TUNTWIN's Workshop

Session A: Basics in Synchrotron Techniques for Environmental and Food from Basics to Application

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Session: Spectroscopy techniques

Small/wide angle X-ray scattering (SAXS/WAXS)

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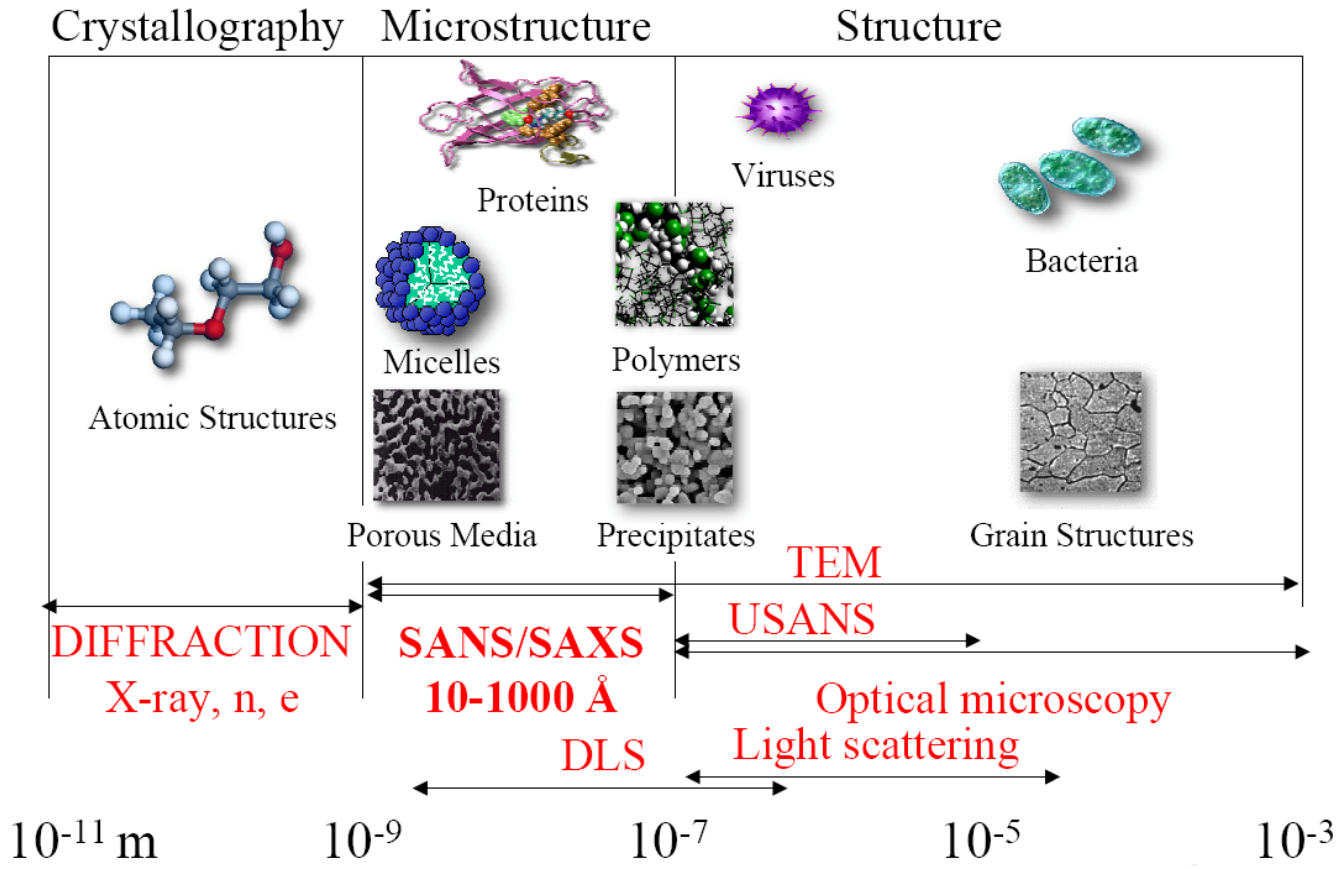
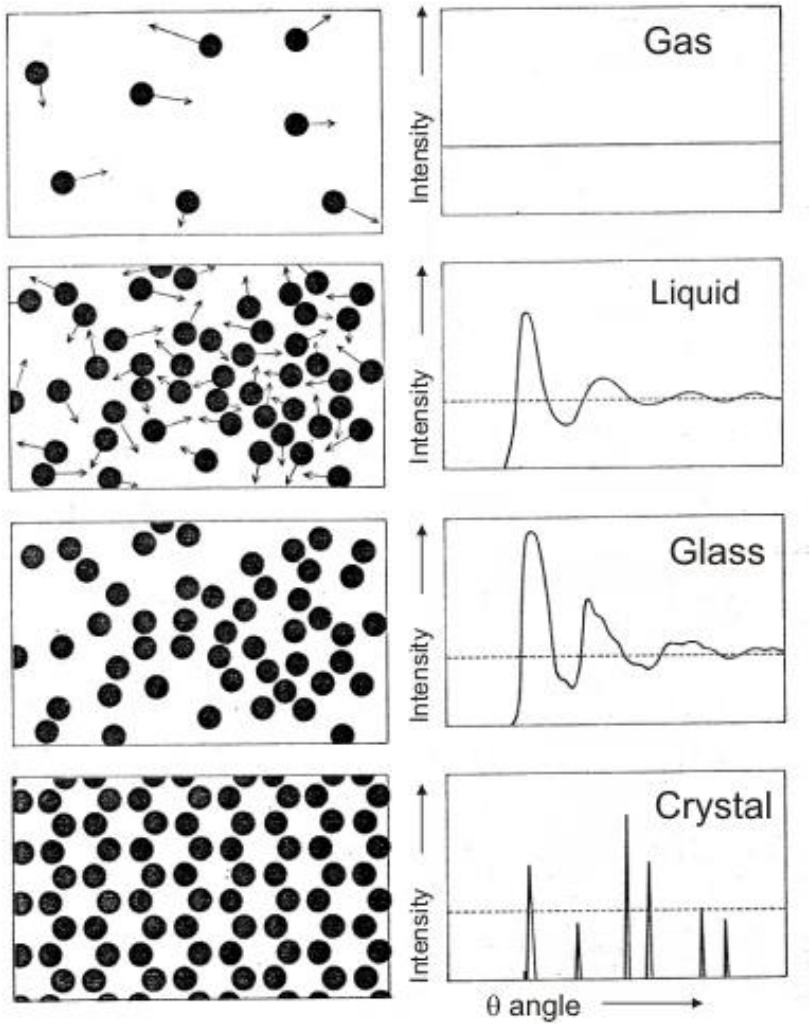
X-ray diffraction and scattering



Diffraction is a coherent process and **scattering** is an incoherent process.

Diffraction requires that the surface/medium is regular on distances comparable to the wavelength of the light being diffracted.

X-ray diffraction and scattering



https://www.xtal.iqfr.csic.es/Cristalografia/parte_05-en.html

X-rays scattered by a set atoms produce X-ray radiation in all directions, leading to interferences due to the coherent phase differences between the interatomic vectors that describe the relative position of atoms.

In the crystal, where the phase relations are fixed and repetitive, the scattering profile becomes sharp with well defined peaks, whereas in the other diagrams the peaks are broad and somewhat continuous. In the crystal case the scattering effect is known as diffraction.

The scattering phenomenon reflects the internal order of the sample -- the positional correlations between atoms.

X-ray scattering – Non crystalline diffraction

Small-angle, non-crystalline diffraction provides essential information on the structure and dynamics of large molecular assemblies in low ordered environments.

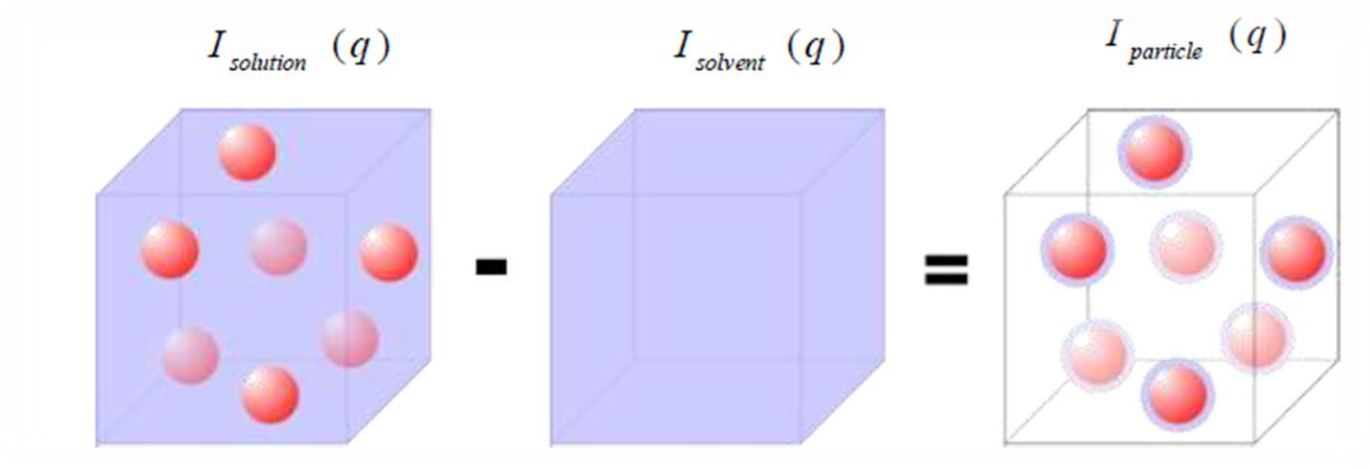
These are characteristic of living organisms and many complex materials such as polymers and colloids.

X-ray scattering is probing distances that are large compared to inter-atomic distances. Characteristics are:

- Random orientation of particles (i.e. no long-range order) leads to scattering rather than diffraction (determination of size and shape)
- Electron density variations at the particle-matrix interface cause x-rays to scatter.
- The scattered intensity, I(q), is measured in terms of the scattering vector, q.

X-ray scattering – Non crystalline diffraction

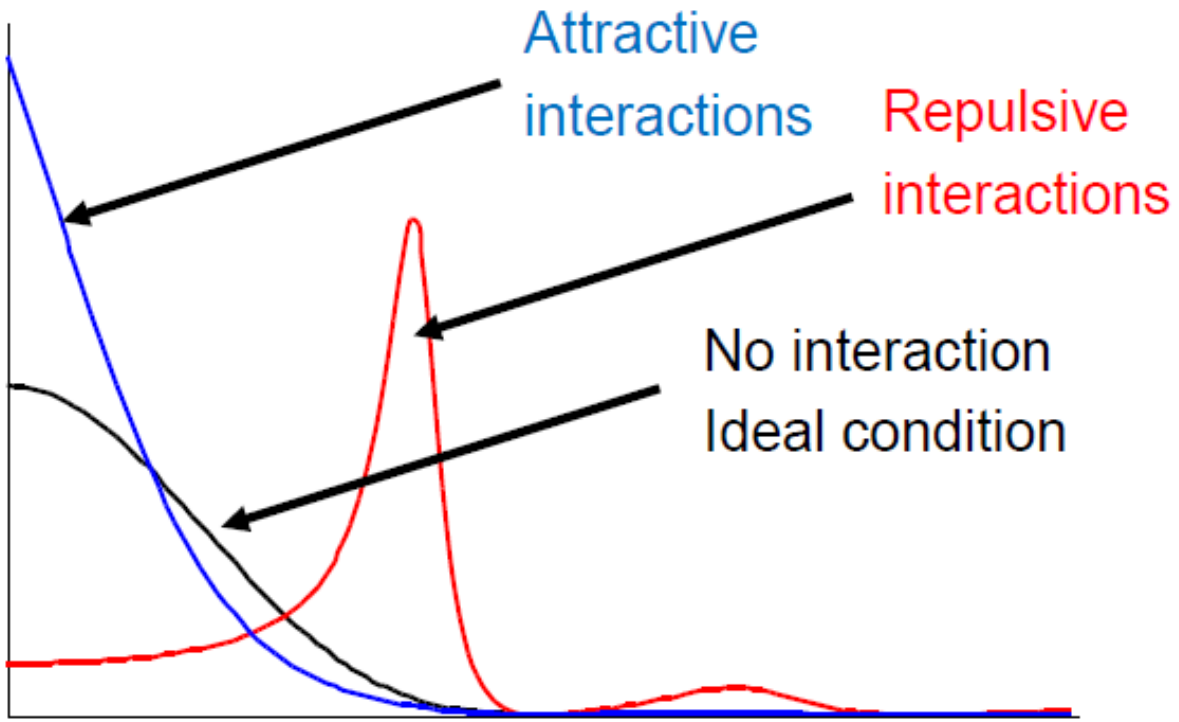
The electronic density of the particle MUST NOT match the electronic density of the matrix.



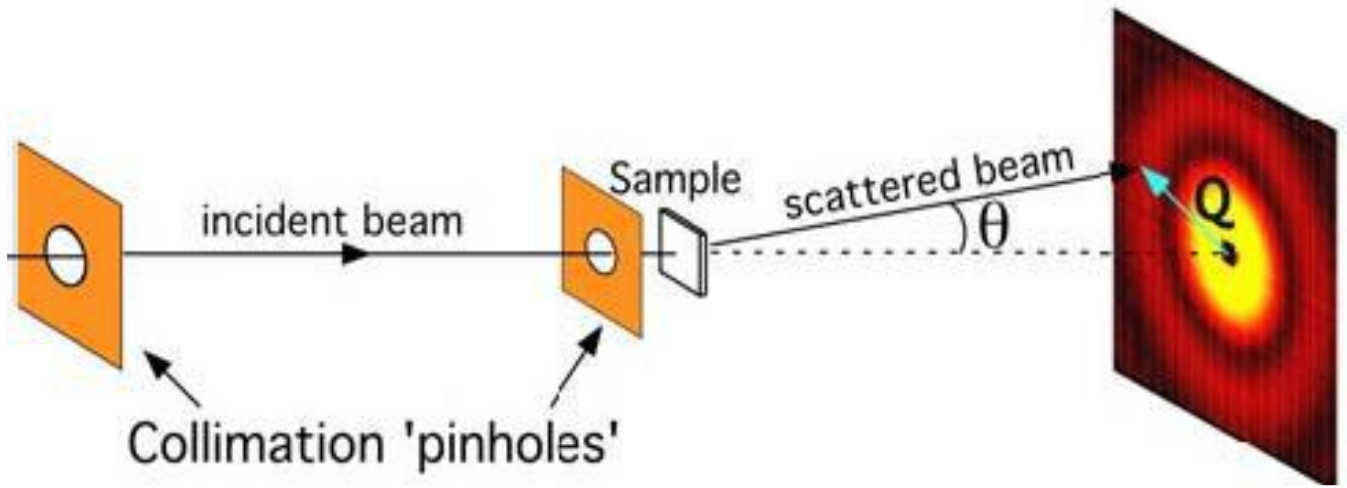
Courtesy of Marc Malfois (SAXS Workshop 2014, ALBA)

X-ray scattering – Non crystalline diffraction

- Big particle scatter more!
- Higher concentration better signal BUT can complicate the data analysis…
- Minimum concentration for synchrotron ~1mg/ml



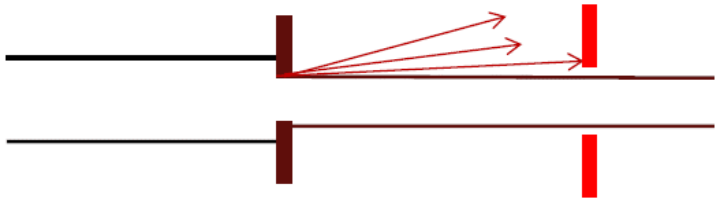
X-ray scattering – Non crystalline diffraction



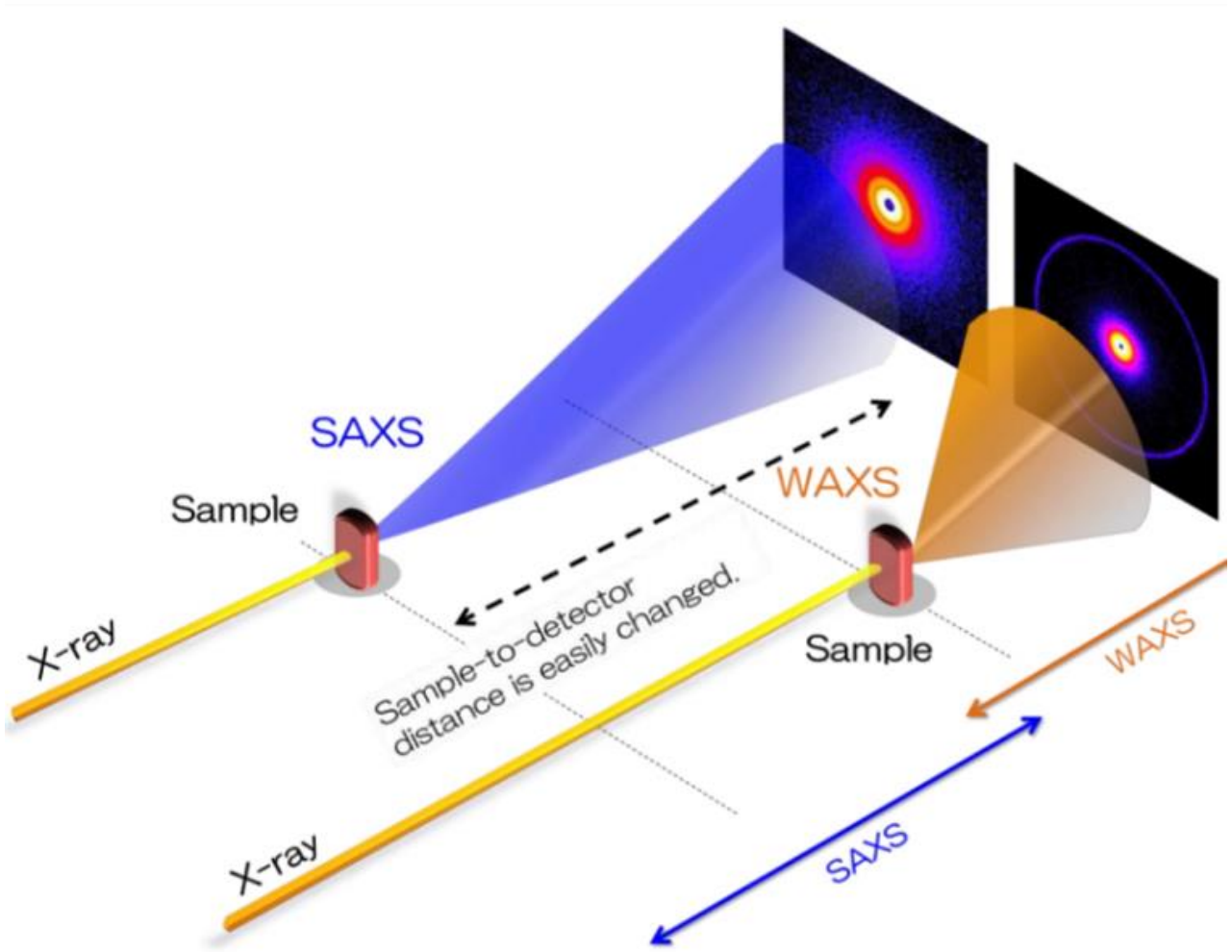
Scattering angle $2\theta < 5\text{-}10^{o}$ (these are the "small" angles)

Collecting at small angle (to access long spacing distances in real space) → Put detector far away from sample

Beam defining slits (pinhole) + Beam 'cleaning' slits (pinhole) to stop the beam dispersed from the first slits/pinhole.



Small angle and wide angle X-ray scattering (SAXS/WAXS)

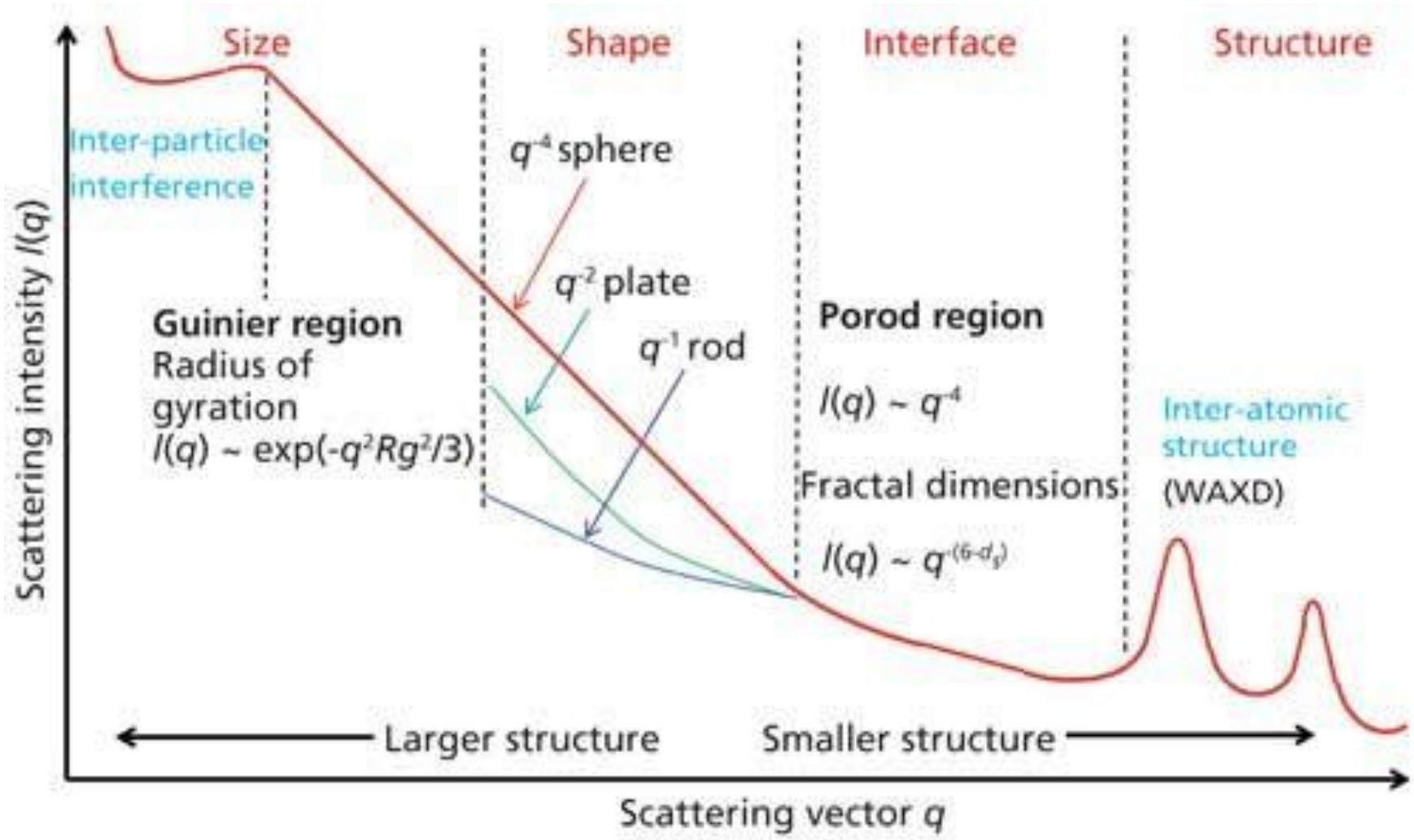


- Scattering light as a function of the angle.
- Depending on where is the detector placed:

	SAXS	WAXS
Angle (θ)	0,1º - 5º	5º - 60º
Length scale	nanometers	microns to Å
Information	particle sizes, shapes, distribution,	chemical composition

https://www.princetoninstruments.com/learn/x-ray-scattering/intro-to-x-ray-scattering

Small angle and wide angle X-ray scattering (SAXS/WAXS)

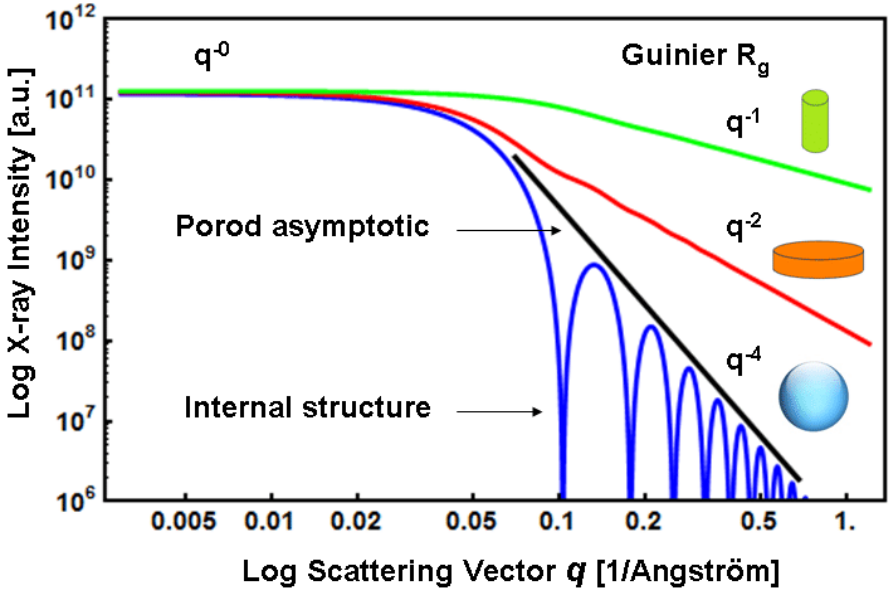


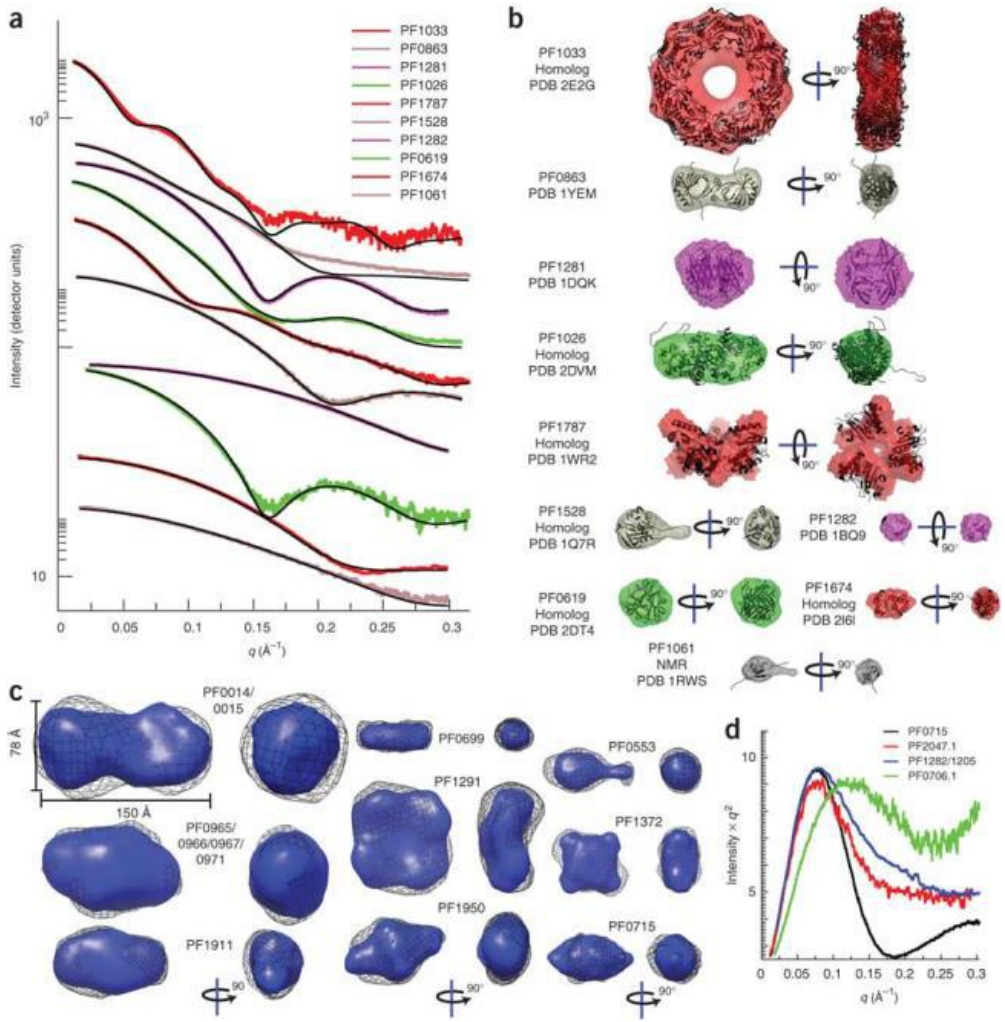
https://www.spectroscopyonline.com/view/recent-developments-small-angle-x-ray-scattering

Small angle and wide angle X-ray scattering (SAXS/WAXS)

From SAXS pattern:

- Particle size
- Particle shape
- Polydispersity
- Kinetics





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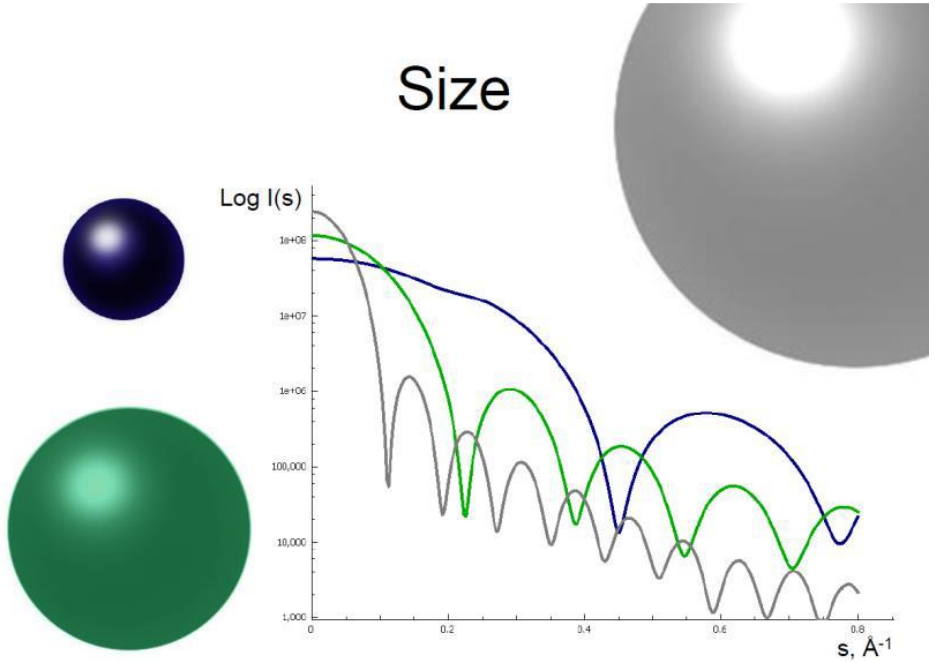
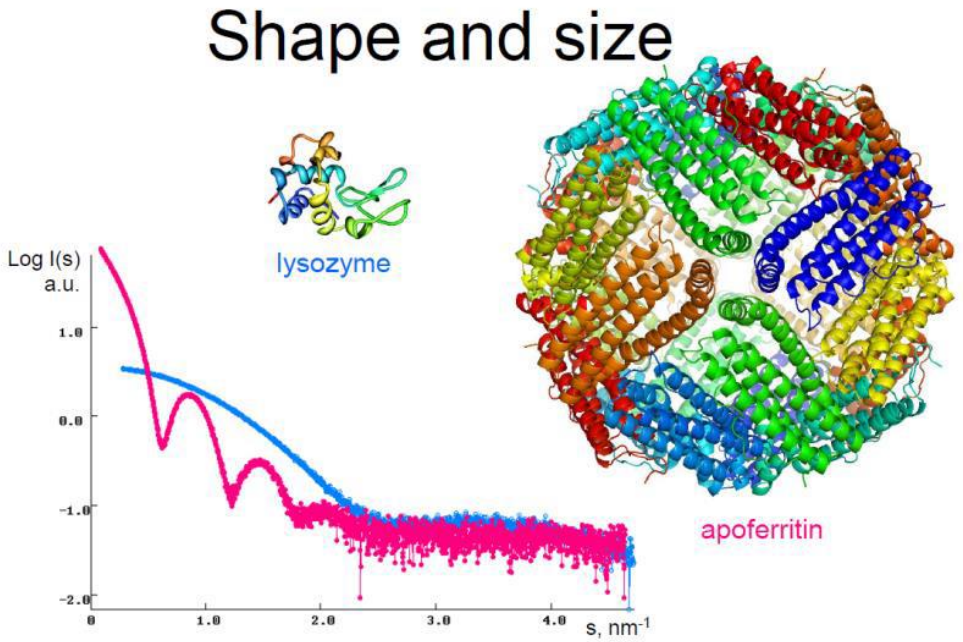
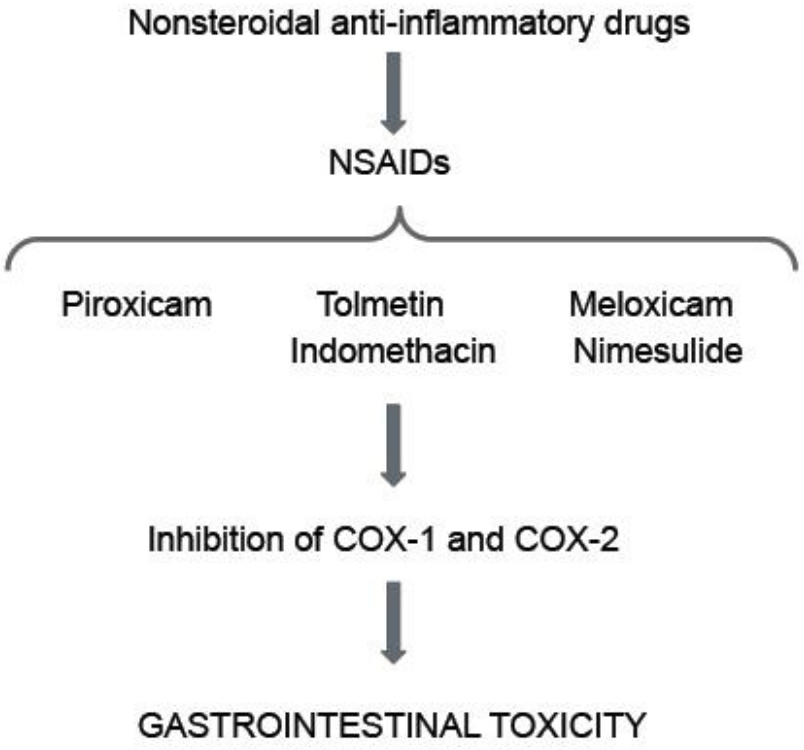
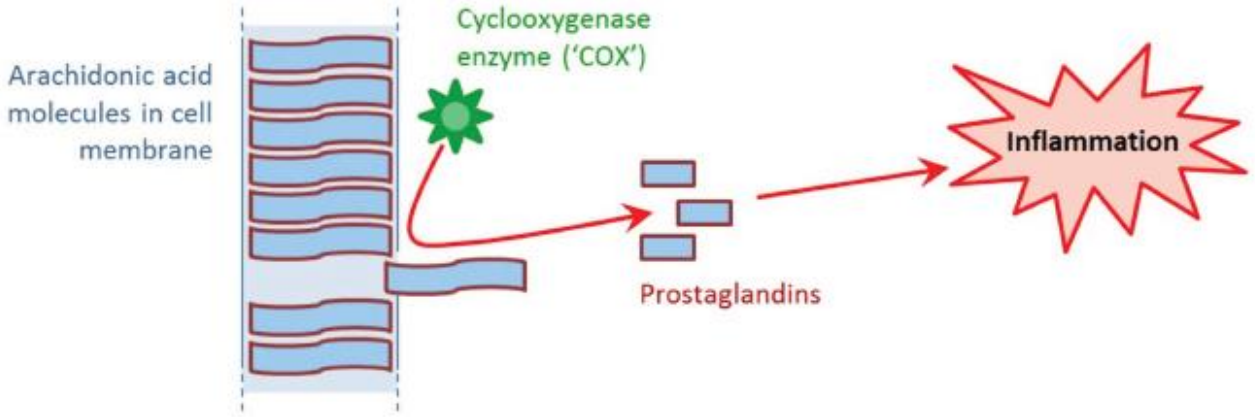




EXAMPLE: Study of the interactions of NSAIDS with Lipid membranes



The main mechanism of action of NSAIDs is based on their ability to **inhibit the enzyme cyclo-oxygenase (COX)**



J. Phys. Chem. B 2011, 115, 24, 8024–8032; https://doi-org.are.uab.cat/10.1021/jp2025158

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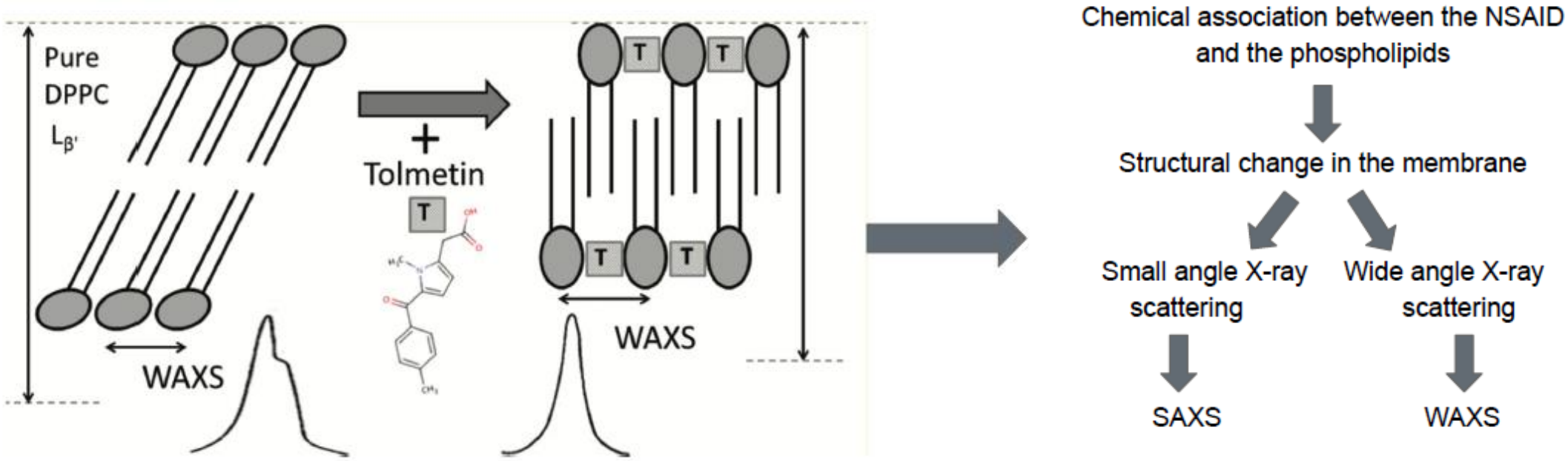

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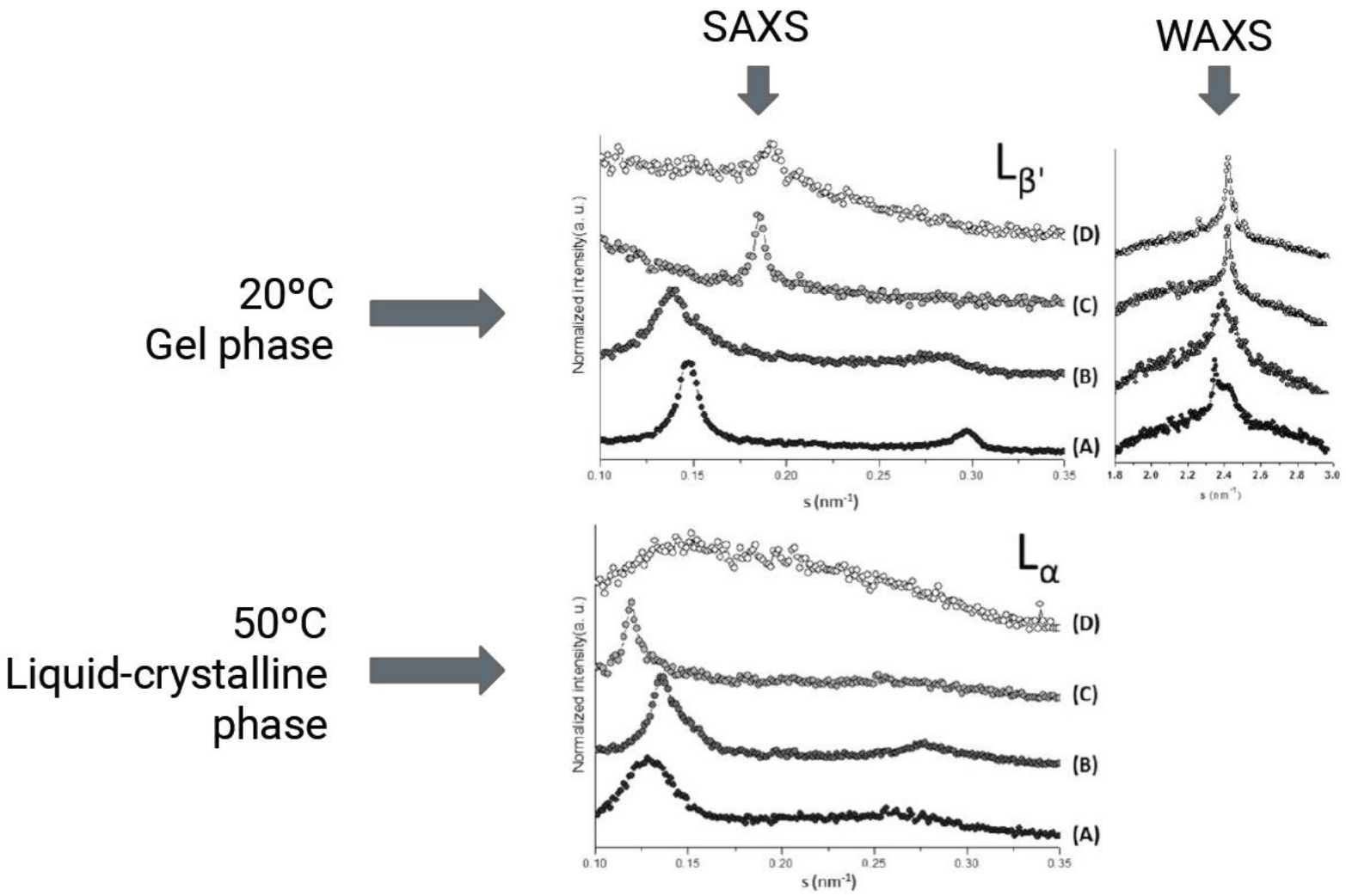

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EXAMPLE: Study of the interactions of NSAIDS with Lipid membranes

NSAID drug	Modification of lipid bilayer	Effect in the body
Meloxicam	Strong effect in the membrane due to the charge.	Low doses ✓ GI tolerability ✓ COX-2 selectivity High doses ✗ GI tolerability ✗ COX-2 selectivity
Piroxicam	Low effect with the membrane but interact with the lipid.	Low and High doses ✗ GI tolerability ✗ COX-2 selectivity
Tolmetin	Strong interaction with the headgroups.	Low and High doses ✗ GI tolerability ✗ COX-2 selectivity
Indomethacin	Great interaction with the membrane.	Low and High doses ✗ GI tolerability ✗ COX-2 selectivity
Nimesulide	Not perturb the lipid packing.	Low and High doses ✓ GI tolerability ✓ COX-2 selectivity

The different NSAIDS present different effects on the Gastro Intestinal tract.

SAXS and WAXS have allowed to determine the structural modification of the lipidic bilayer caused by NSAIDS.

J. Phys. Chem. B 2011, 115, 24, 8024–8032; https://doi-org.are.uab.cat/10.1021/jp2025158

EXAMPLE: the structure of the bone

Long d-spacing systems

(a) macroscopic bone

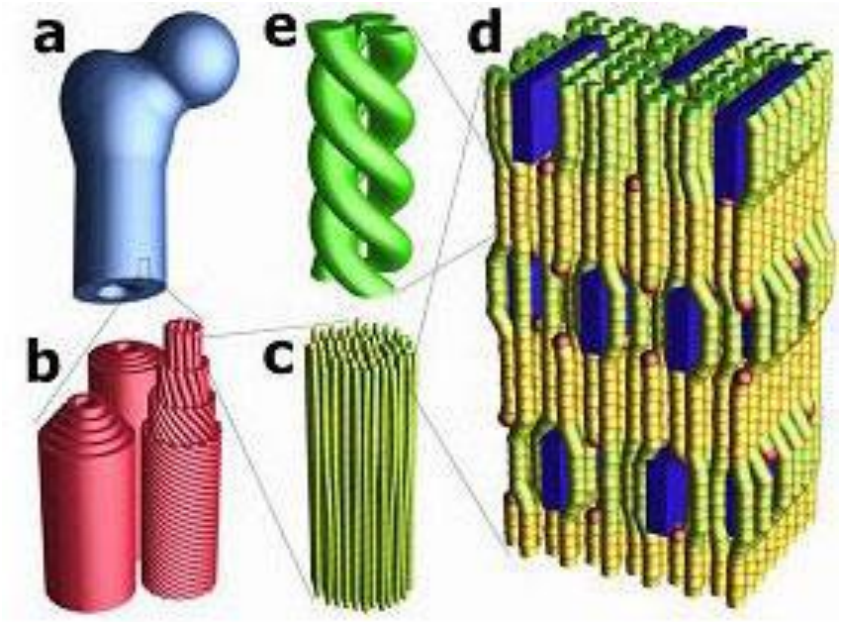
(b) osteons (~100μm in diameter) with circular arrangements of differently oriented collagen fibers

(c) A collagen fiber (~5μm in diameter) consisting of bundles of collagen fibrils (each with a diameter of ~500nm)

(d) A striped collagen fibril (each period is ~68 nm in length) consisting of a staggered arrangement of collagen molecules (each having a diameter of ~1.5 nm) with embedded mineral crystals (with diameters from ~2 to 20 nm and lengths of 30 nm)

(e) A collagen molecule triple helix

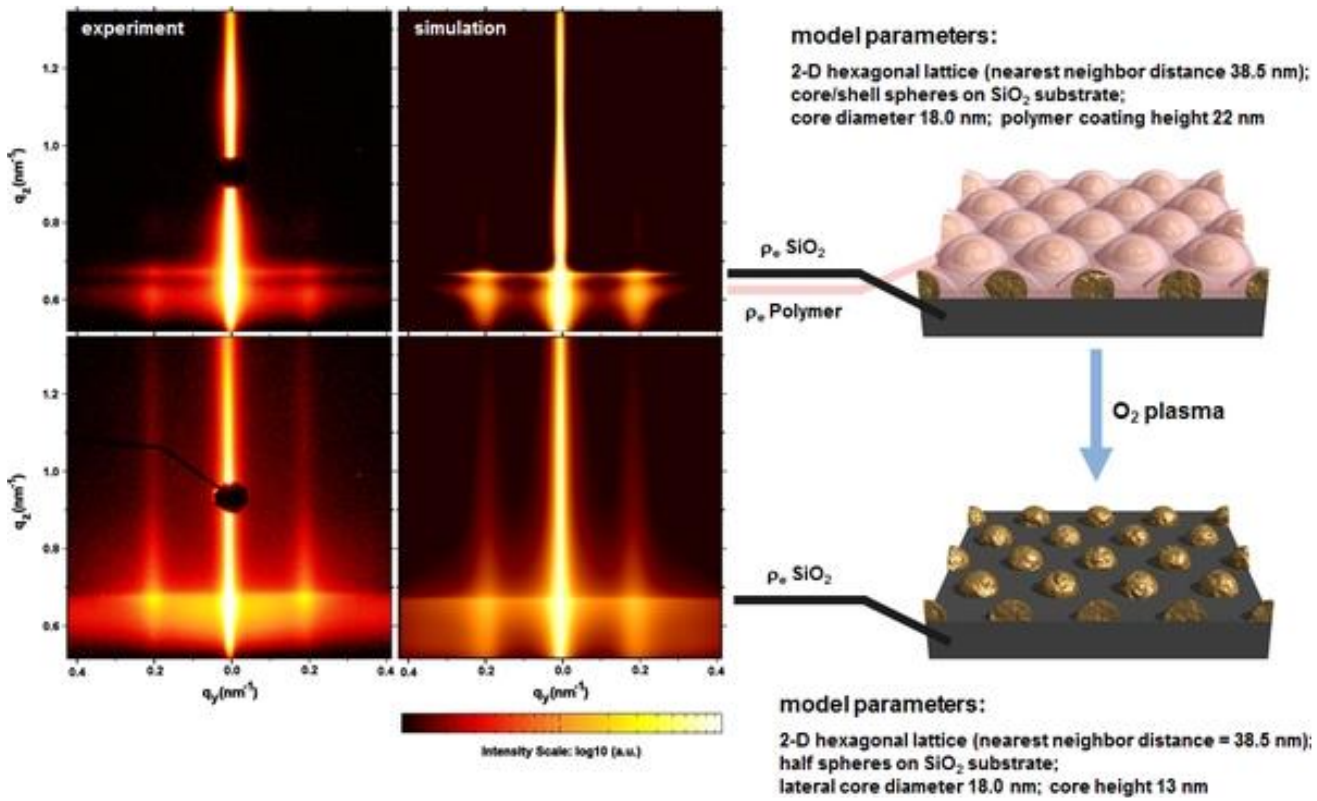
Strain, stress, and other mechanical parameters determination at small scales (<100nm) in nanostructured biomineralized composites



Karunaratne et al., Methods in Enzymology, ***532,*** *2013, Pages 415-473*

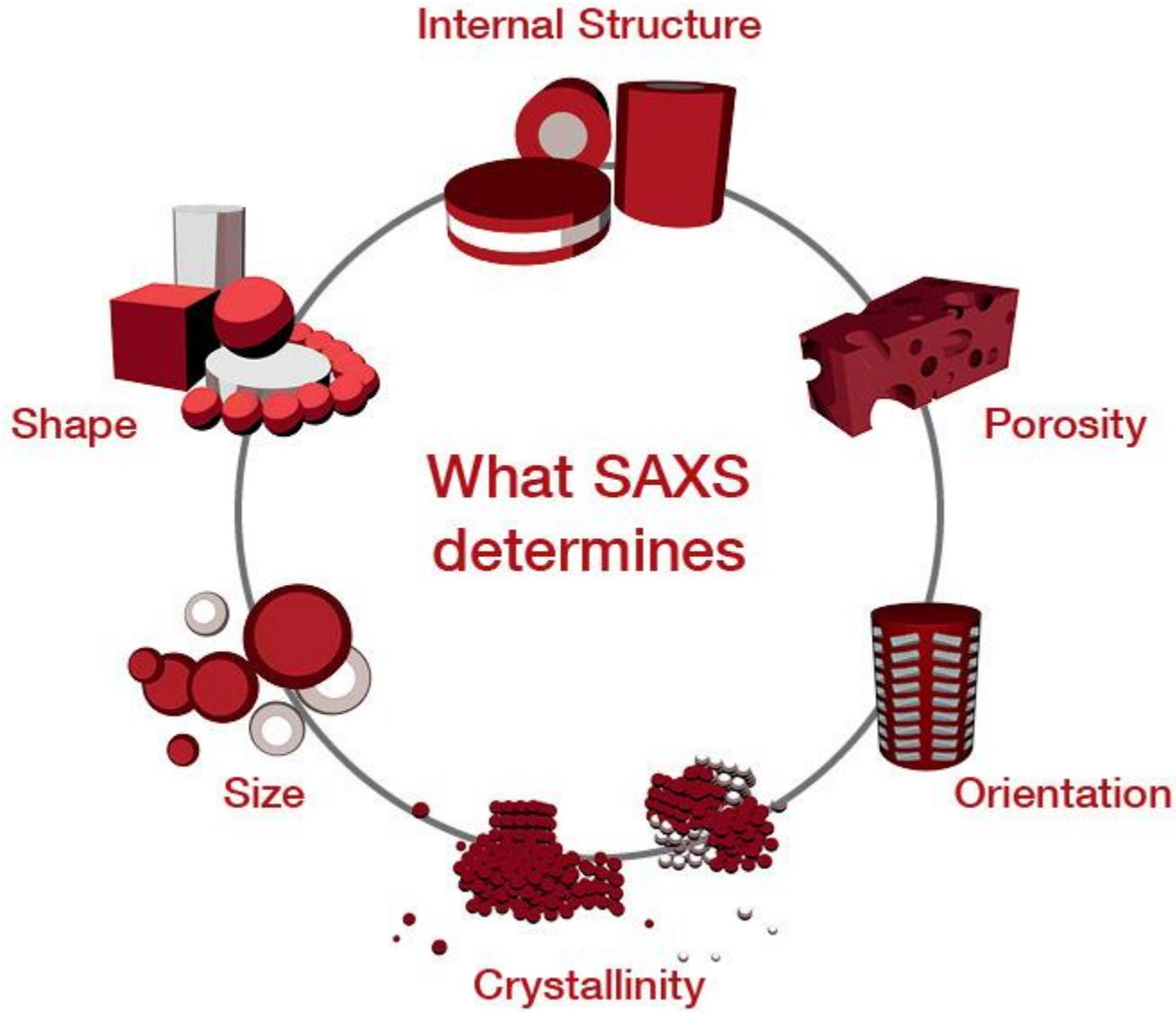
Grazing incidence SAXS

Surface sensitive technique



Experiment and simulation before and after O_2-plasma treatment of SiO_2 filled diblock copolymer micelles on a silicon wafer

small 2007, 3, No. 5, 880 – 889


Internal Structure
Porosity
Orientation
Crystallinity
Size
Shape
What SAXS determines

TUNTWIN's Workshop

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Merci!

Thank you!

¡Gracias!

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