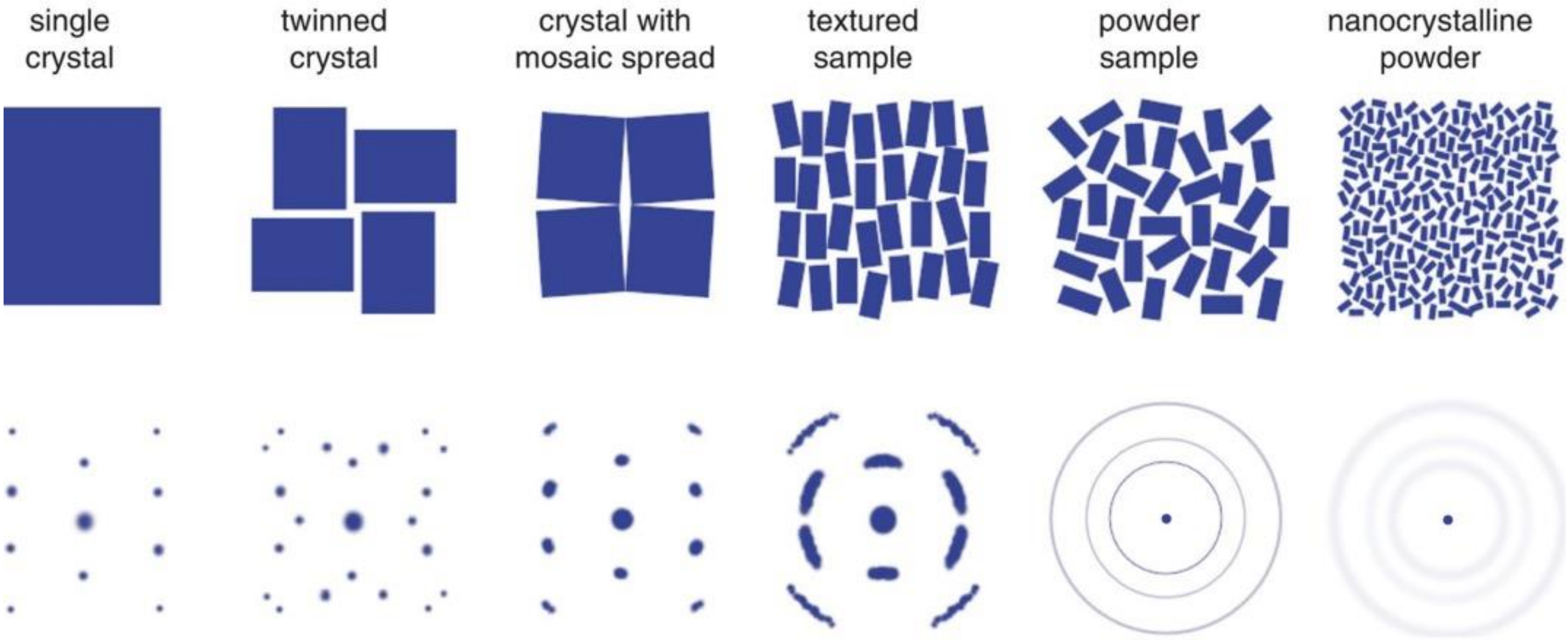
All h k l combinations allowed

h + k + l = 2n (i.e. even)

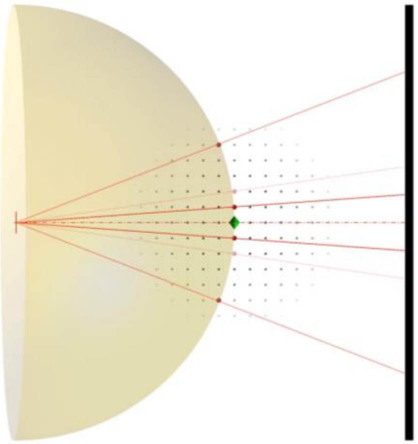
h k l all even, or h k l all odd

h k l all even AND h+k+l = 4n, or h k l all odd

Sample types

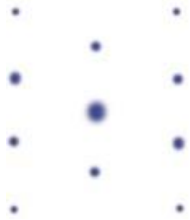


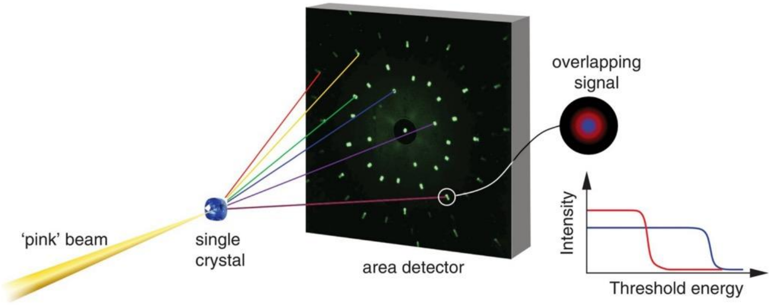
Sample types and experiments



rotation method with
monochromatic light

By rotating the crystal around an axis perpendicular to the incident beam (ϕ), diffraction maxima pass through the surface of the Ewald sphere and are registered on a 2D x-ray detector



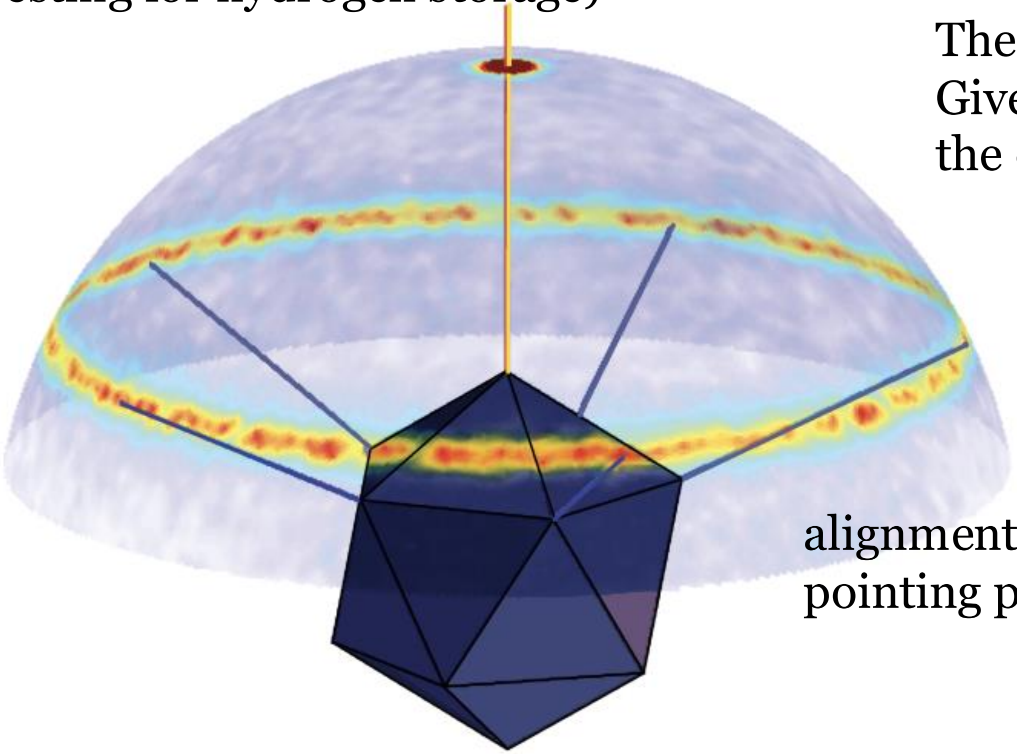


Laue diffraction
pink beam = many wavelength

Multiple Ewald spheres with different radius intersecting with several Brapp pints from the reciprocal space lattice

Textured sample and pole figure

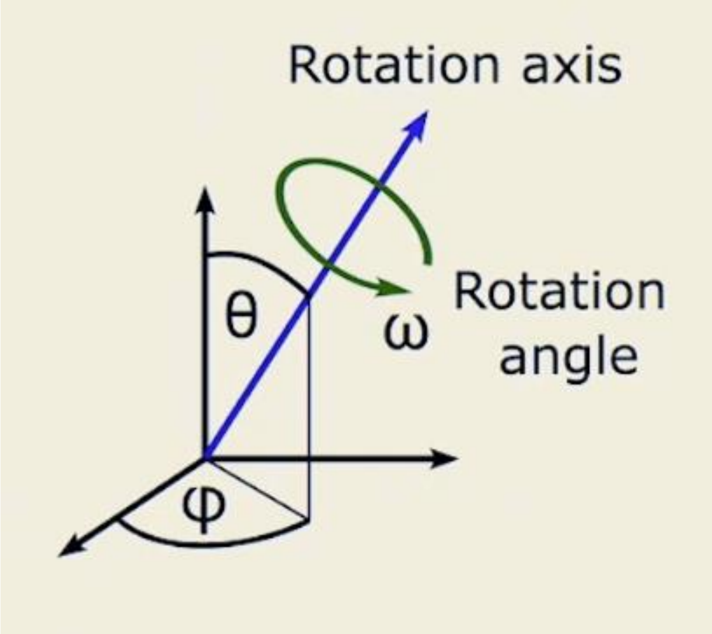
Ti-Ni-Zr alloy thin films
(interesting for hydrogen storage)

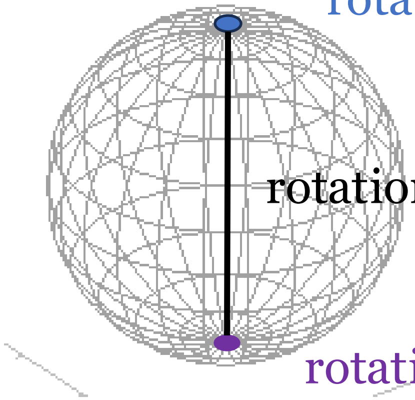


Given a specific set of reciprocal lattice vectors, *{hkl}*
The pole figure $P_{hkl}(q)$
Gives the probablity of finding that plane in the direction, q

alignment of one of the symmetry axis pointing perpendicular out of the thin film

Textured samples: orientation information



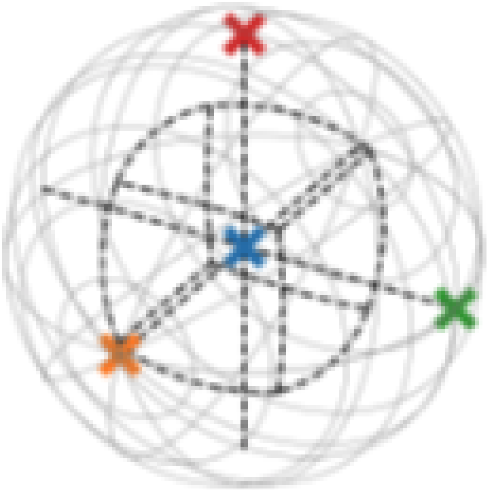


axis-angle representation of 3D orientation
one vector defining the axis, and an angle defining the rotation around it

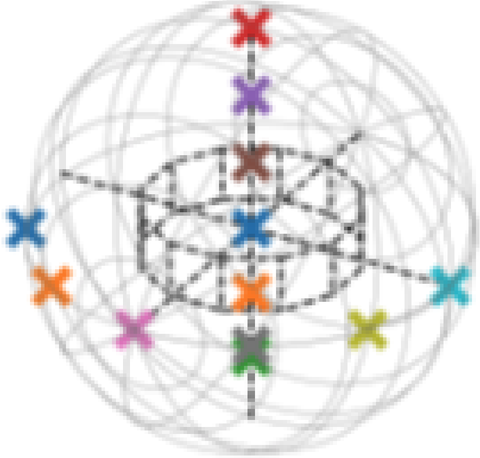
if there is a two-fold **symmetry** around that axis, rotation of 0° and 180° and -180° are equivalent!

what defines if certain orientations are equivalent?

Orientation of a crystal and crystal symmetry



point group 222



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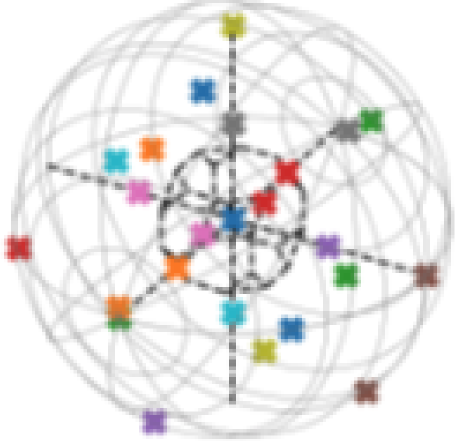


432

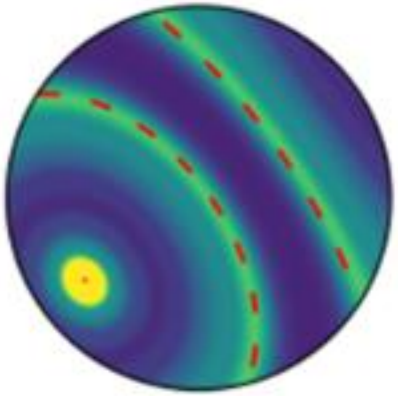
crystal system

the more symmetry elements a point group has, the smaller is the fundamental zone since more and more orientation become equivalent

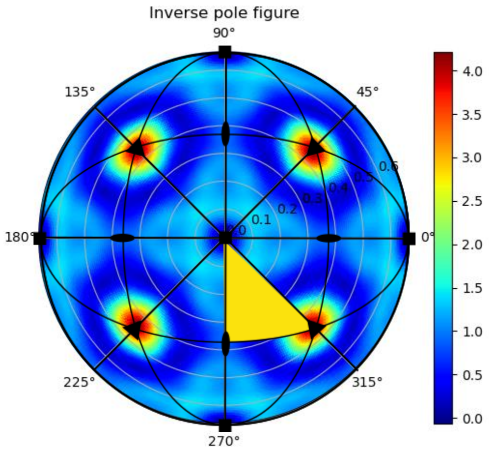
→ this also means for a full dataset in single crystal diffraction fewer orientations of a crystal need to be measured if there is a higher symmetry

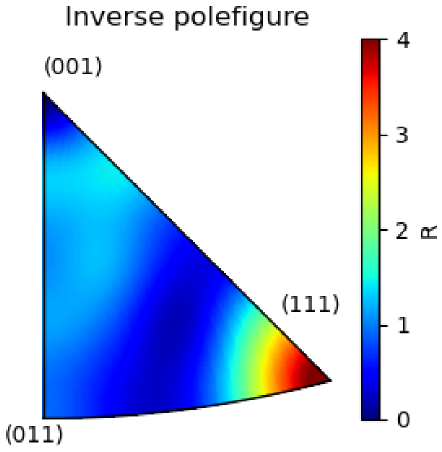
Texture analysis

- The pole figure
  - Given a specific set of reciprocal lattice vectors, *{hkl}*
  - The pole figure gives the probablity of finding that plane in the direction, q

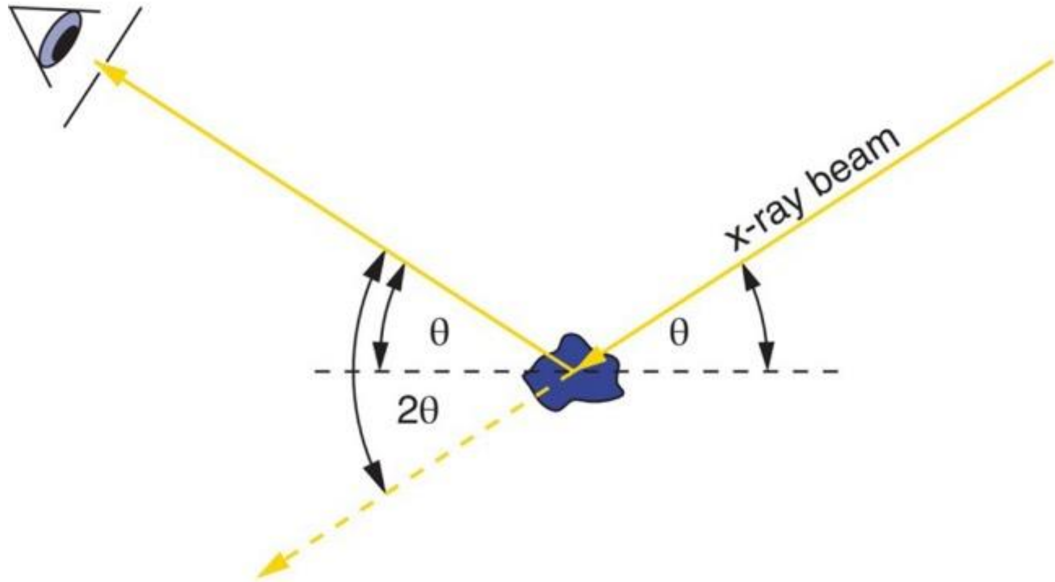


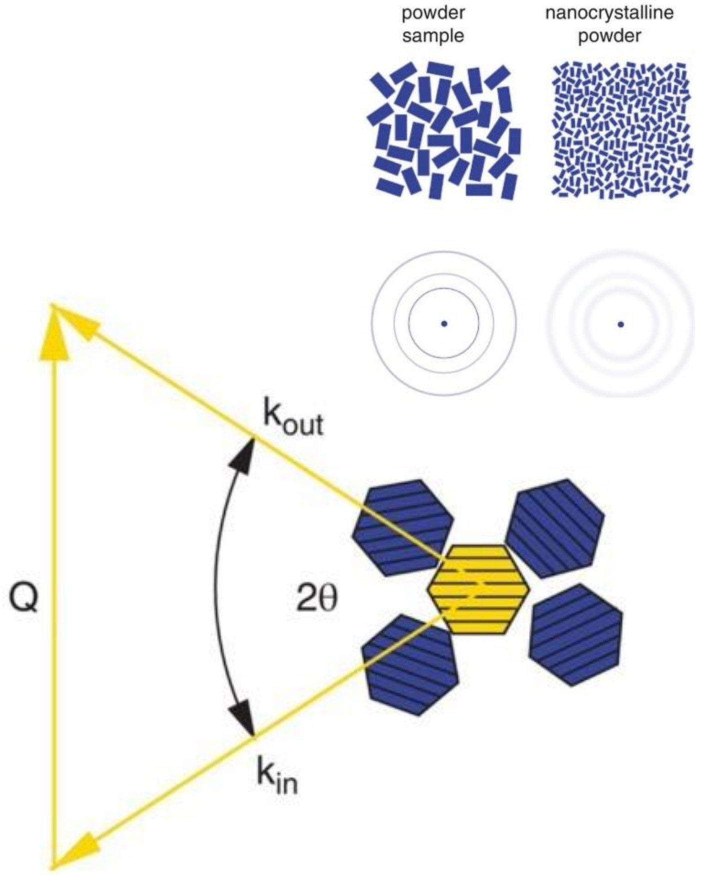
- The inverse pole figure
  - Given a specific direction *y* in the sample (here: the wire direction = draw direction)
  - The inverse pole figure gives the probability that *y* falls in a certain lattice orientation.





Powder diffraction



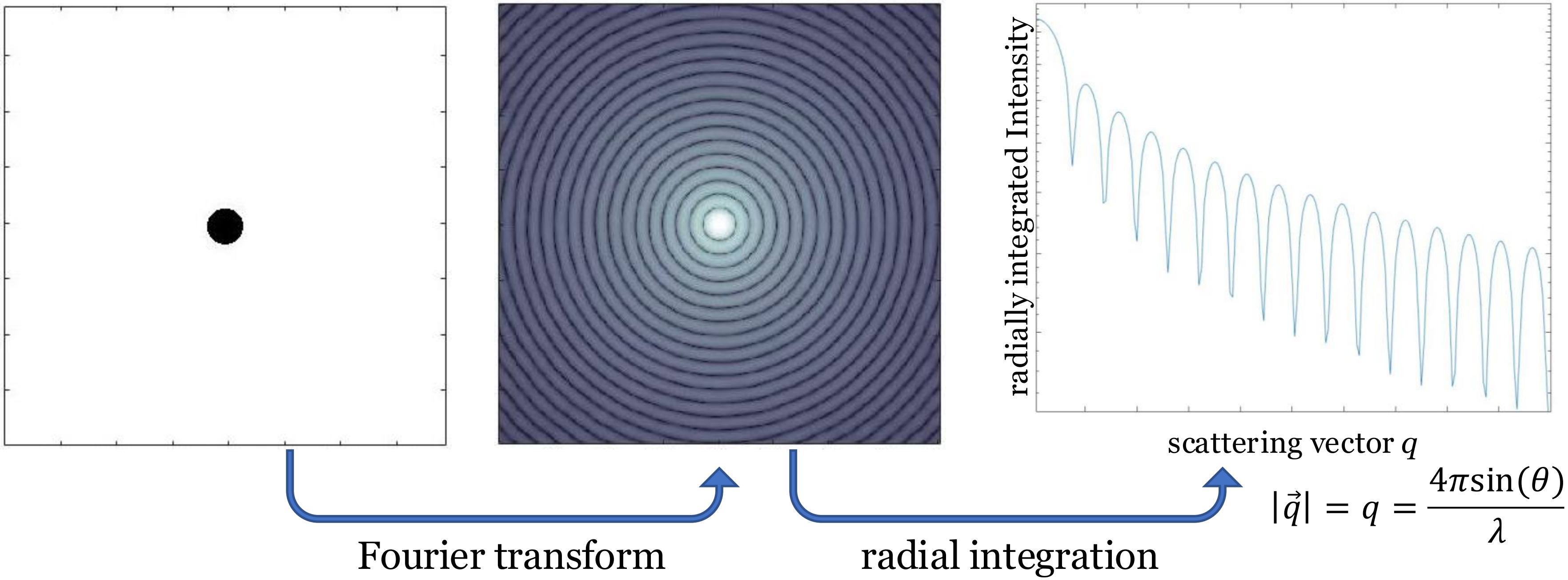


Conditions for diffraction in a powder sample. A detector will only see a diffracted signal if the d_{hkl} spacing, the orientation of the crystallite, and the angle of the detector 2θ to the incident x-ray beam lead to the diffraction condition being satisfied. This is fulfilled by the yellow-highlighted crystallite.

XRD
Imperfect microstructure

- large crystal with perfect atomic arrangement give rise to perfectly sharp peak (except of instrumental broadening)
- imperfections such as grain boundaries, defects at dislocations, stacking faults, stresses → peak broadening, as well as possibly peak position shifts
- small crystal size: “defect” as the long-range atomic arrangement is disrupted at the interface → peak broadening
  - Scherrer width $B = \frac{K \cdot \lambda}{D \cdot \cos\theta}$
- when looking at more than one order of a reflection, the effect of ”size” and “strain” can be separated
- Rietfeld refinement to get all information out of powder diffraction data

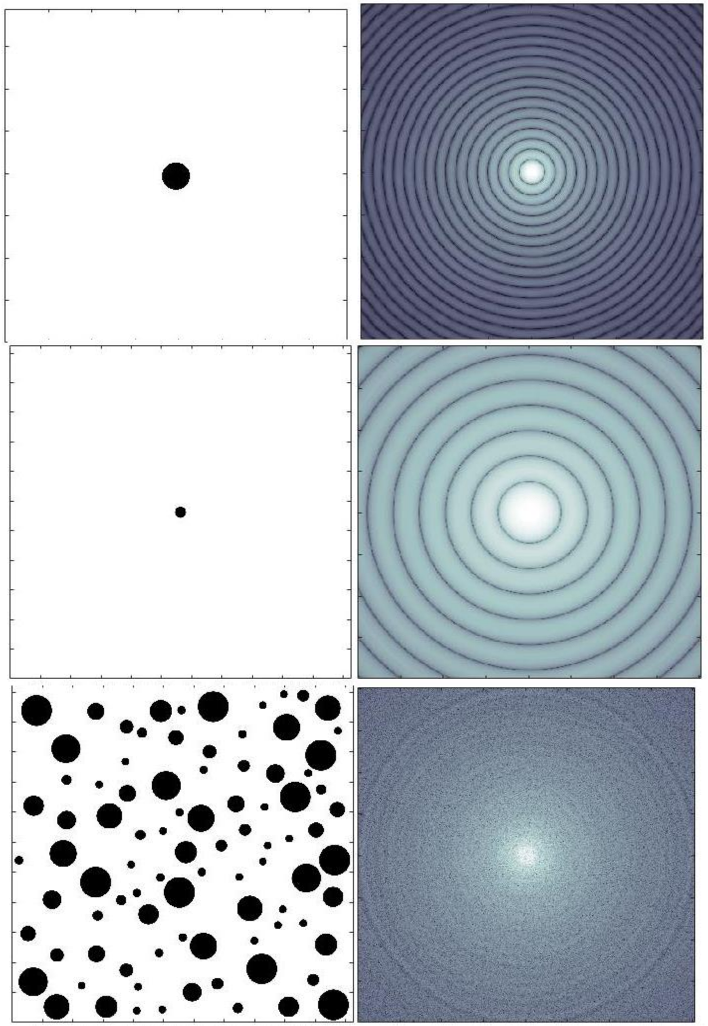
Scattering/Diffraction



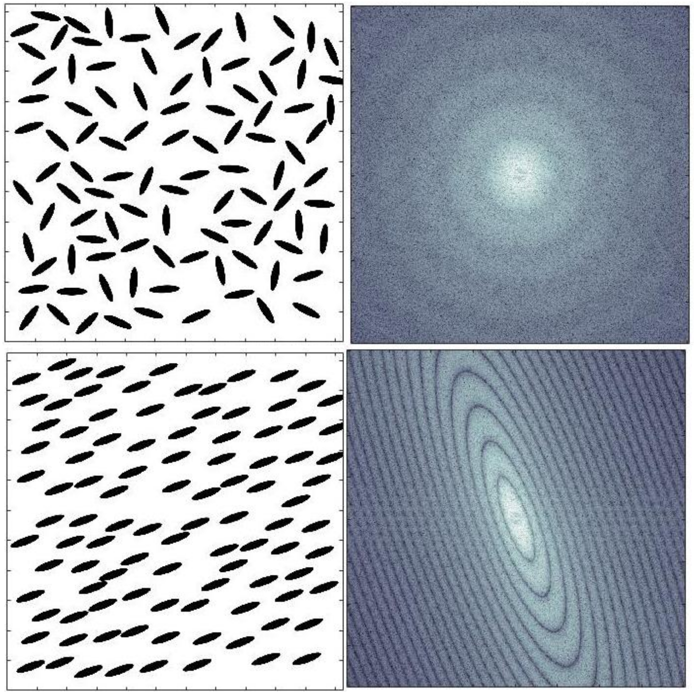
$$|\vec{q}| = q = \frac{4\pi \sin(\theta)}{\lambda}$$

the field distribution at a distant detector is the Fourier transform of the electric field distribution in the exit plane of a sample
BUT we don’t measure field but the intensity, which is the squared field: complex quantity: complex part (the phase) get lost → **the phase problem**

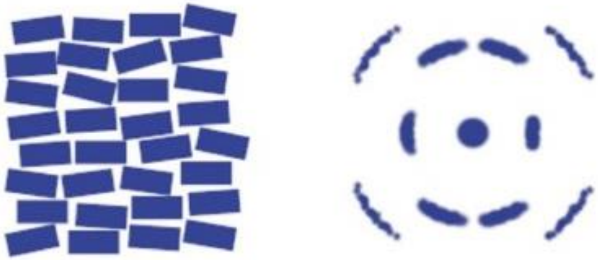
Scattering/Diffraction



larger structures scatter at smaller angles

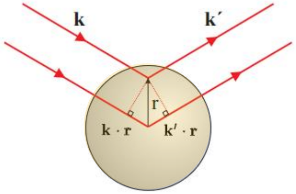


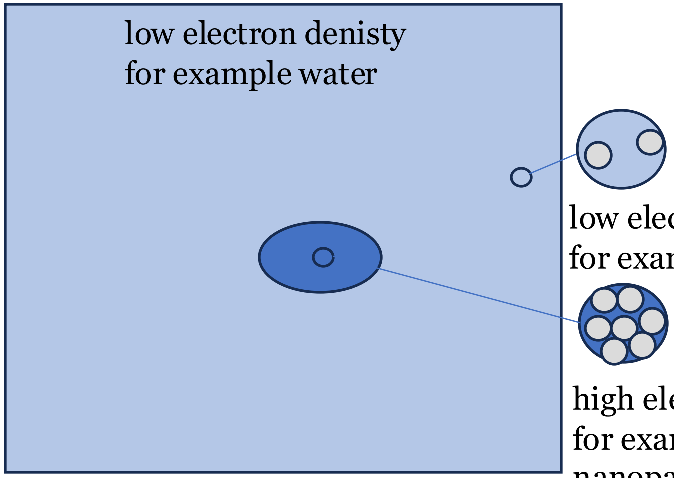
scattering and diffraction can be used to study orientation of nanostructures or crystalline planes



WAXS/XRD and SAXS

Electron distribution $\rho(\vec{r})$





low electron denisty
for example water

low electron denisty
for example water

high electron density
for example solid
nanoparticle

at large **Q**: small structure
atomic scales

Scattering amplitude: $F(\vec{Q}) = -r_0 \boxed{\int \rho(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} d\vec{r}}$

Fourier Transform of electron
density distribution ! → atomic form factor

at small **Q**: larger structures
nanometer scales

$$I_1^{SAXS}(Q) = (\rho_{sl,p} - \rho_{sl,0})^2 \left| \int_{V_p} e^{i\mathbf{Q}\cdot\mathbf{r}} \, dV_p \right|^2$$

Fourier Transform of electron density (but now at the nanoscale)
and with

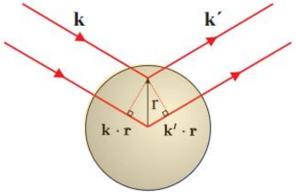
$$\mathcal{F}(\mathbf{Q}) = \frac{1}{V_p} \int_{V_p} e^{i\mathbf{Q}\cdot\mathbf{r}} \, dV_p,$$

→ single particle form factor
depends on size and shape of the particle

$$I_1^{SAXS}(\mathbf{Q}) = \Delta\rho^2 \, V_p^2 \, |\mathcal{F}(\mathbf{Q})|^2 .$$

Structure factor in SAXS

Electron distribution $\rho(\vec{r})$

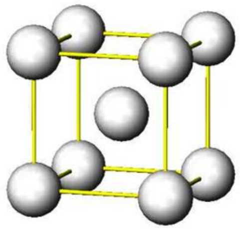


at large **Q**: small structure
atomic scales

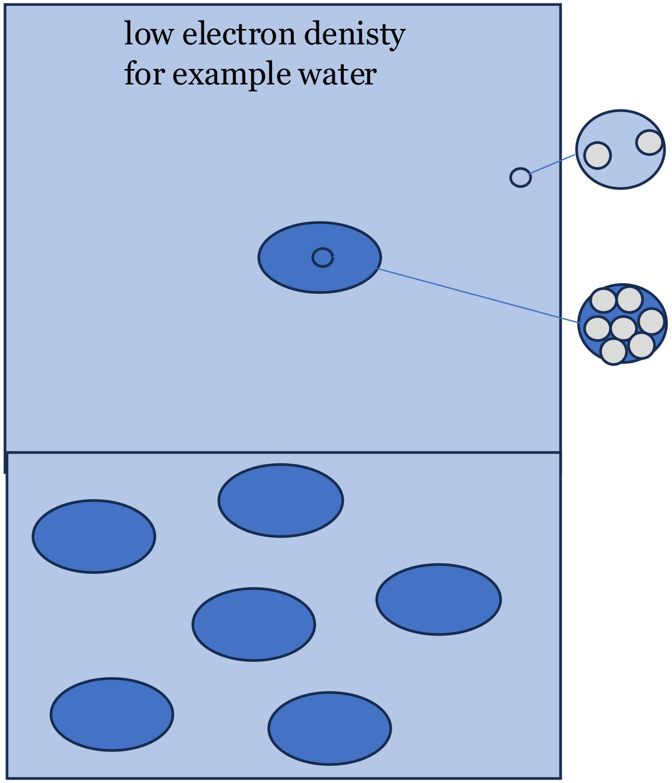
Scattering amplitude: $F(\vec{Q}) = -r_0 \boxed{\int \rho(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} d\vec{r}}$

Fourier Transform of electron density distribution ! →atomic form factor

scattering from unit cell:
structure factor



at small **Q**: larger structures
nanometer scales



$$I_1^{SAXS}(\mathrm{Q}) = (\rho_{sl,p} - \rho_{sl,0})^2 \left| \int_{V_p} e^{i\mathbf{Q}\cdot\mathbf{r}}\, dV_p \right|^2$$

Fourier Transform of electron density (but now at the nanoscale) and with

$$\mathcal{F}(\mathbf{Q}) = \frac{1}{V_p} \int_{V_p} e^{i\mathbf{Q}\cdot\mathbf{r}}\, dV_p$$

→ single particle form factor
depends on size and shape of the particle

$$I_1^{SAXS}(\mathbf{Q}) = \Delta\rho^2 V_p^2 |\mathcal{F}(\mathbf{Q})|^2 .$$

non-dilute system: inter-particle interaction

$$I^{SAXS}(\mathrm{Q}) = \Delta\rho^2 V_p^2 |\mathcal{F}(\mathbf{Q})|^2 \mathcal{S}(\mathrm{Q})$$

→ particle structure factor

SAXS data analysis

The phase problem

→we cannot directly calculate back with an inverse Fourier transform the particles shape and size, different approaches to retrieve information from the scattering pattern

- model independent
- mathematically model the SAXS curve
- iterative phase retrival
- pair distance distribution function (PDDF)

Small-angle scattering

low q: information about interaction s between the particles and particle size, no information about shape of particle
intermediate q: in the order of the particle size, particle shape
high q: Porod's region contrast at the interface between the particle and their surrounding, measure of surface area

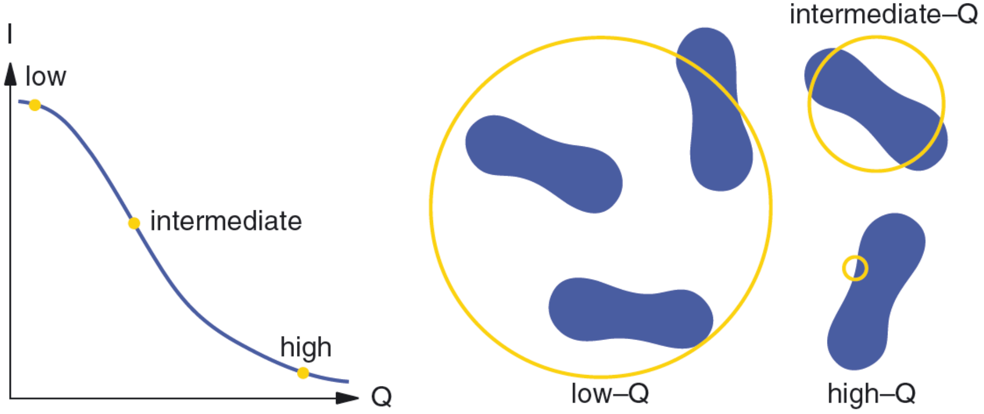


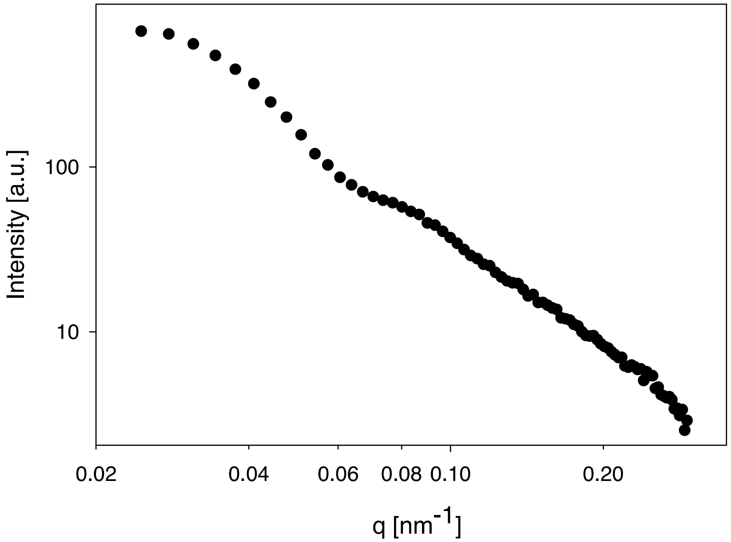
Figure 5.67 *The three Q-domains of SAXS.*

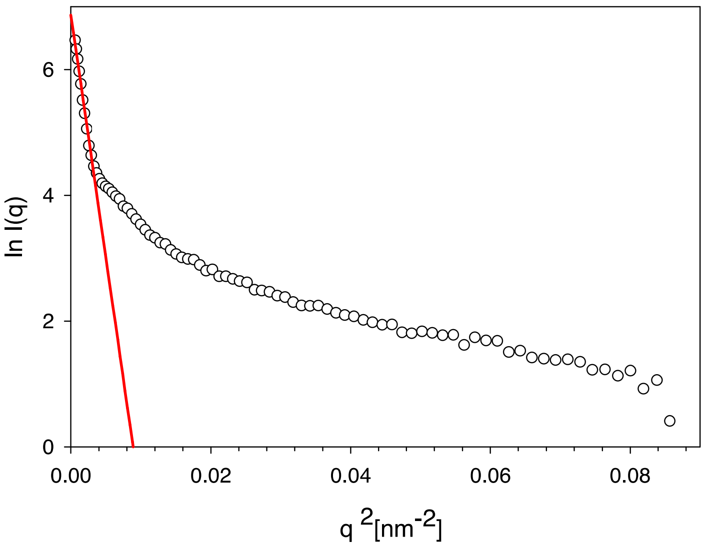
Willmott, P. (2011). Scattering Techniques. An Introduction to Synchrotron Radiation, John Wiley & Sons, Ltd: 133-221.

Guinier approximation

Guinier approximation valid only in the region of small q values, R_G can be derived

$$I(q) \approx I(0)e^{-(1/3)q^2R_G^2}$$





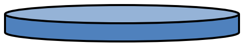
A not existing linear range indicates the presence of very large structures which scatter at low *q*, perhaps outside the accessible *q* range → change detector distance, change λ, check with SLS

Guinier approximation

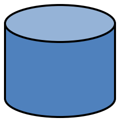
- Radius of gyration R_G: “weight average” of all radii present in the sample in analogy to mechanics

solid sphere radius R: $R_G^2 = \frac{3}{5} R^2$

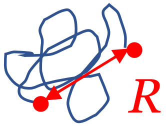
thin rod length L: $R_G^2 = \frac{1}{12} L^2$



thin disc radius R: $R_G^2 = \frac{1}{2} R^2$



cylinder of height h and radius $R_G^2 = \frac{R^2}{2} + \frac{h^2}{12}$



For a polymer coil with end to end distance $R_G^2 = \frac{1}{6} R^2$

Small-angle scattering: Power law

Slope of the scattering curve: power law behavior

q^{-D} with D the **fractal dimension**

How does the mass changes as a function of the size

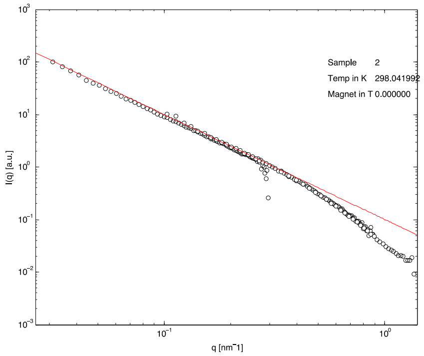
rod-like D=1

disk-like D=2

in general: the higher D, the more compact is the structure

D=4 Porod scattering

→sharp interphase of two phases, information about surface area



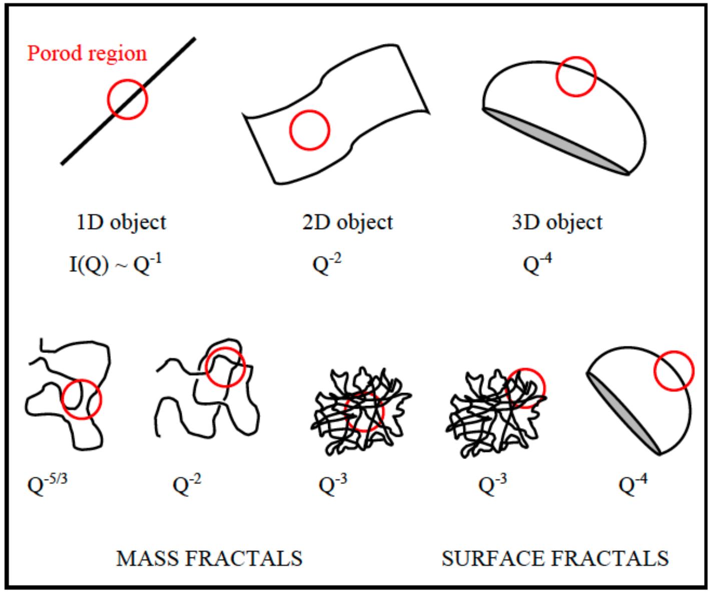
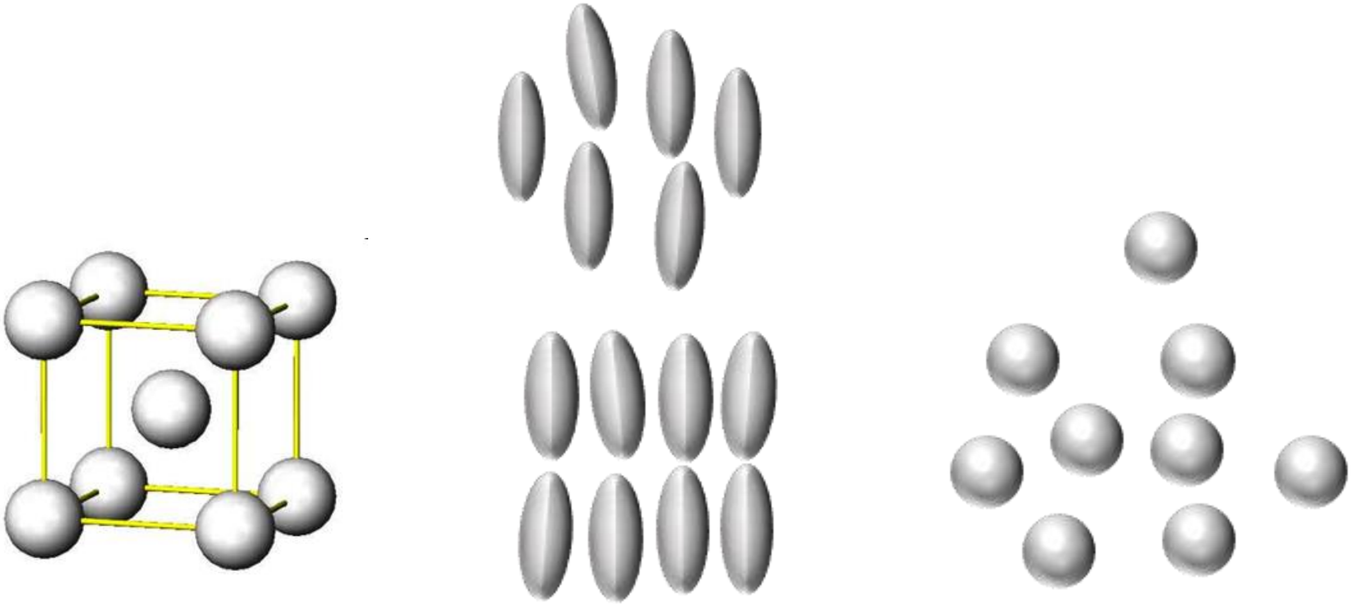


Figure 7: Assortment of Porod law behaviors for different shape objects.

Order and disorder



→ how to describe structure of amorphous materials?

long-range order: periodic distribtuion of atoms ordered over large distances

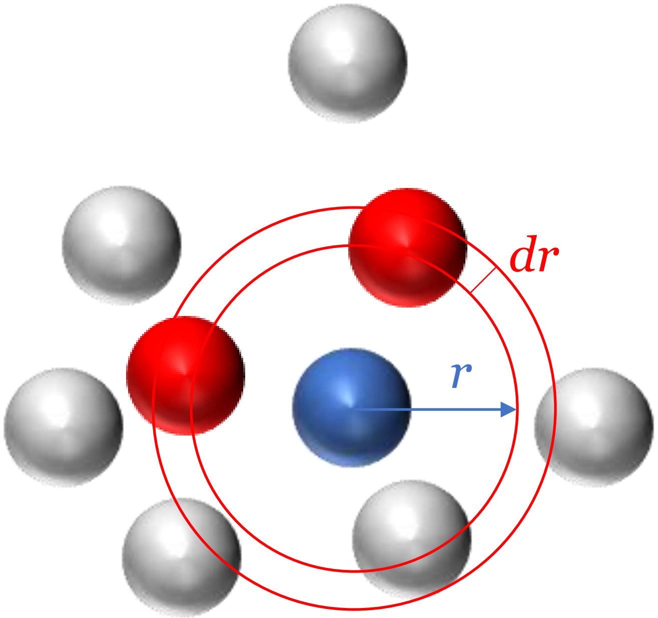
exact location from an atom can be inferred relative to a chosen atom at the origin
→ **atomistic**

short-range order: over short distances (some atomic diameters) a certain periodicity in the distribution of atoms still exists.

some randomness in the position of the atoms: structural order can only be described **statistical**

Pair distribution function (PDF)

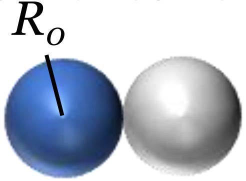
- probability of finding an atom/molecule at a certain distance normalized over the overall density → local density in the structure surrounding a typical atom



$$\boxed{g(r) = \frac{dn(r,r+dr)}{dv(r,r+dr)}\frac{1}{\rho_0} = \frac{\rho(r)}{\rho_0}}$$

$4\pi r[\rho(r) - \rho_0]$: excess particle number density in a spherical shell at radius r

h(r) = g(r)-1 total correlation function, deviation from uncorrelated behavior

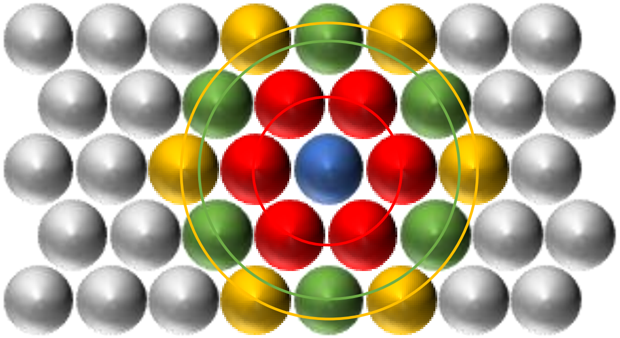


$$g(r < 2R_o) = 0$$

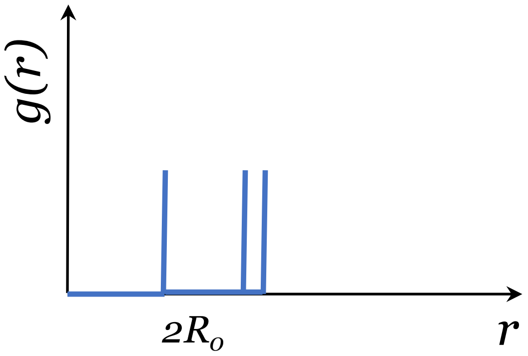
dn : number of atoms in a spherical shell
dv : spherical shell volume = $4\pi r^2 dr$
r : distance of the shell from an arbitary atom selected as the origin
ρ_0: average particle density
$\rho(r)$: atomic pair density
R_o = radius of atom (solid sphere model)

Pair distribution functhon

crystal

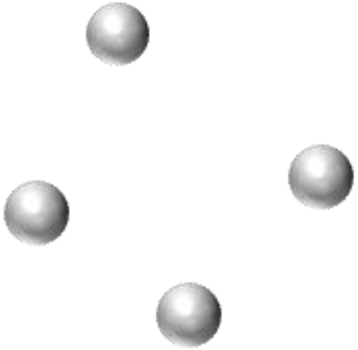


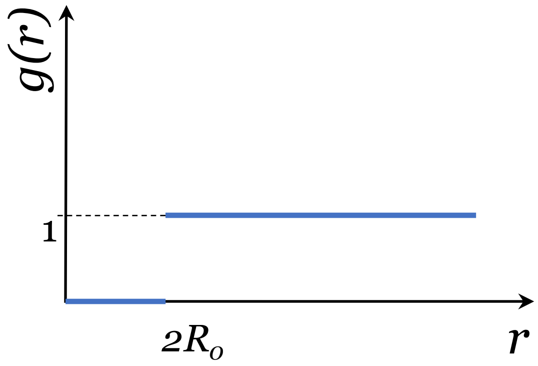
$g(r < 2R_o) = 0$



g(r) infinite series of discrete peaks (delta functions) at the values of interatomic separation, depending on crystal structure

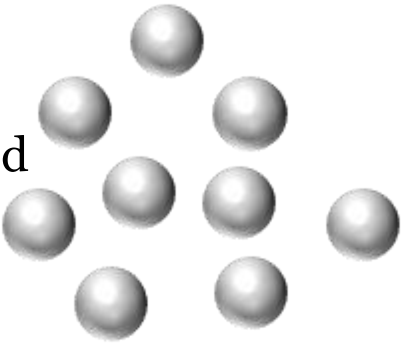
gas

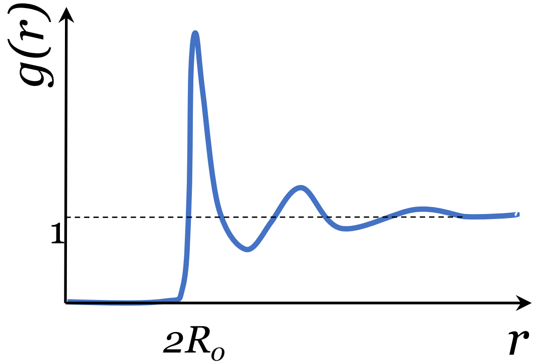




Beyond the hard sphere diameter, the probability of finding another atom is equal to the average gas density, $g(r) = 1$

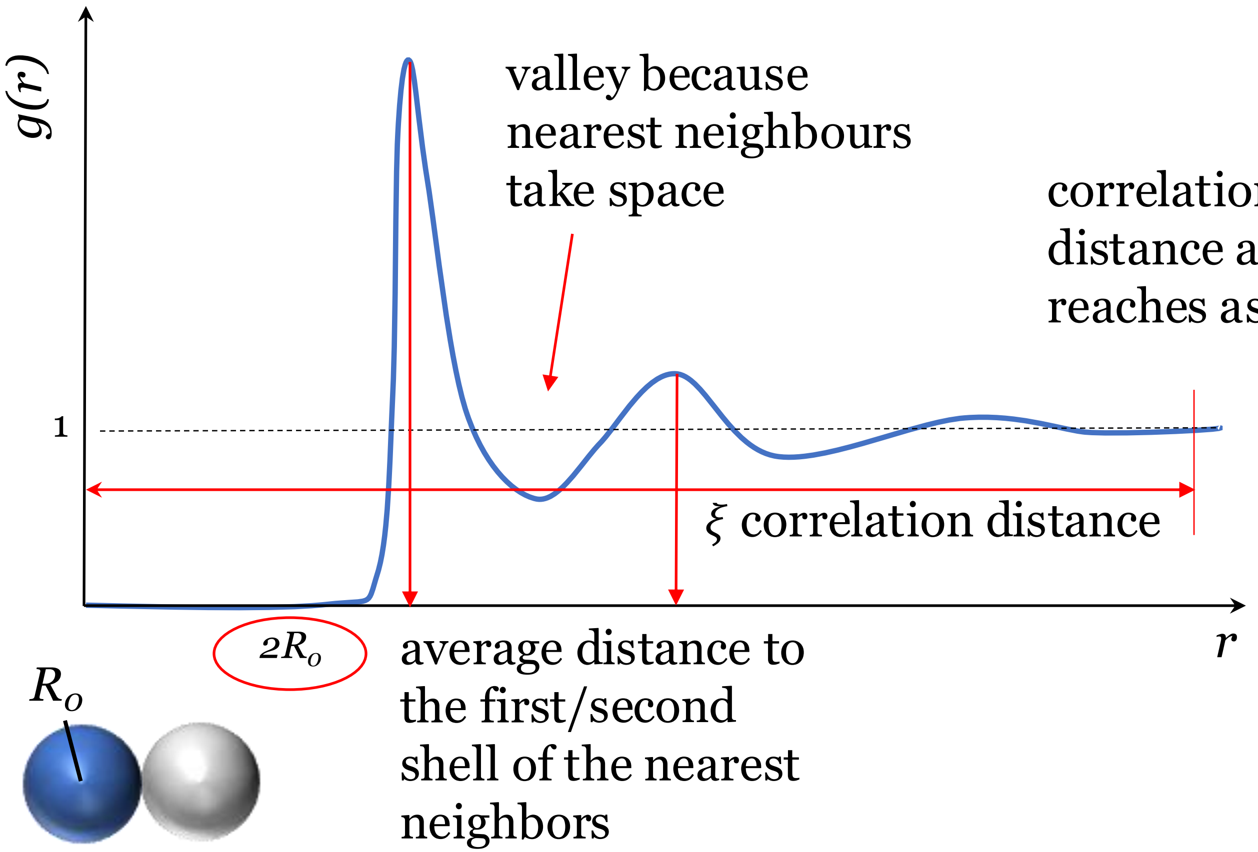
liquid
amorphous solid





g(r) several broad peaks and valleys until reaching a constant value at large distance r

Pair distribution function for liquid/glass



valley because nearest neighbours take space

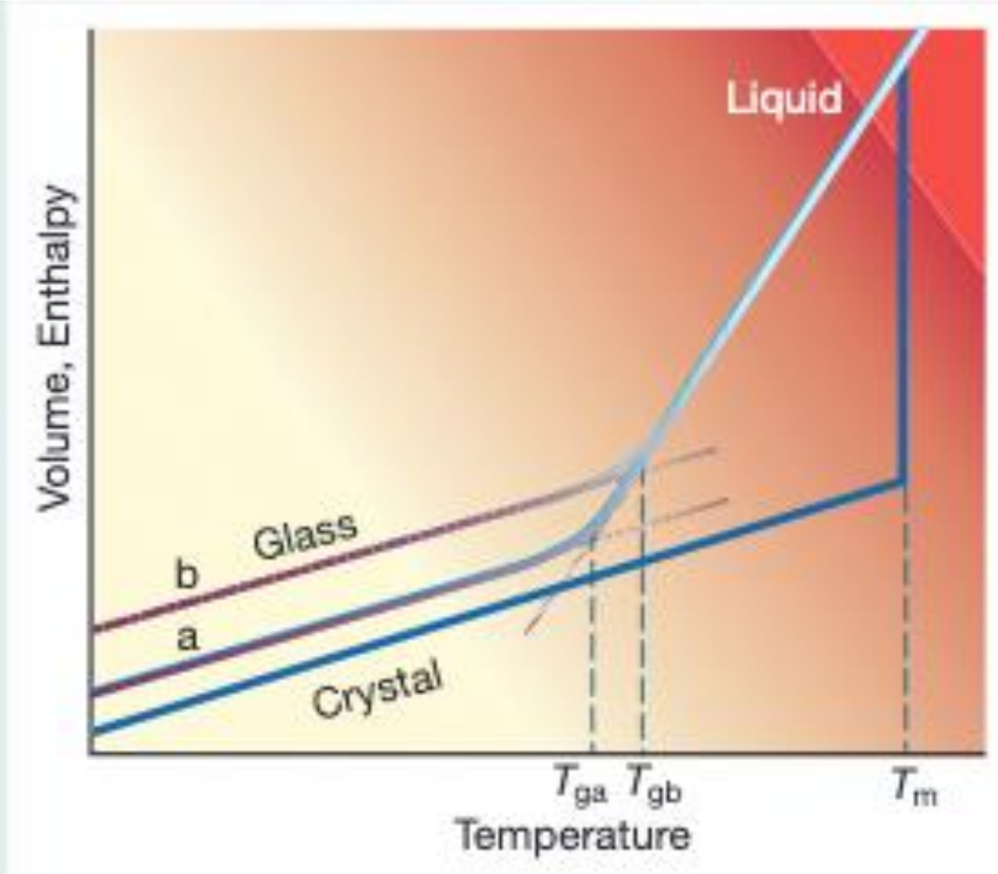
correlation distance ξ distance at which $g(r)$ reaches asymptotic 1

ξ correlation distance

average distance to the first/second shell of the nearest neighbors

$g(r < 2R_o) = 0$

Glass formation and glass transition temperature



Crystallization happens at a well defined melting temperature T_m with an abrupt change in the specific volume

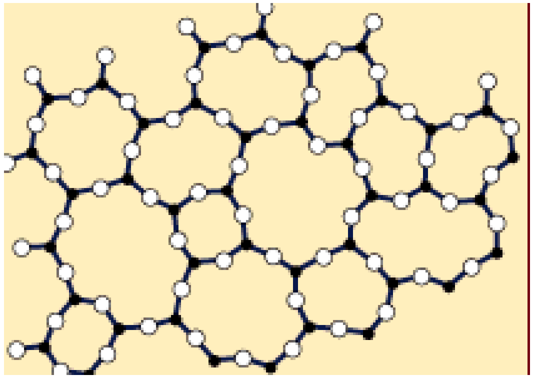
Glass transition: The temperature where the glass transition happens depends on the cooling rate
→ glass a) with a slower cooling rate than glass b)

thermal expansion coefficient changes (different slope) but no abrupt change in specific volume

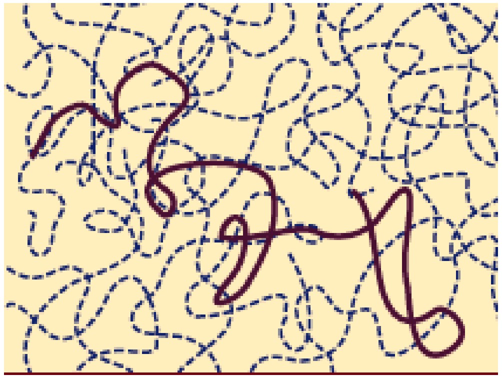
Debenedetti, P. G., & Stillinger, F. H. (2001). Review article Supercooled liquids and the glass transition. *Nature*, *410*(March), 259.

Atomic scale structure: models

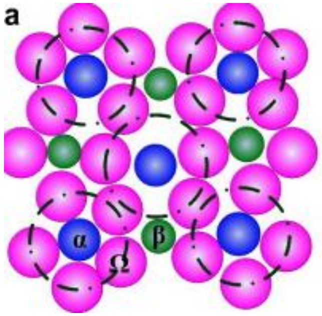
random-network model → covalently bonded glasses (amorphous silicon, oxide glasses)
random-coil model → polymer-chain organic glasses
random close-packing model → metallic glasses



continous random-network model for network glasses



random-coil model for polymeric glasses

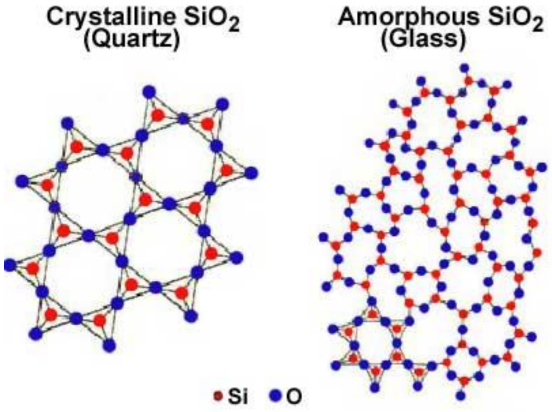


random close-packing model
“efficient cluster packing”
for metallic glasses

Enyclopaedia Britannica

Continous random network model

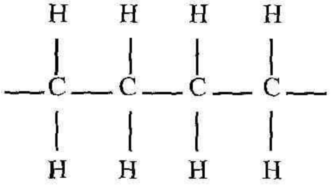
- Based on the observation that oxid glasses have similar mechanical properties (elastic modulus etc) as crystals: properties are driven by the local bonding
- → contionous random network model: three-dimensional network of bonded units that lack translational symmetry, but respects bond functionality and can be extended indefinitely (W.H. Zachariasen 1932)
- chemical species which enter into the structure of the network forming strong chemical bonds with oxygen are called network formers. Chemical species such as Na or Ca, which do not bond directly with the network but sit (in ionic form) within its interstitial holes are called network modifiers → they modify interaction (depending on type of bonding strenghten or weaken!)



What is a polymer?

Chain-like molecules where chemical groups (at least to some extend) repeat
Covalent bonds between the units.
→ long string like molecules

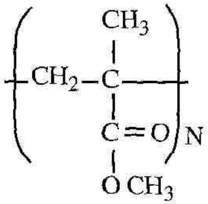
Polyethylene



or $(CH_2)_N$

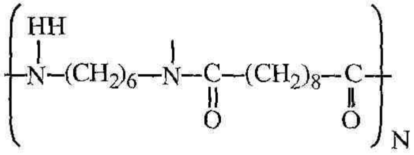
where N = degree of polymerisation

Polymethyl methacrylate

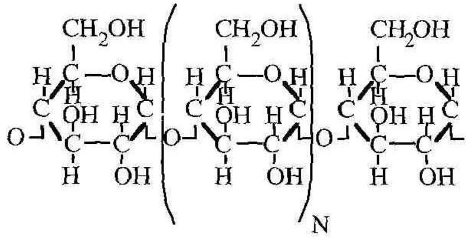


PMMA or Perspex (ICI trade name)

Nylon 6-10

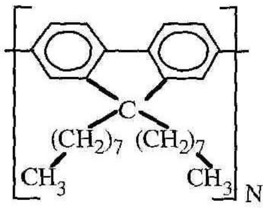


Amylose

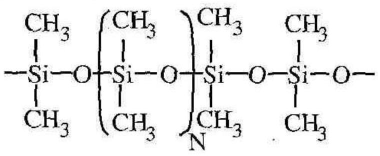


Starch

Poly(di-octyl fluorene)



Polydimethyl siloxane



PDMS or silicone oil

main elements forming the basis:
C, O, Si

Molecular weight

There is almost always a distribution in molecular weight M because the degree of polymerization N, i.e. the number o monomers, is a random variable

number average : $$M_n = \frac{\sum n_i M_i}{\sum n_i}$$

weight average: $$M_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i M_i}{\sum n_i M_i}$$

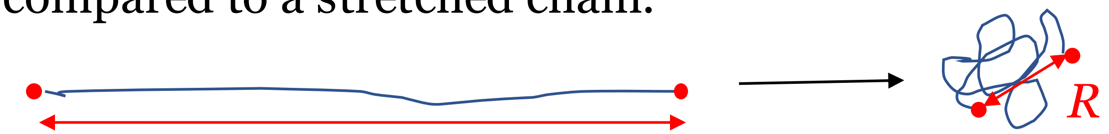
n_i and w_i are number and weight fractions of molecules/chains with molar mass M_i

The polydispersity index is given by M_w/M_n

Viscosity of molten polymers depends on its molecular weight!

Size of polymer chains

- Polymers normally form **random coils** due to the entropy gain.
- The number of microstates is much higher for a random coil configuration compared to a stretched chain.



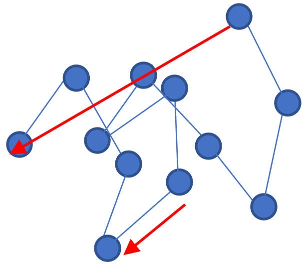
$r_{max} = Na$

contour length

N the number of monomers
a the length of one monomer

- **Freely jointed** chain segment model: At each “connection point” a new direction is acquired by random. If each segment is equal to the chemical monomer in size the “walk” along the chain consists of *N* vectors at each point in a random direction (**random walk**).

$$\vec{r} = \sum_{i=1}^{N} \vec{a}_i$$



$R = aN^{1/2}$

expected value R of the end-to-end distance for the random variable r

Real chain: Kuhn length or persistence length

- In real chains there are **steric limitations**: not free to rotate but constrained to have certain definite bond angles, but some freedom to rotate
- thus after a certain distance, the statistical step length, called the **Kuhn length** b which is larger than the monomer length a, the segments are freely jointed, the number of segments for the random walk is now aN/b

$$R = b(Na/b)^{1/2} = (abN)^{1/2}$$

$$C_\infty = \frac{a^2}{b^2}$$ is the Flory's characteristic ratio

- For stiff polymers an alternate model is used: continuously bending worm-like chains.

- but also here: there is a loss of correlation of direction over a certain distance, the **persistence length** l_p. Correlation decays exponentially

$$R = (2l_p aN)^{1/2}$$

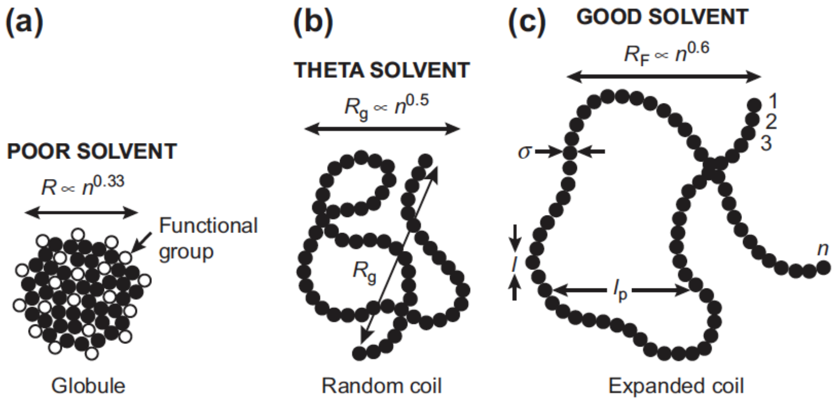
Interaction with the solvents

In a “good solvent”: repulsion between the chains: volume exclusion effect, coil expands:
$R=aN^{\upsilon}$, $\upsilon>1/2$, from experiments in general $v \approx 0,6$

”Theta solvent”: no interactions (repulsive effect is exactly cancelled by attractive effects), this is also true for a polymer melt: same interaction within chain as with other chains around, “normal random walk”
$R = aN^{1/2}$

in a “bad solvent”: segments attract each other, collapse into a compact structure

$$R = aN^{1/3}$$



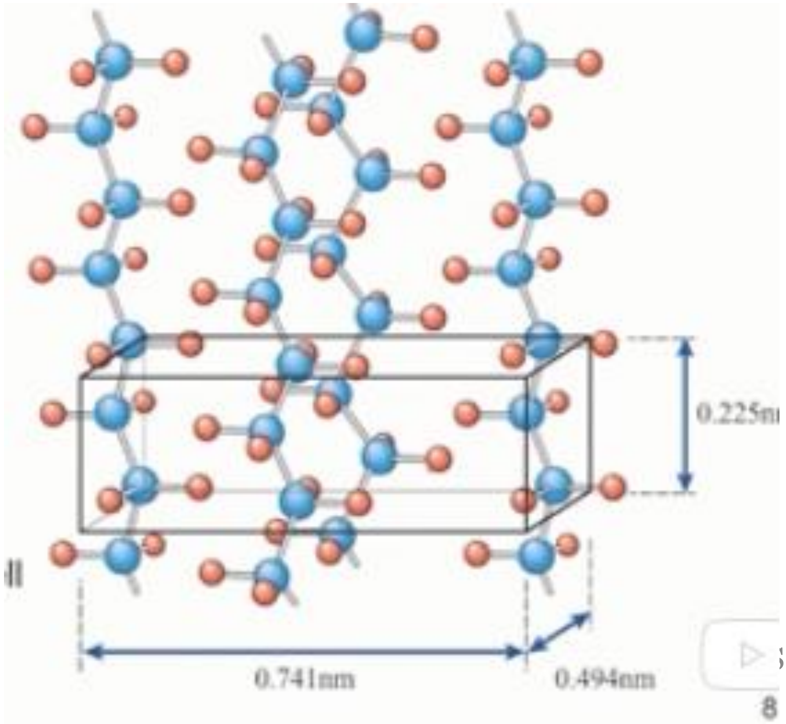
Crystal structure of polymers

crystallization: basic requirement chain into straight perfectly ordered form
pack lattice by orienting the chains uniformly in one direction

→ monomeric units as structure units

→ strong anisotropy in binding force: covalent bond in one direction of the unit cell, van der Waals in the two other directions, if Hydrogen bonds are possible: stronger interaction

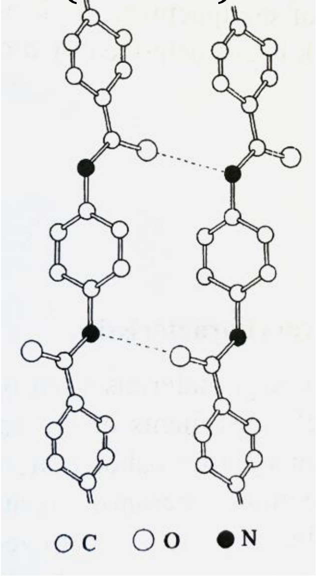
polyethylene unit cell (stretched zig-zag)



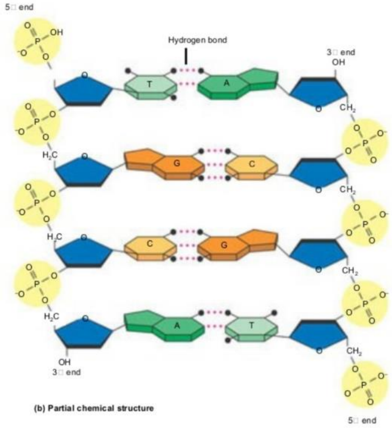
helical twist

hydrogen bonds in the plane

Aramid fibers (Kevlar)



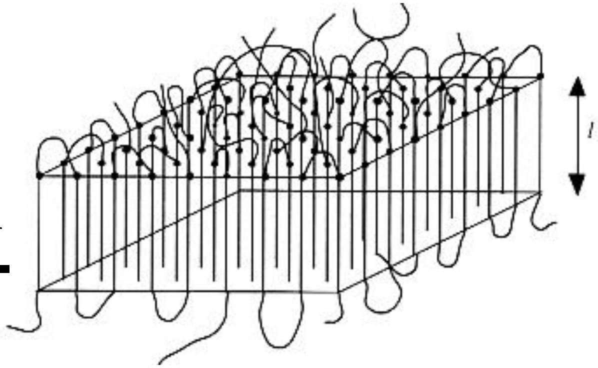
DNA



Crystallinity

Polymer molecules show some degree of ordering. Depending on molecular symmetry, molecular weight (kinetics) and branching, etc.

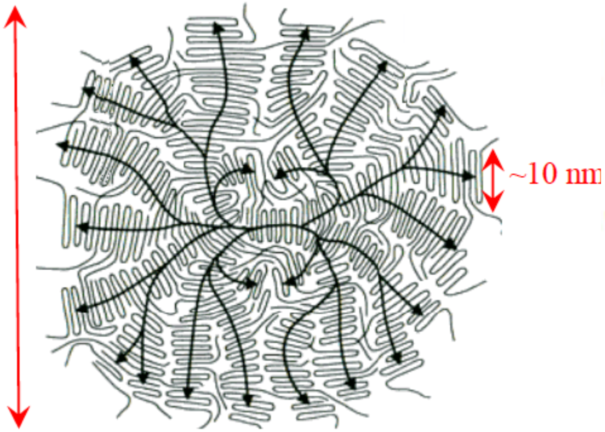
Polymers never fully crystals because of the entanglement of the chains in the melt



Lamellar growth direction ~10 µm

Lamella thickness
~10 – 20 nm

spherulite: lamellae branches grow from a nucleation center



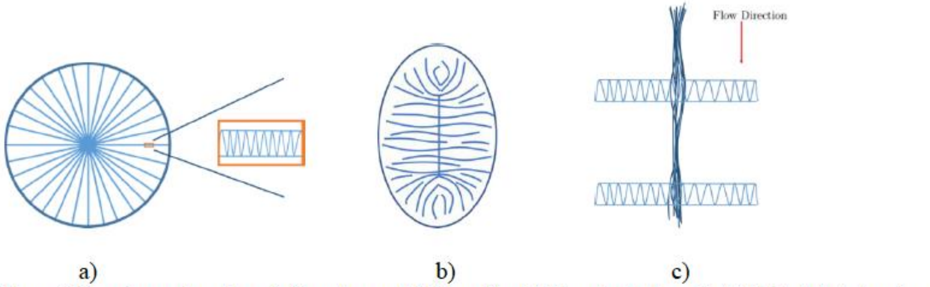
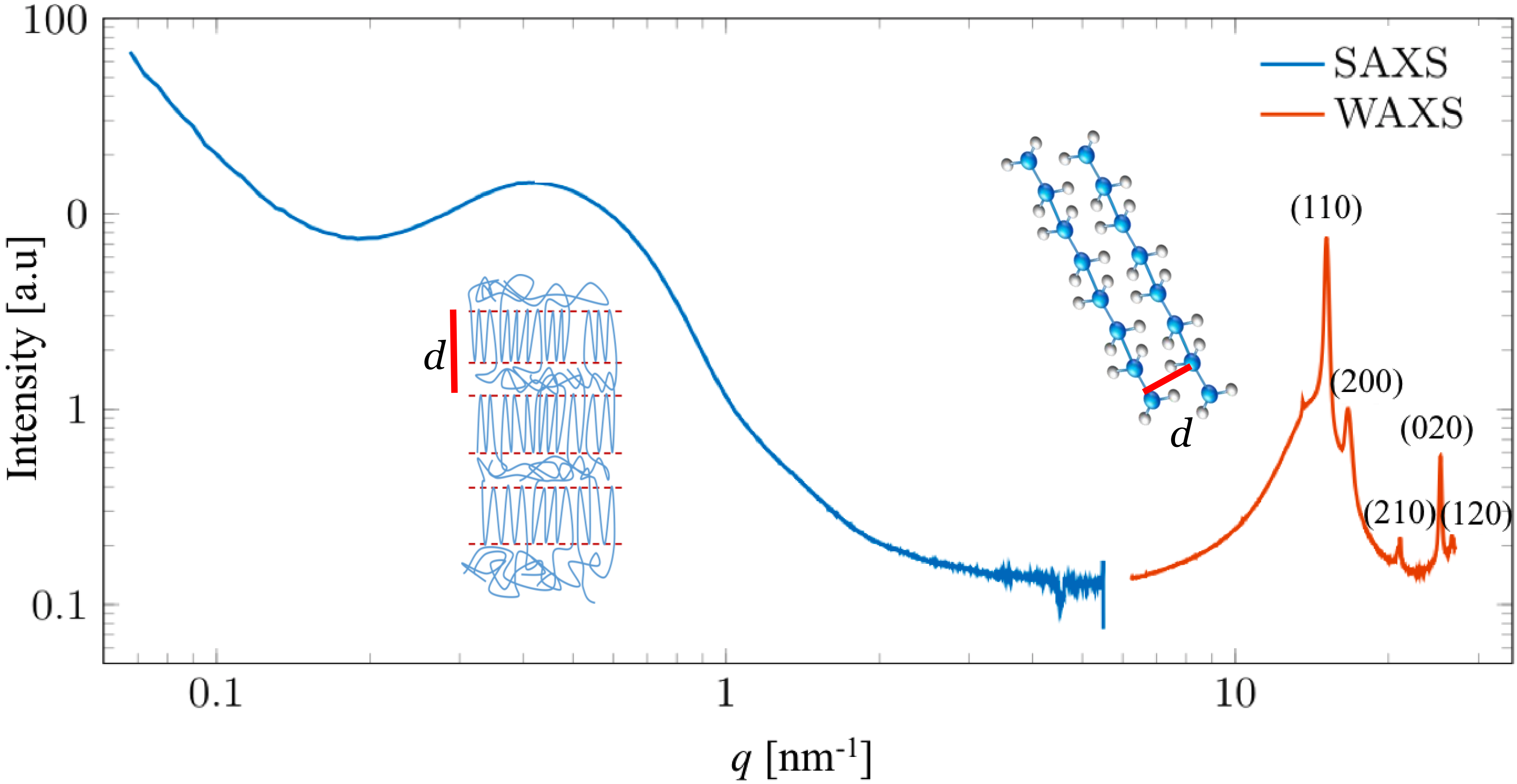


Figure 2: Structures of semi-crystallin polymers (a) Spherulite (b) Elongated spherulite (c) Shish-kebab structure

Semi-crystalline polymer:

competition between polymer stretching and coiling and reduction in free energy for crystal formation on the other hand determines lamellar thickness



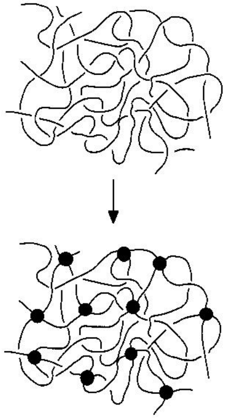
Thermoplastic materials

- linear or slightly branched polymers
- At high temperature (above 170 – 300°C) molten state

→soften when heated and harden when cooled → reshaping

- process is reversible and can be repeated → materials can be recyled
- bonds between individual molecules is relatively week (e.g. van der Waal bonding)
- above glass transition: polymer molecules can slide and be molded
- amorphous, semi-crystalline (or liquid-crystalline)
- examples: polyethylene, polystyrene, poly(vinil chloride)

Thermosetting polymers



- permanently hard (after curing) do not soften upon heating
- network polymers are covelently linked → three-dimensional structure
- at high temperature become damaged and degraded
- examples: vulcanized rubbers, epoxies, polyamides

Polymer gels are highly elastic when they consist of long chains connected with few cross-link points. Small chains and many cross-link points lead to a higher Young's modulus

Elastomer: low number of cross-links (e.g. car tires 1 per 100 units)

Thermosets: high number of cross-link density (10-100 times more)

Structure – mechanical property: crosslinks

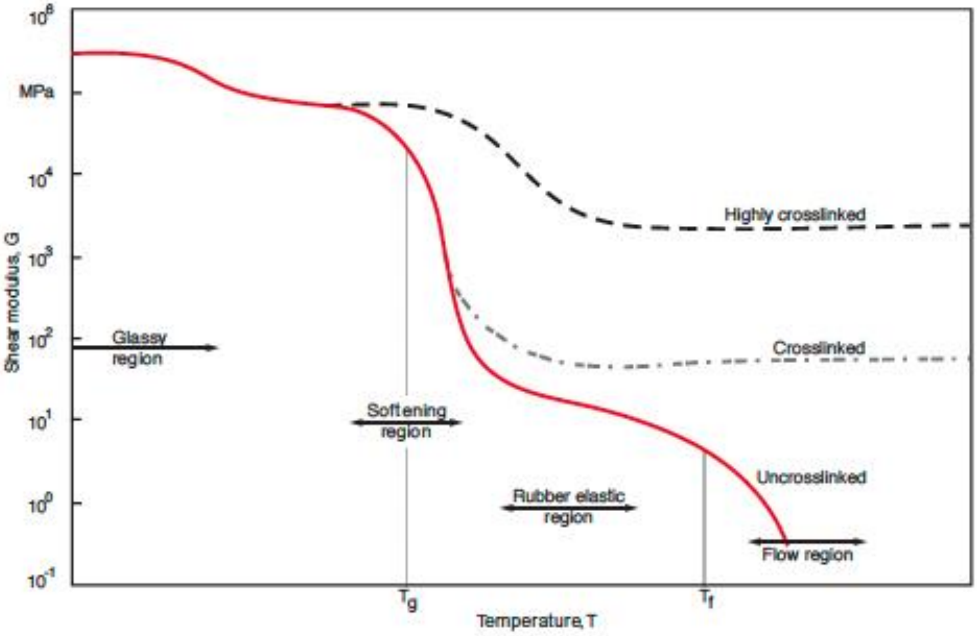
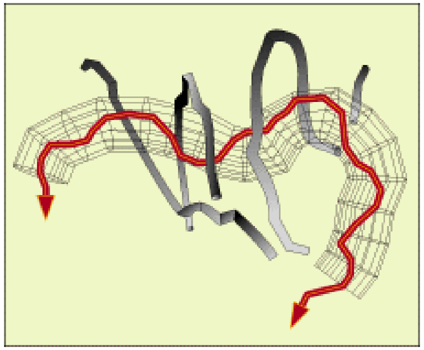


Figure 9.66 Shear modulus and behavior of cross-linked and non-crosslinked polymers

In a cross-linked polymer the elastic modulus depends on the average molecular mass between cross-links M_x, R ,T and the density ρ:

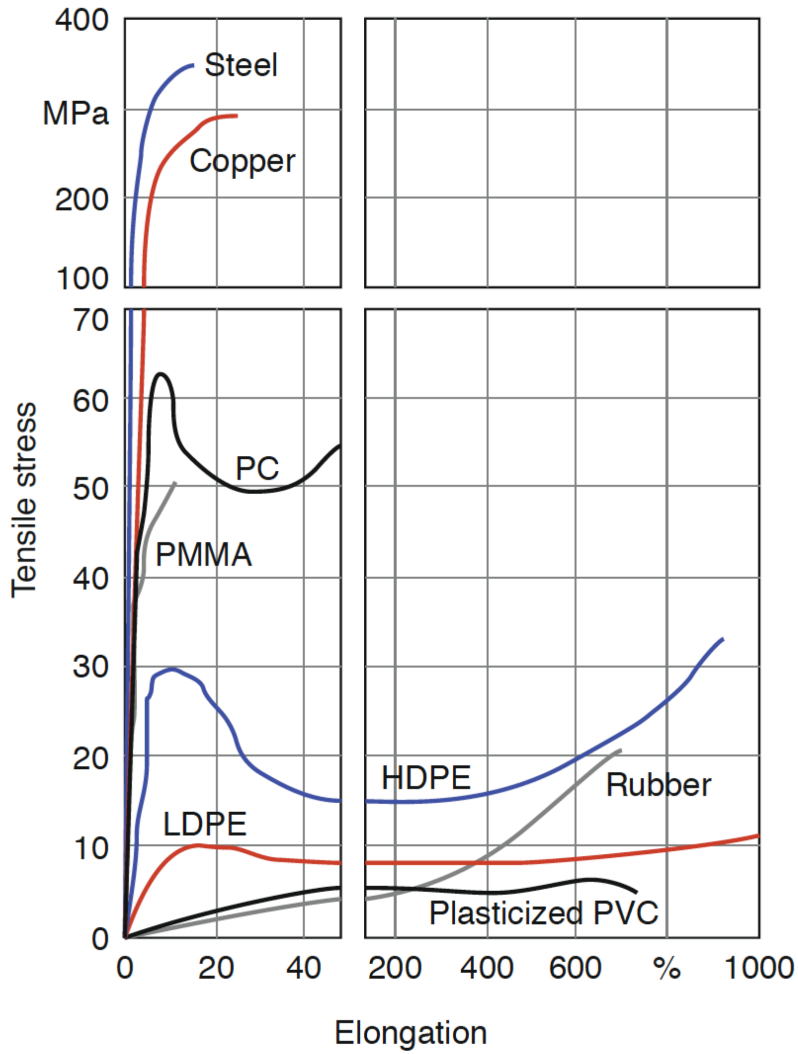
$$G = \frac{\rho RT}{M_x}$$

rubber plateau in non-crosslinked polymers: entanglement of polymer chains creates temporary cross-links



Structure – mechanical property

Tensile stress-strain curves for several materials



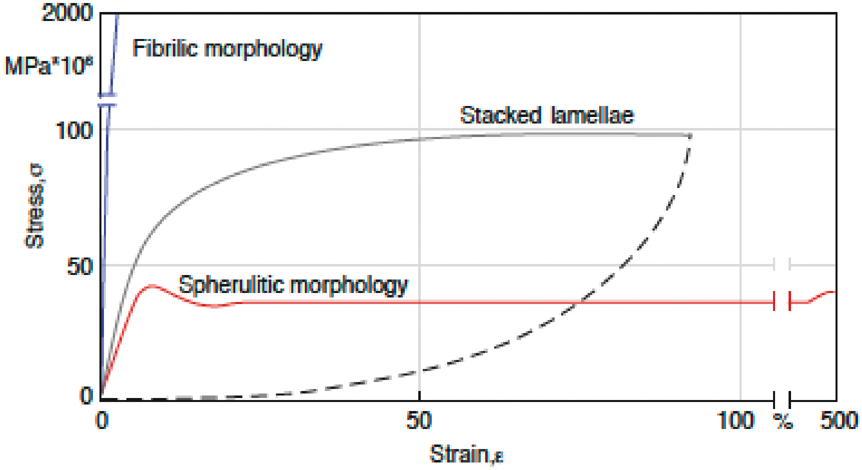


Figure 9.62 Stress-strain behavior of polyethylene with various morphologies

Materials science of polymers for engineers (Oswald, Menges)

Biological Materials: main components of life

- Polymeric molecules:
  - Nucleic acids (DNA, RNA)
  - Proteins
  - Polysaccharide (random sequence)

- Lipids: fats and oils

- Amphiphilic molecules (self-assembly)
  - phospholipids

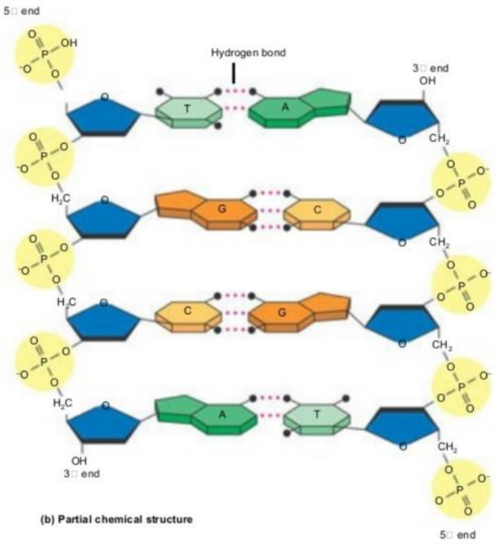
- Biominerals
  - Calcium phosphate (example: hydroxyapatite in bone)
  - Calcium carbonate (example aragonite and calcite in mollusk shells)
  - Silicates (diatoms)

DNA base pairs

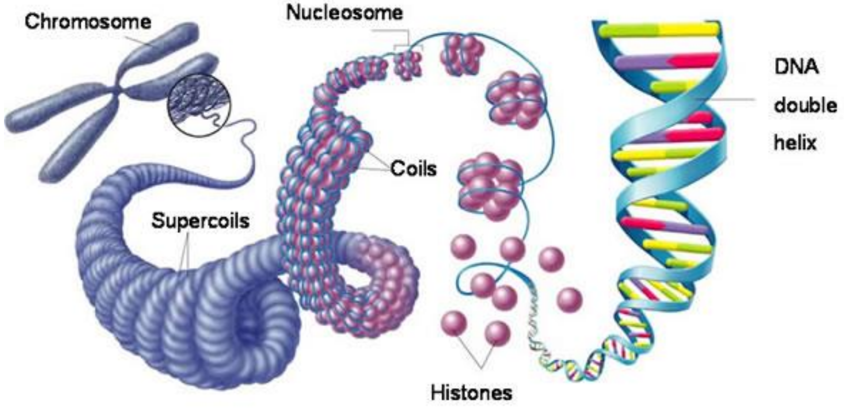
DNA backbone: phosphate and deoxyribose
4 different bases: thymine (T), cystosine (C), adenine (A) and guanine (G)

specific base pairing (A-T and C-G)
allows to reproduce a copy from a first strand (DNA replication)
very stiff polymer chain, pack into complex hiearchical structure with the help of proteins to fit into the nucleus of the cell: no random walk

RNA slightly different chemical composition, single stranded, involved in transcription of genetic information to proteins



(b) Partial chemical structure



Biology, Neil Campbell and Jane Reece
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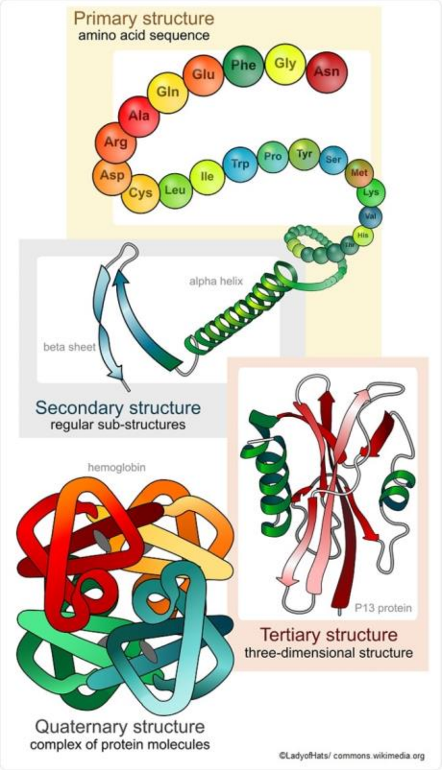
Protein

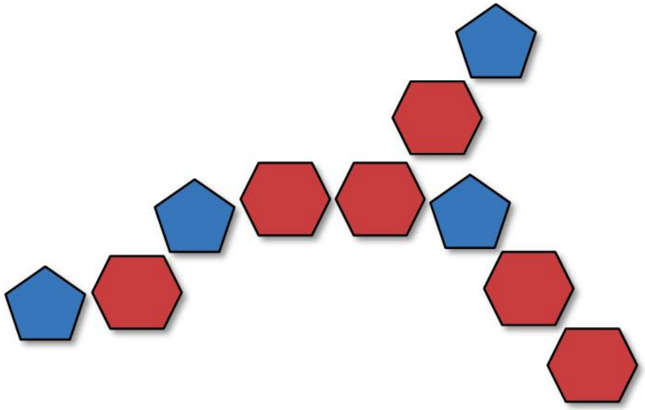
- Amino acid sequence = primary structure, determined by genetic code
- 22 different proteinogenic amino acids with hydrophobic (unpolar), hydrophilic uncharged (polar) or hydrophilic and charged (acidic or basic)
- hydrophilic and hydrophobic parts in the same molecule → specific interactions along the chain: don0t follow random walk but assisted self-assembly

- specific function due to very specific 3D structure:
- enzymes, signaling, transport, immunsystem, muscle movement…



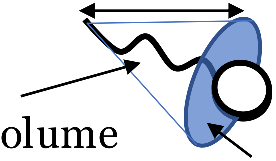
Polysaccharides

- carbohydrates, general formula $C_x(H_2O)_y$, monomers: various sugars
- no defined sequence and architecture (side-chains)
- store energy: starch (amylose and amylopectin), glycogen
- structural polymer: cellulose, chitin



Aggregates of amphiphiles

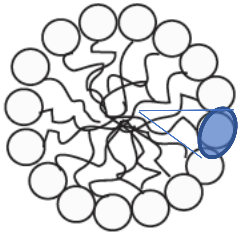
The aggregates formed is determined by the geometry of the amphiphile, maximizing the contact of the hydrophilic head with water while minimizing its contact with the hydrophobic tail



Radius $r \leq l_C$ critical chain length

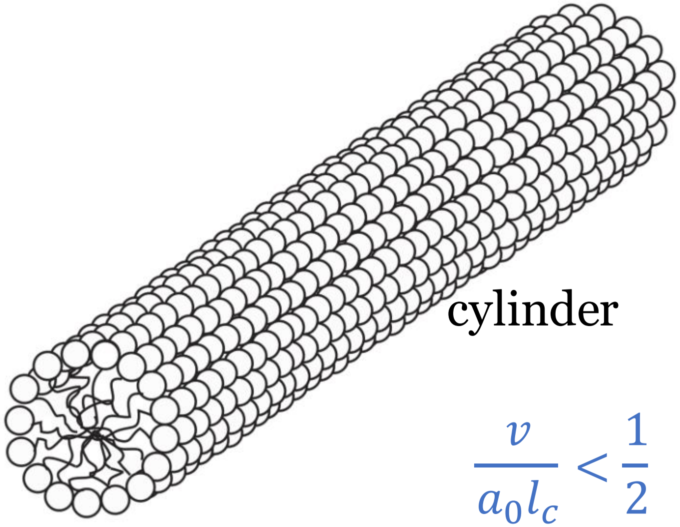
v chain volume

a_o optimal headgroup area



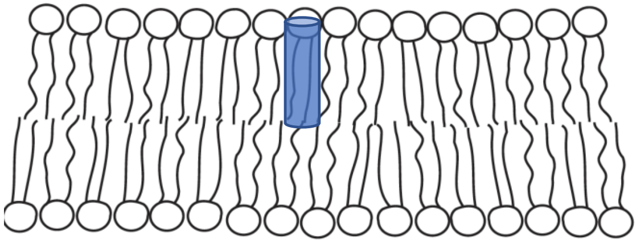
sphere

$$\frac{v}{a_0 l_c} < \frac{1}{3}$$



cylinder

$$\frac{v}{a_0 l_c} < \frac{1}{2}$$



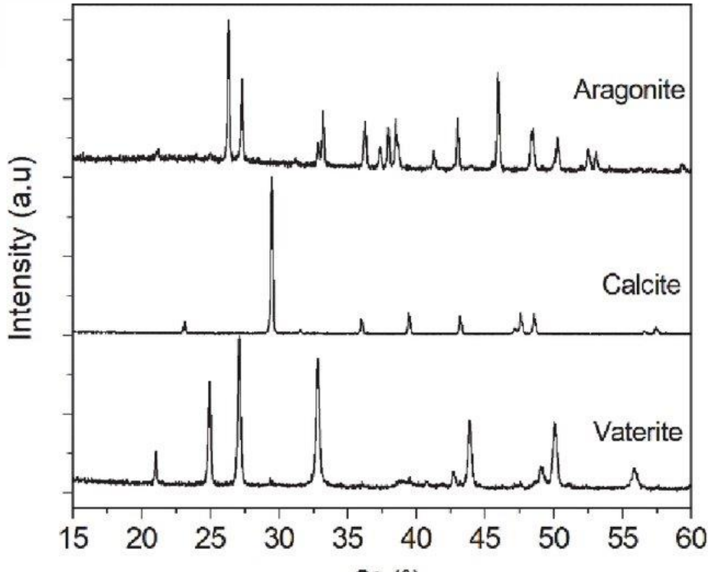
bilayer

$$\frac{v}{a_0 l_c} \approx 1$$

Biomineral: example calcium carbonate

The crystalline structure of Calcium carbonate: Polymorph

trigonal orthorombic hexagonal



Hybrid materials/Composite materials

composite materials: mixture on the microscopic scale of several phases

hybrid materials are composites consiting of two consituents at the nanometer or molecuar level

not a strict separation between composite and hybrid material. Both combine properties from from than one material with distinct structure and chemocal composition, contributing synergistically to the physical, chemical or mechanical properties

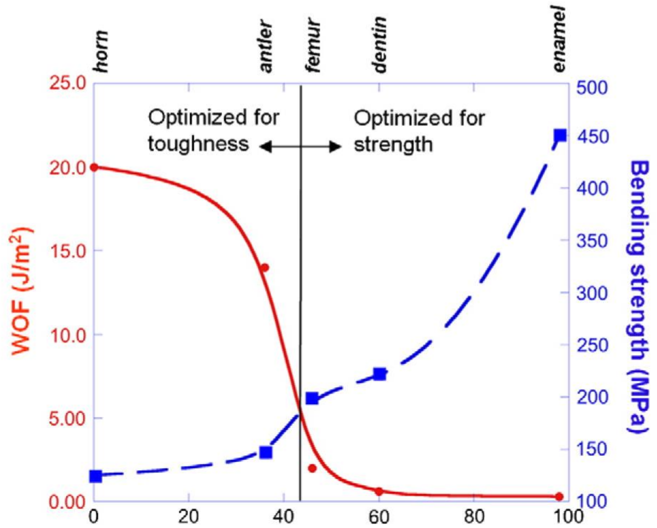
Composite materials

- Reinforced composites:
  - fiber composites: continous matrix reinforced with high strenght fibres
    - short (discontinous) fibers
    - long (continous) fibers
  - particulate composites: (isotropic) particles immersed in a matrix
  - flake composites: flat reinforcements aligned in plane in matrix

  matrix can be for example: polymer (**thermoset** or thermoplastics (PEEK)), metalceramic, carbon
- sandwich structures: combining various materials used to form functional structures
- functional composites: example composites with sensing functionality

Biocomposites

- often (but not only) a combination of biominerals (high stiffness, low thoughness) with a biopolymer (high thoughness, low young's modulus)
- Hierarchical structure to balance stiffness, strength and thoughness. While strength decreases due to the existence of flaws, thoughness increases with more hierarchical levels, since a growing crack will encounter barriers as it propagates



mineral fraction