MSE-238
Structure of Materials

Week 12 – biological materials and hybrid materials

Spring 2025

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- Q&A session: June 27 between 13-15 room DIA 003

Overview

- biological materials
- structure of some important biological building blocks:
  - nucelic acids (DNA/RNA)
  - proteins
  - polysaccharides
  - lipids
  - amphiphilies
  - biominerals
- hybrid materials/composite materials
- reinforced composites
- functional composites
- biocomposites
- hierachical materials

Additional reading

- ”Soft Condensed Matter”, Jones, Oxford
- “Introduction to Materials Science” Mercier, Zambelli, Kurz, Elsevier
- “Introduction to soft matter: synthetic and biological self-assembling materials”, Hamley, Wiley

Biological Materials: main components of life

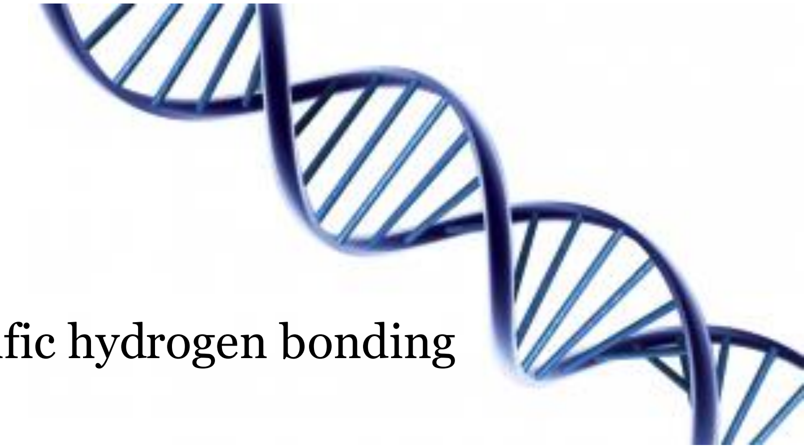
- Polymeric molecules:
  - Nucleic acids (DNA, RNA)
  - Proteins
  - Polysaccharide (random sequence)

- 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)

Nucleic acids



DNA (deoxyribonucleic acid)

- store and transmit information
- genetic code: complementary base pairs with specific hydrogen bonding
- double helix
- robust polymer
- free energy about 3kBT/basepair: melting into single strands at 50-90°C

RNA (ribonucleic acid)

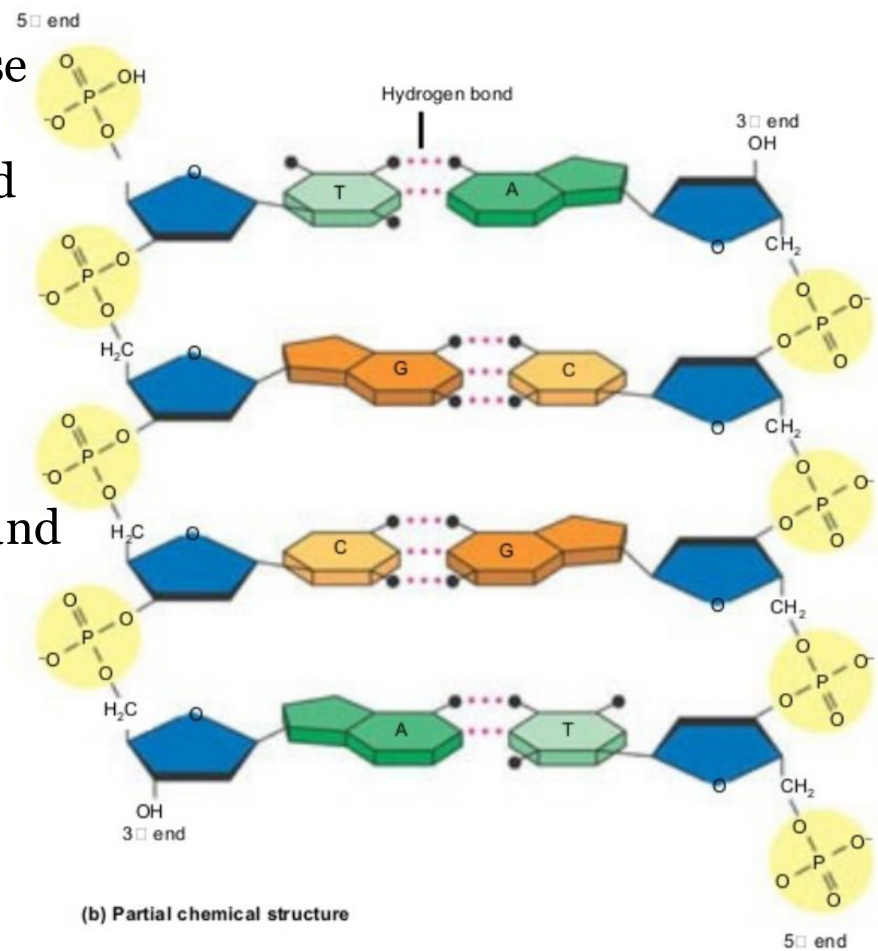
- involved in transcription of information into proteins
- slightly different chemical composition
- single stranded

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 (hydrogen bonds)

allows to reproduce a copy from a first strand
--> DNA replication



(b) Partial chemical structure

Chromosome

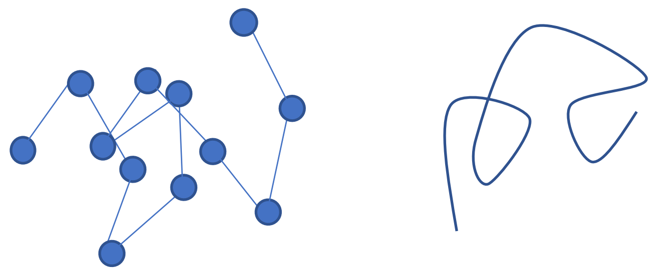
- double helix: rigid molecule, at length scales smaller than the persistence length l_p = 60 nm the molecule is stiff (compare to $a = 0.34\ nm$)
- larger length scales: random walk
- largest human DNA has 280×10^6 monomers units

- what is the total contour length?
- what is the end-to-end distance?

- worm-like chain model end-to-end distance: $\left[2 l_p a N\right]^{1/2}$

Worm-like chains: persistence length

- 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

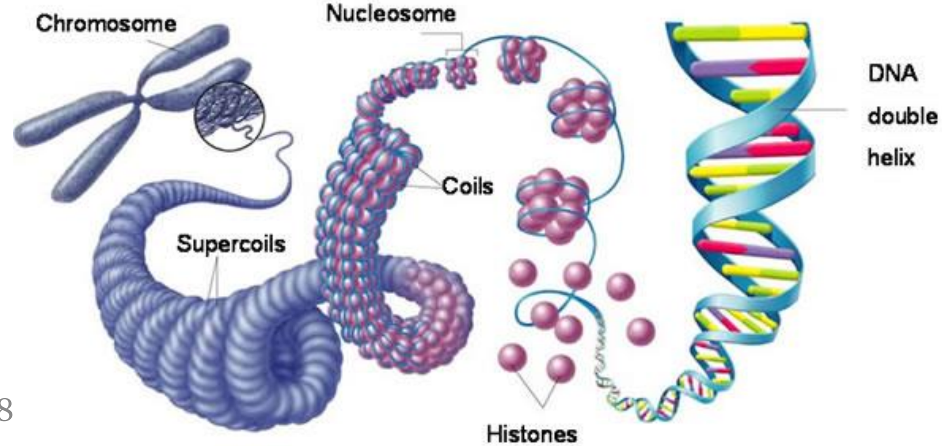
$$R_{\mathrm{wlc}} = \left[2 l_\mathrm{p} r_{\max} \left[1 - \frac{l_\mathrm{p}}{r_{\max}} \left[1 - \exp\left(-\frac{r_{\max}}{l_\mathrm{p}} \right) \right] \right] \right]^{1/2}$$

for $r_{\max} = Na >> l_\mathrm{p}$ the random walk is recovered $R\big|_{r_{\max} >> l_\mathrm{p}} \approx \left[2 l_\mathrm{p} r_{\max} \right]^{1/2} = \left[2 l_\mathrm{p} a N \right]^{1/2}$

comparing to the Kuhn length: $R = [abN]^{1/2}$ so $b = 2l_p$

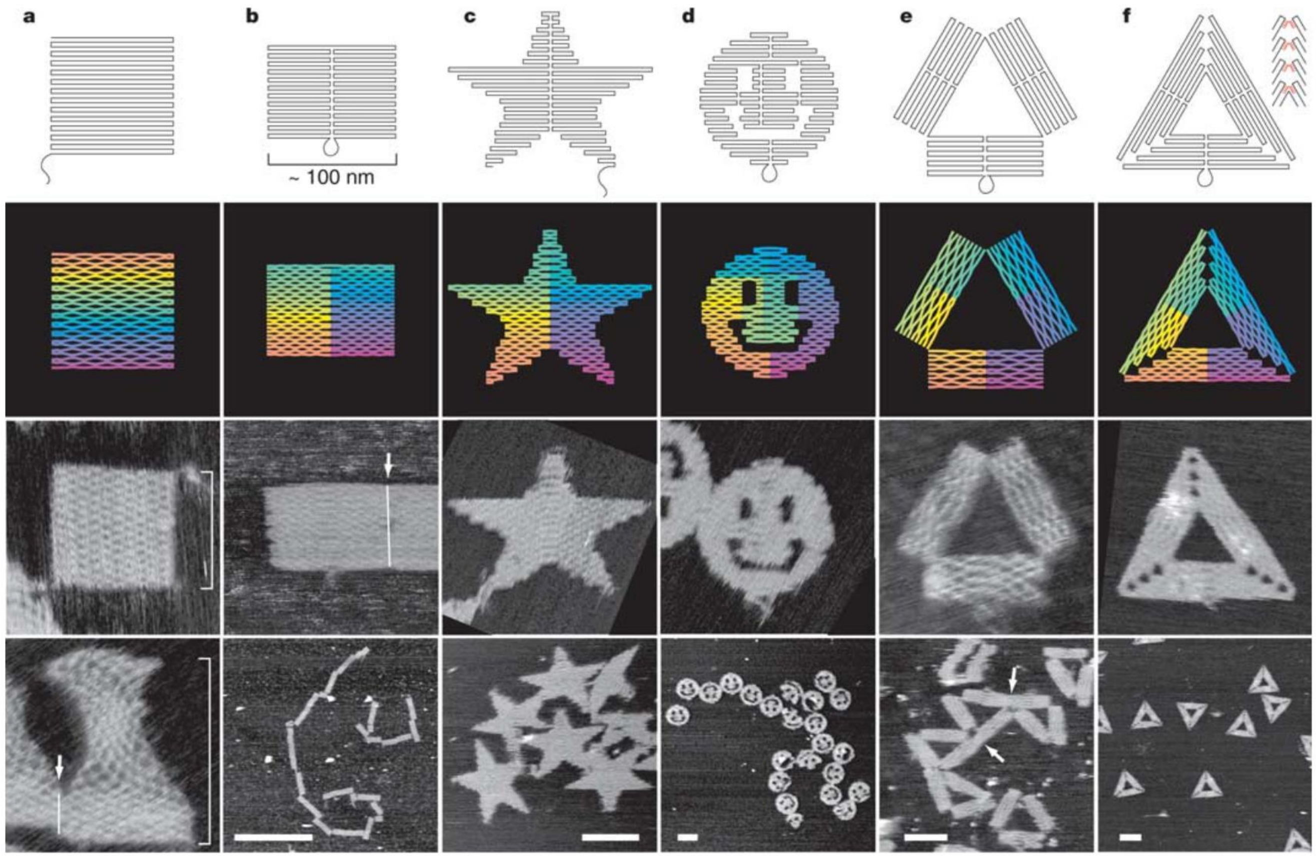
Chromosome

- double helix: rigid molecule, at length scales smaller than the persistence length l_p = 50-60nm the molecule is stiff (compare to a = *0.34 nm*)
- larger length scales: random walk
- worm-like chain model end-to-end distance: $\left[2 l_p a N\right]^{1/2}$
- largest human DNA has 280×10^6 monomers units
- for the end-to-end distance of the largest human DNA molecule with a total contour length of 95 mm results in about 100µm: no space in the cell nucelus (around 6µm)!
- complex, hierarchical structure including proteins and supercoiling
- → Chromosome (human cell contains 24)



DNA origami

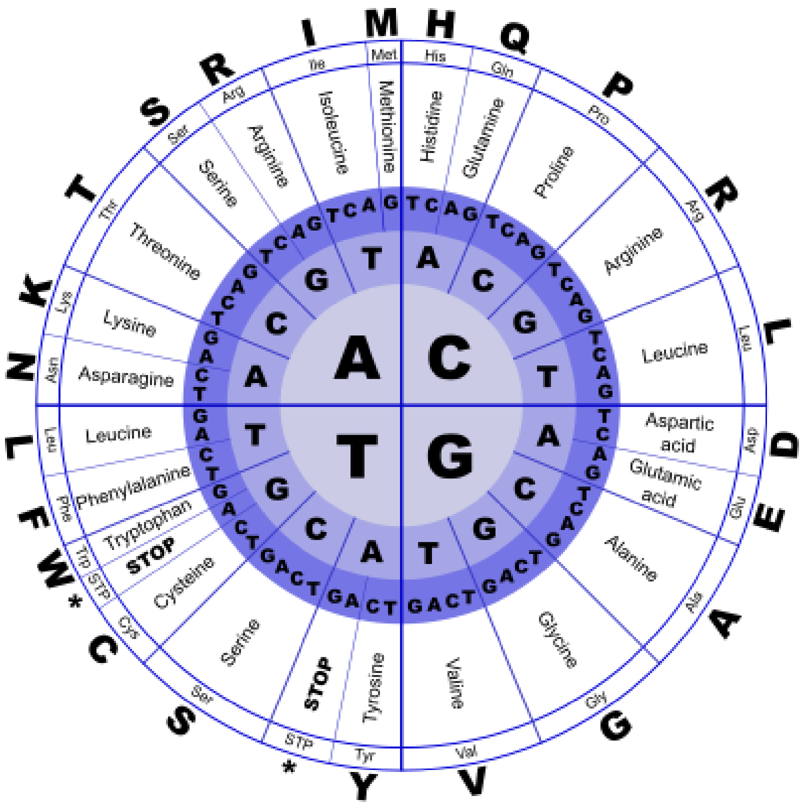
utilizing the possibility to create DNA sequences and their specific hybridization, well defined self-assembly of 2D structures
each oligonucleotide can serve as a 6-nm pixel

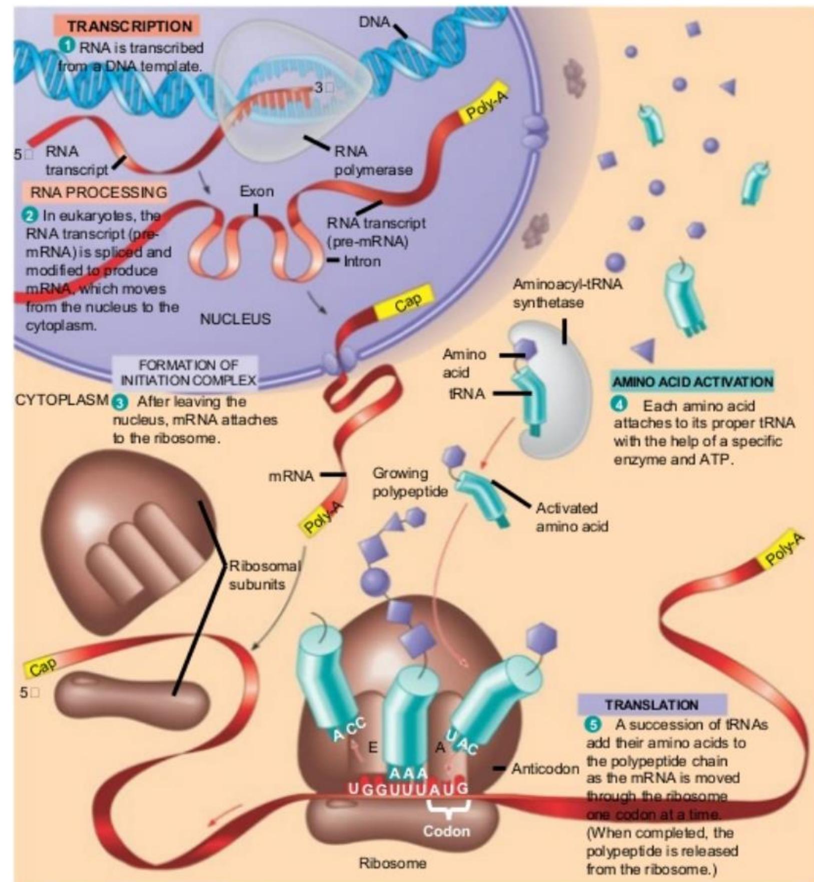


Rothemund, Nature, 440,297, 2006

from Gene to Protein

- DNA molecule codes for the amino acid sequence of the protein
- RNA transcription and Protein translation





Protein

- Amino acid sequence = primary structure, determined by genetic code
- 22 different proteinogenic amino acids
- all proteinogenic amino acids (except glycine) are **chiral**, only the L-enatiomer exists in biological systems
- hydrophobic (unpolar)
- hydrophilic uncharged (polar)
- hydrophilic and charged (acidic or basic)

- hydrophilic and hydrophobic parts in the same molecule → self-assembly to minimize contact between hydrophobic groups and water, maximize contact hydrophilic and water

Protein functions

- Enzymes: biological catalysts
- cell signaling and signal transduction, e.g. insulin
- membrane proteins: regulate transport and sense the environment (receptor)
- adaptive immune system (antibodies)
- transport proteins, e.g. Haemoglobin transporting oxygen
- structural proteins: cytoskeleton, collagen, spider silk
- molecular motors: convert chemical energy to mechanical motion

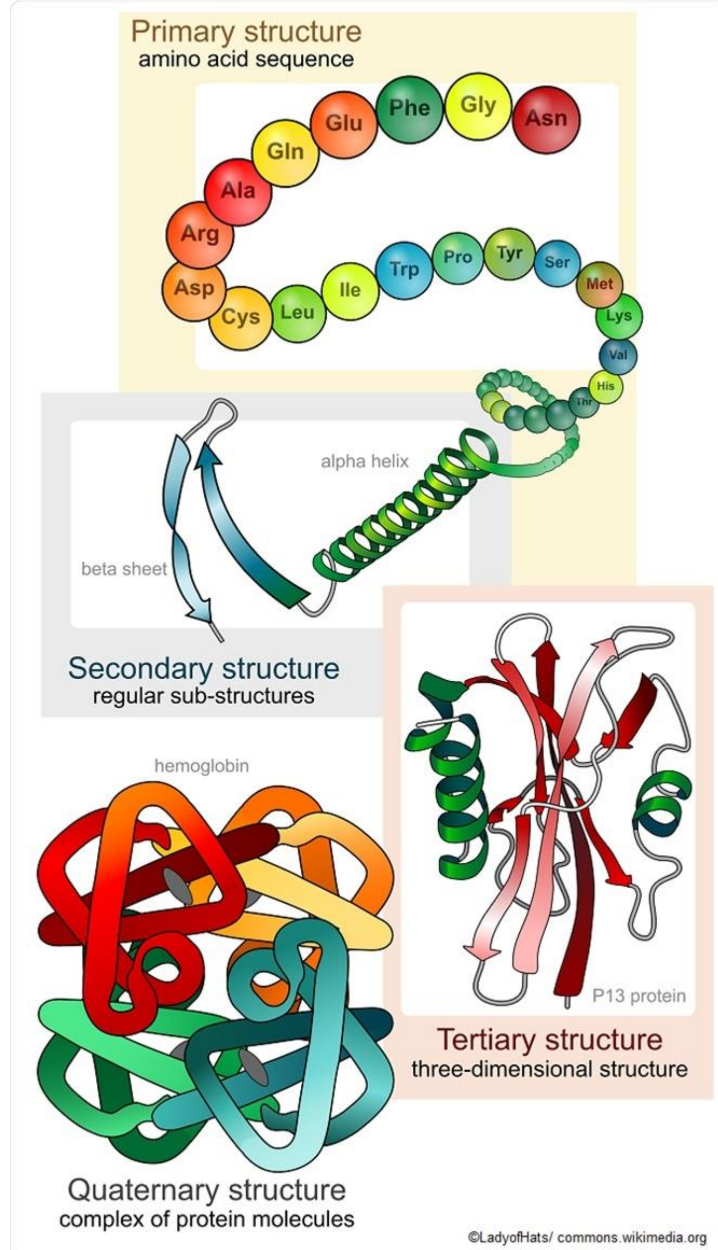
Proteins: hierarchical structure

function with 3D structure:

protein folding into secondary and tertiary structure

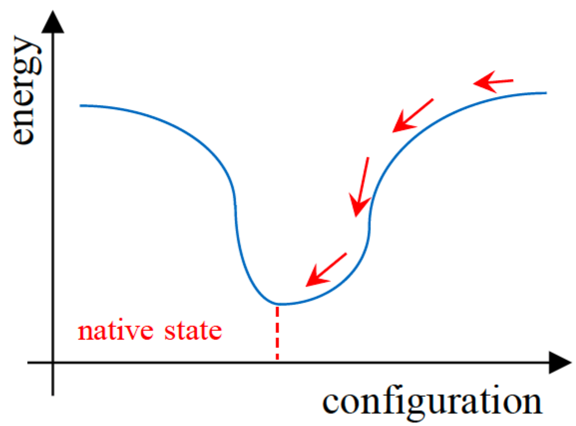
assisted self-assembly (chaperones)

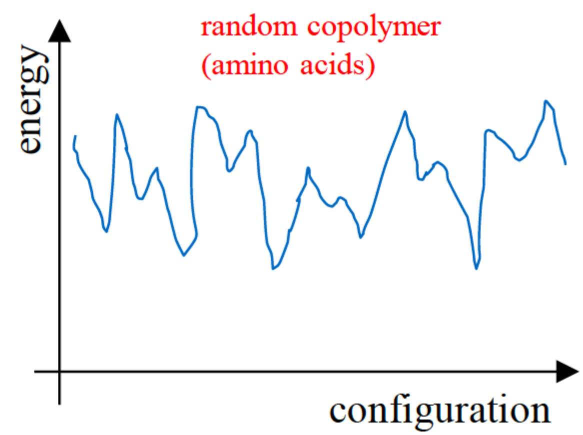
→ don't follow random walk model of polymers



Proteins

- native form: single, well-defined structure, compact
- denaturated form: more open, random conformation, tertiary structure and maybe also secondary structure is destroyed: loss of biochemical activity, can be irreversible
- protein sequences are not random, they have evolved specifically to have the property of one well defined structure
- energy landscape, protein folding towards successively lower energy

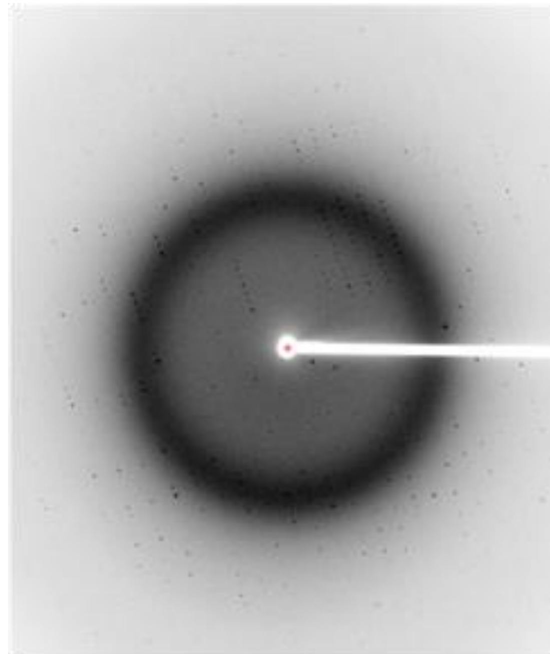


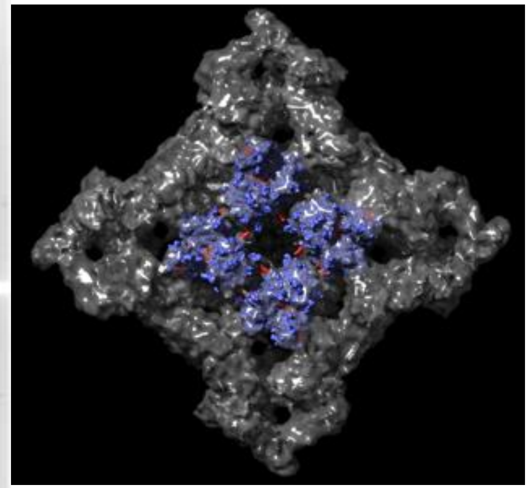


Reminder: protein crystallography

study the three-dimensional structure of biological macromolecules.

Data collection: wave length = 0.097nm, Canadian Light Source - 1 second per frame,
total of ~360 frames,
step size 0.5 degrees





Courtesy: F. Van Petegem, UBC, Canada

For structure determination from single crystal diffraction one needs to retrieve…

in order to solve this problem, the space group will restrict the model **fewer atoms** because symmetry will automatically place equivalent atoms.
→ Refine the structure more efficiently using fewer parameters.

to reach higher resolution in the structure determination one needs….

Protein Crystallography

Reminder:

14 Bravais lattices

32 point groups

230 space groups


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.

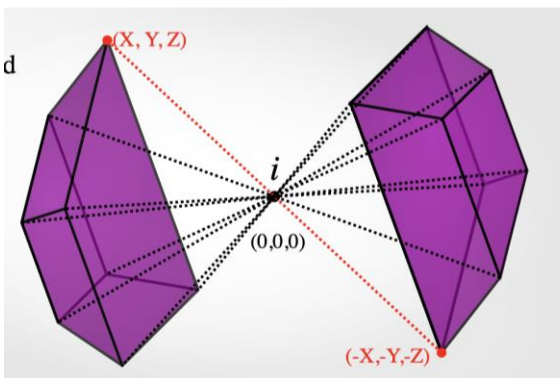
Point Symmetry operations in 3D

- **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

Protein Crystallography

Reminder:

14 Bravais lattices

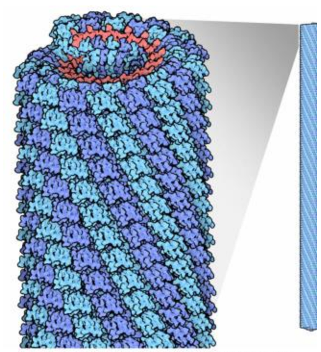
32 point groups

230 space groups

- proteins are chiral, chiral molecules cannot exist in crystals with symmetry operations that invert handedness, such as:

Protein crystallography

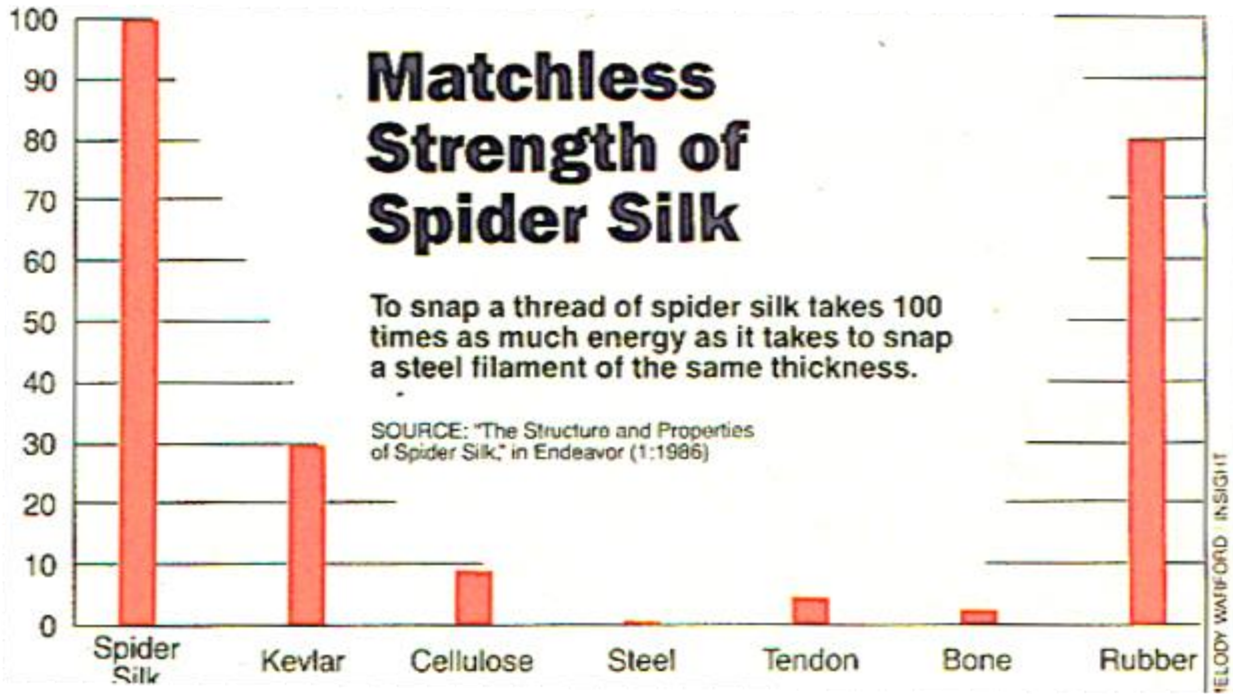
- from the 65 possible space groups for proteins, only 50% of them have been observed for proteins.
- one particular space group (P212121 (No. 19) makes up more then 30% of all known protein crystals
- Orthorhombic and monoclinic crystal systems dominate
- symmetric proteins, often as quaternary structure crystallize on the other hand more often in space groups which can accommodate for that symmetry, often in the tetragonal or trigonal structure with helical screw symmetries



Tobacco mosaic virus, with the RNA genome in red.

Wukovitz & Yeates *Nature structural biology* 1995 *2,12*

Spider Silk

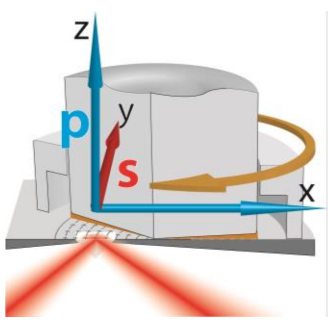


A cable made of spider silk which is no thicker than 5 cm diameter could support an aeroplane

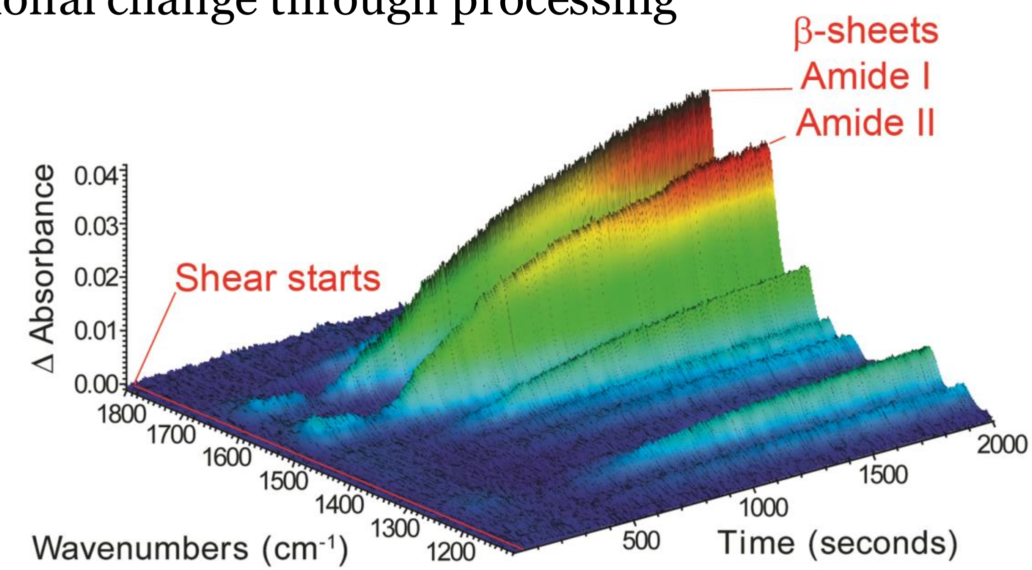
Spider silk

silk protein in solution

conformational change through processing

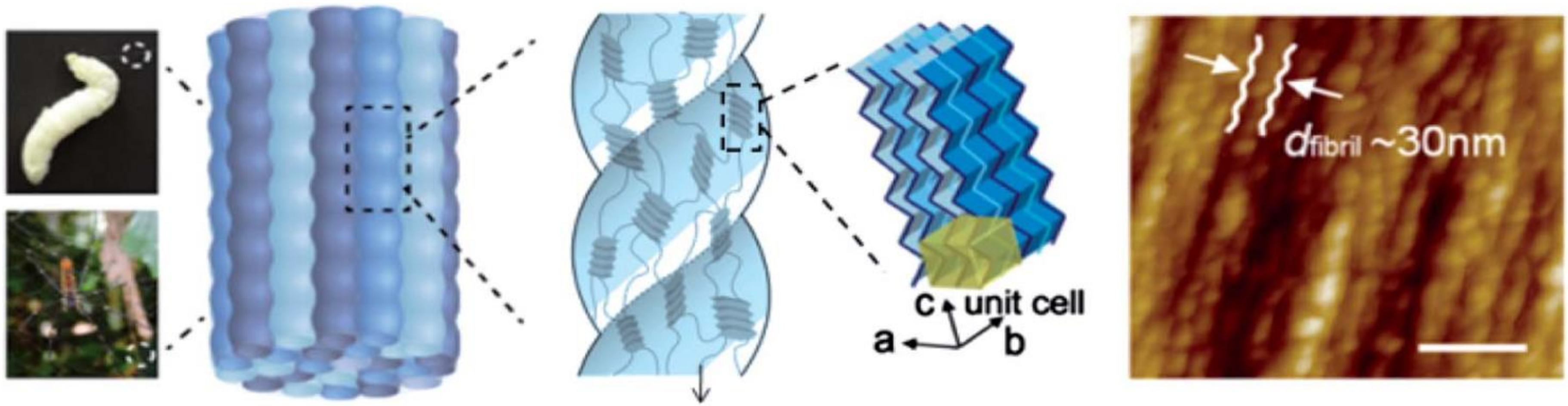


Oxford Silk Group



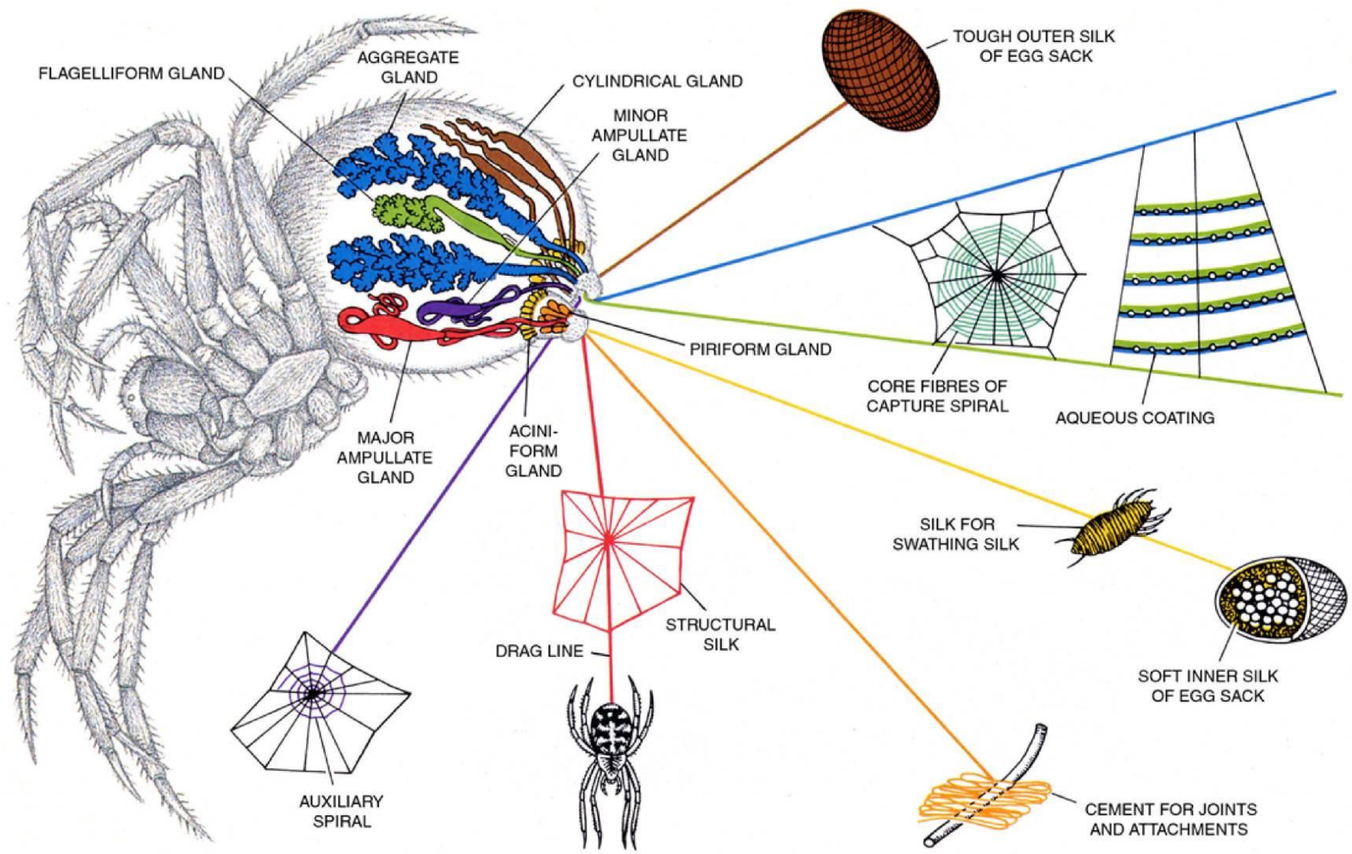
Spider Silk

Fiber Nano-fibril Nano β-crystallite



Xu et al. SoftMatter, **10**, 2116 (2014)

7 different types of spider silk



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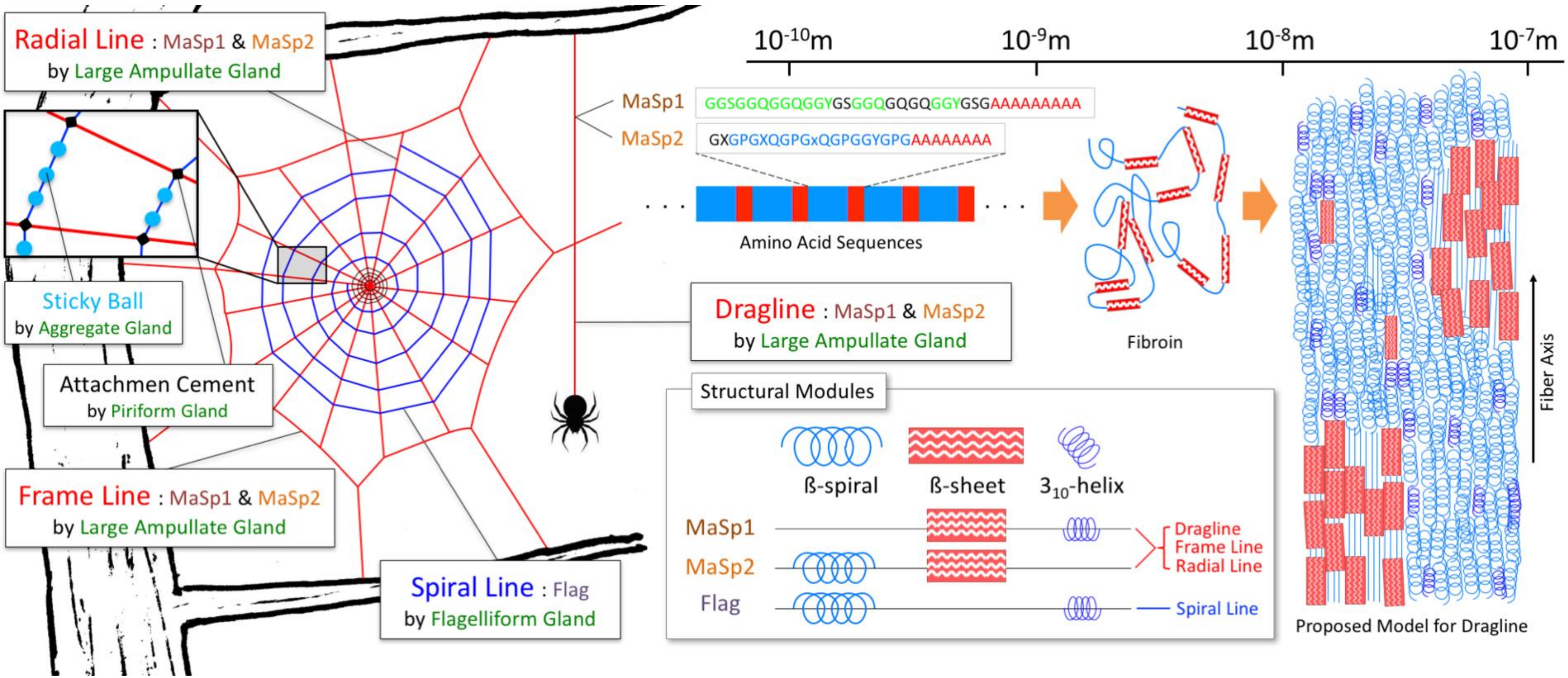
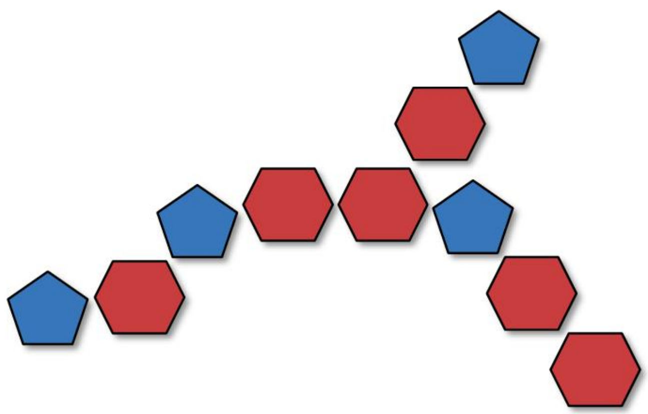
Spider silk



Zhao, Yet al. Appl. Phys. B (2017) 123: 188.

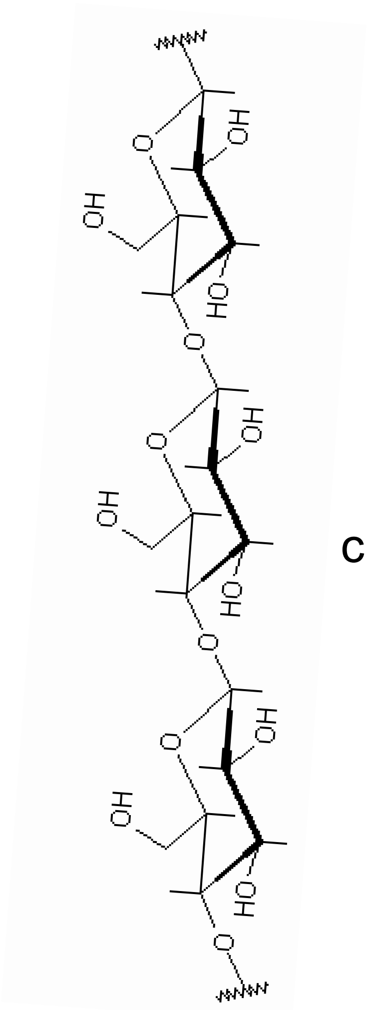
Polysaccharides

- 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
- amylose, amylopectin, glycogen and cellulose same chemical composition

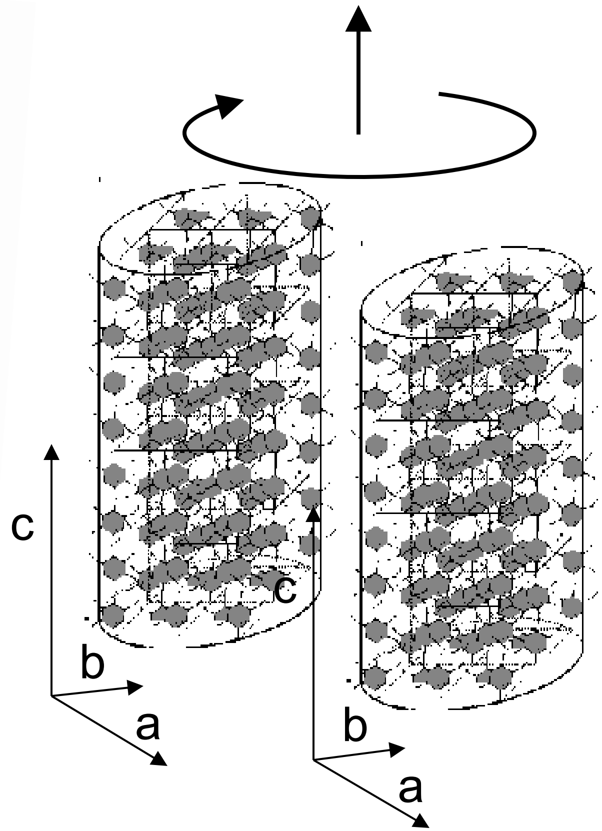


Cellulose: X-ray diffraction

cellulose fiber

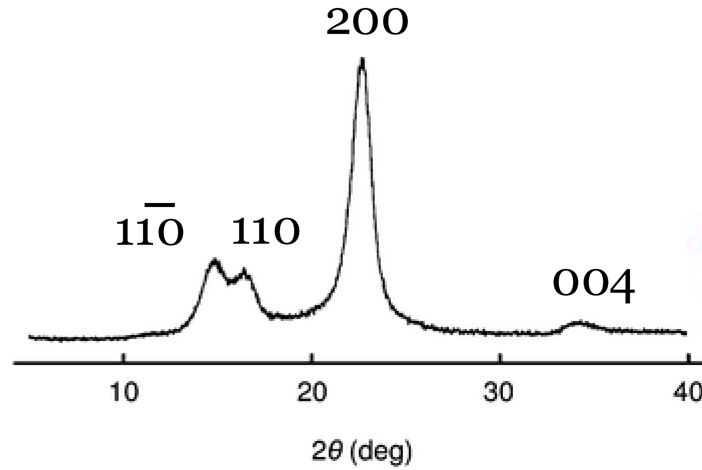


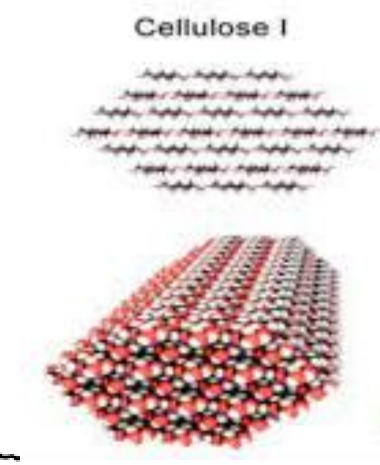
Cellulose molecule



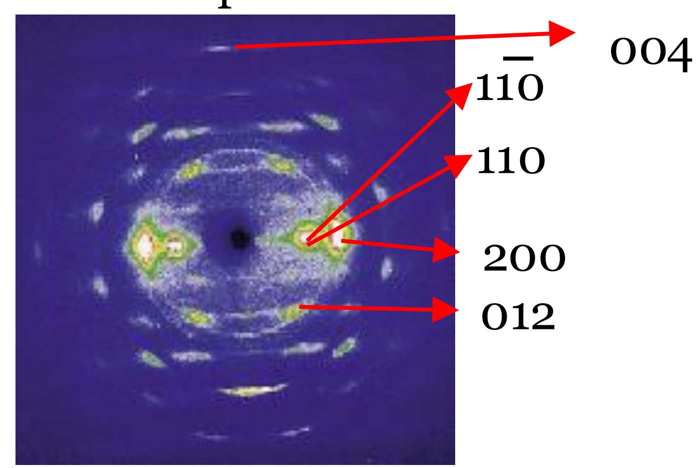
Crystalline cellulose fibers

Powder diffraction pattern





2D diffraction pattern



Copolymer

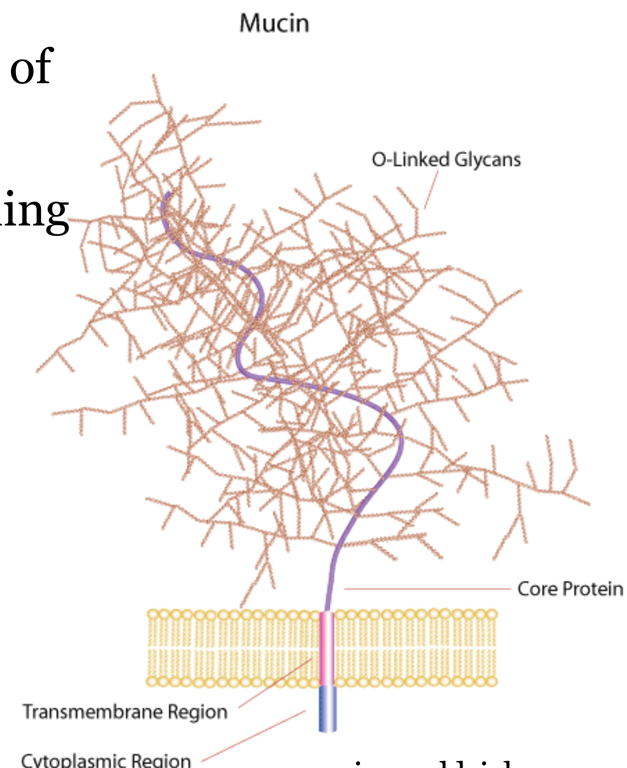
Polysaccharides can form copolymers together with proteins

→ glycoproteins or peptidoglycans

Glycosylation: attachment of sugars to existing proteins

One example is mucin contained in mucus: the slimy surface of exposed tissue like nose, lung, stomach

prevents particles and infectious microorganisms from reaching the cell



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Biological Materials: main components of life

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

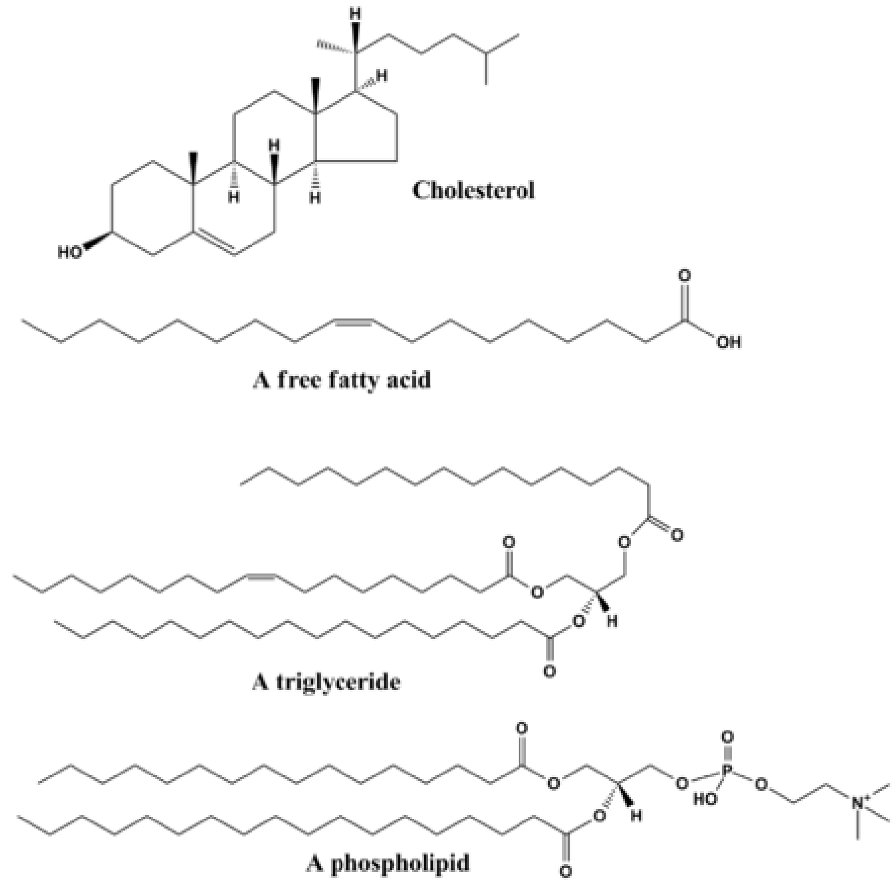
- **Lipids: fats and oils**

- Amphiphilic molecules (self-assembly)
  - phospholipids

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

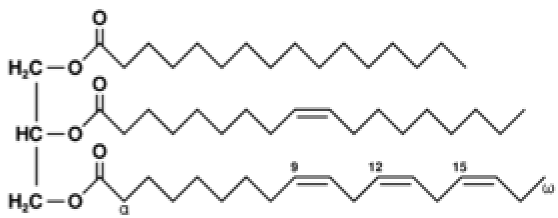
Lipids

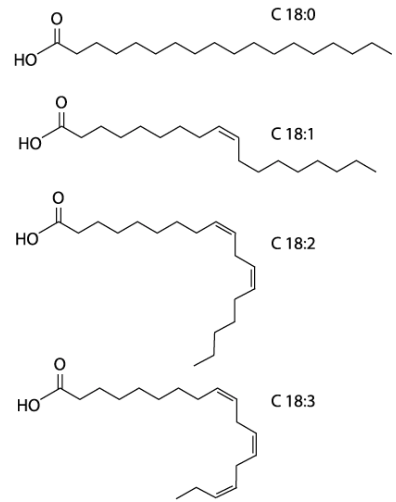
- hydrophobic or amphiphilic molecules
- biological functions:
  - storing energy
  - structural components of cell membranes
  - signaling
  - vitamins
- eight categories
  - fatty acids
  - **glycerolipids**
  - **glycerophospholipids**
  - spingolipids
  - saccarolipids
  - polyketides
  - sterol lipids (e.g. cholesterol, steroids)
  - prenol lipids (fat soluble vitamins)



Triglyceride

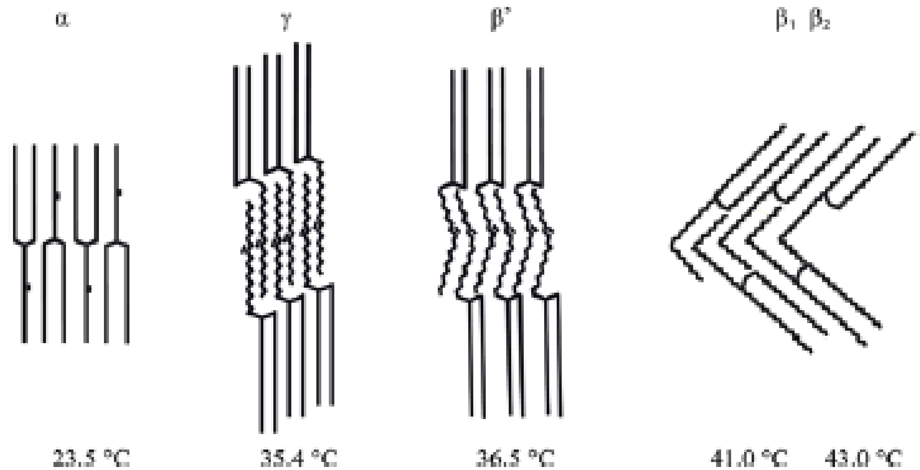
- energy storage: main constituents of body fat and vegetable fat/oil
- in food: fat dissolves most aroma compounds
- saturated and unsaturated

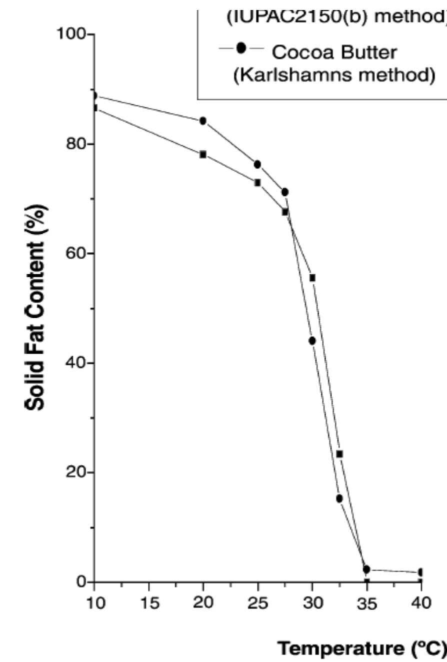




Chocolate

- cacao butter, main component POS and many other triglycerides
- polymorphism: 6 different crystalline forms: γ, α, III, β_{IV}, β_V, β_{VI}
- β_V: desired form due to melting behaviour gloss, texture and breaking behaviour BUT: is not the thermodynamically most stable form





Biological Materials: main components of life

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

- Lipids: fats and oils

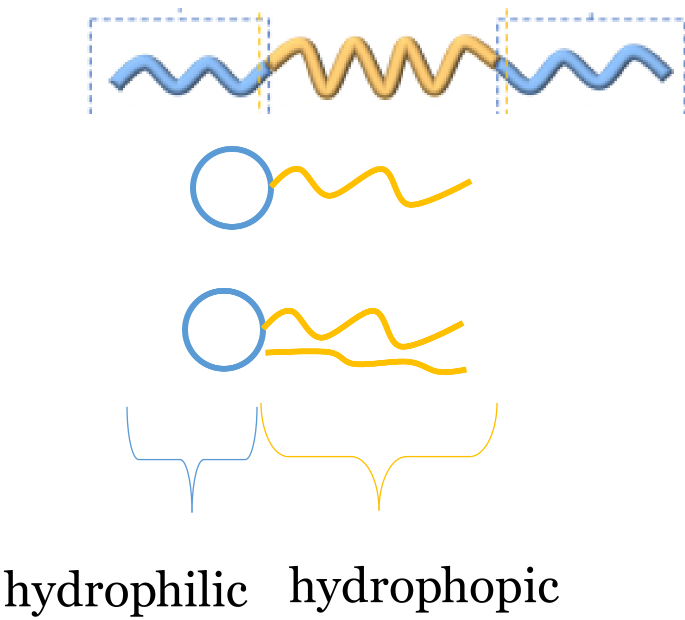
- **Amphiphilic molecules (self-assembly)**
  - **phospholipids**

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

Amphiphilic molecules

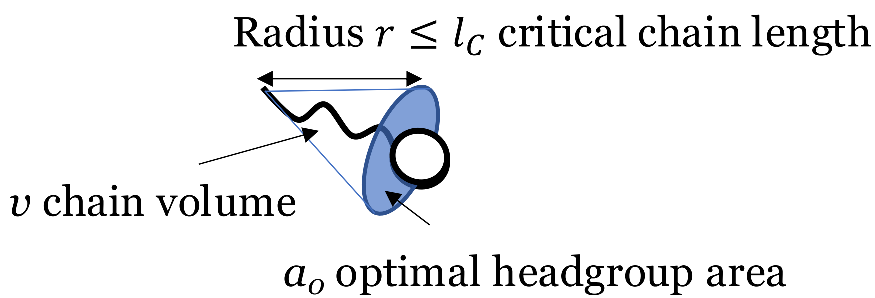
Amphiphiles: contain hydrophobic group and hydrophilic group

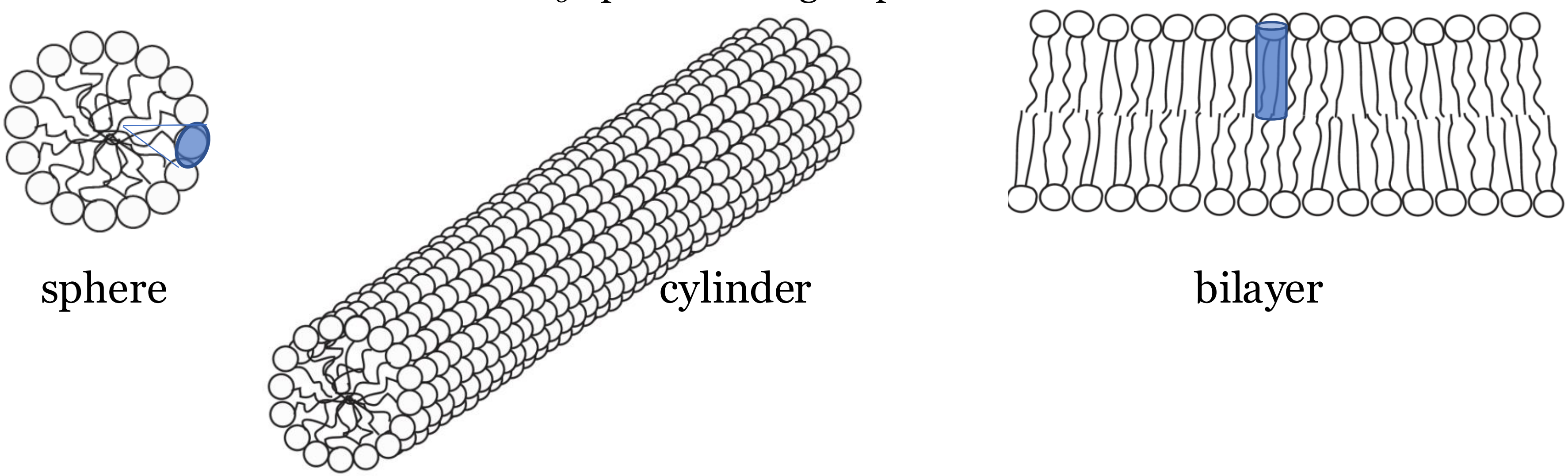
Surfactant: surface active molecule, often used for man-made amphiphiles



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

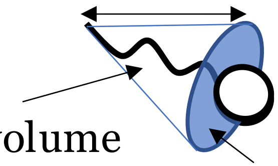




Packing parameter

Packing parameter $\frac{v}{a_0 l_c}$

Radius $r \leq l_c$ critical chain length



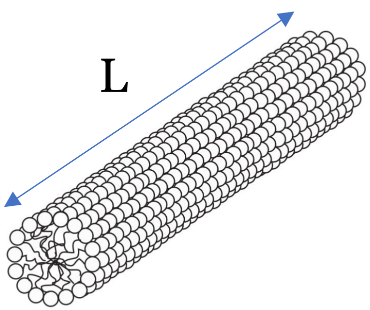
v chain volume

a_o optimal headgroup area

For micelle:

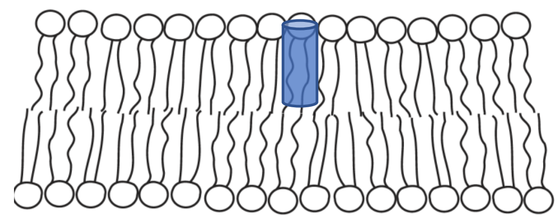
$$V = \frac{4\pi r^3}{3} = Nv$$
$$A = 4\pi r^2 = Na_0$$
$$r = \frac{3v}{a_0}$$
$$\frac{v}{a_0 l_c} < \frac{1}{3}$$

For a cylinder:



$$V = \pi r^2 L = Nv$$
$$A = 2\pi r L = Na_0$$
$$r = \frac{2v}{a_0}$$
$$\frac{v}{a_0 l_c} < \frac{1}{2}$$

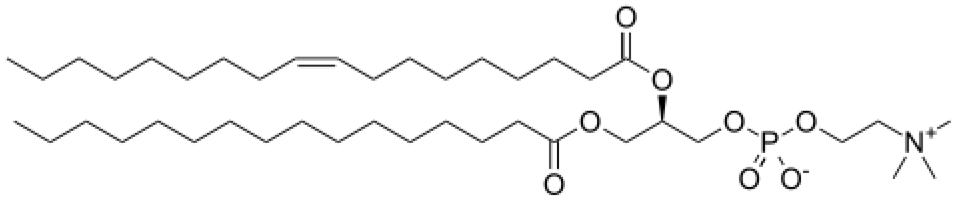
For a bilayer: $\frac{v}{a_0 l_c} \approx 1$



For inverted structures: $\frac{v}{a_0 l_c} > 1$

Biological amphiphiles

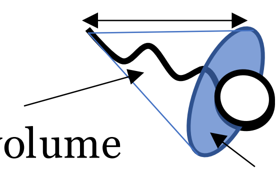
Phospholipids



1-palmitoyl-2-oleyl-*sn*-glycero-3-phosphatidylcholine POPC

- large hydrocarbon volume compared to headgroup: bilayer assembly

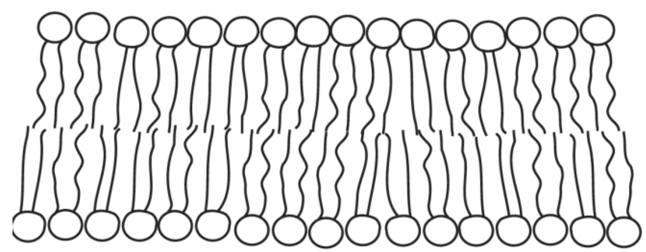
Radius $r \leq l_C$ critical chain length



v chain volume

a_o optimal headgroup area

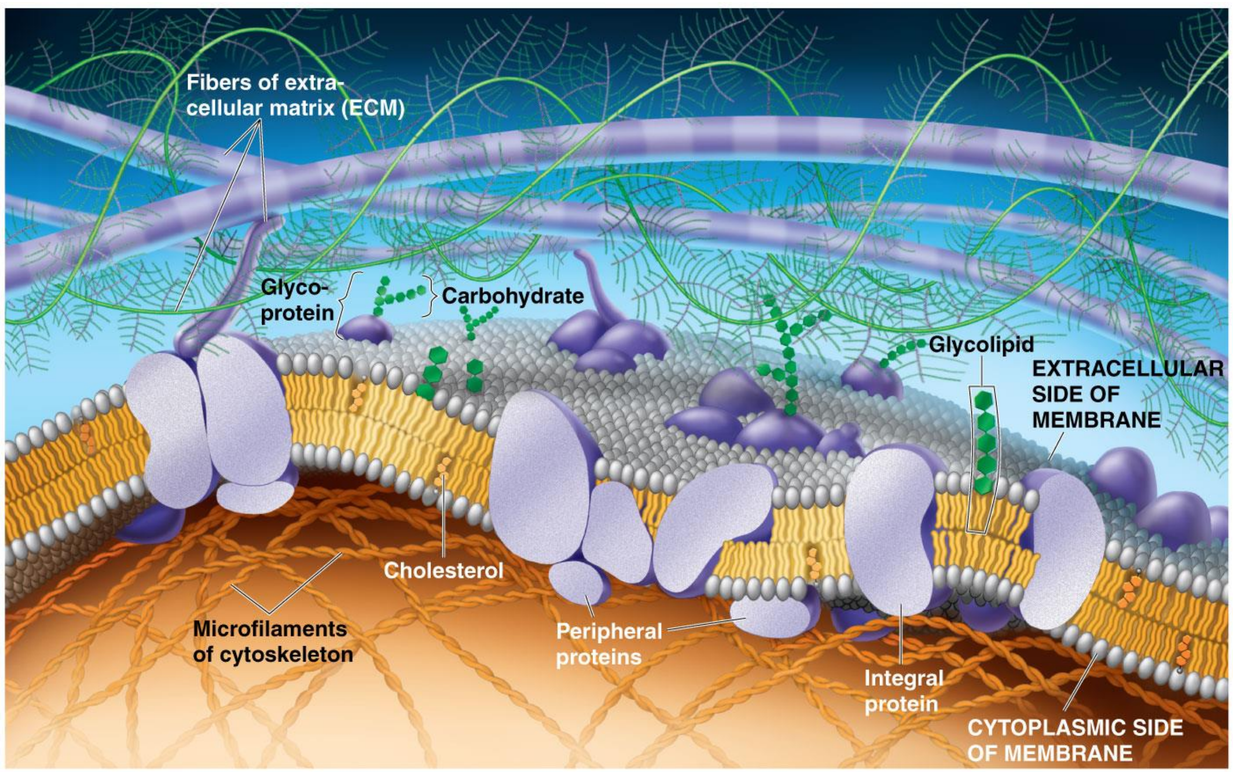
$$\frac{v}{a_0 l_c} \approx 1$$



- two chains: very insoluble, stable as membrane
- quite big headgroup: low probability for flipflop: different sides of membranes

Membrane properties

- bilayer provides barrier for ions, charged, polar and large molecules: allows compartmentalization into different environments
- cell membrane: complex mixture, raft formation, cholesterol alter stiffness and permeability, membrane proteins, asymmetric, outside polysaccharides, inside link to cytoskeleton



www.thinglink.com

Vesicle

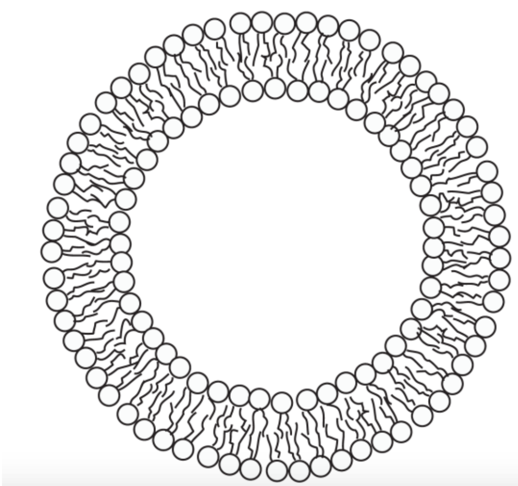
A self-closed bilayer is called a vesicle

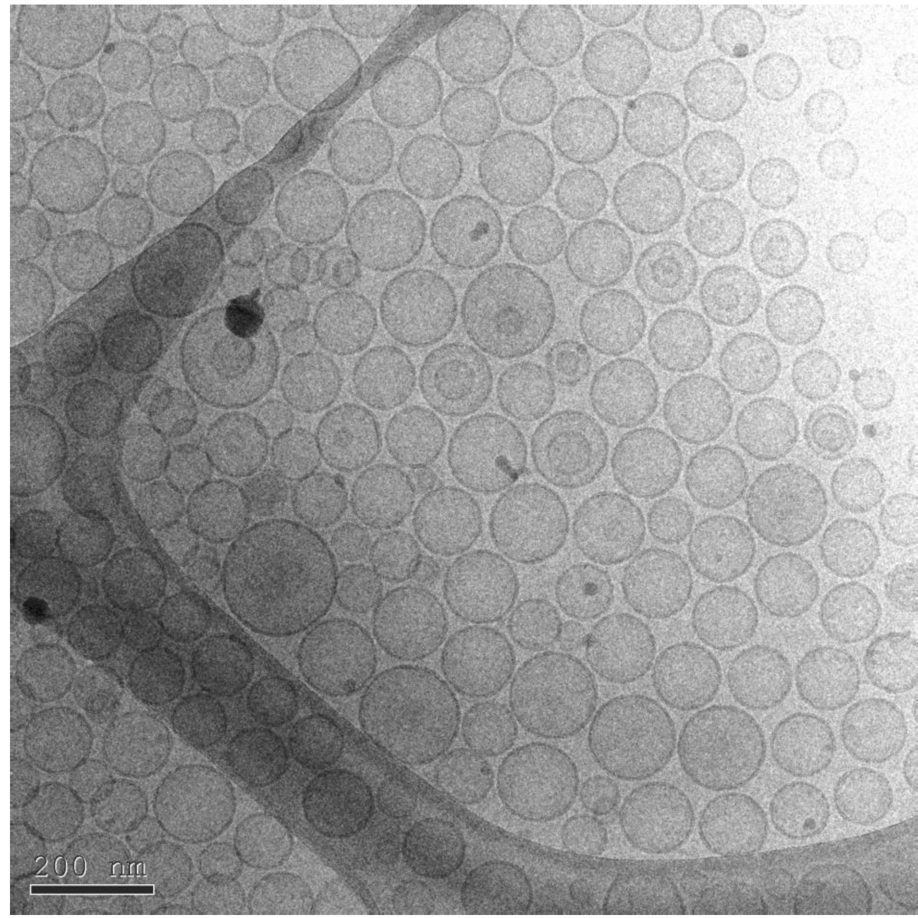
In human body for cell-cell communication

Encapsulation of objects, drug delivery

Model of cells and cell membranes

Minireactor in chemistry





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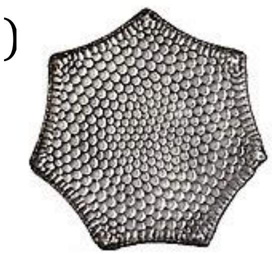
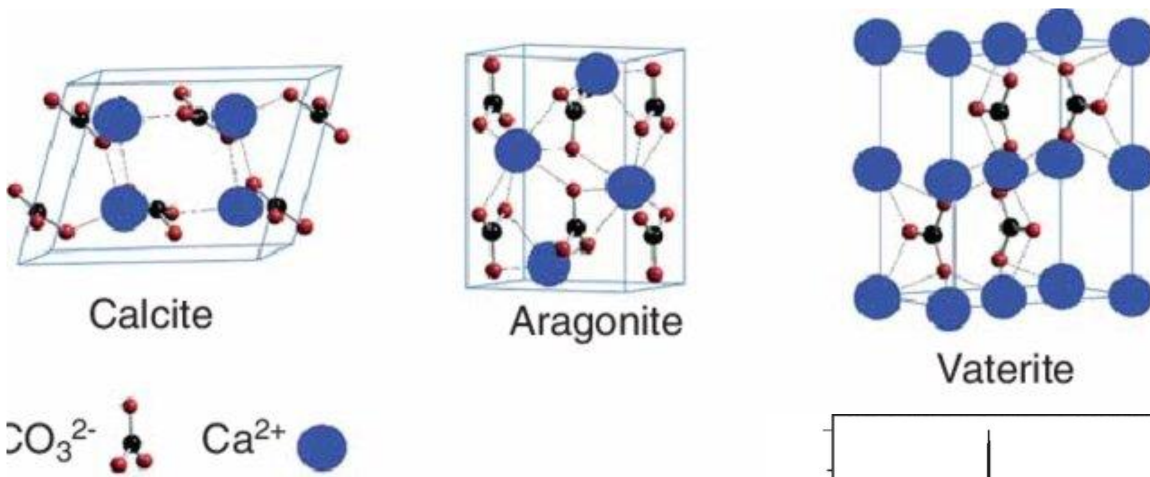
- **Biominerals**
  - **Calcium phosphate** (example: hydroxyapatite in bone)
  - **Calcium carbonate** (example aragonite and calcite in mollusk shells)
  - **Silicates** (diatoms)

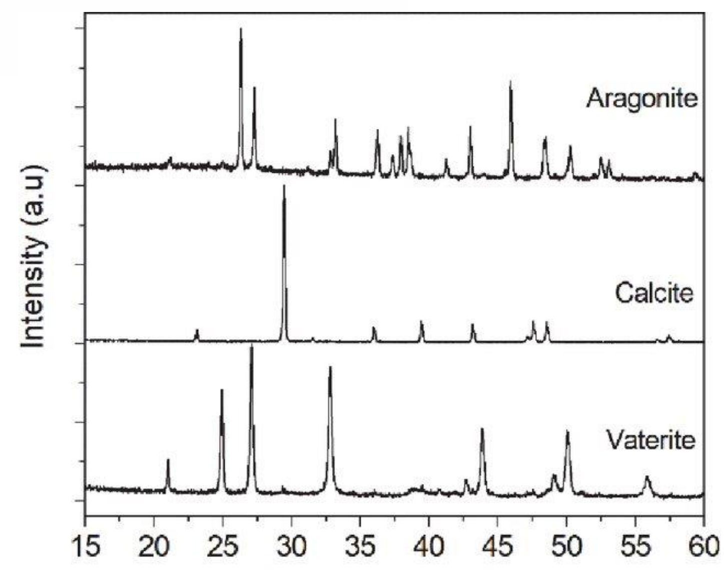


Biomineral: example calcium carbonate

The crystalline structure of Calcium carbonate: Polymorph

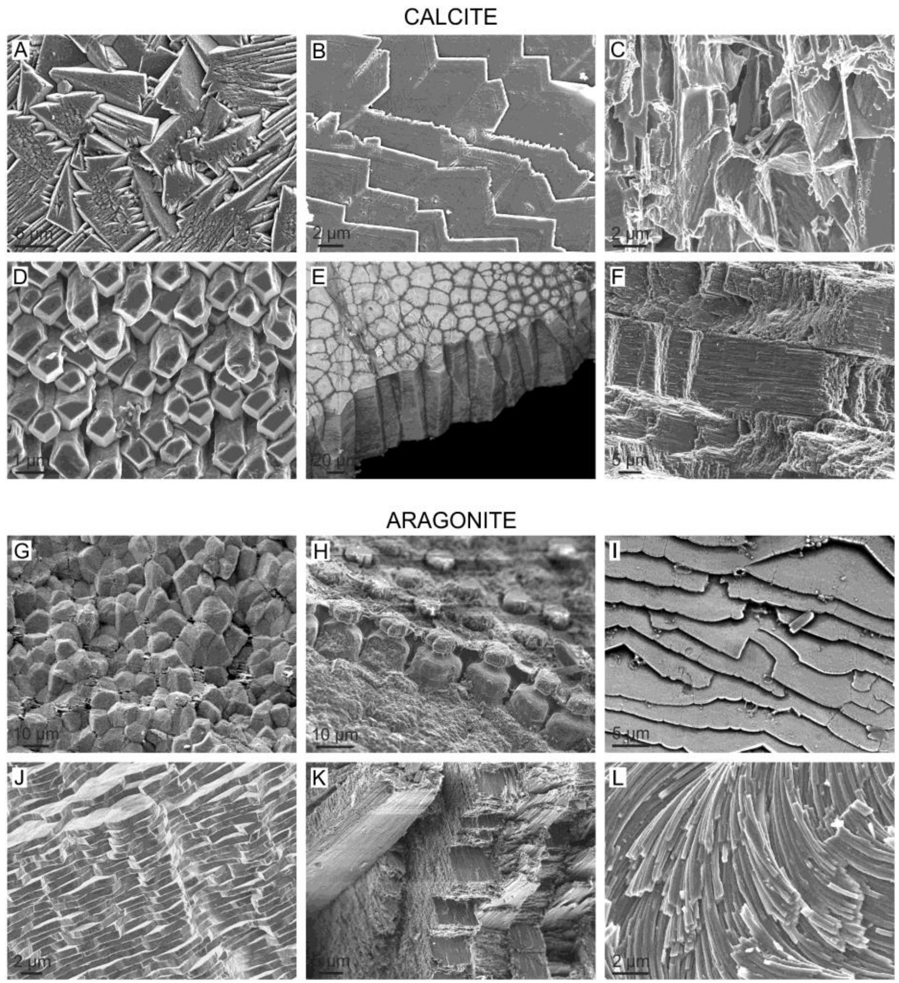
trigonal orthorombic hexagonal





Biomineral: example calcium carbonate

The crystalline structure of Calcium carbonate: Polymorph

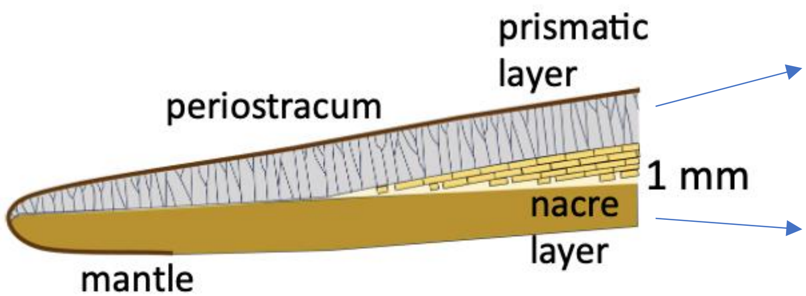


and different microstructure for the same crystal structure

Checa A.G. "Physical and Biological Determinants of the Fabriation of Molluscan Shell Microstructure", Front. Mar. Scie, 2018, 5

Example: Mollusk shell

The crystalline structure of Calcium carbonate: Polymorph



prismatic layer: mainly calcite

nacre layer: mainly aragonite

composite material of crystalline component (95-99%) and an organic fraction (0.1-5%)

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

Summary biological materials

- biological materials
- structure of some important biological building blocks:
  - nucleic acids (DNA/RNA), specific base pairing for replication and encoding of protein structure, chromosome and random walk
  - proteins, hierarchical structure, specific 3D structure for function (not random walk!), chiral space groups
  - polysaccharides: carbohydrates, energy & strutcture
  - lipids
  - amphiphilies, aggregates formed depend on the molecular packing parameter
  - biominerals, crystal structure polymorph and strictly controlled in biological crystallization

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

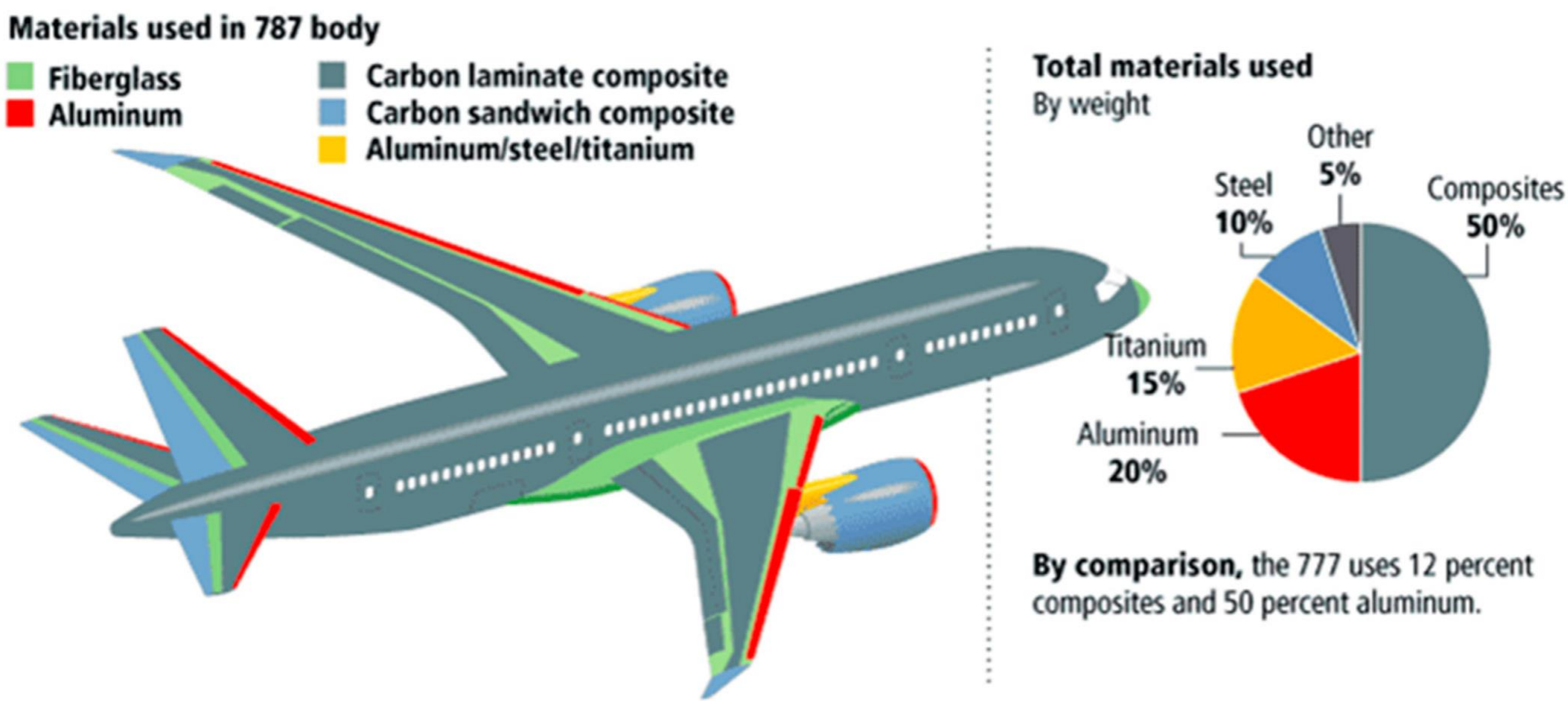
- Mobility (automotive, aeronautics and space)
- Sport (marine, ski, bike, …)
- biomedical (encapsulation, prosthethics)
- electronic devises (encapsulation, flexibel electronics)
- energy (wind turbines, solar panels integration)
- bio-inpired composites
- construction (cement reinforced with steel)


yrs.edu


composite.com.au


sampe.org

Applications: example Boeing 787

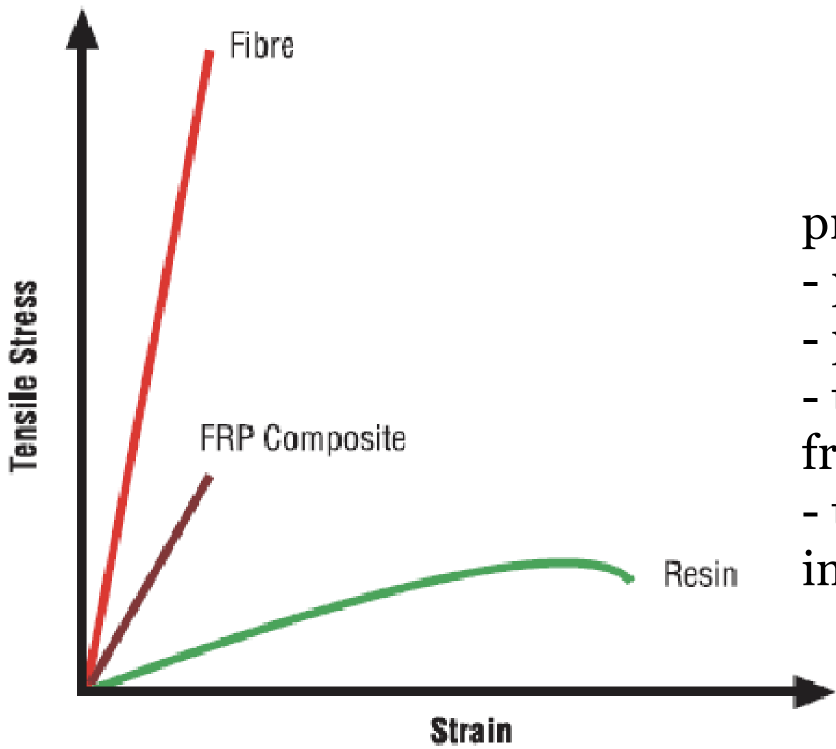


Composite materials

- 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

Polymer fiber composites



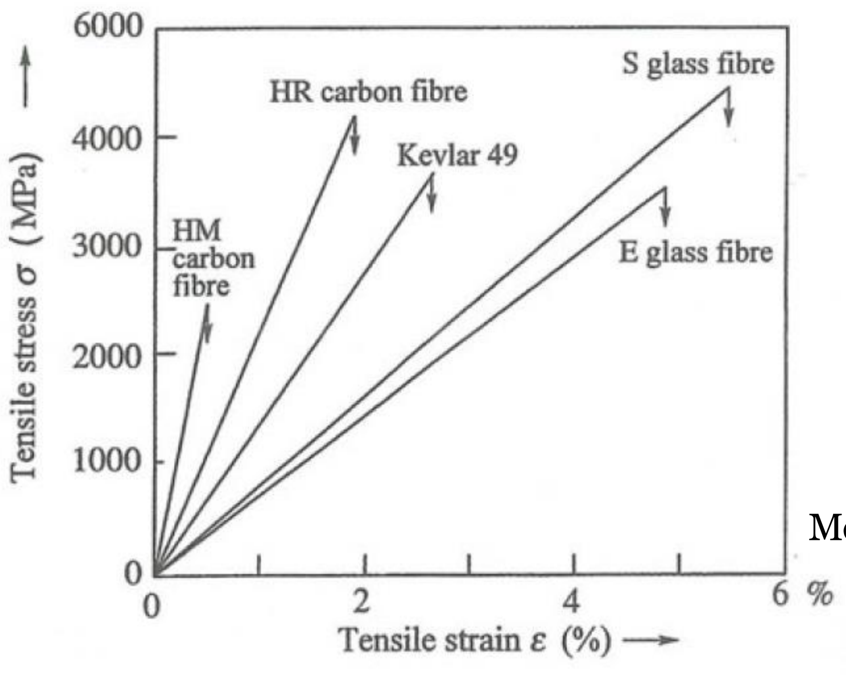
properties of the composite determined by
- properties of the fibre
- properies of the resin
- the ratio of fibre to resin (Fibre volum fraction)
- the geometry and orientation of the fibres in the composites

Polymer fiber composites

- 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

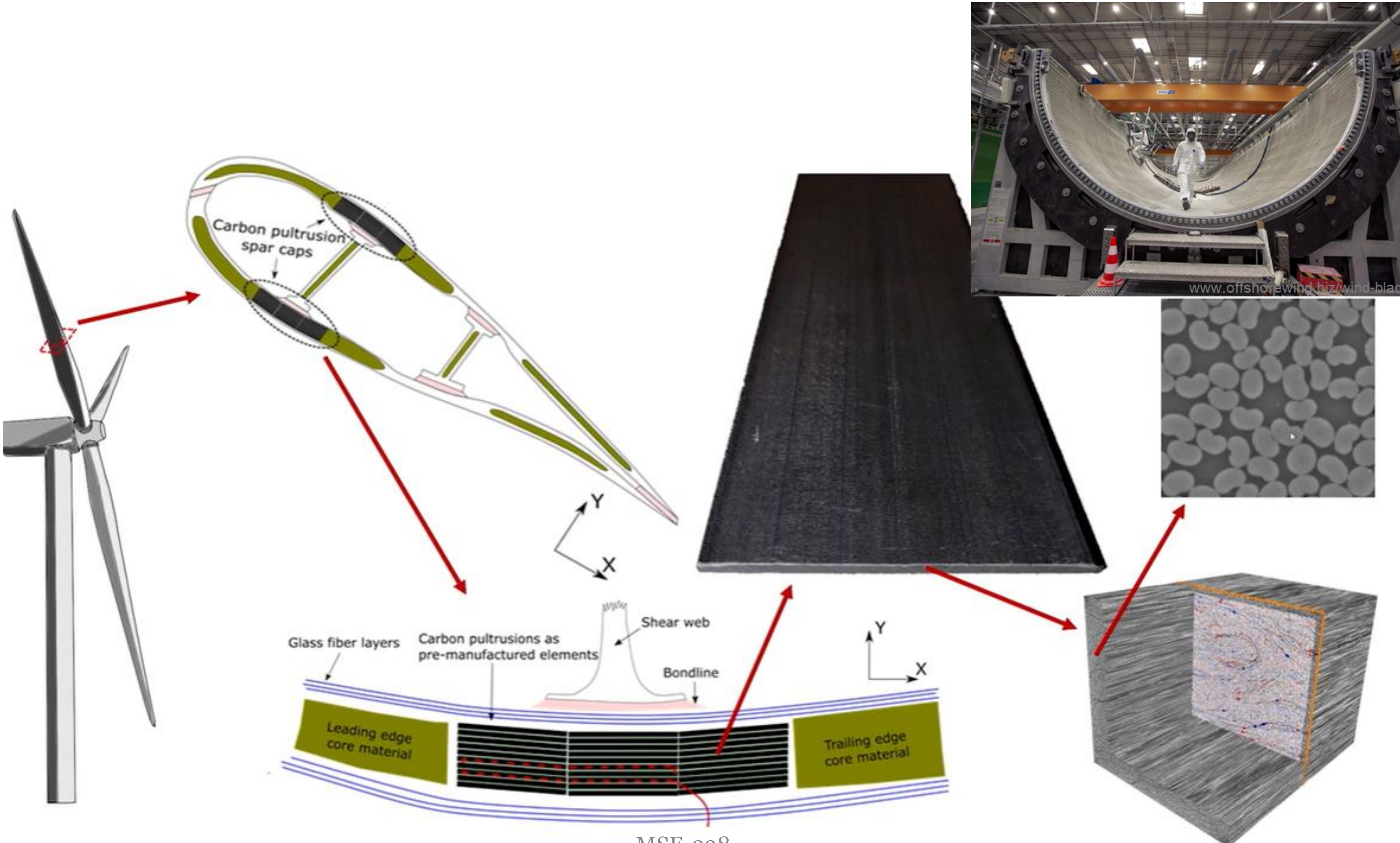
- uniaxially oriented fiber, short fiber composites, woven fibers…
- glass fibers, mainly aluminium borosilicates, S glass fibers high mechanical strength
- carbon fibers (high modulus fibres HT and high-strength fibres HR)
- Kevlar



- 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

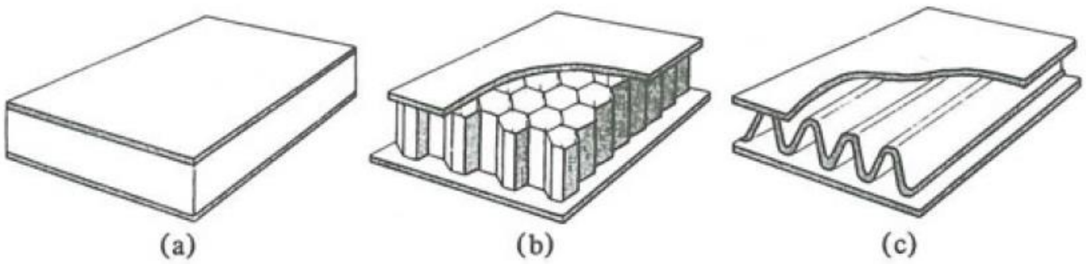


Figure 16.11. Various sandwich structure constructions: (a) solid core (foam-balsa); (b) honeycomb; (c) corrugated core.

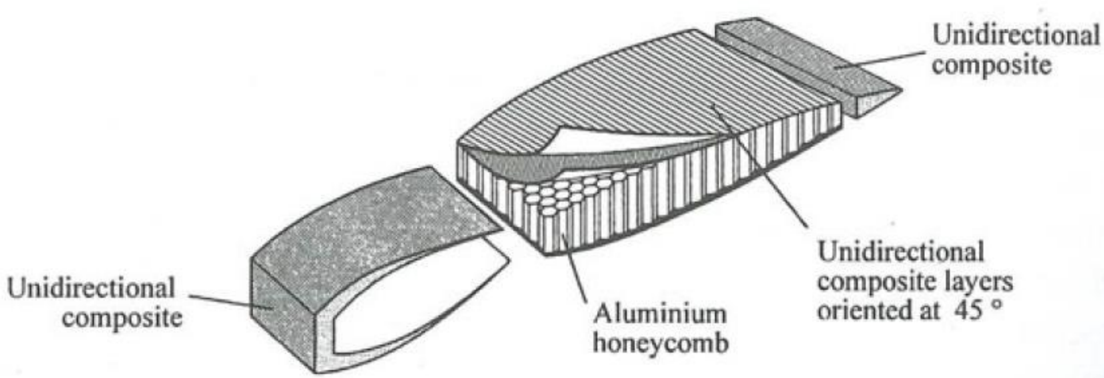
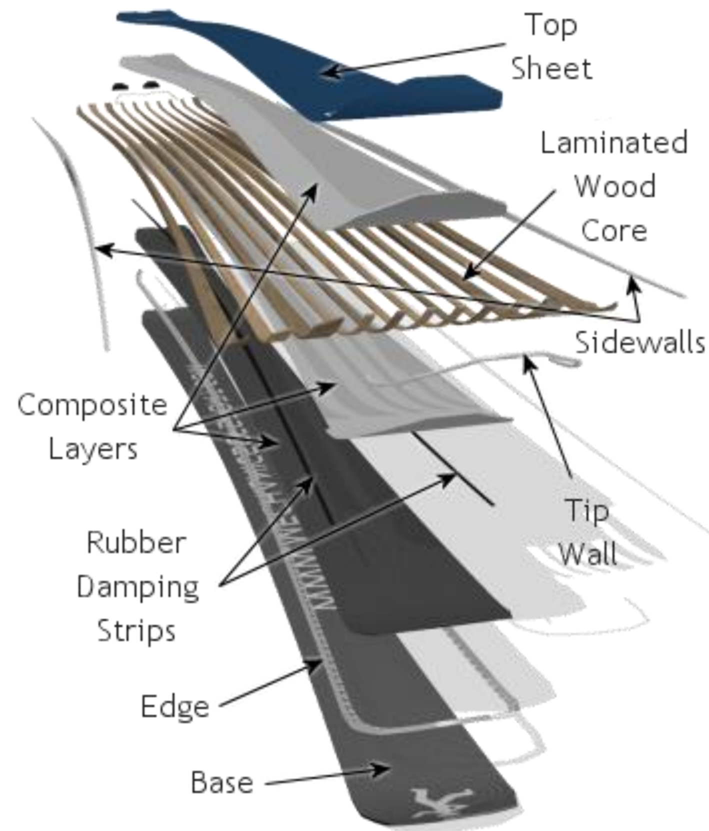


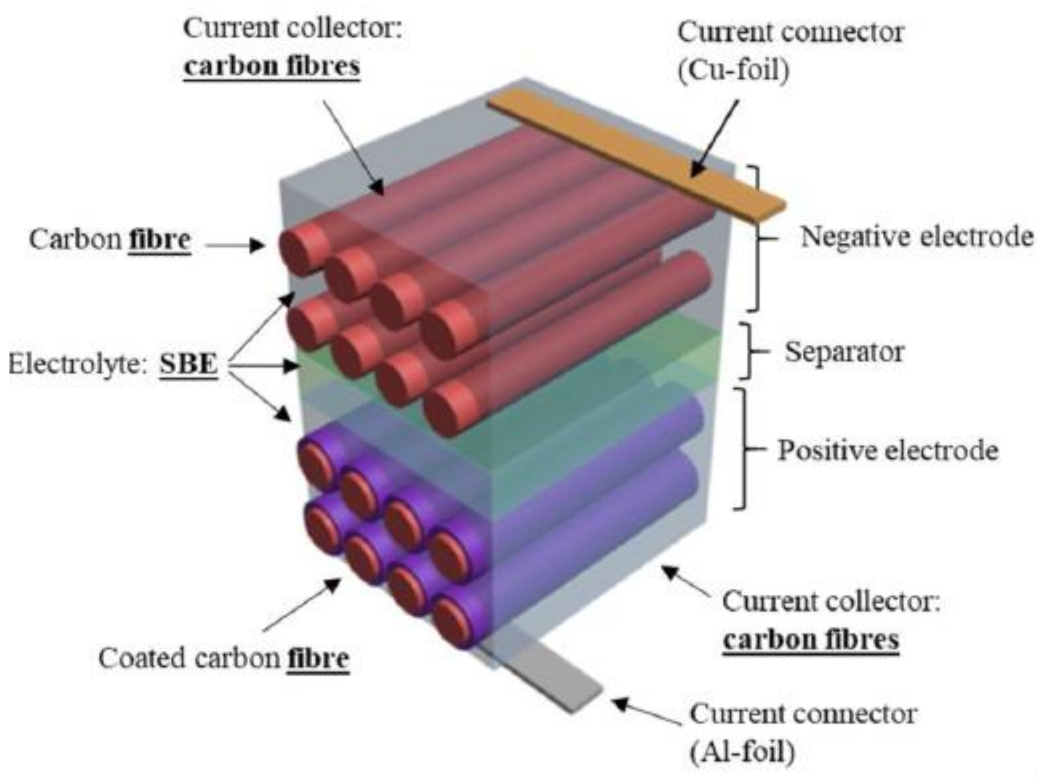
Figure 16.12. Helicopter rotor blade (after Golé, 1979).



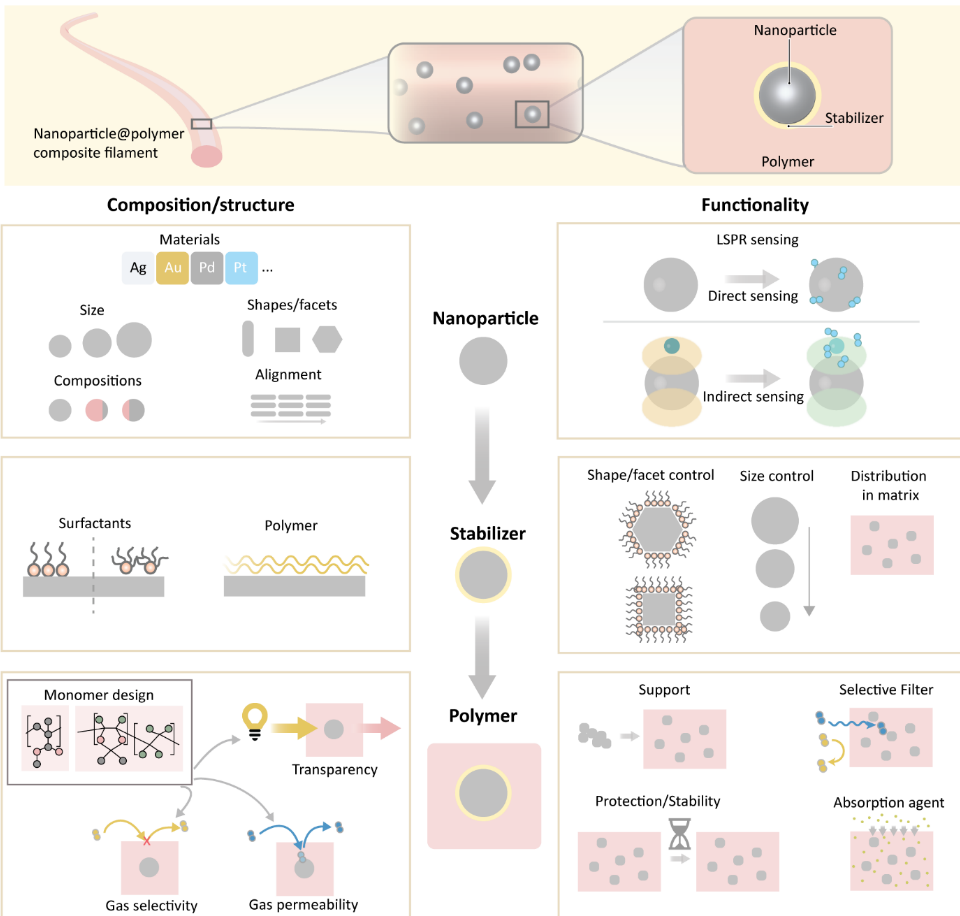
Mercier, Zambelli, Kurz, “Introduction to Materials Science”, Elsevier

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

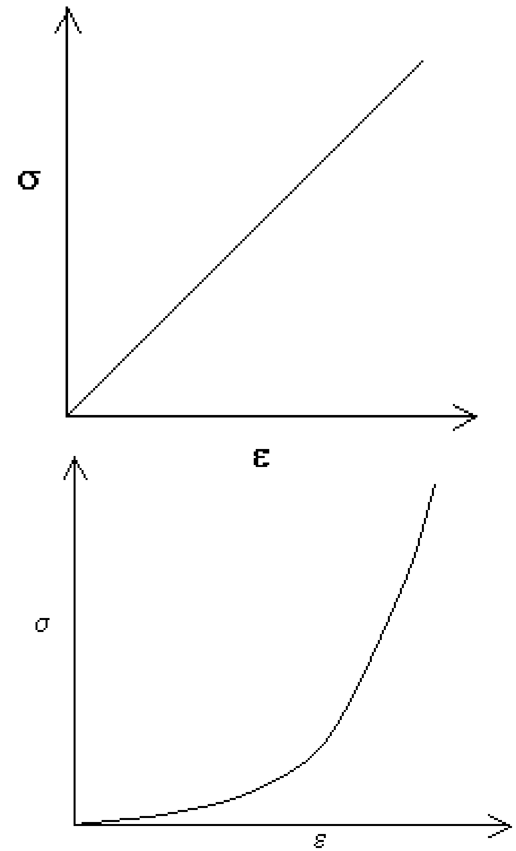
(ii) surfactant/stabilizer molecules on the nanoparticle surface

(iii) polymer matrix, and how they can be tailored from a composition/structure and functionality perspective.

Biocomposites

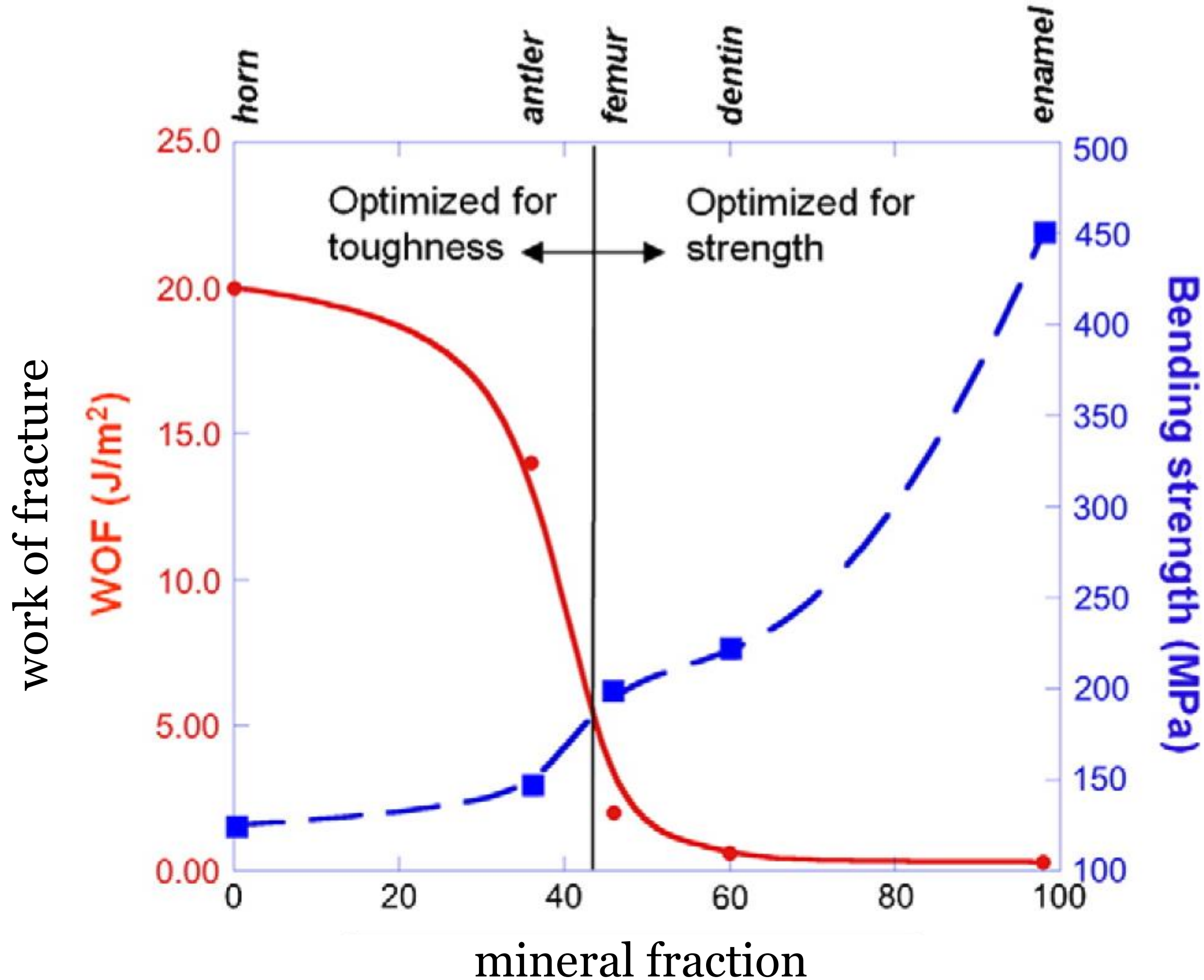
Biominerals
- Linear elastic stress-strain plot
- In general high stiffness, low toughness

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.

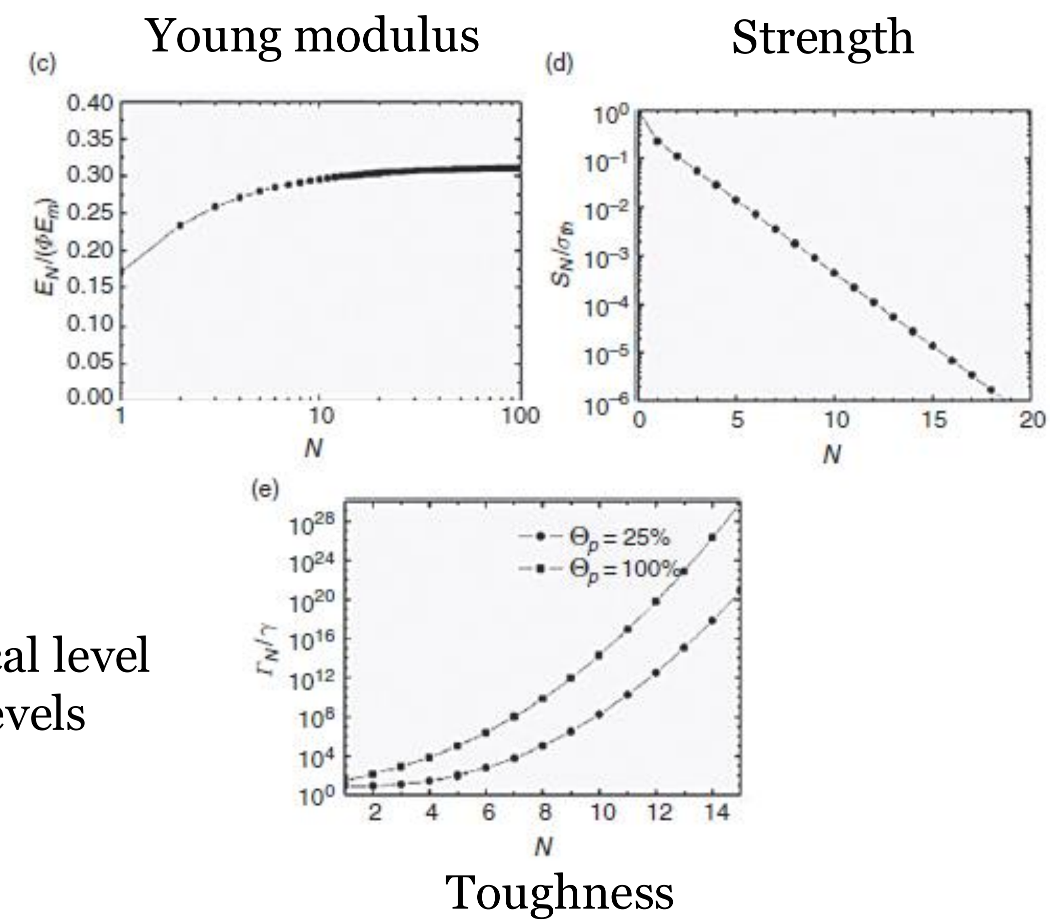
Biocomposite: toughness and strength



McKittrick et al. 2010 Materials Science and Engineering C

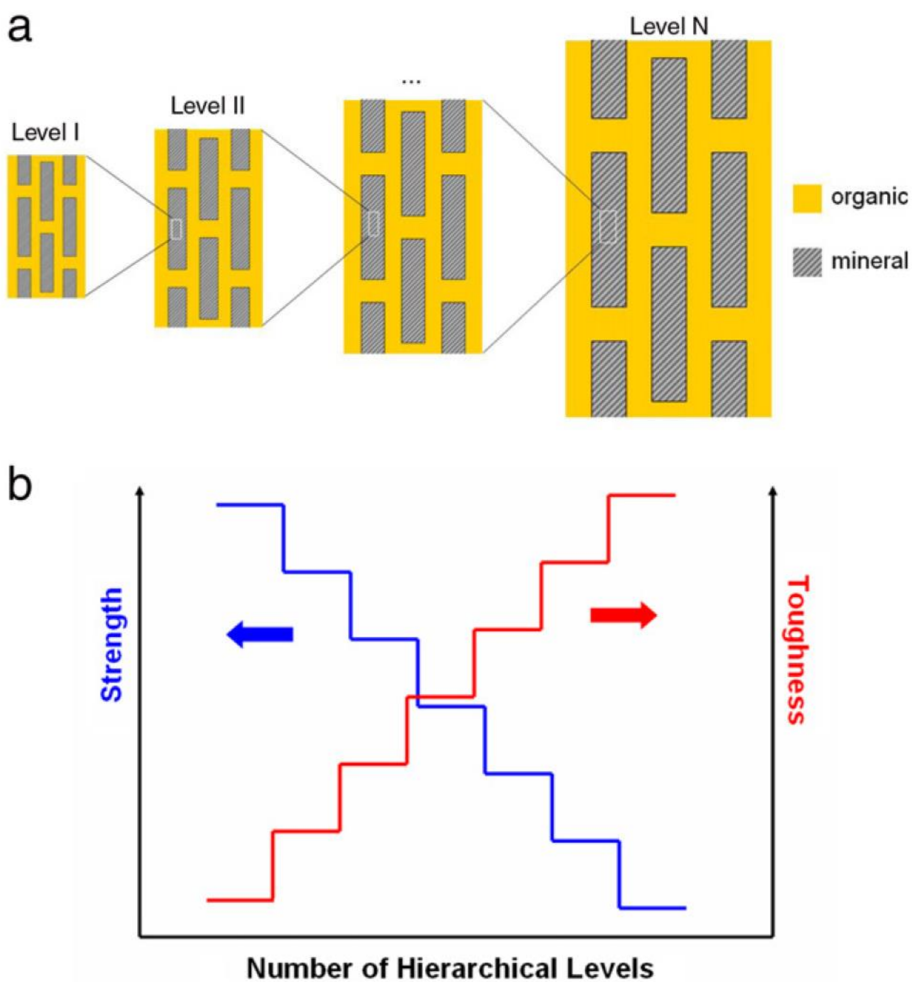
Hierarchical materials

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



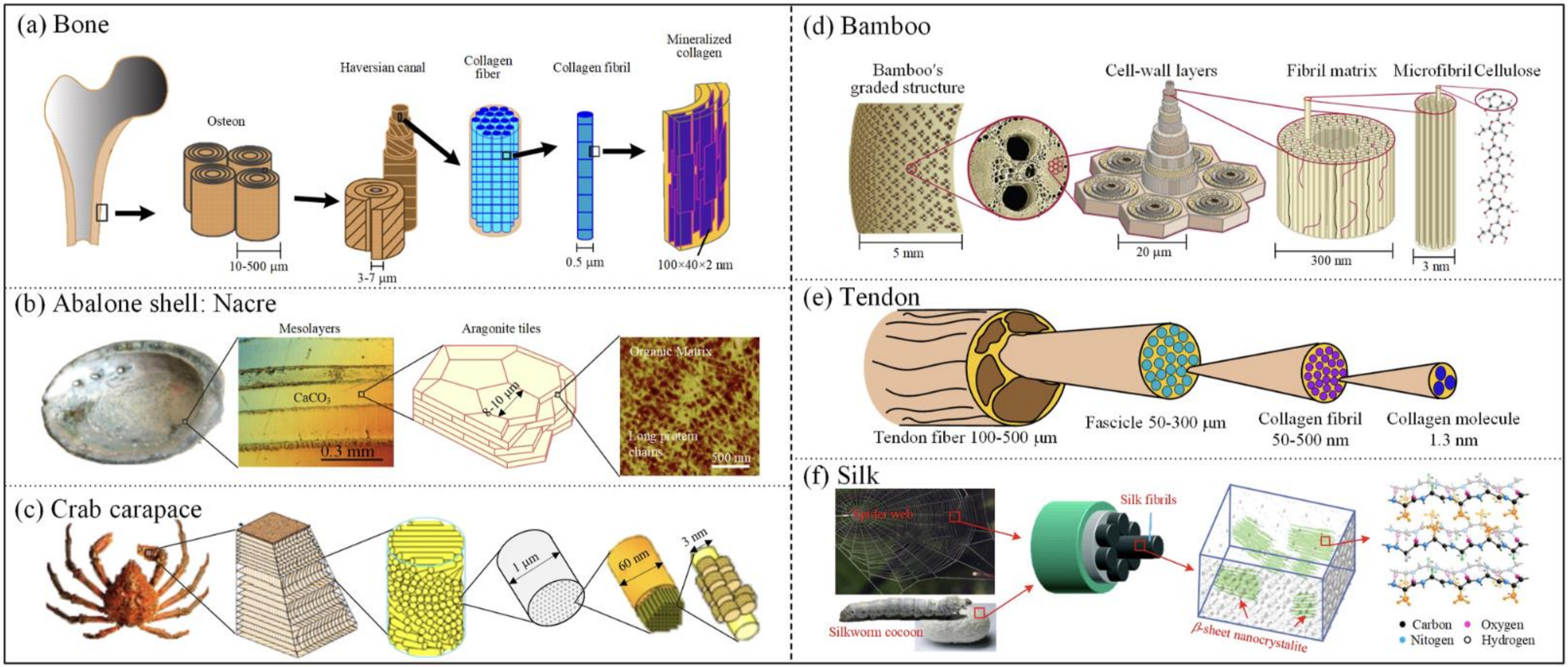
Φ= aspect ratio
Θ= strain
σ_{th}= strength at th hierarchical level
N= number of hierarchical levels
Γ= Fracture energy
γ= surface energy

Hierarchical materials



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

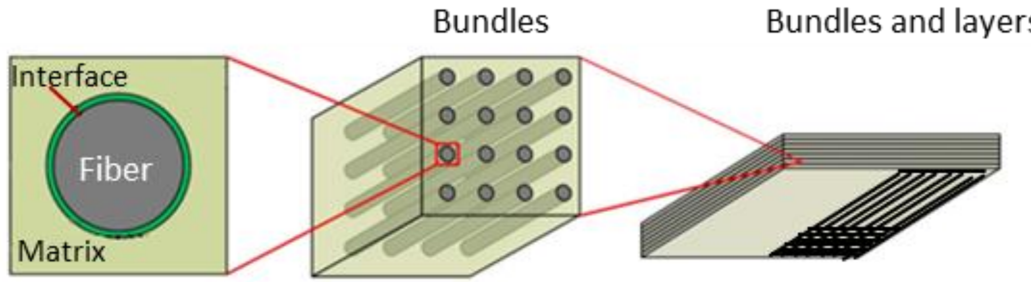
Bio-composites: hierarchical structure



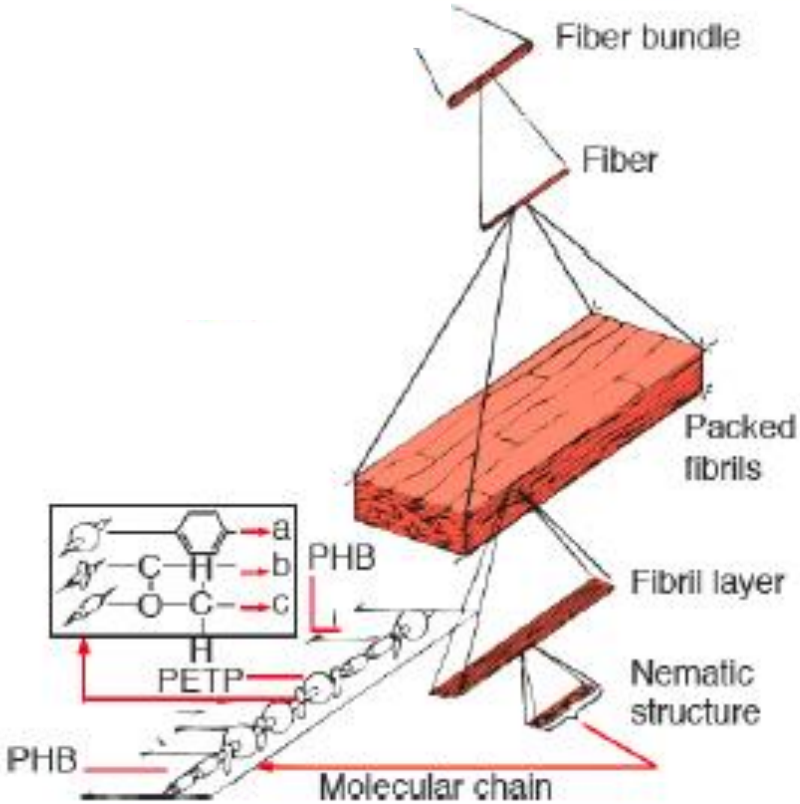
Chen, Y., et al. (2021). Advances in mechanics of hierarchical composite materials. *Composites Science and Technology*, *214*, 108970.

Fiber composite: hierarchical structure

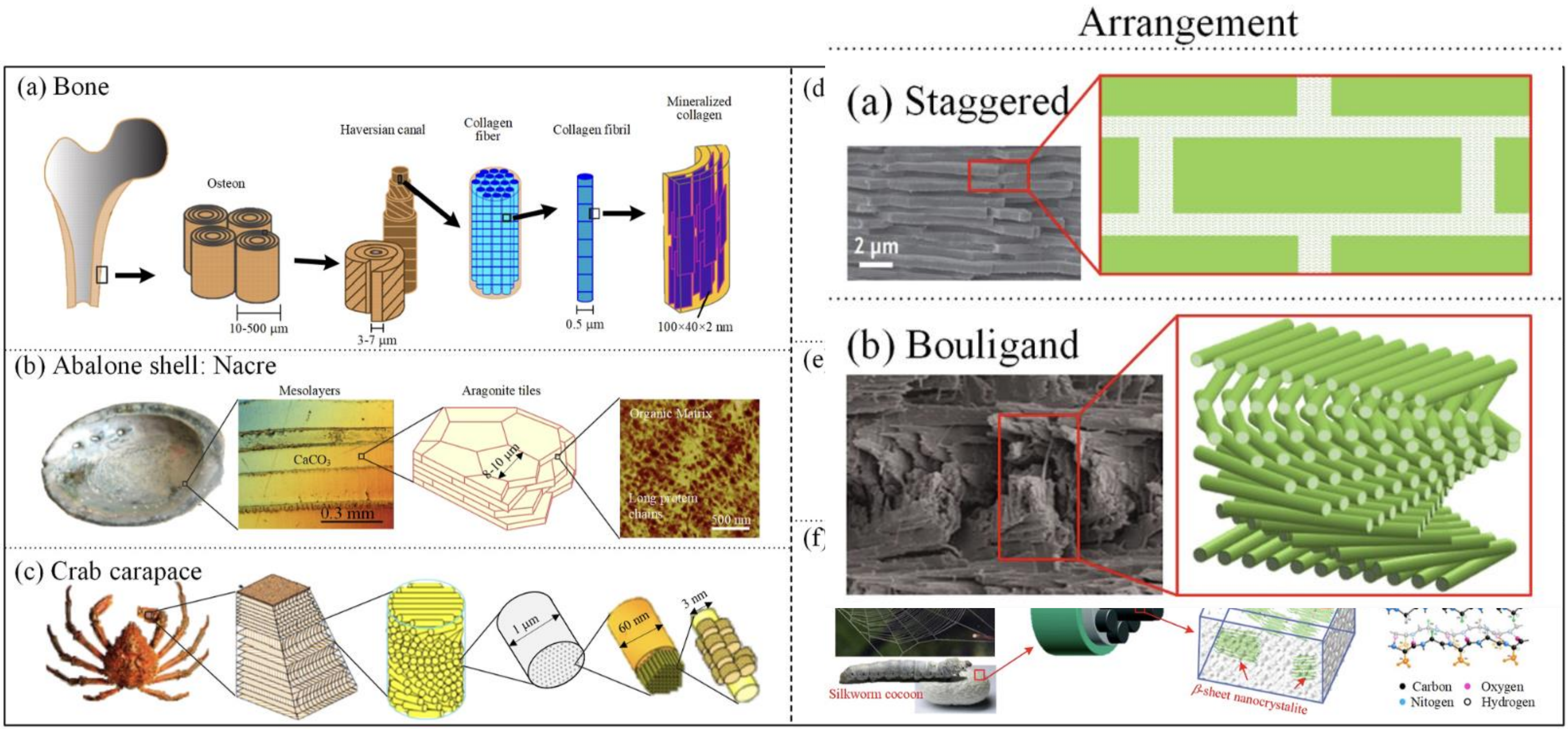
example: Aramid (Kevlar) fiber composite



unidirectional or woven structures



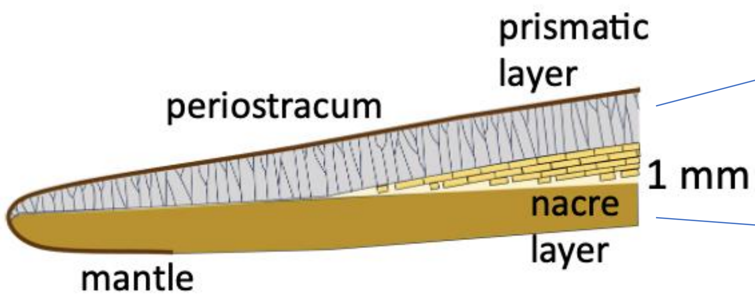
Bio-composites: hierarchical structure



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

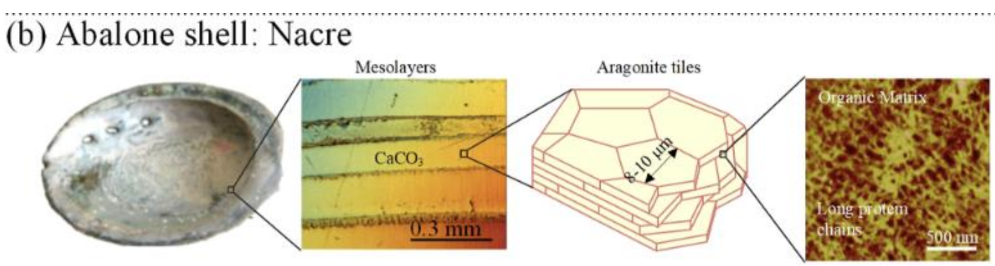
Example: Mollusk shell

The crystalline structure of Calcium carbonate: Polymorph



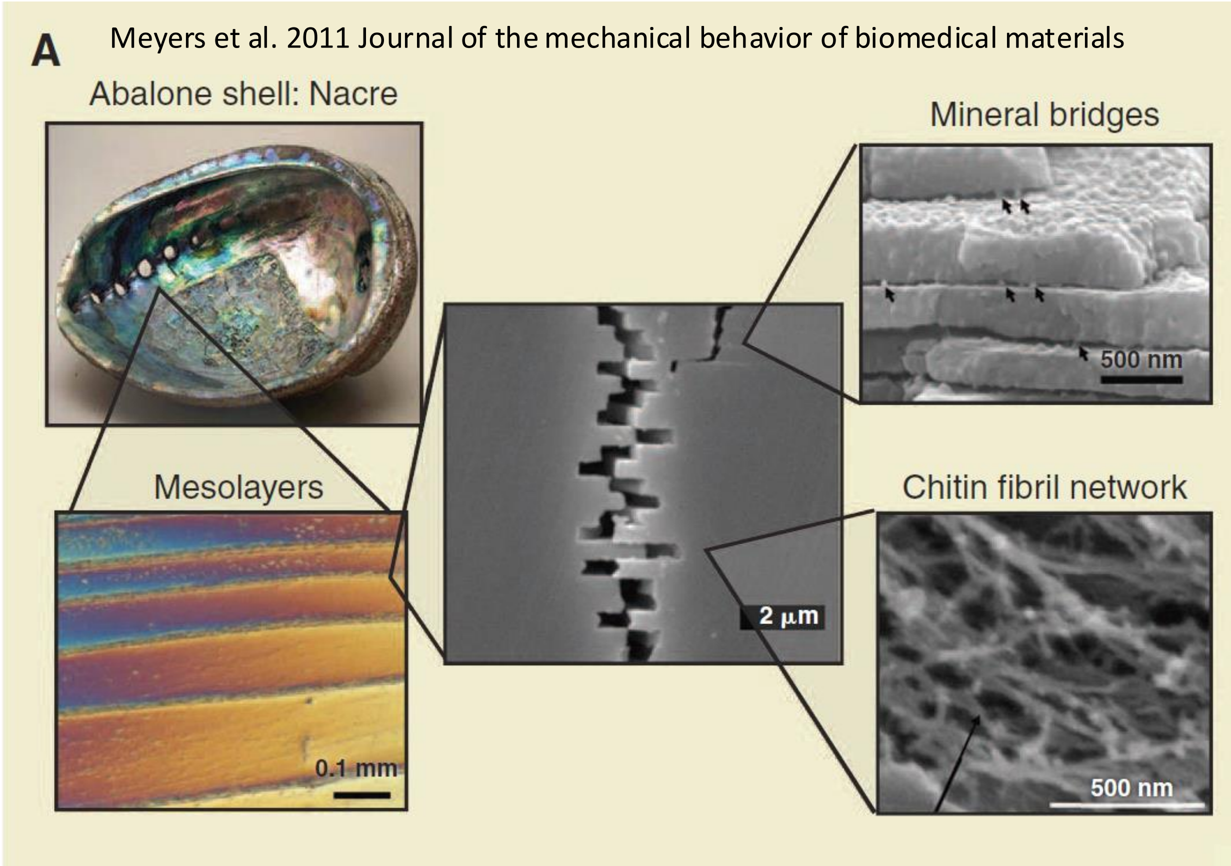
prismatic layer: mainly calcite

nacre layer: mainly aragonite



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

Abalone nacre:
a superior fracture toughness

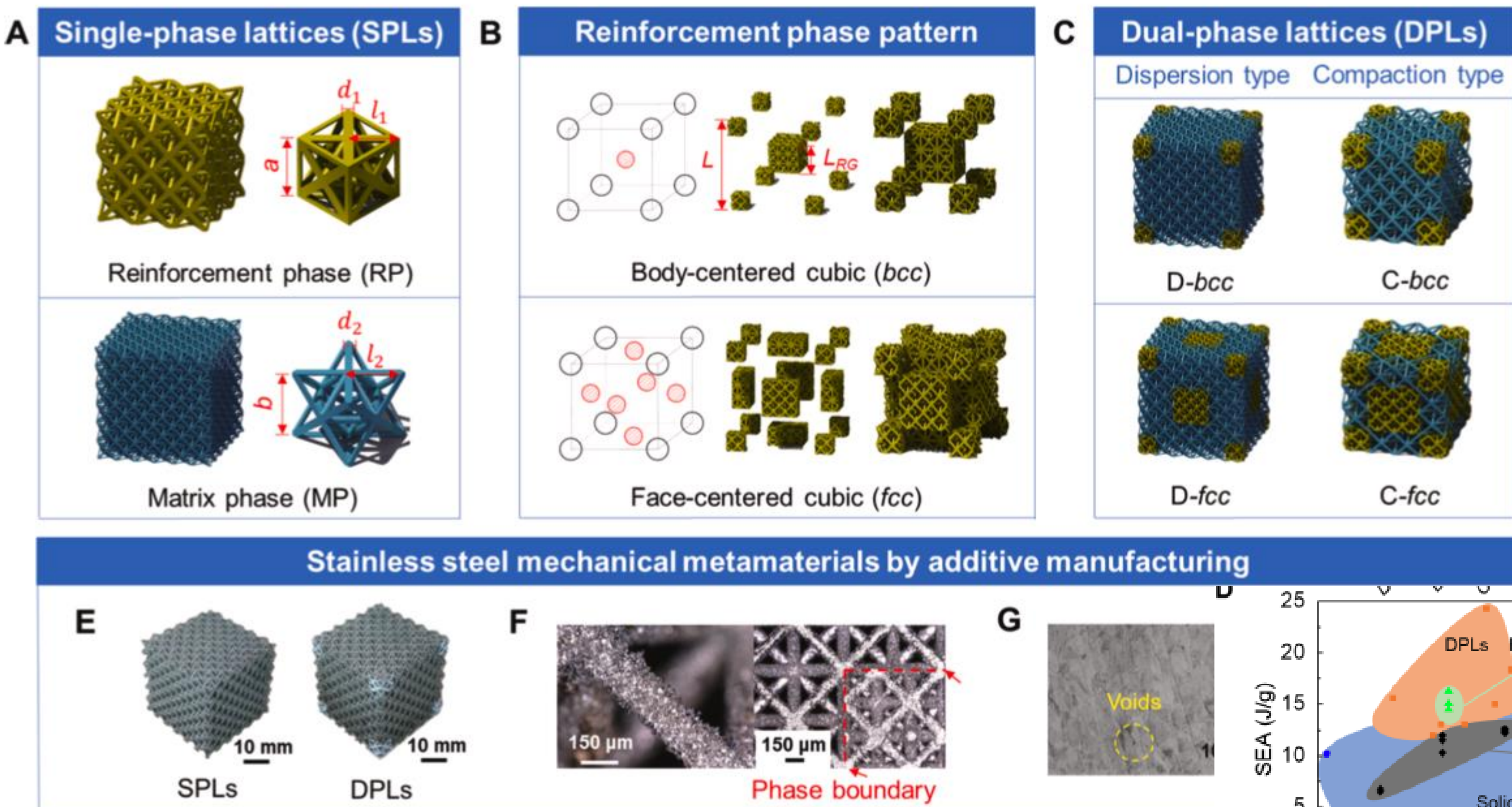


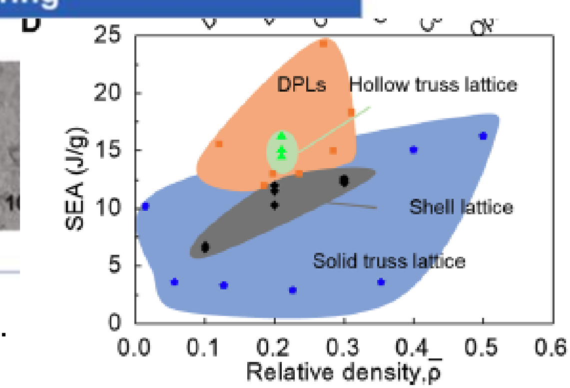
Three contributions to the mechanical performance

- 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*.