SOLEIL SYNCHROTRON

A small introduction to Small Angle X-rays Scattering

Thomas Bizien, SWING Beamline

Introduction

SAXS - What’s that ?

Scattering from individual objects

Scattering from Lattices and Complex Organizations

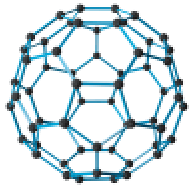
Where can I do this?

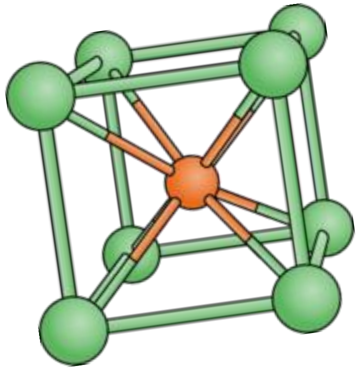
What can we get from SAXS, a few examples

Probing lentgh-scales

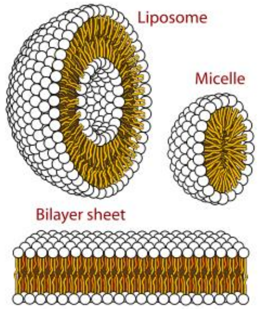
Crystallography | Microstructure | structure

Atomic structure

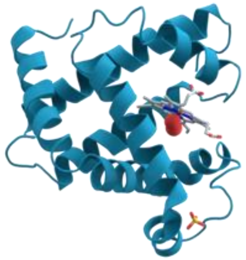




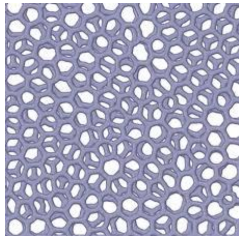
Micelles …



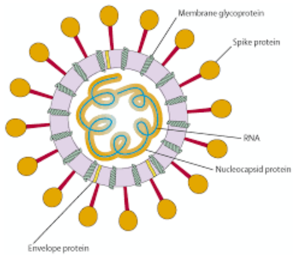
Proteins



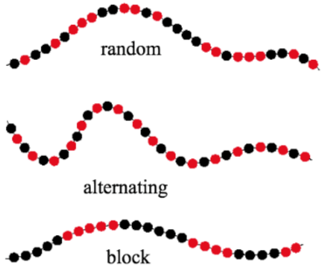
Porosity



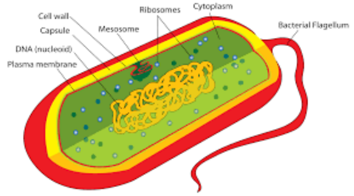
Virus



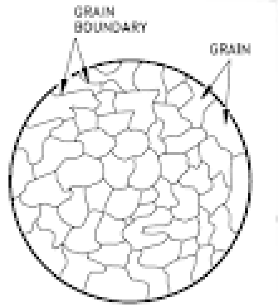
Polymers



Bacteria



Grain structure



Optical microscopy

Electron Diffr.

Electron microscopy

X-ray Diffr.

X-ray Small Angle Scattering

Ultra small X-ray Small Angle Scattering

Neutron Diffr.

Neutron Small Angle Scattering

Various spectroscopic method (inelastic scattering)

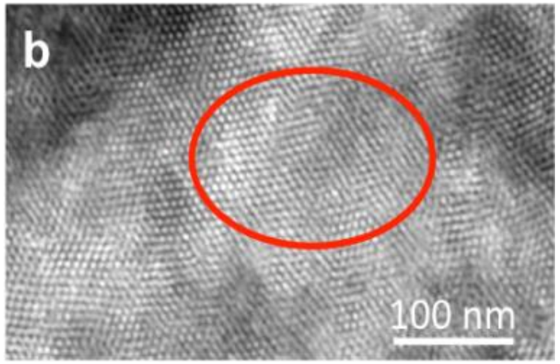
10^{-9} 10^{-7} 10^{-5}

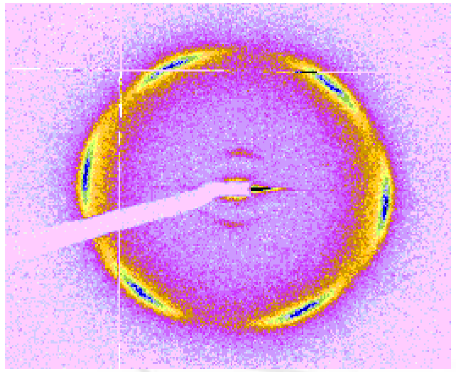
Pro:

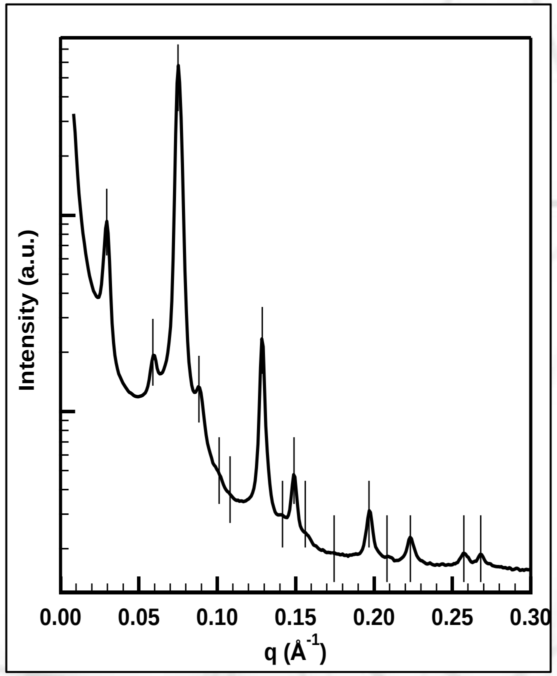
- Fast
- Meaningful global average
- Probing of buried 3D structure
- In-situ and almost non-destructive :
  - Probing in liquid state, during kinetics, working devices

Cons:

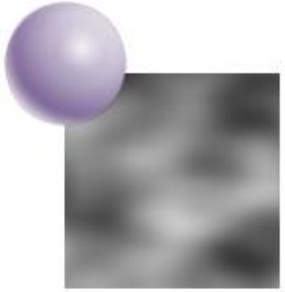
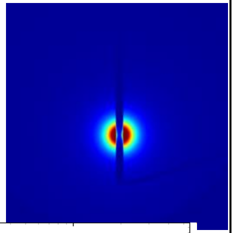
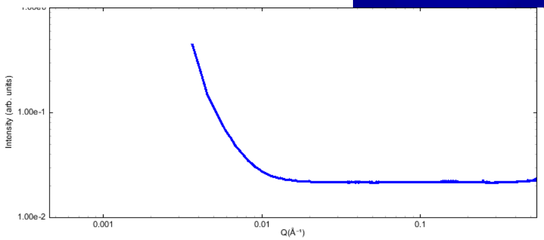
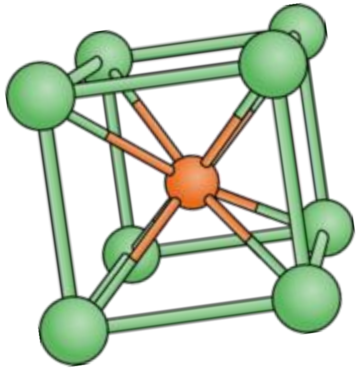
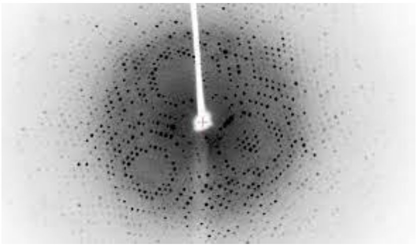
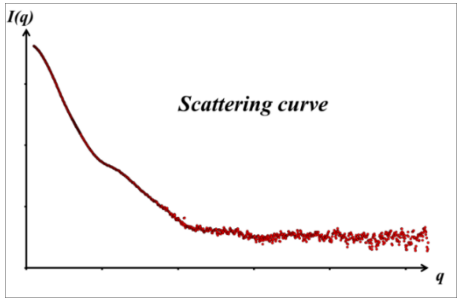
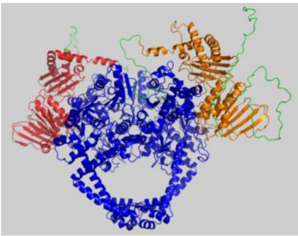
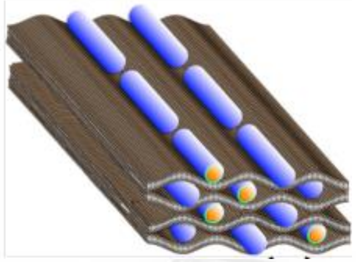
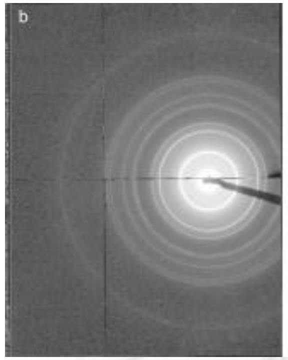
- Hard to interpret data (sometimes)







What scatter?

<table>
<tr><td></td><td></td><td colspan="2">Organization of constituents
« Structure Factor »</td></tr>
<tr><td></td><td></td><td>Random</td><td>Periodic</td></tr>
<tr><td rowspan="2">Constituents
« Form Factor »</td><td>Simple</td><td>Gases, liquids, glasses, …
</td><td>Crystals, …
</td></tr>
<tr><td>Arbitrary</td><td>Colloids, proteins in solutions, …
</td><td>Lithography, nano-particles lattice, …
</td></tr>
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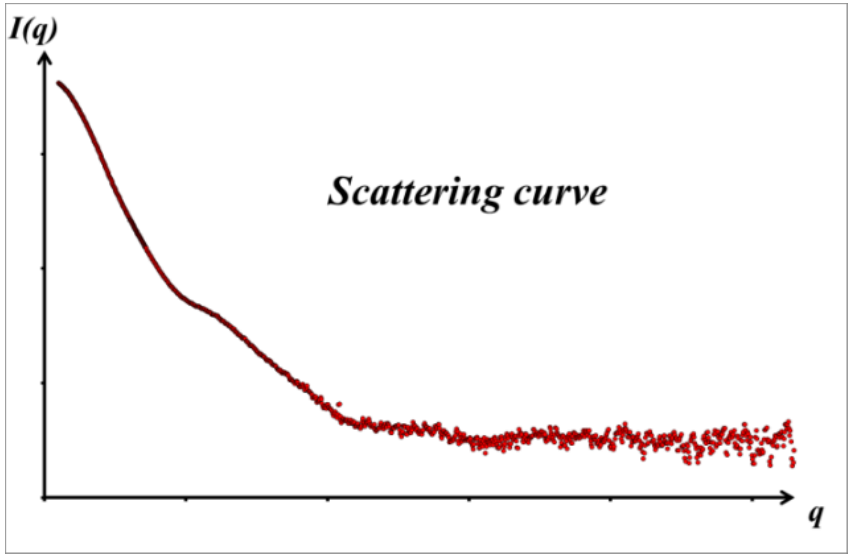
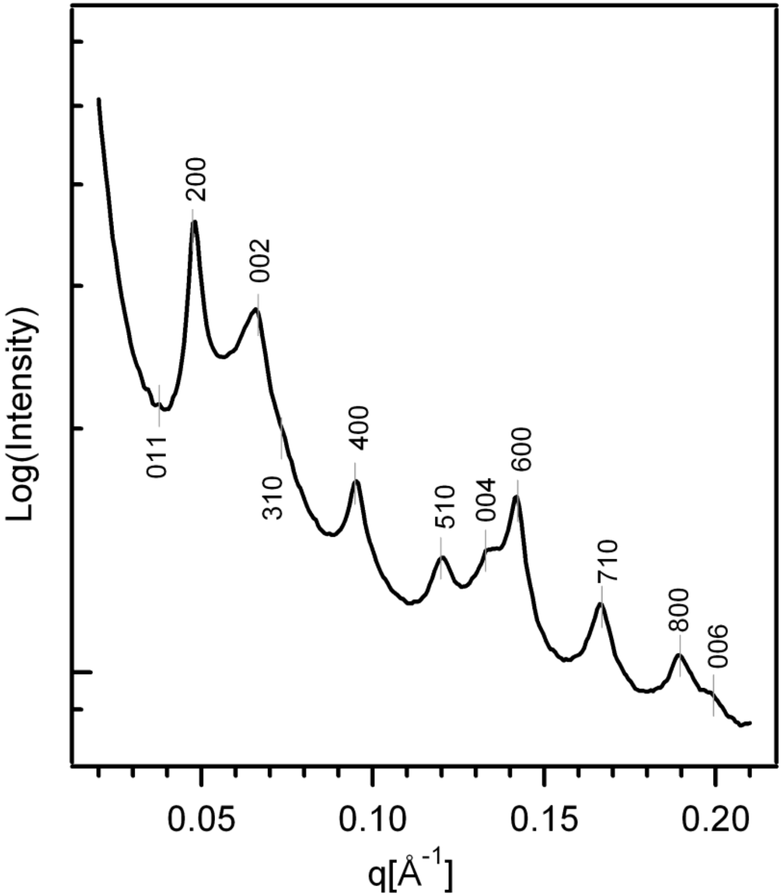
What can we measure?

- Size of scatterrer
- Amounts of them
- Polydispersity
- Distribution
- Shapes
- Morphology
- Structures



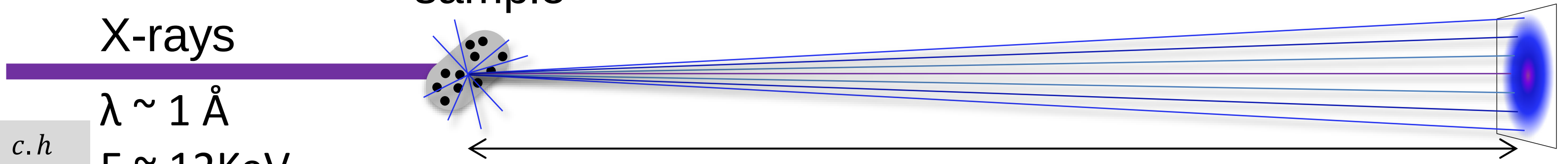


There is a really strong dependence between some of these terms

SAXS Plus *other measurement* can provide really rich information about
The sample microstructure

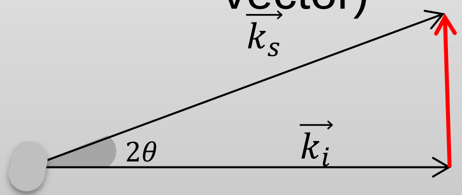
SAXS - What’s that ?

- **Small Angle X-ray Scattering**



$$E = \frac{c.h}{\lambda}$$

Angle => momentum transfer (scattering vector)



$$\vec{q} = \overrightarrow{k_s} - \overrightarrow{k_i}$$

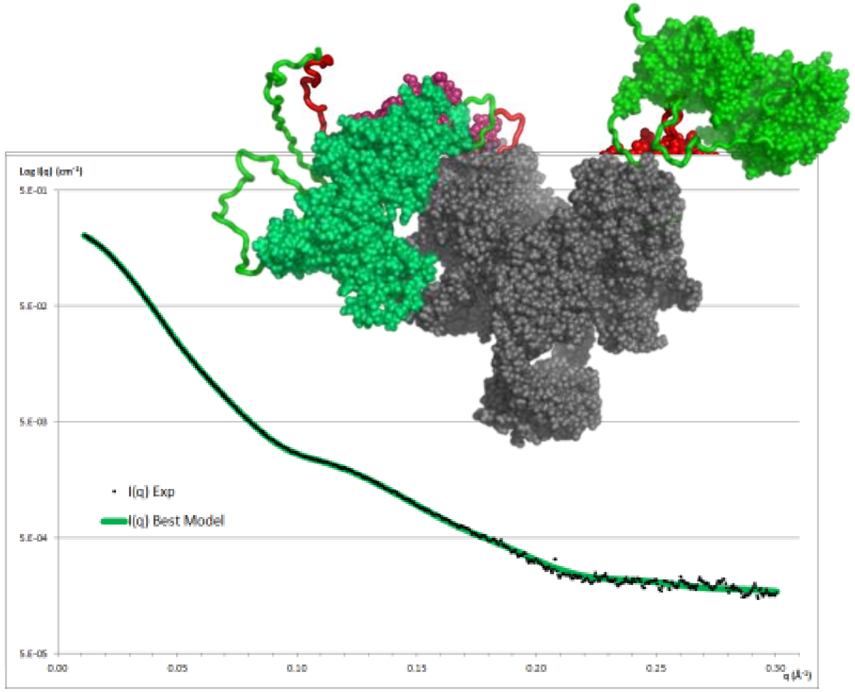
$$q = \frac{4\pi \sin\theta}{\lambda}$$

SAXS Curve : $I(q) = |F(q)|^2\ |S(q)|$

First things to know :

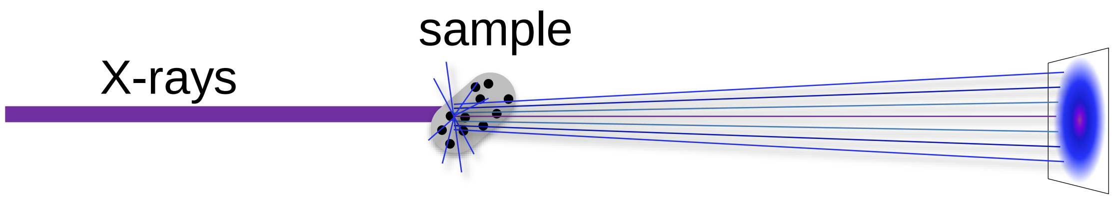
All obtained SAXS data are interpretated using analytical models
Therefore, you **HAVE TO**
- know SAXS and
- know about your sample morphology in real space

SAXS – Scattering from indidual objects

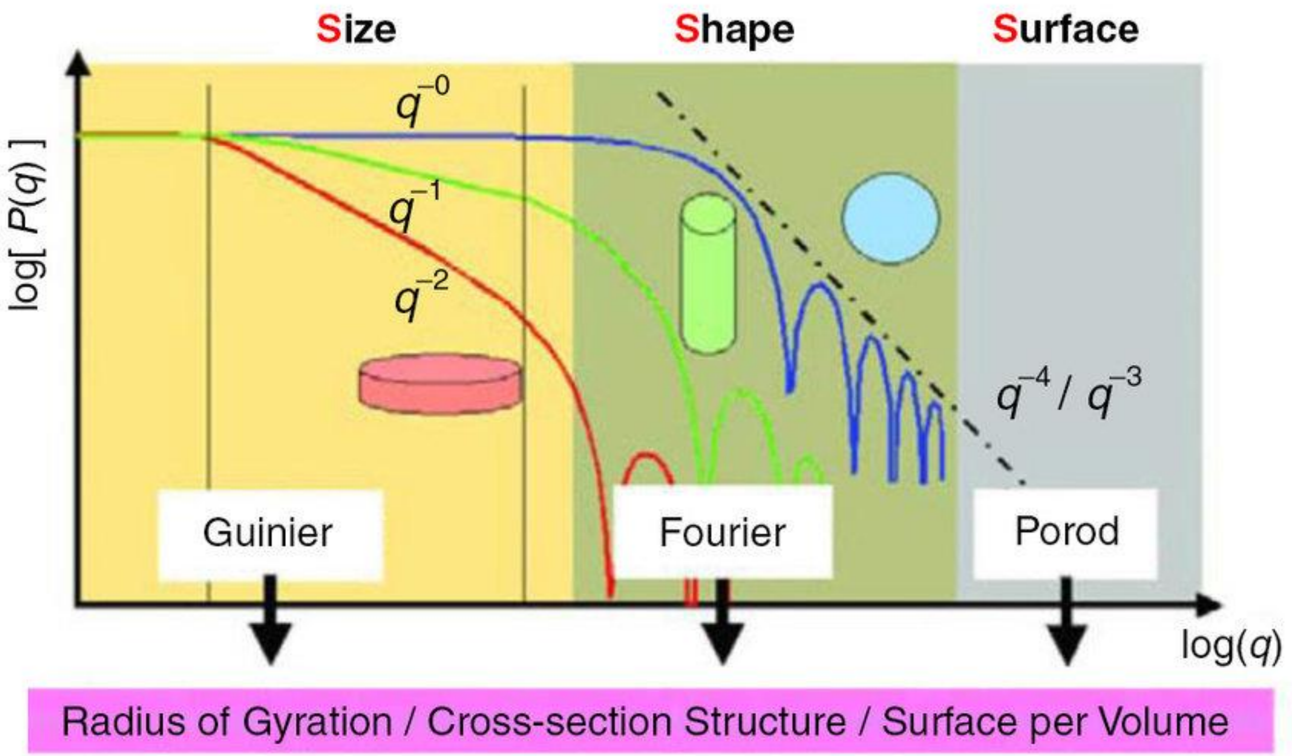


- **Form factor**

For a dilute system



Low q region



In solution, the scattering is isotropic, so the intensity depends only on **q**

Boldon, L.,(2015). *Nano Reviews*, *6*(1).

SAXS – Scattering from indidual objects

- **What are we measuring?**

Measure quantity is :

$$I(q) \propto \frac{d\,\Sigma(q)}{d\Omega} = \frac{N}{V} V^2 particles(\rho 1 - \rho 2)^2\, P(q)S(q)$$

Diluted system => independence of scatterers = **No interparticle effects**

Thus

$$I(q) \propto \frac{d\,\Sigma(q)}{d\Omega} = \frac{N}{V} V^2 particles(\rho 1 - \rho 2)^2\, P(q)\cancel{S(q)}$$

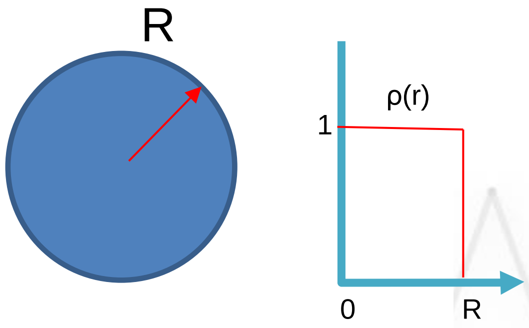
= Sum of individual particle scattering

P(q) or F(q)= form factor – **SHAPE** and **SIZE** information

SAXS – Scattering from individual objects

• A few examples :

Simple shapes objects form factor have analytical formula expression. For example : **Spheres** are widely used to characterize spheroids Nanoparticles, of even globular proteins.



Simple sphere : homogenous electron density and Radius *R*

$$F(q) = \frac{3(\sin(qR) - qR\cos(qR))}{(qR)^3}$$

$$I(q) = F^2(q) = \left(\frac{3(\sin(qR) - qR\cos(qR))}{(qR)^3}\right)^2$$

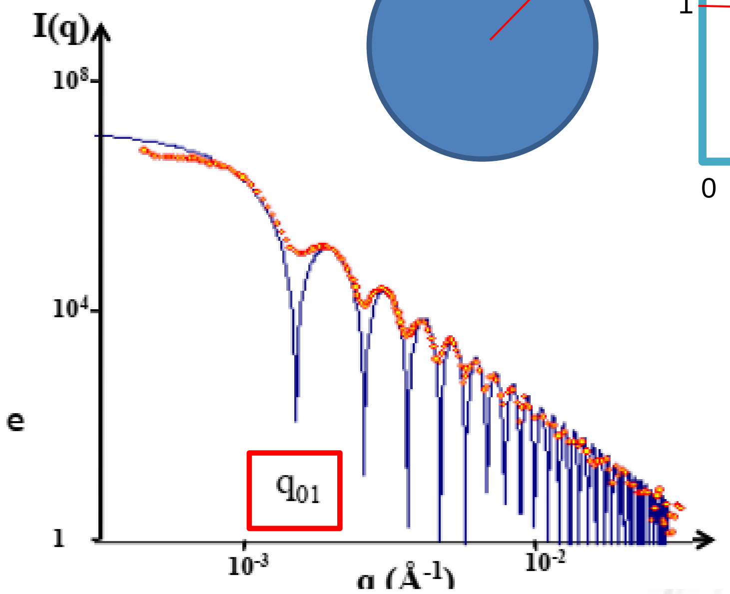
For centro-symmetric object:

$$A(\vec{q}) = \int \rho(\vec{r})\exp(-i\vec{q}\cdot\vec{r})\, d\vec{r}$$

$$A(q) = 4\pi \int_0^\infty \rho(r)\frac{\sin(qr)}{qr} r^2 dr = 4\pi \int_0^R \frac{\sin(qr)}{qr} r^2 dr$$

$$= \frac{4\pi}{q}\int_0^R \sin(qr)\, r dr = \ldots \quad \text{(partial integration)}\ldots$$

$$= \frac{4}{3}\pi \boxed{R^3 \frac{3[\sin(qR) - qR\cos(qR)]}{(qR)^3}}$$



From the curve we estimate :

$$R \approx \frac{4{,}4493}{q_{01}}$$

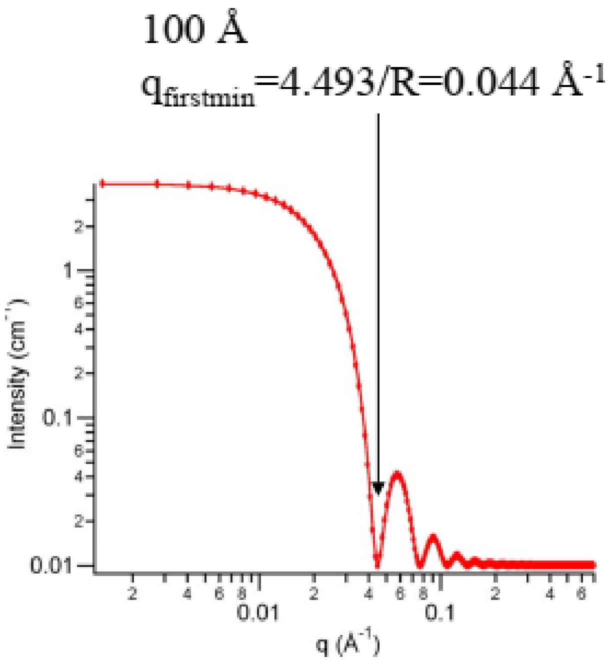
- profile of silica spheres (red) and simulation based on perfect sphere (blue)
- Discrepancy of silica scattering from sphere model due to size polydispersity, imperfect spherical shape, etc

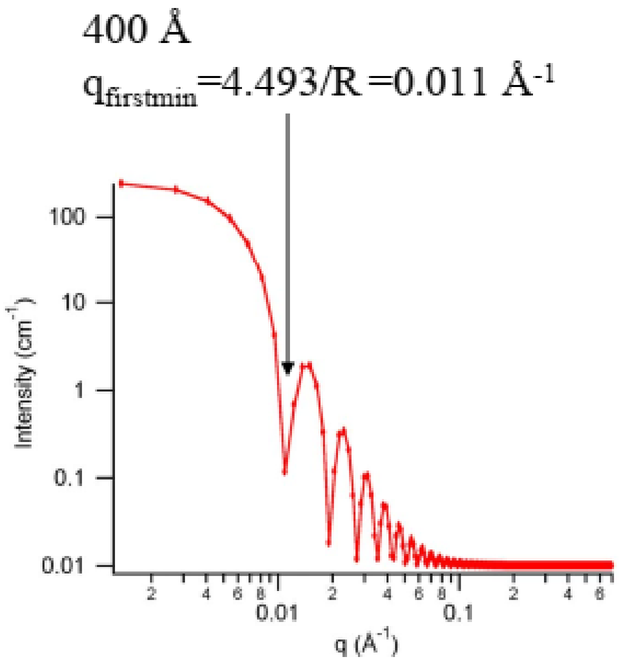
Figure modified from: Lambard, Lessieur and Zemb, J. Phys. I France, 1992, (2) 1191

SAXS – Scattering from individual objects

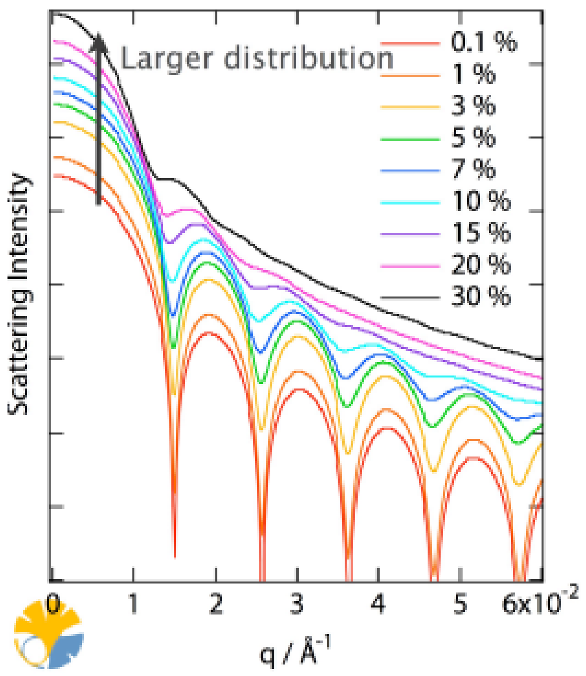
- **A few examples :**
  - **Effect of size and polydispersity**

Size





Polydispersity



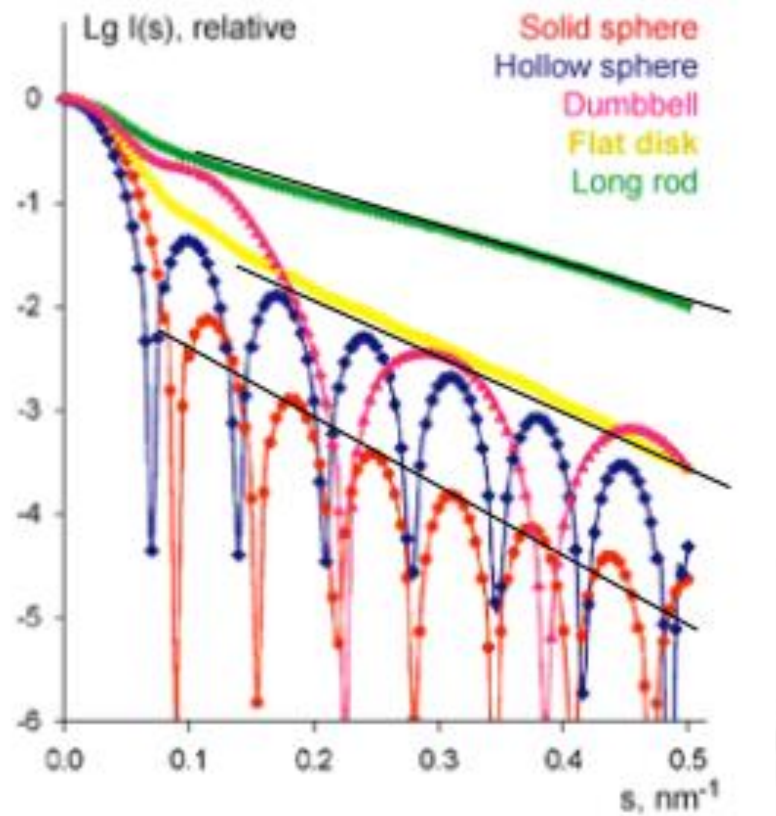
Instrument resolution is paramount and can affect the data, e.i. masking of the « true » distribution => Sample is not so polydisperse as it looks on the 2D curve

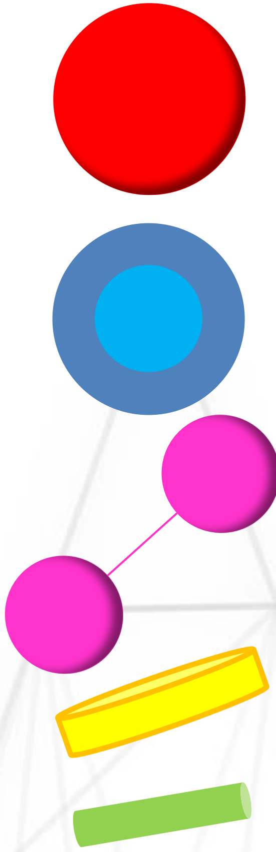
SAXS – Scattering from individual objects

- **A few examples :**
  - **Other shapes**

Morphologies	P(q) or P²(q) – depends on source	Morphologies
Spheres (radius :R)	$\frac{9}{(qR)^6}[\sin(qR) - qR\cdot\cos(qR)]^2 = A^2_{sph}(qR)$	
Spherical shells (outer radius: R_1 inner radius: R_2)	$\frac{[R_1^3\cdot A_{sph}(qR_1) - R_2^3\cdot A_{sph}(qR_2)]^2}{(R_1^3 - R_2^3)^2}$	
Triaxial ellipsoids (semiaxes: a,b,c)	$\int_0^1\int_0^1 A^2_{sph}[q\sqrt{a^2\cos^2(\pi x/2) + b^2\sin^2(\pi x/2)(1-y^2)_1 + c^2y^2}\,]\,dx\,dy$	
Cylinders (radius: R length: L)	$4\int_0^1 \frac{J_1^2[qR\sqrt{1-x^2}\,]}{[qR\sqrt{1-x^2}\,]^2}\,\frac{\sin^2(qLx/2)}{(qLx/2)^2}\,dx$ $J_1(x)$ is the first kind Bessel function of order 1	
Thin disk (radius: R)	By setting L = 0 $\quad \frac{2 - J_1(2qR)/qR}{q^2R^2}$	
Long rod (length: L)	By setting R = 0 $\quad \frac{2}{qL}\int_0^{qL}\frac{\sin(t)}{t}\,dt - \frac{\sin^2(qL/2)}{(qL/2)^2}$	

"Structure Analysis by Small Angle X-Ray and Neutron Scattering" L. A. Feigen and D. I. Svergun

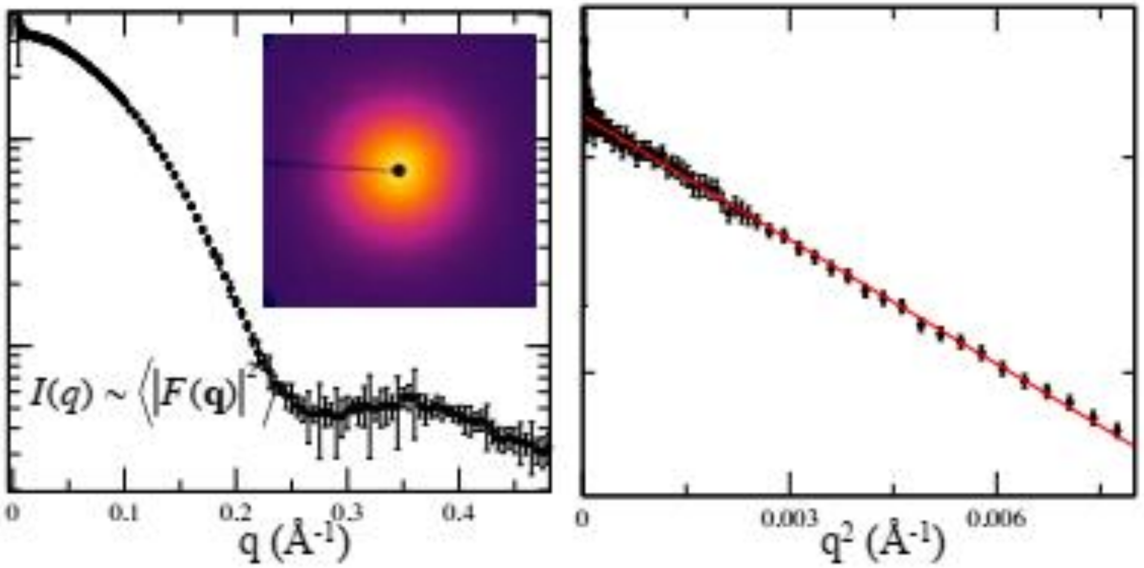




SAXS – Scattering from individual objects

- **Radius of gyration and Guinier's law:**

Prof. André Guinier
1911-2000
Orsay, France



Guinier Law is valid when qRg <1,3

$$I(q \to 0) \sim I_0 \exp(-\frac{q^2 R_g^2}{3})$$

$$lnI(q) \sim lnI_0 - \frac{R_g^2}{3} q^2$$

Guinier law allows finding a Rg without any model assumption

Guinier region won't be a linear if there is aggregation in the sample

- **Radius of gyration and Guinier's law:**

  - Scatterers' characteristics are mainly encoded in the low-q scattering thanks to **radius of gyration (*Rg*)**
  - Rg is calculated as the root mean square distance of the object's parts from its center of gravity

Sphere

$$R_g^2 = \frac{3}{5} R^2$$

Thin rod

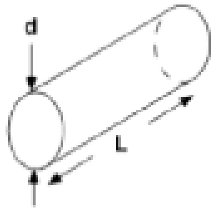
$$R_g{}^2 = \frac{L^2}{12}$$

Thin disc

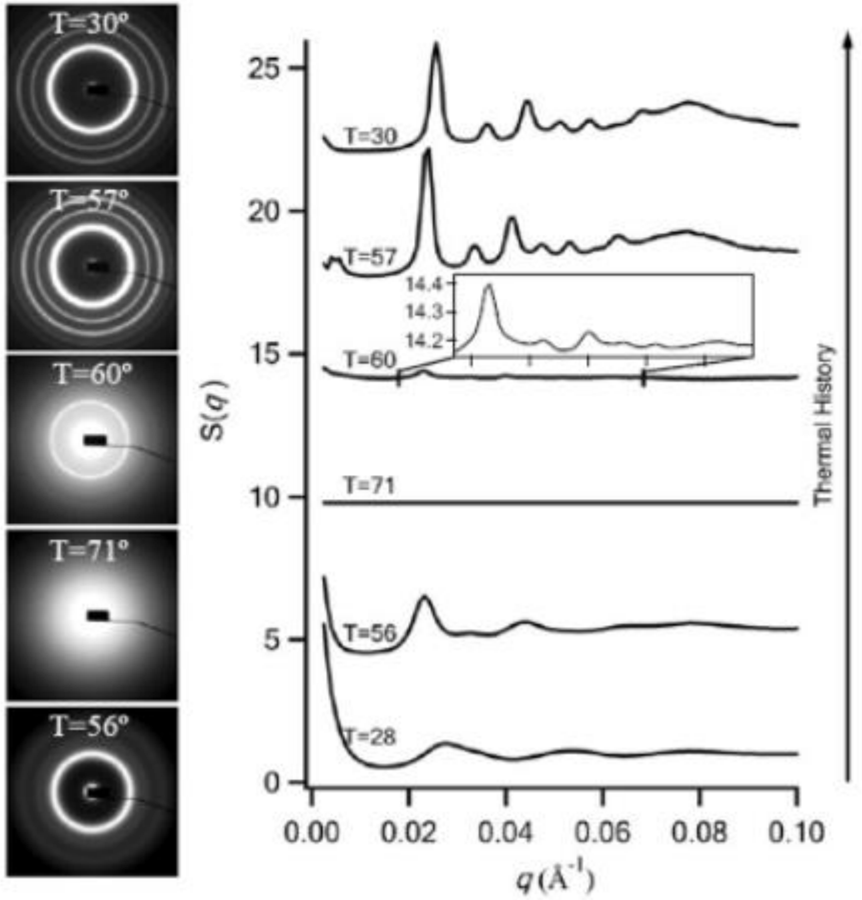
$$R_g{}^2 = \frac{R^2}{2}$$

Cylinder

$$R_g{}^2 = \frac{d^2}{8} + \frac{L^2}{12}$$



Scattering from Lattices and Complex Organizations



D. Nykypanchuk, M. Maye, D. Van der Lelie, and O. Gang, ***Nature, 451, 549 (2008)***

SAXS – Lattices and Complex Organizations

- **What are we measuring?**

Measure quantity is :

$$I(q) \propto \frac{d\,\Sigma(q)}{d\Omega} = \frac{N}{V} V^2 particles(\rho 1 - \rho 2)^2\, P(q)S(q)$$

concentrated system => dependence of scatterers = **interparticle effects**

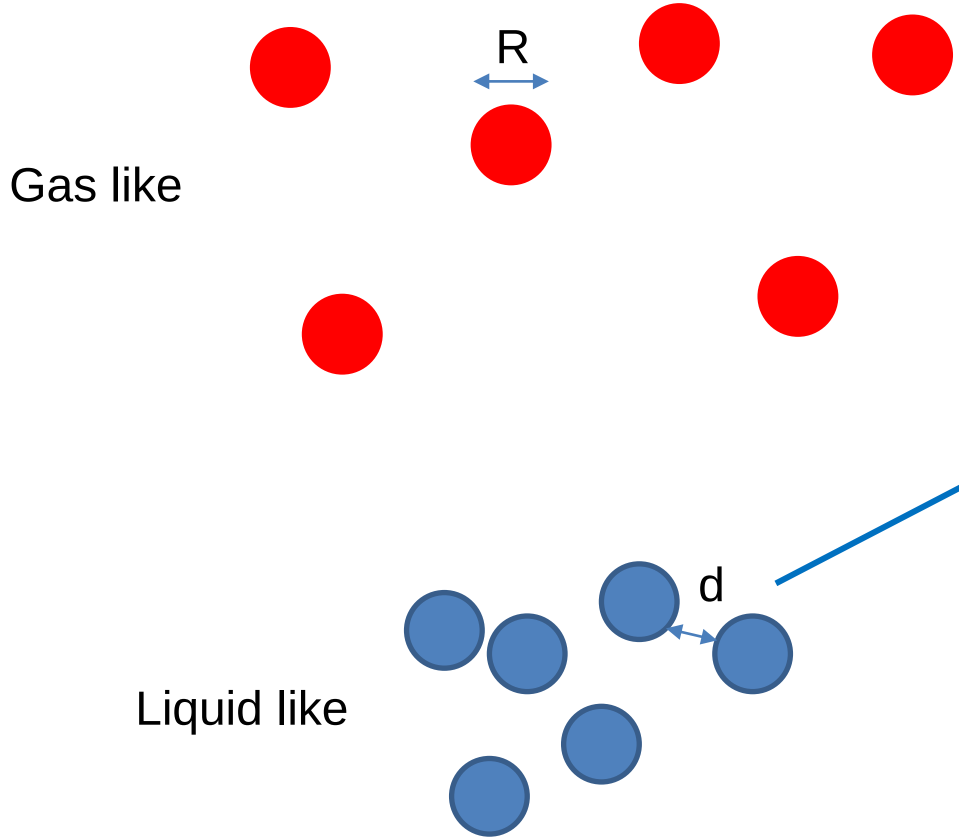
Thus

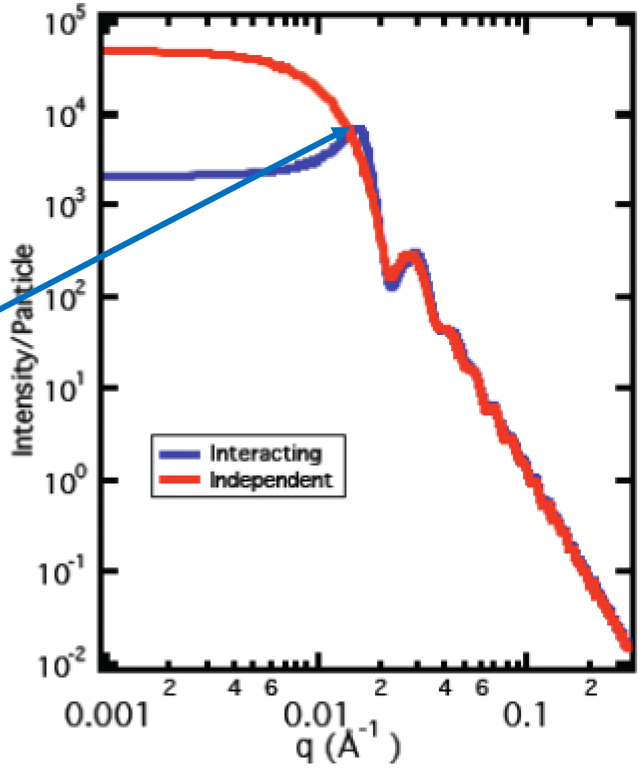
$$I(q) \propto \frac{d\,\Sigma(q)}{d\Omega} = \frac{N}{V} V^2 particles(\rho 1 - \rho 2)^2\, P(q)S(q)$$

S(q)= structure factor and at the same time P(q) = form factor

Scattering from Lattices and Complex Organizations

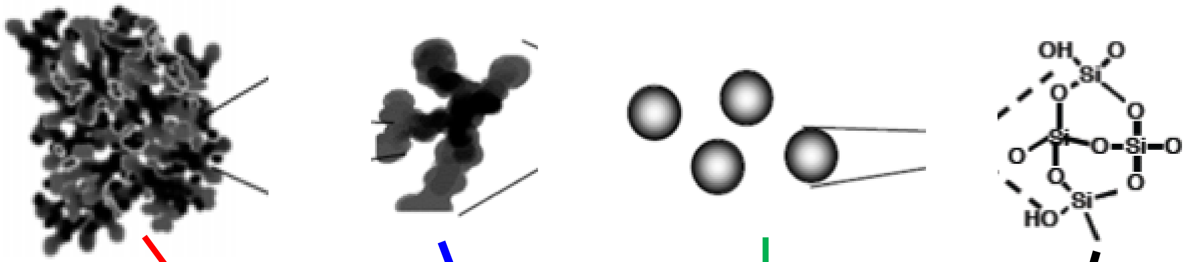
- **Particles interaction**





- **Hierarchical structure**

Four length scales



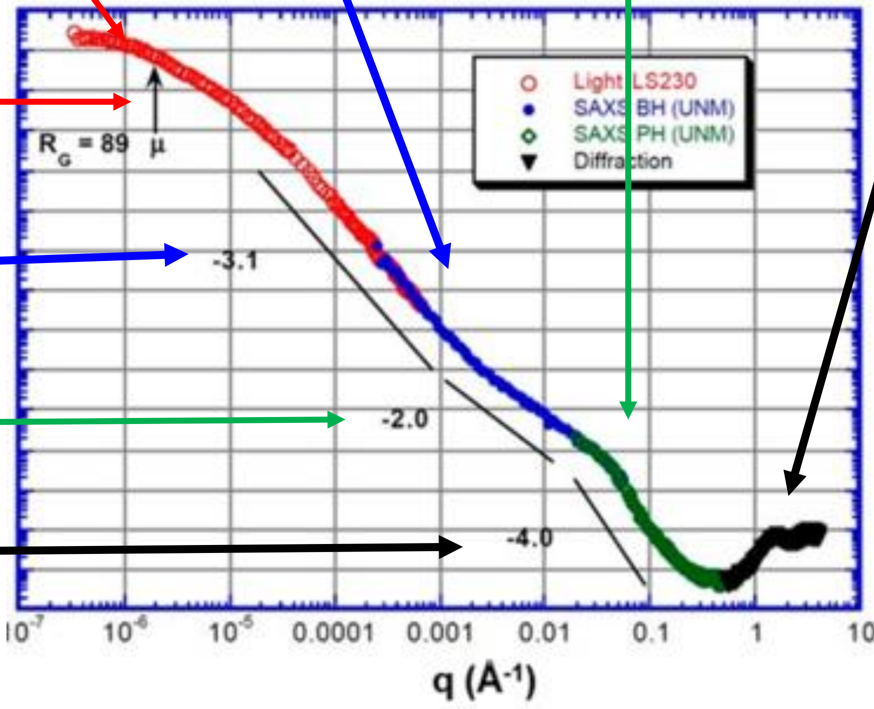
« Agglomerate » Aggregate Polymer particle Polymer network

« Rg = 89 µm »

Slope -3,1 = rough surface

Slope -2 = mass fractal

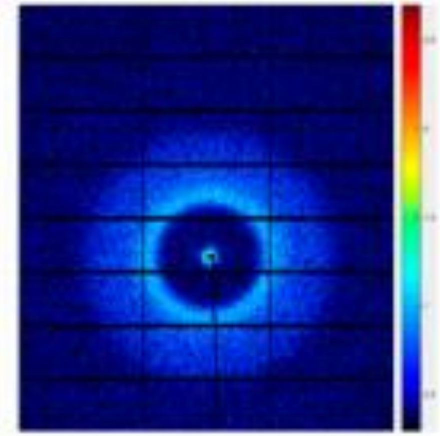
Slope -4 = sphere



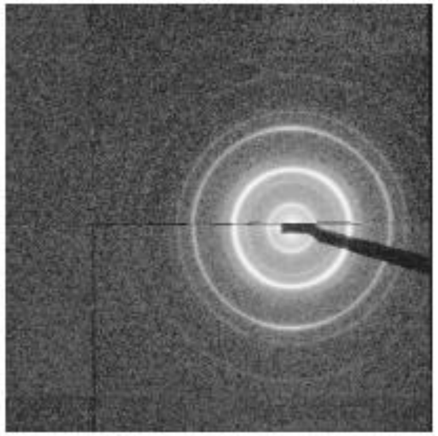
Li, T., Senesi, A.J., & Lee, B. (2016). Small Angle X-ray Scattering for Nanoparticle Research. *Chemical reviews, 116 18*, 11128-80 .

Scattering from Lattices and Complex Organizations

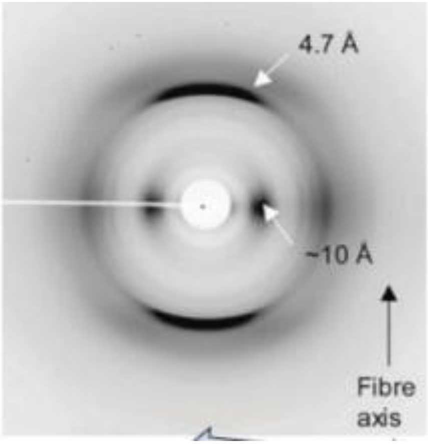
- **Scattering from structures**
  - **Easily infer amount of order**



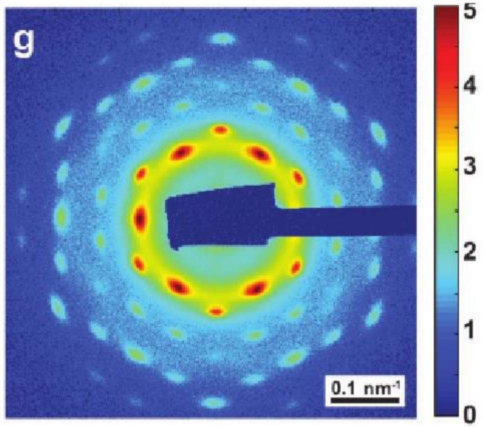
amorphous



Polycrystaline = powder



Orientation

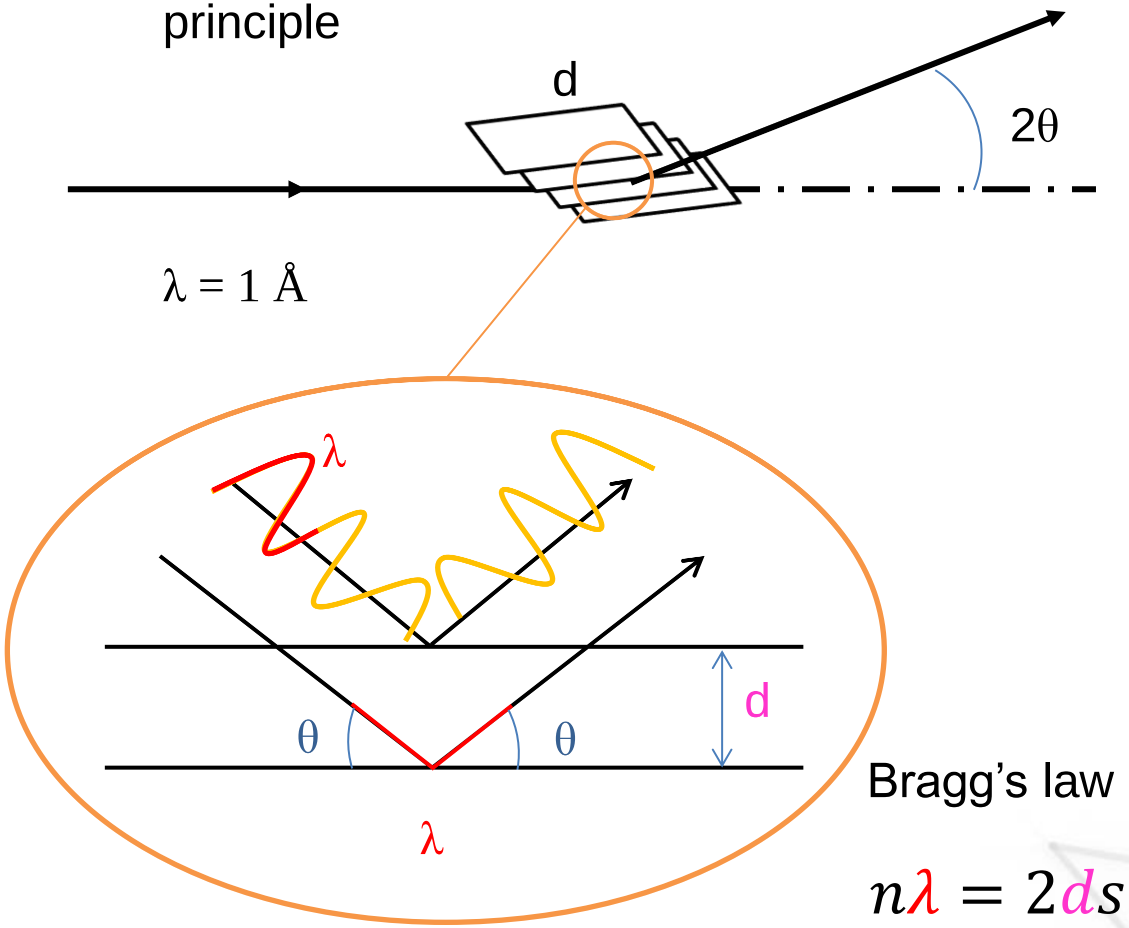


Single crystal

Roger, K., et al. (2016). ." Proceedings of the National Academy of Sciences **113**(37): 10275.

Scattering from Lattices and Complex Organizations

- **Small Angle X-ray Scattering**



Bragg's law

$$n\lambda = 2d\sin\theta$$

$$d \cdot q = 2\pi$$

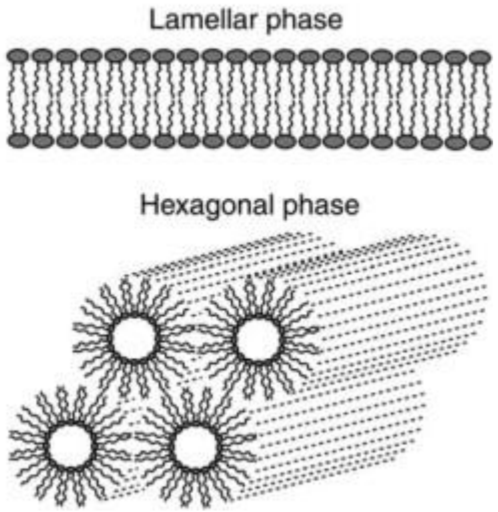
d-space ⟷ q-space

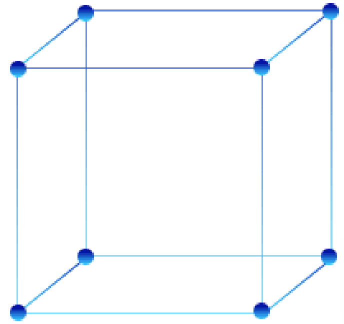
Fourrier transform

Time (t) ⟷ Pulsation (ω)

- **Long- and short-range positional order**
  - **Diffraction peak position for common latices**

Lamellar : 1, 2, 3, 4, 5,…
Cubic : 1, $\sqrt{2}$, $\sqrt{3}$, 2, $\sqrt{5}$,…
Hexagonal : 1, $\sqrt{3}$, 2, $\sqrt{7}$, 3,…



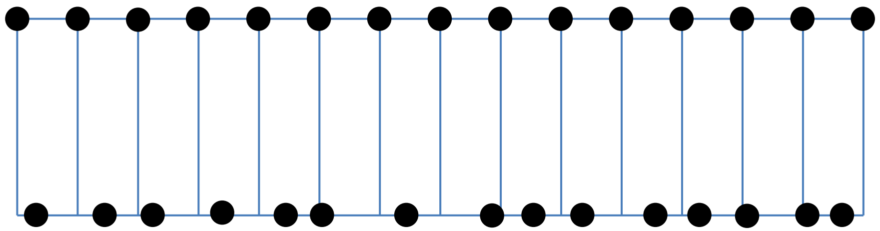


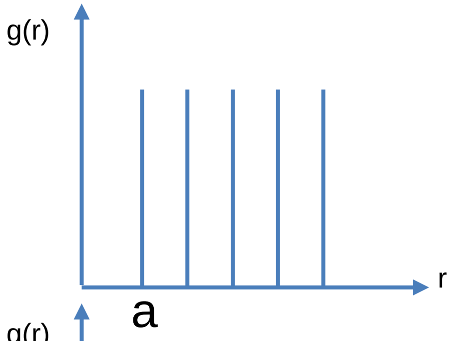
Cubic

radial distribution function or g(r)
defines the probability of finding a particle at a distance r from another tagged particle

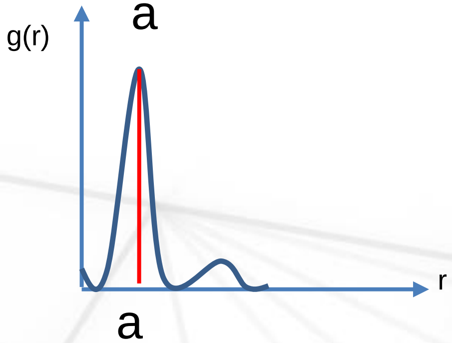
Solid

« liquid »





Long range order

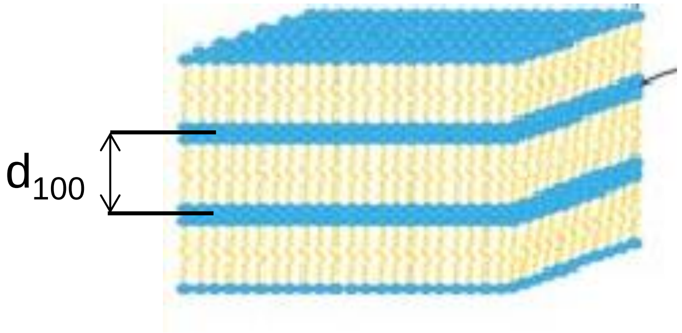


Short range order

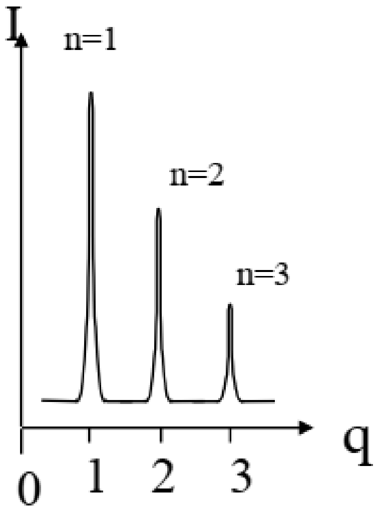
•Israelachvilli J.N. Intermolecular and Surface Forces.Academic Press, London1991

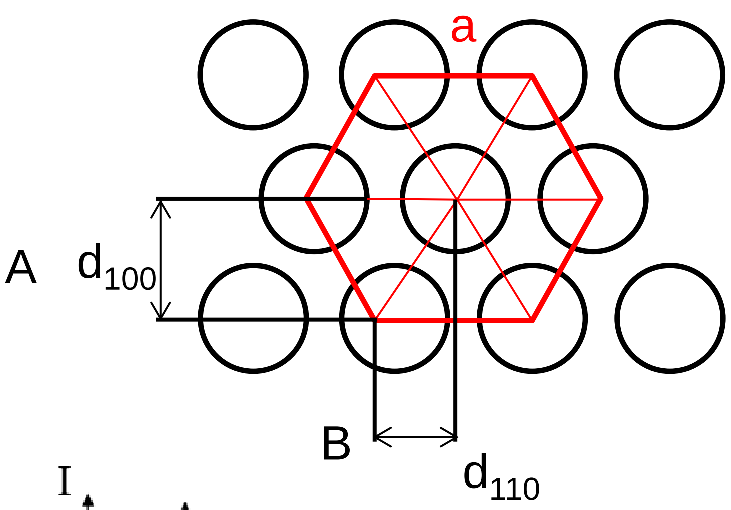
Scattering from Lattices and Complex Organizations

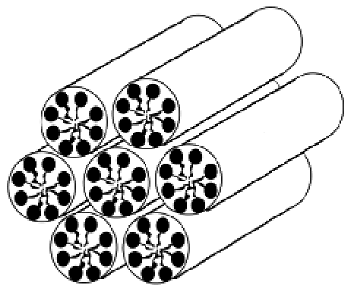
- **Typical scattering from Lamellar and columnar mesophases**

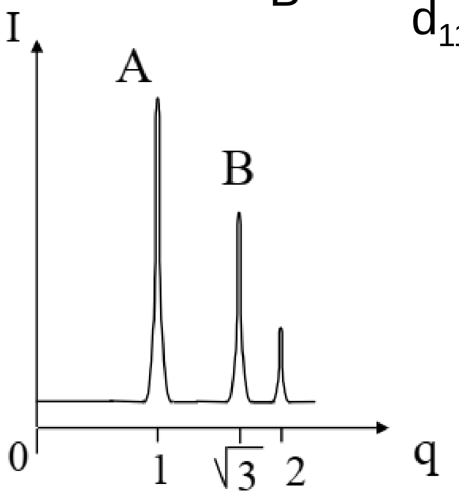


$$q_{n00} = 2\pi n/d_{000}$$









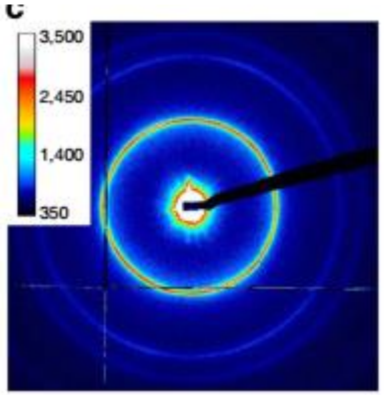
$$q_{100} = 2\pi/d_{100}$$

$$d_{100} = \sqrt{\frac{3}{2}}a$$

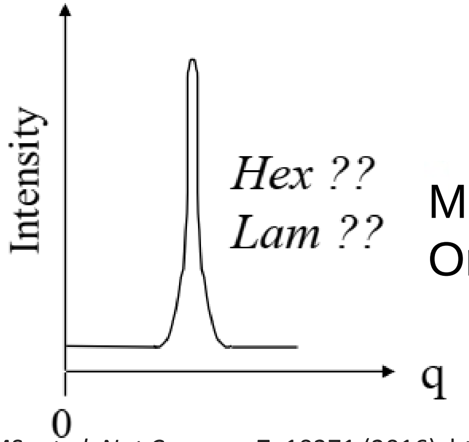
Scattering from Lattices and Complex Organizations

- **Polycrystaline samples: powder diffraction pattern**

Many small single crystals domains

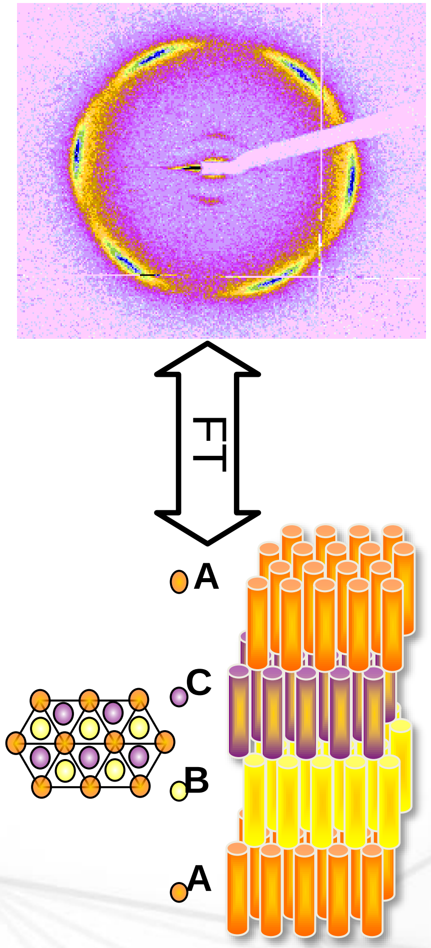


Integration



More peaks needed
Or use of another method

Single crystal



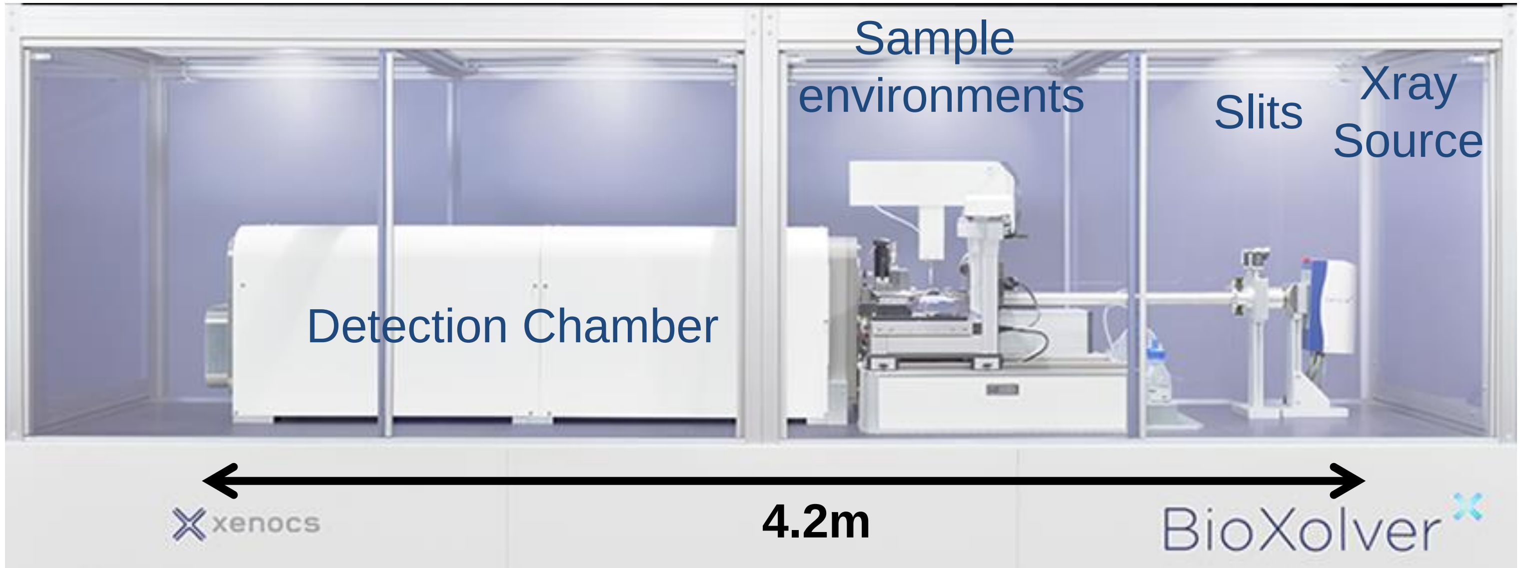
Paineau, E., Krapf, ME., Amara, MS. *et al*. *Nat Commun* **7,** 10271 (2016). https://doi.org/10.1038/ncomms1027

Bizien, T., et al. (2021). Journal of Nanomaterials **2021**: 1790976.

SAXS – Where can I do this?

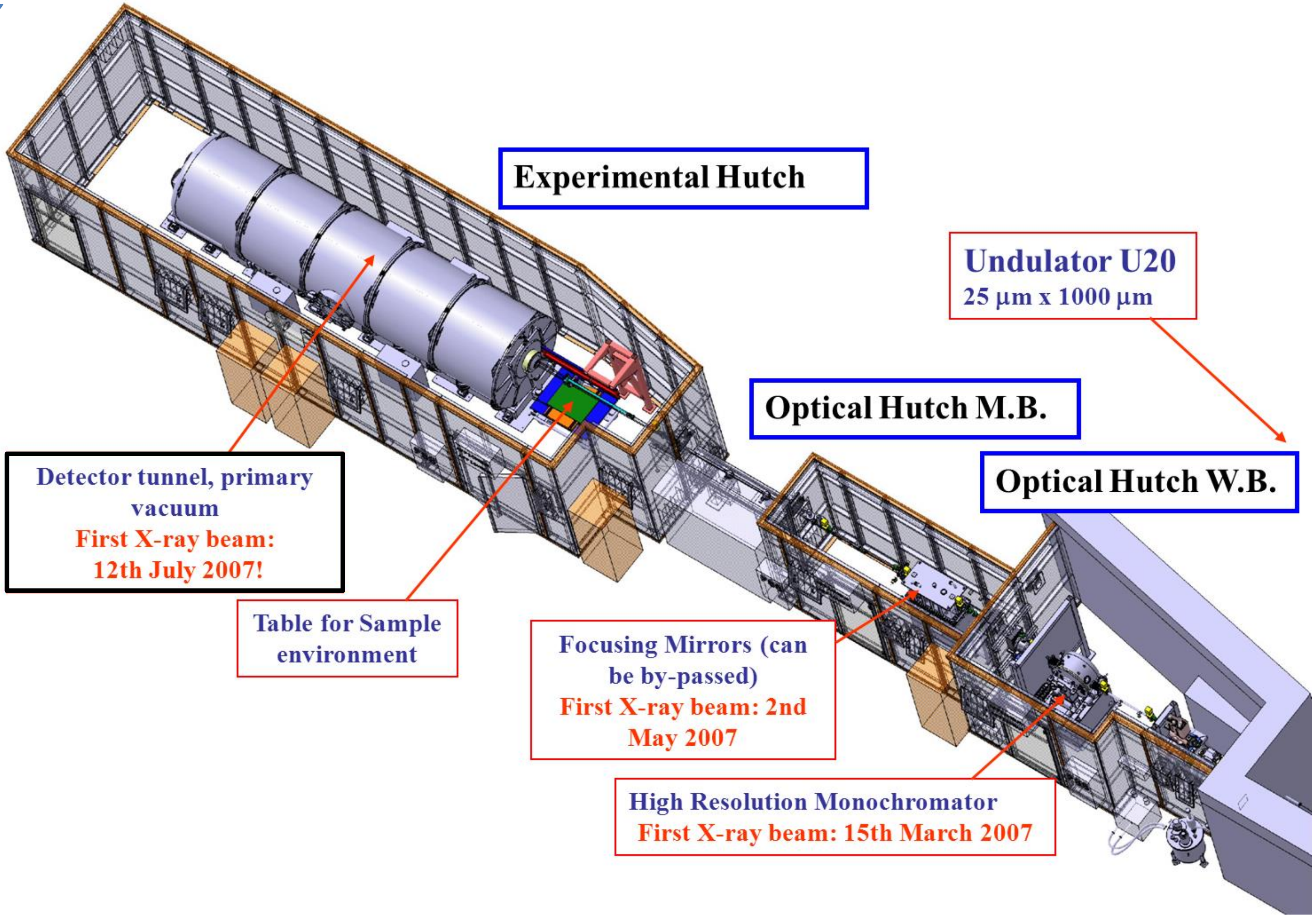
SAXS – Where can I do this?

- Where can we perform the experiment ?
  - Lab
    - Flux: 10^6 to 10^9 ph/sec

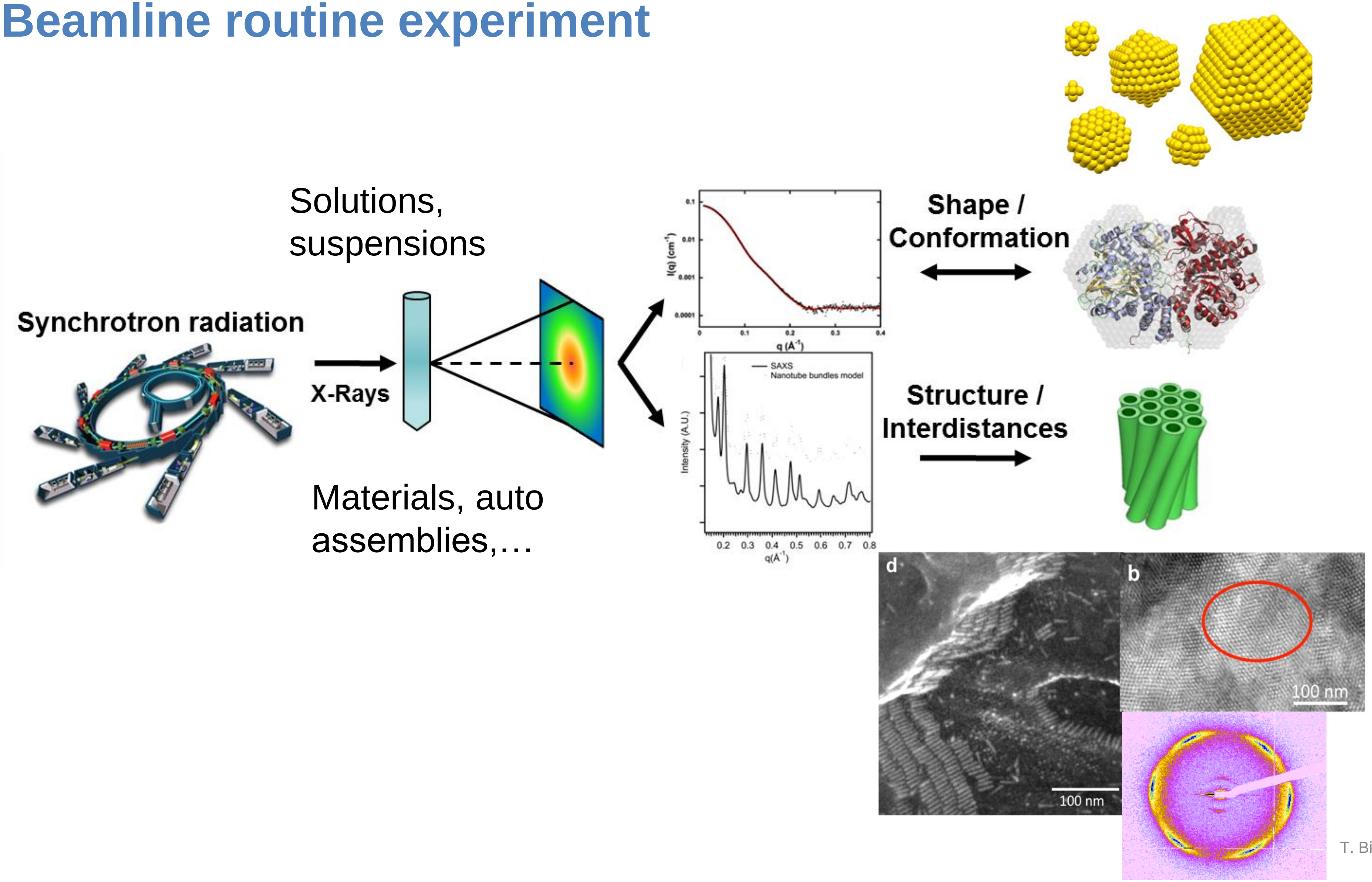


SAXS – Where can I do this?

- **SWING Beamline**

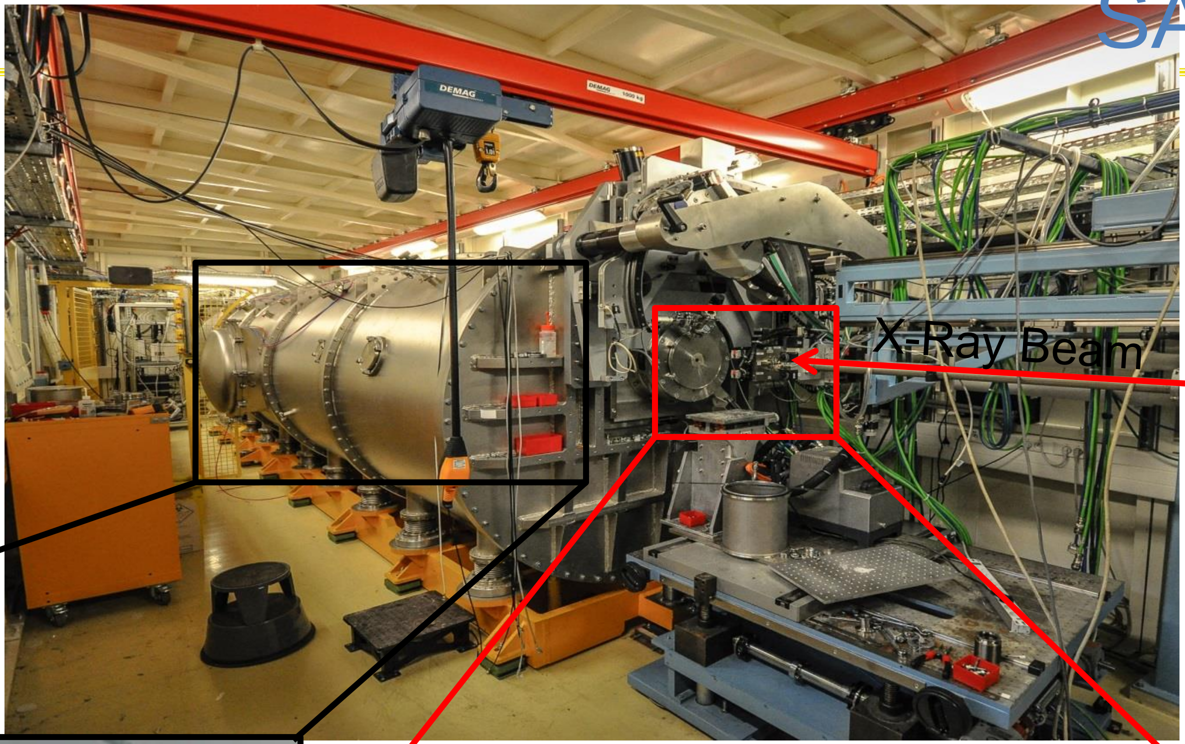


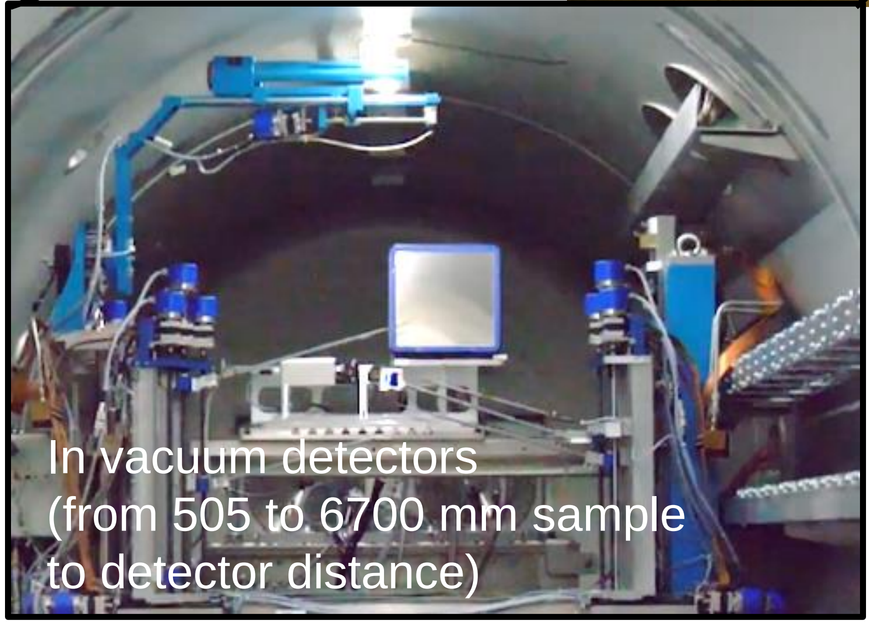
- **SWING Beamline routine experiment**

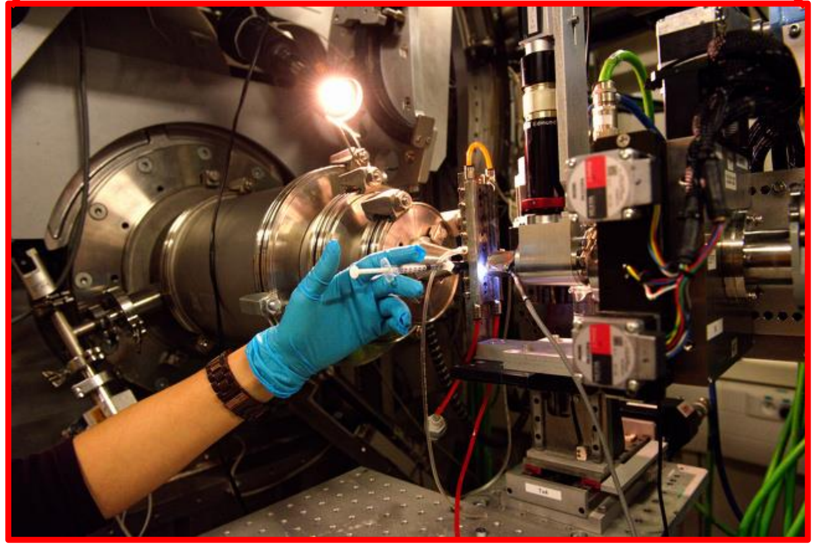


SAXS @ SWING

SWING beamline
Experimental hutch







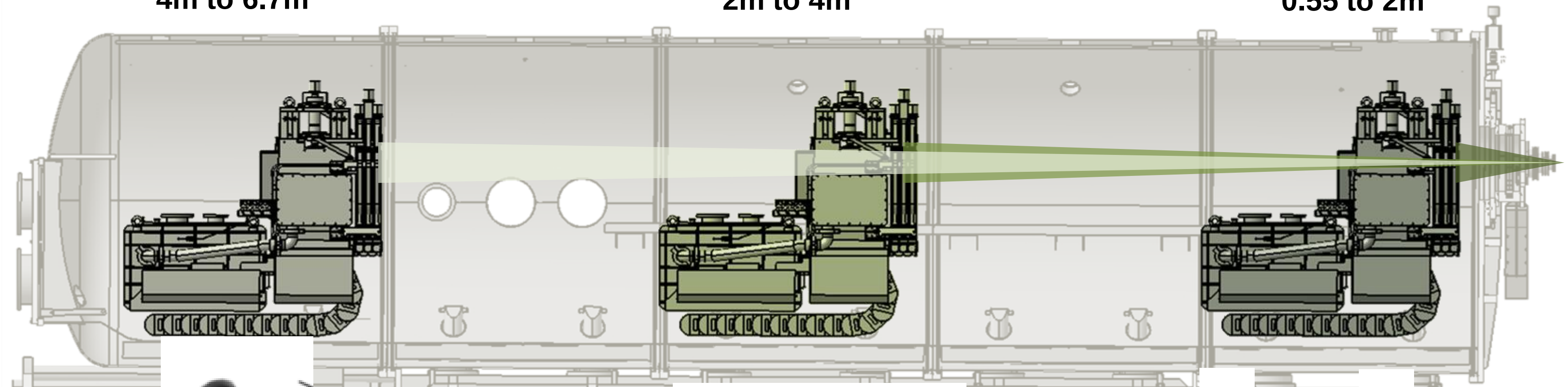
Users environment

Why such a tunnel?

"Long distance"
4m to 6.7m

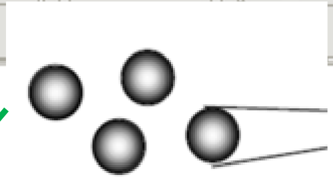
"Medium distance"
2m to 4m

"Short distance"
0.55 to 2m

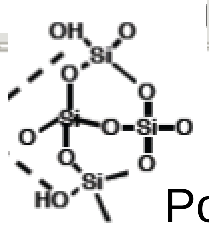


Scattered
beam

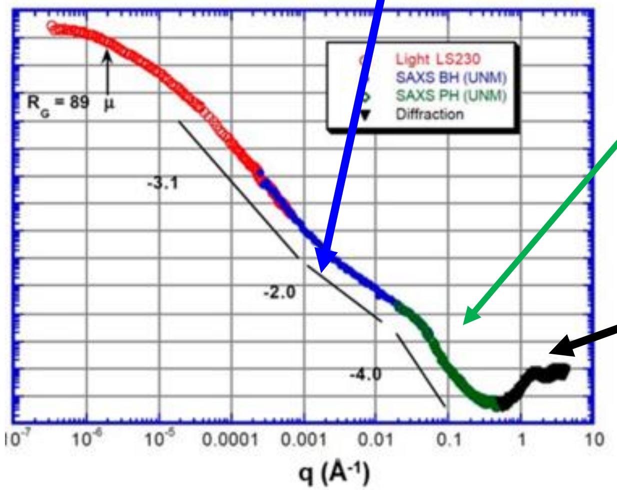
Aggregate



Polymer particle

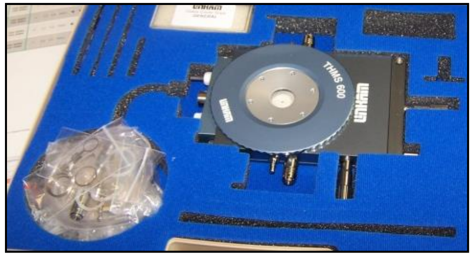


Polymer network

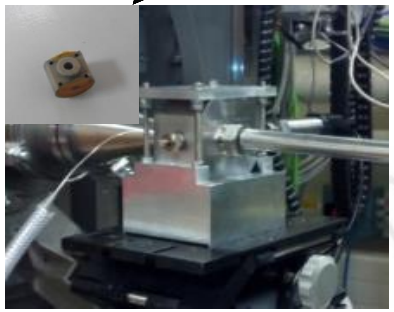


- **Samples environments**

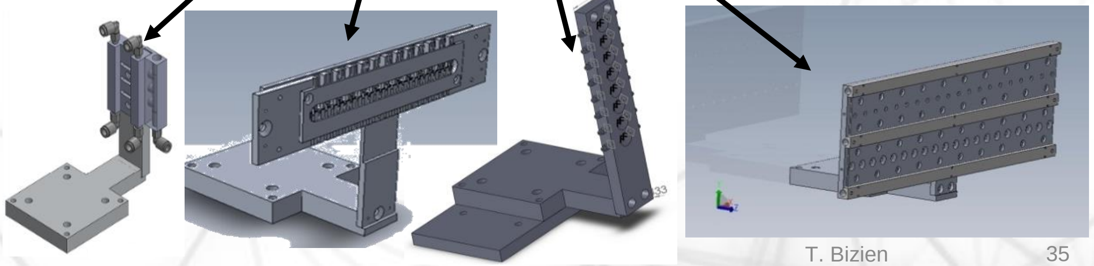
Thermostated Anton Paar Rheometer (collab. LPS, Orsay, France)
Biologic SFM400 Stopped-Flow for chemistry/biology (courtesy Biology Lab)
Linkam Hot stage for capillaries (T < 600°C)



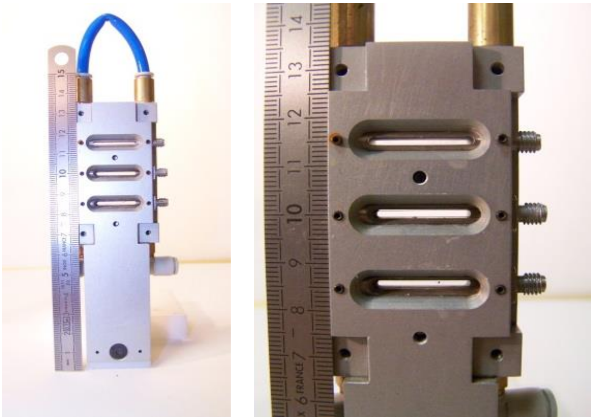
Automated High Pressure Cell for liquid samples (P < 5 kBar)



***Interchangeable* sample holders:**
- **Motorized (3 axis), Thermalized (10 – 70°C)**
- **Flow-through thin (10µm) quartz capillaries**
- **For gels**
- **For sealed capillaries**

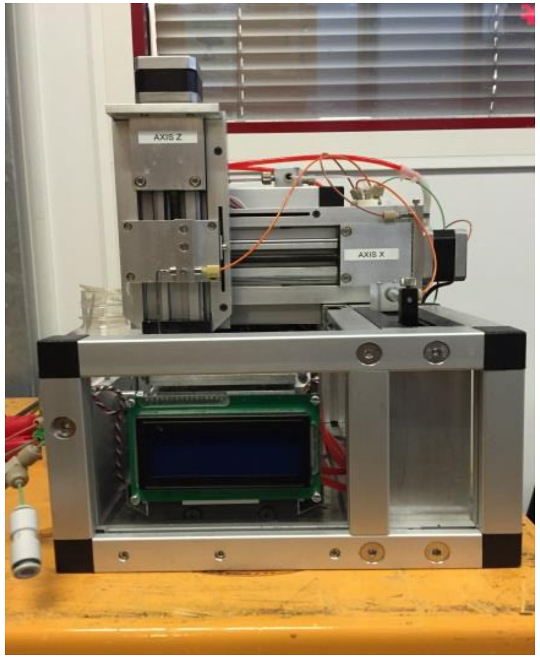


Samples environments, In solutions

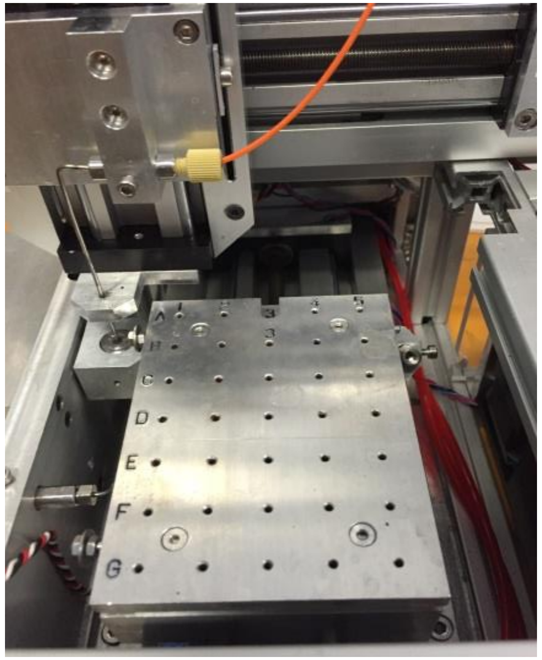


- 3 capillaries of Ø 1,5 mm
- 20 mm horizontal scanning length
- Thermalized 10-75°C

Pipeting and injecting Robot
© Pierre Roblin !!



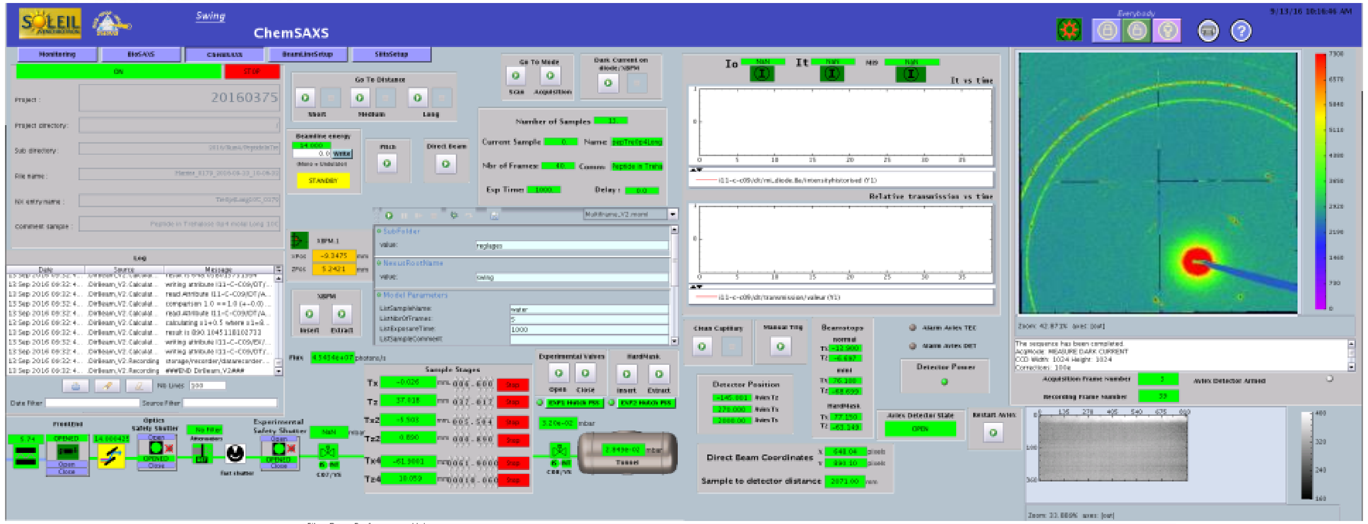
- 34 vials capacity
- Thermalized vials holder (5-10 to 60 °C)
- 1 Injection every 4 minutes (incl. capillary cleaning)
- Injection possible up to 30 % glycerol in water



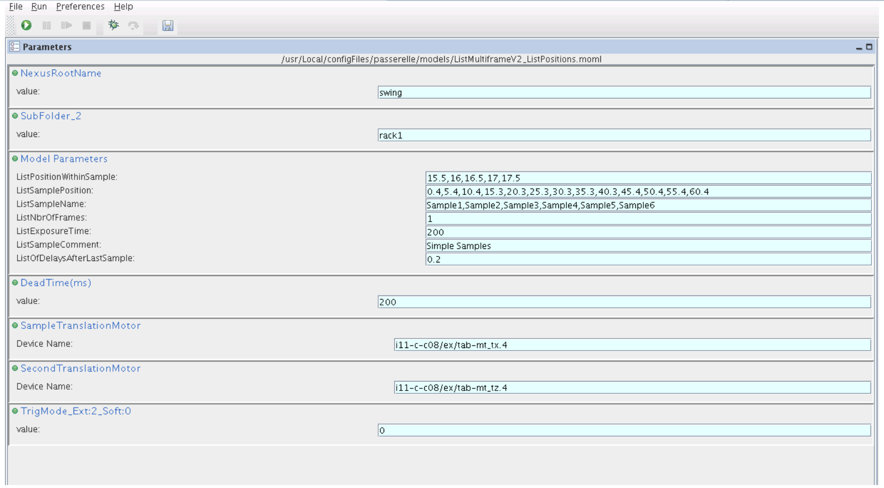
Other Injection modes through the capillaries :

- Peristaltic pump
- Commercial syringe driver
- Manual injection
- Pressure pumps

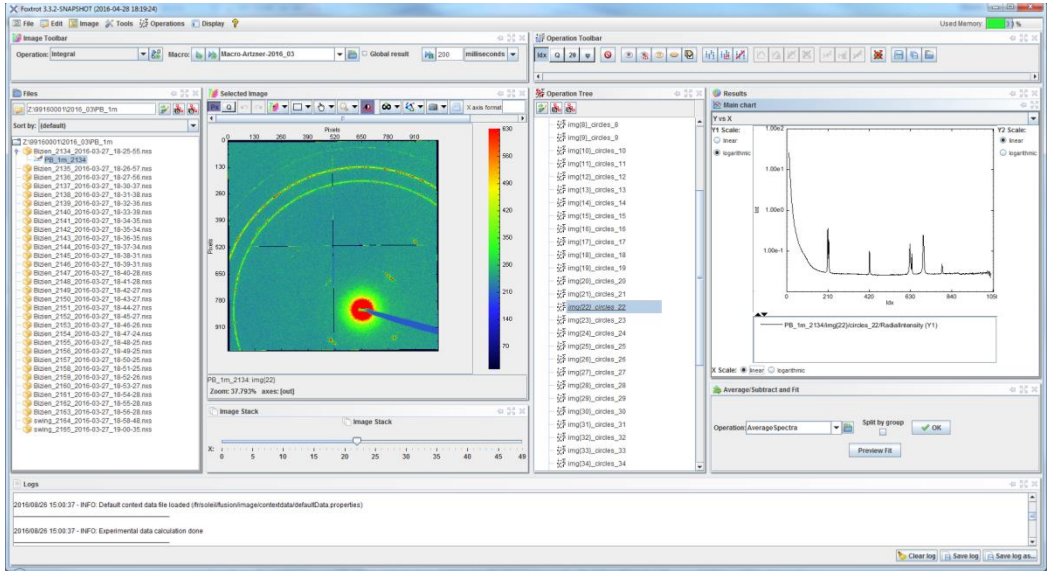
Monitoring, online data reduction



Dedicated GUI for soft-condensed matter allowing direct data monitoring and control of the beamline.

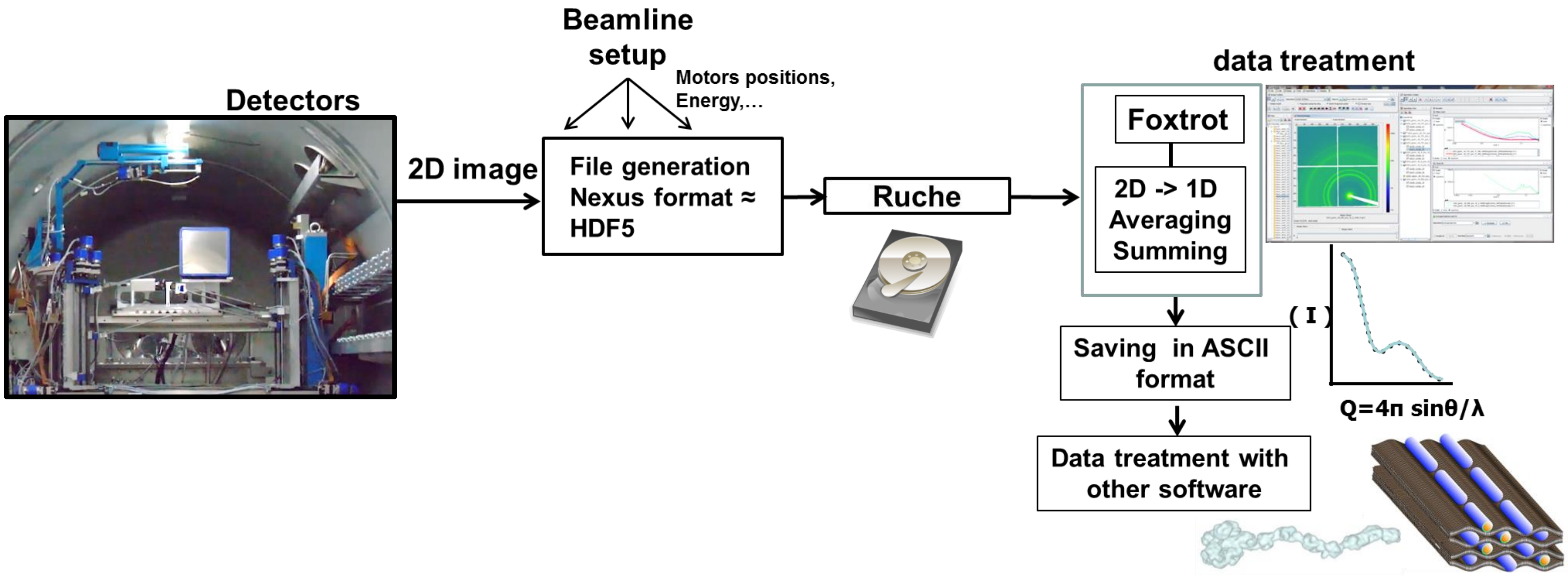


Simplified GUI allowing “on demand” complex data collection strategies



Foxtrot, the SWING data treatment software, gives users direct visualization reduced data and allows data first analysis.

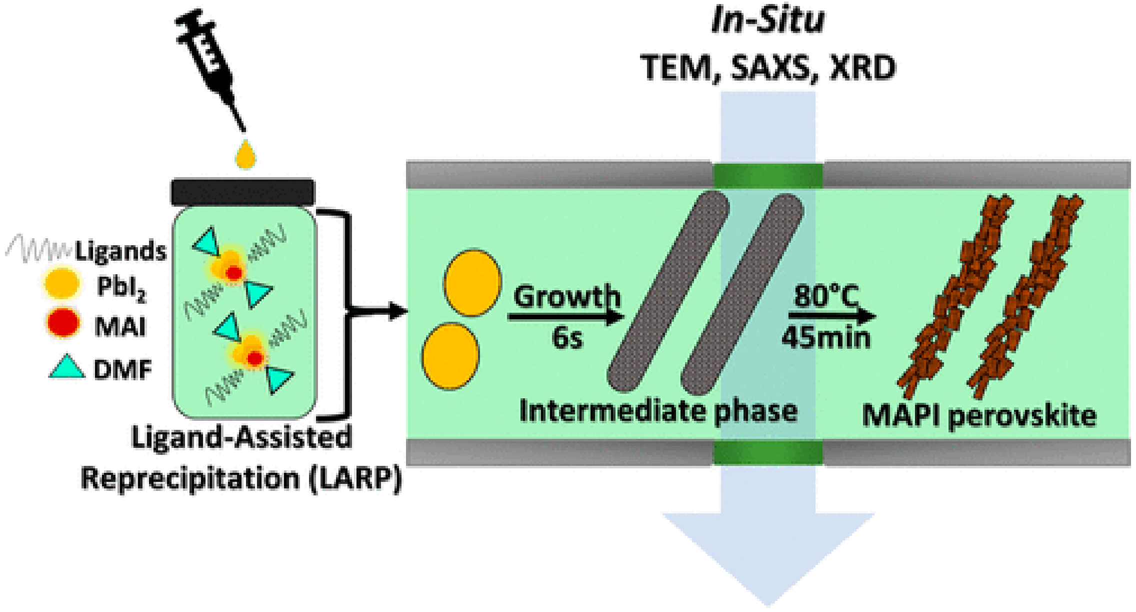
Monitoring, online data reduction

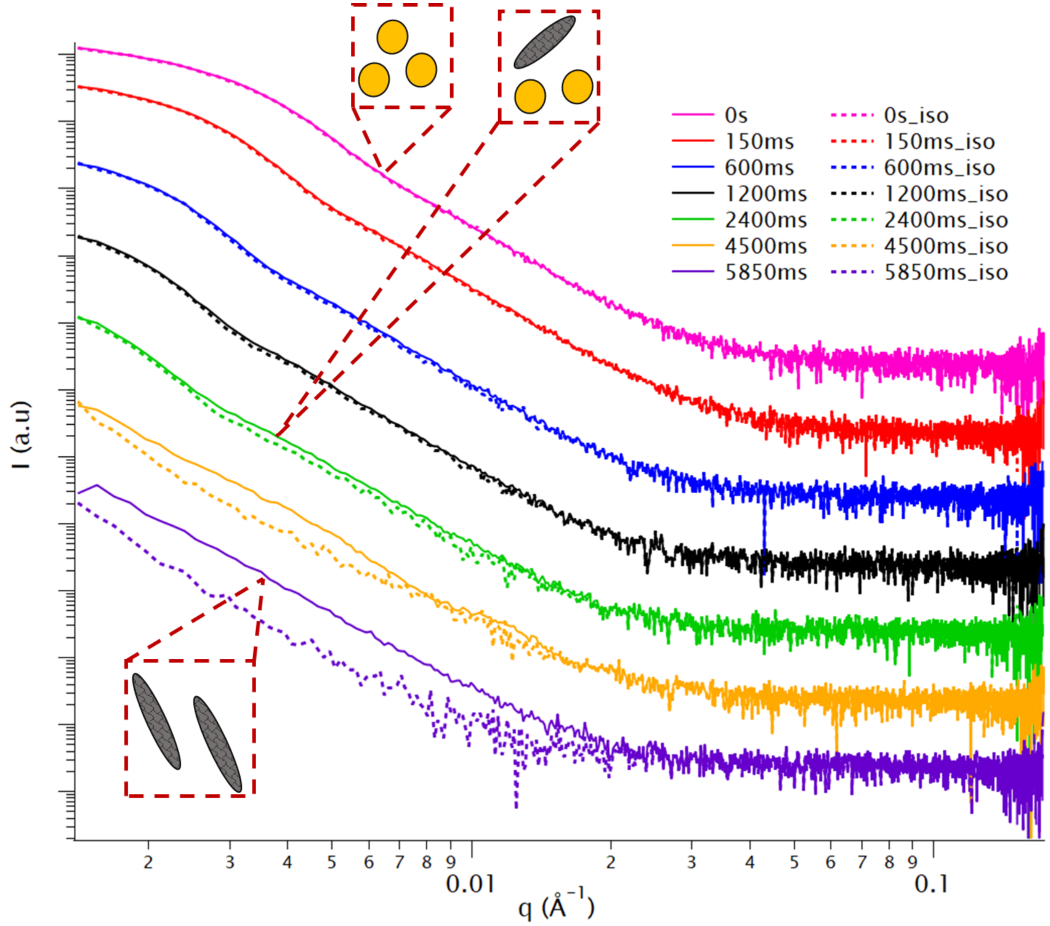


What can we get from SAXS, a few examples

1/ time-resolved SAXS
2/ multiscale Sample characterization
3/ Building structured materials by self-assembly ★

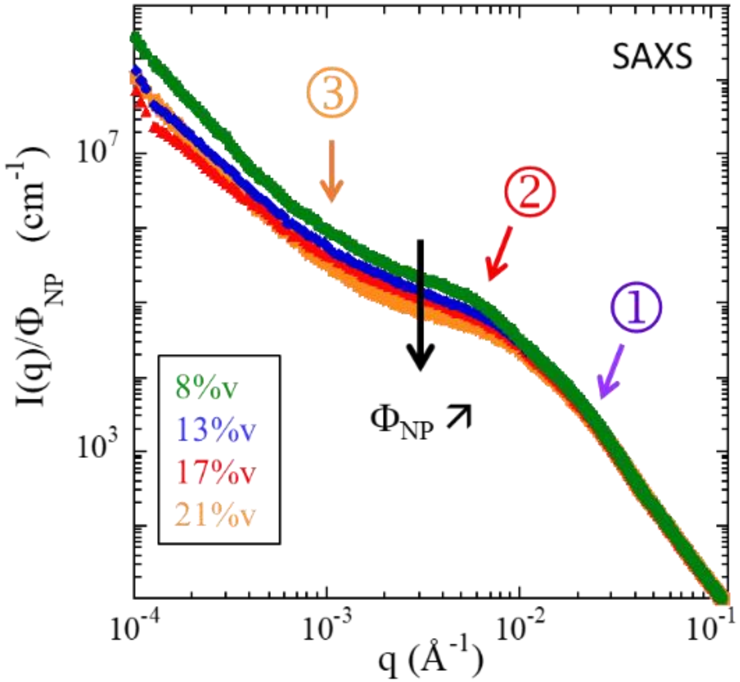
In Suspension supramolecular aggregates formation characterization

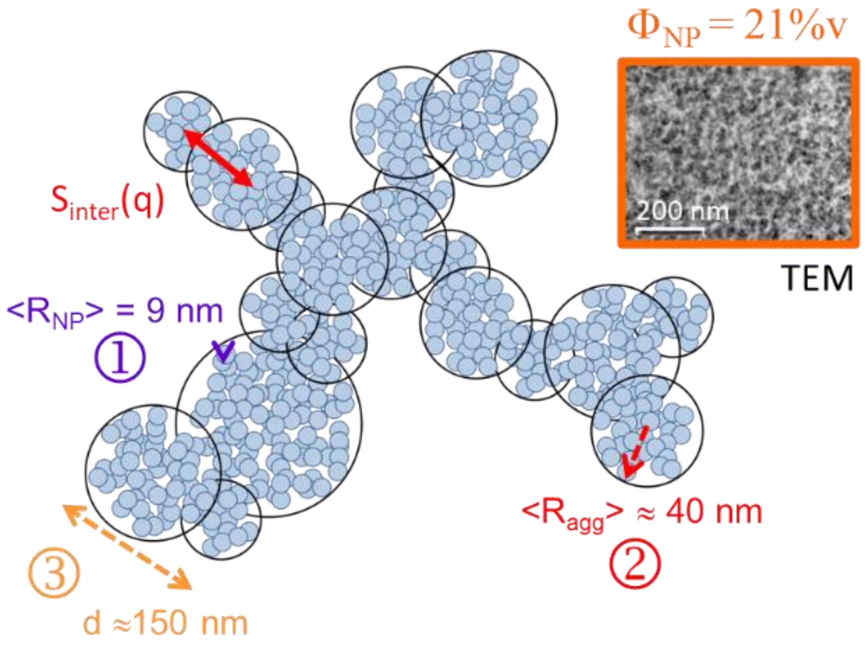




Shedding Light on the Birth of Hybrid Perovskites: A Correlative Study by *In Situ* Electron Microscopy and Synchrotron-Based X-ray Scattering Charles Sidhoum, et al *Chemistry of Materials* **2023** *35* (19), 7943-7956

SAXS scattered intensity for a series of silica volume fractions in styrene-butadiene matrix Arrows indicate the breaks in slope associated with characteristic sizes as illustrated in the scheme for nanoparticles, aggregates, and fractal branches in PNCs.



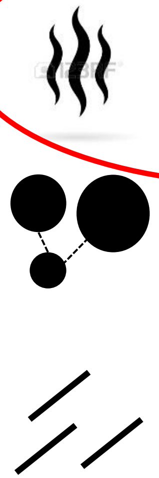


G.P. Baeza, **Multiscale Filler Structure in Simplified Industrial Nanocomposite Silica/SBR Systems Studied by SAXS and TEM**, Macromolecules 46(1) (2013) 317-329.

A.C. Genix, **Recent advances in structural and dynamical properties of simplified industrial nanocomposites**, Eur. Polym. J. 85 (2016) 605-619.

Colloidal synthesis

Self assembly



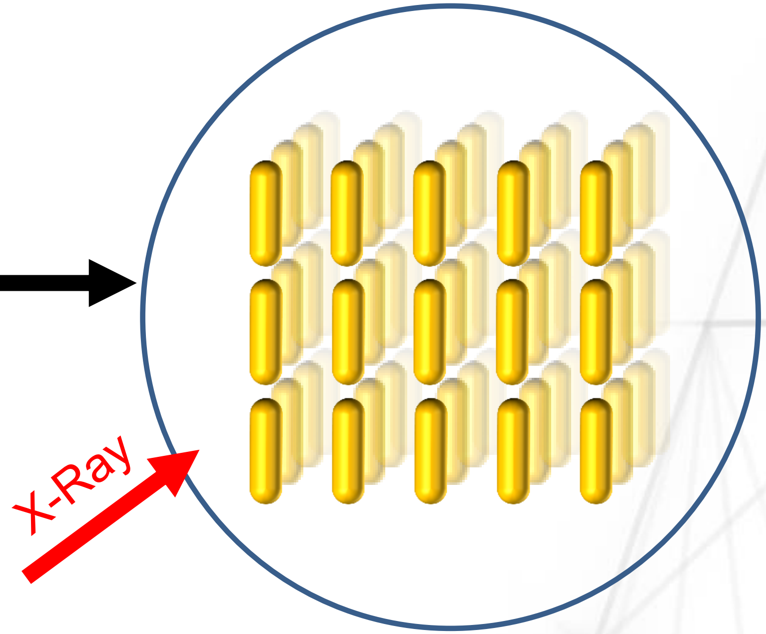
evaporation

Directed assembly

templates

and more…

Material



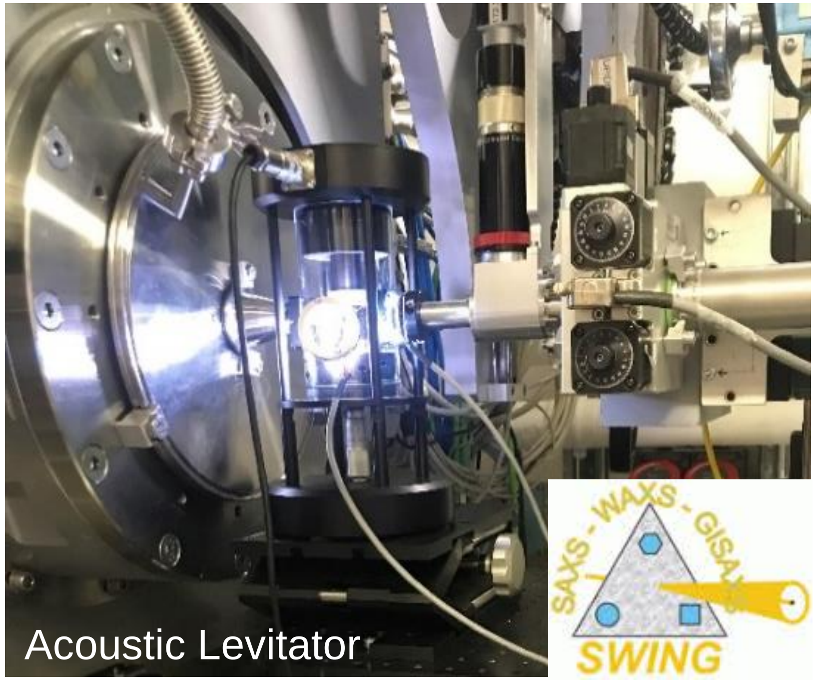
1. Structure
2. Collective physical properties

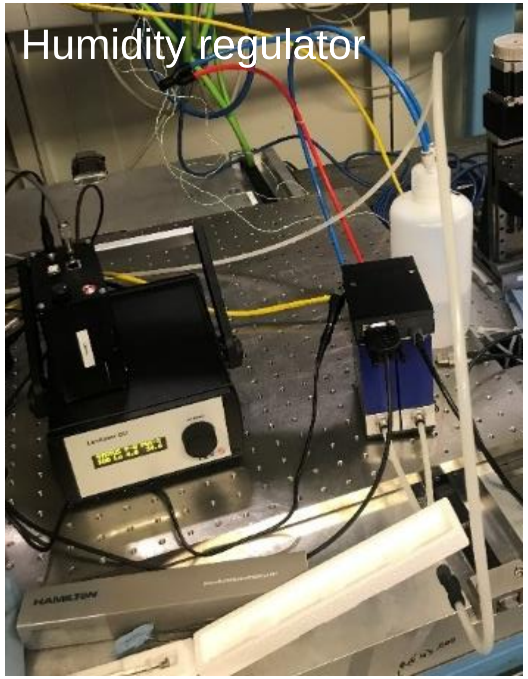
Building materials by self-assembly

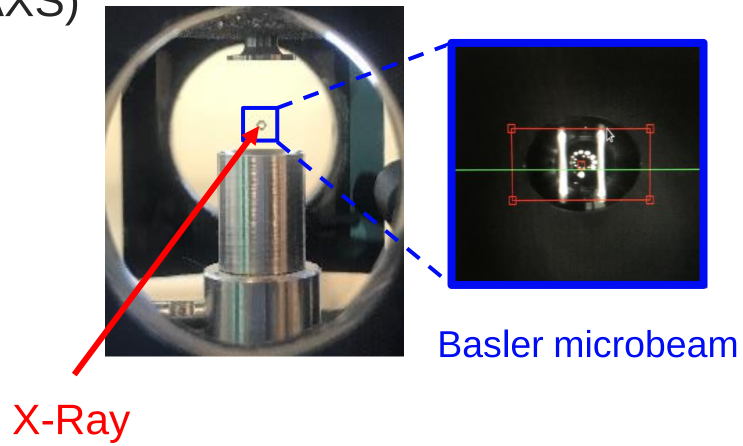
- **In-situ SAXS measurements**

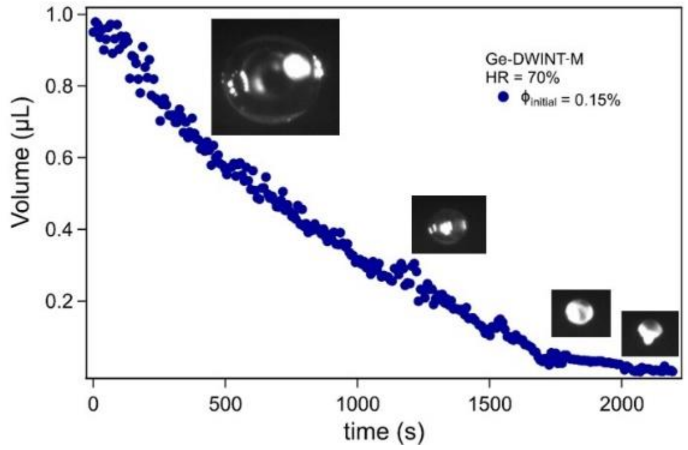
⟶ Time-resolved as a function of relative humidity

⟶ Simultaneous monitoring of drop volume (optical) and interparticle distances (SAXS)









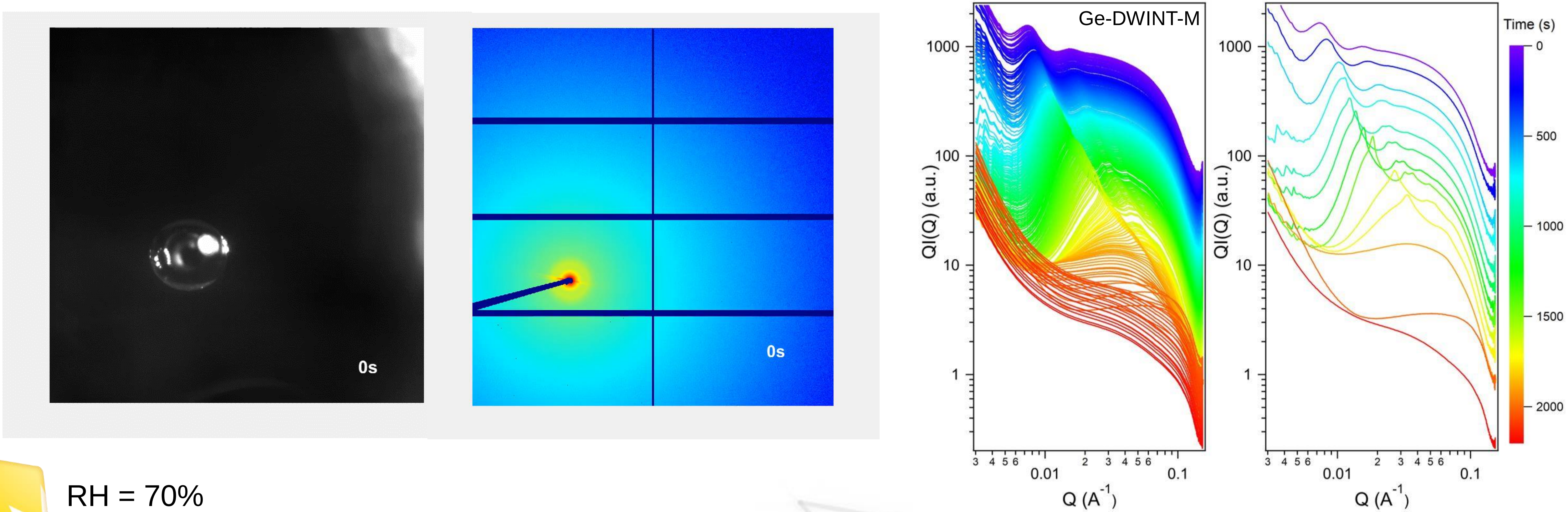
Hotton et al., *Adv. Mater. Interfaces* –**11**(29): art.n° 2400323. (2024).

Building materials by self-assembly

- **In-situ SAXS measurements on Imogolite nanotube**

⟶ Time-resolved as a function of relative humidity

⟶ Simultaneous monitoring of drop volume (optical) and interparticle distances (SAXS)



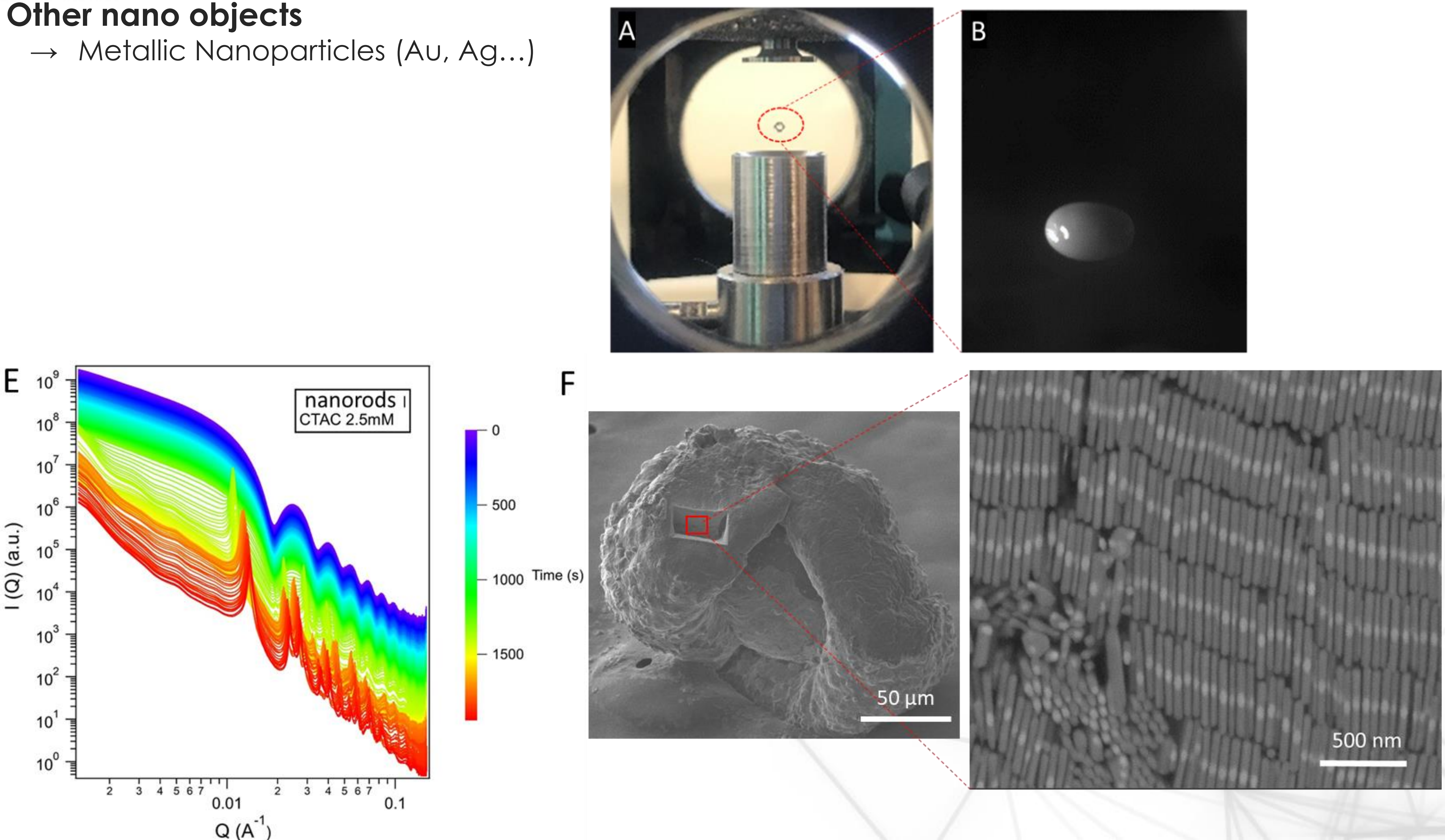
RH = 70%

$\Phi_{initial}$ = 0.15%

Hotton et al., *Adv. Mater. Interfaces* **11***(29): art.n° 2400323. (2024).*

Building materials by self-assembly

- **Other nano objects**
  - → Metallic Nanoparticles (Au, Ag…)

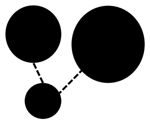


Building materials by self-assembly

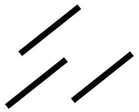
Colloidal synthesis

Self assembly

evaporation



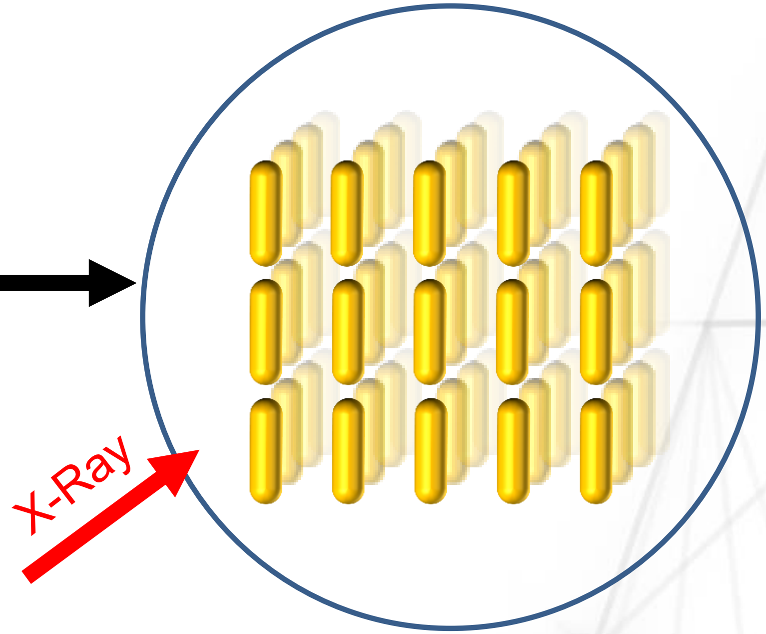
Directed assembly



templates

and more…

Material

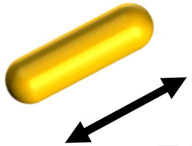


1. Structure
2. Collective physical properties

Building materials by self-assembly

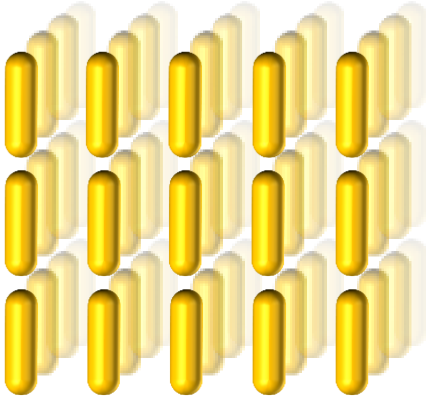
NPs assembly: A multiscale challenge

Monodisperse NPs



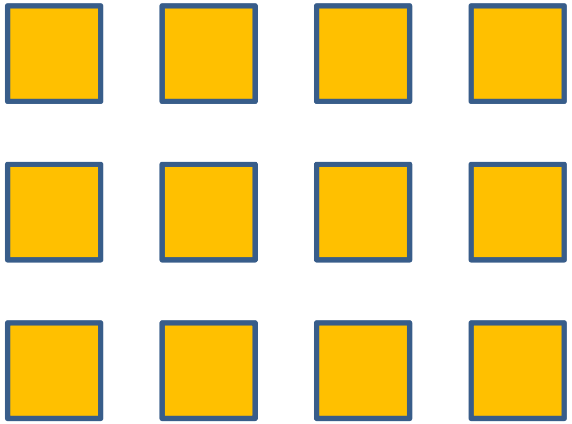
50 nm

Local ordering



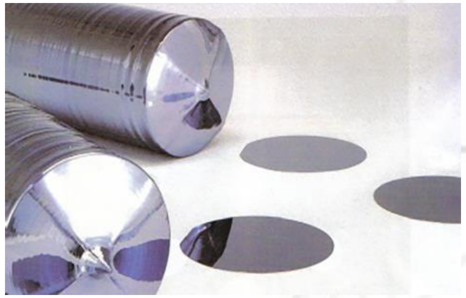
1 µm

macroscale ordering



100 µm

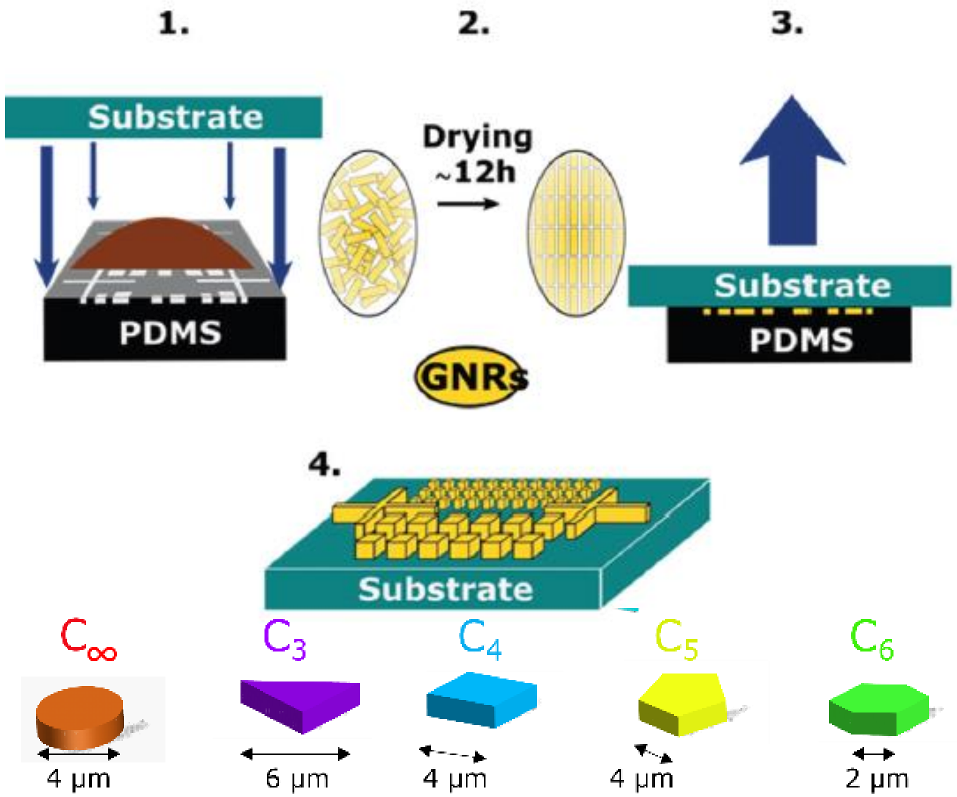
Device scale



10 cm

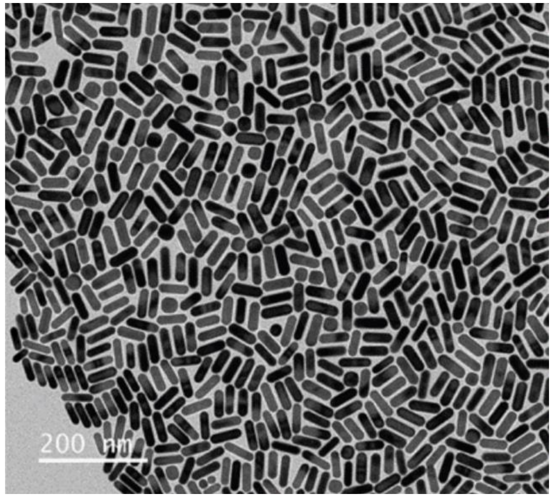
Building materials by self-assembly

Introducing prismatic confinement

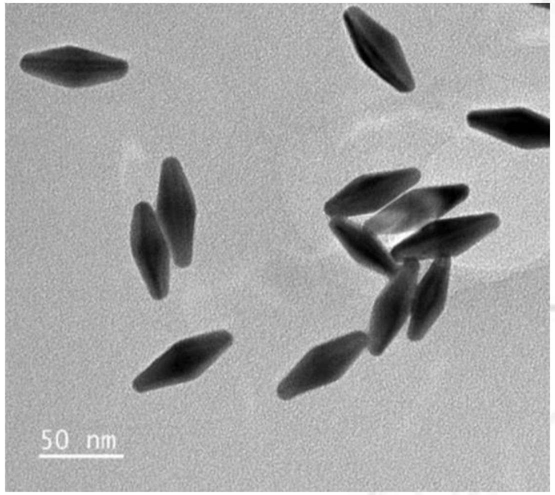


Cavities with prismatic shapes
=> Prismatic confinement

AuNRs (L: 55 ± 5 nm, W: 18 ± 2 nm)



AuBPs (L: 66 ± 4 nm, W: 25 ± 2 nm)



Ligand: CTAC

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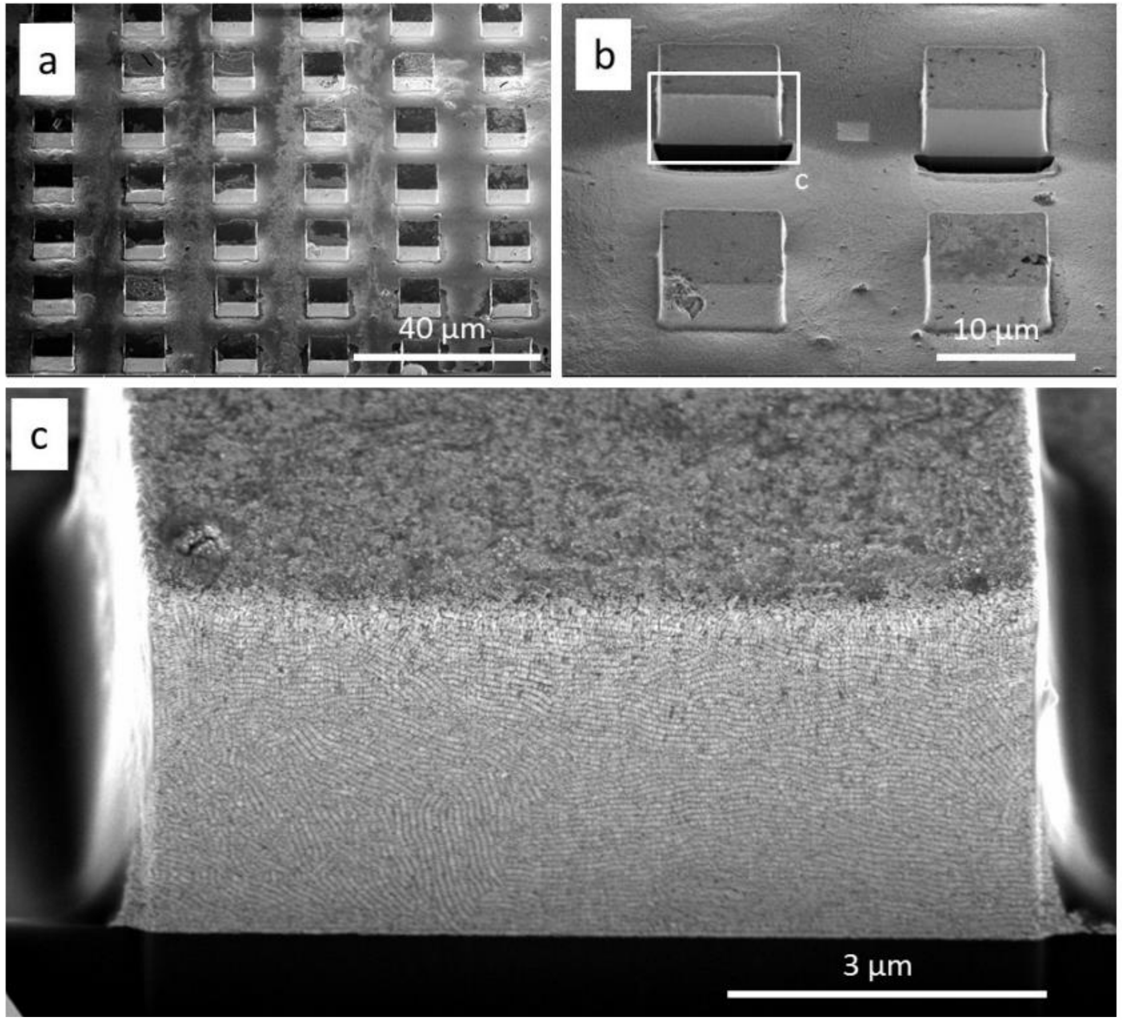
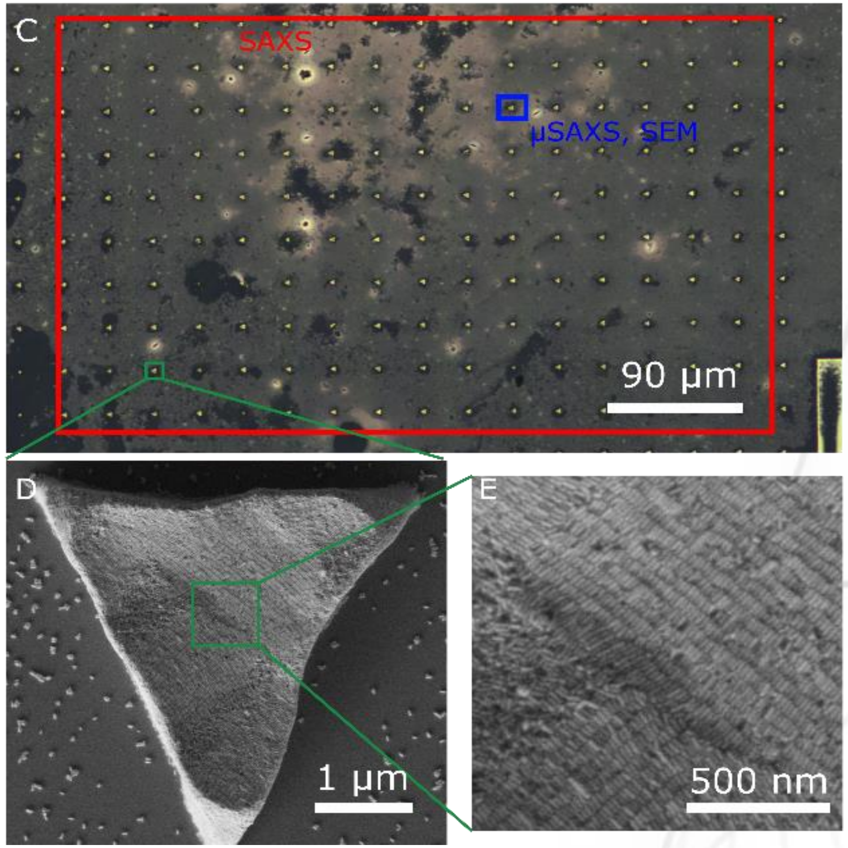
Building materials by self-assembly



µsaxs cartography



SAXS: average measurment on ≈100 supercrystals
µSAXS: measurment on 1 supercrystal

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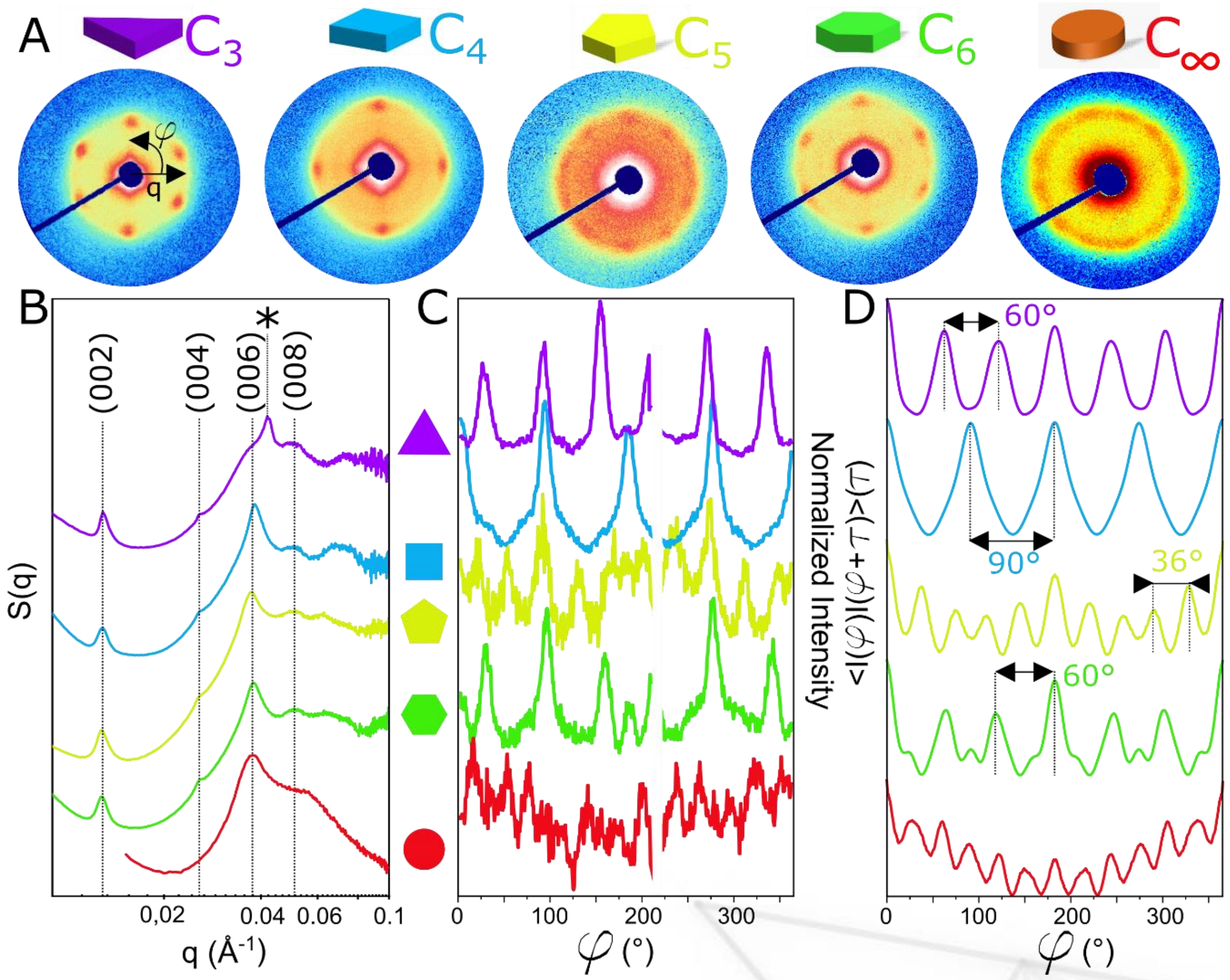
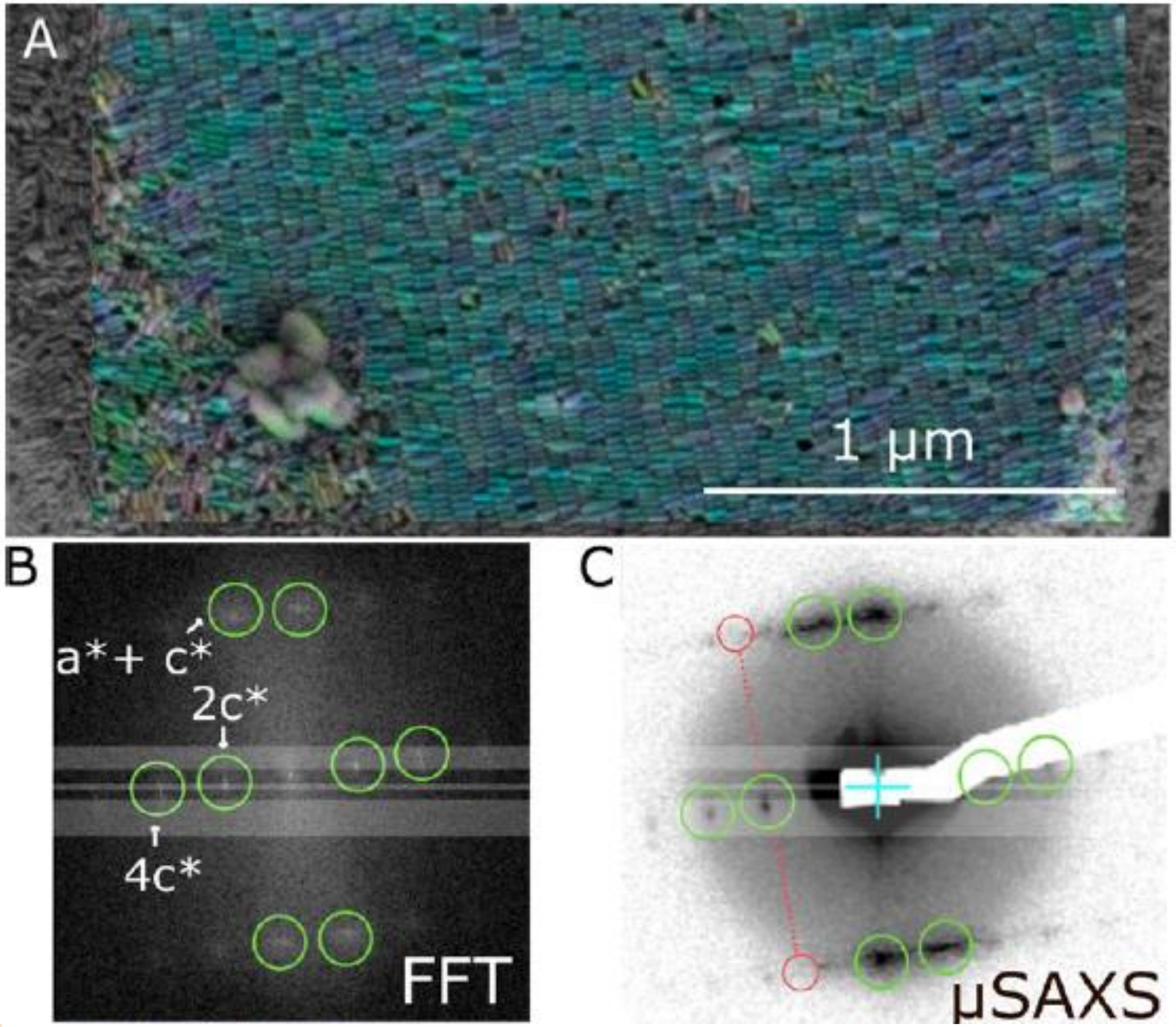
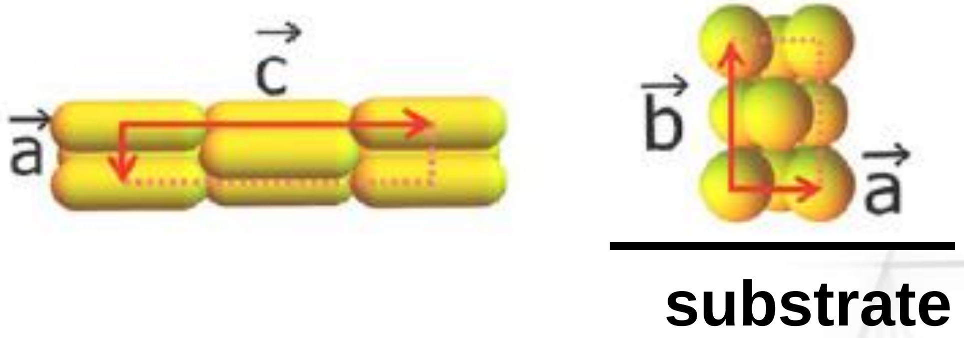
SAXS: average measurment on ≈100 supercrystals



µSAXS: measurment on 1 supercrystal



Orthorhombic lattice



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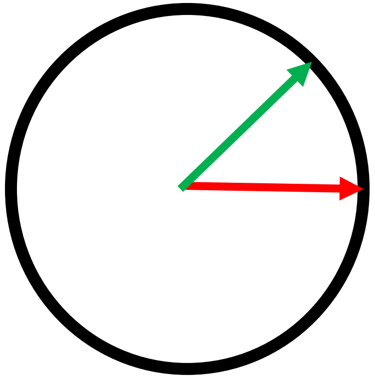
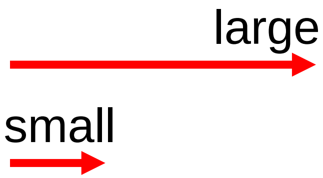
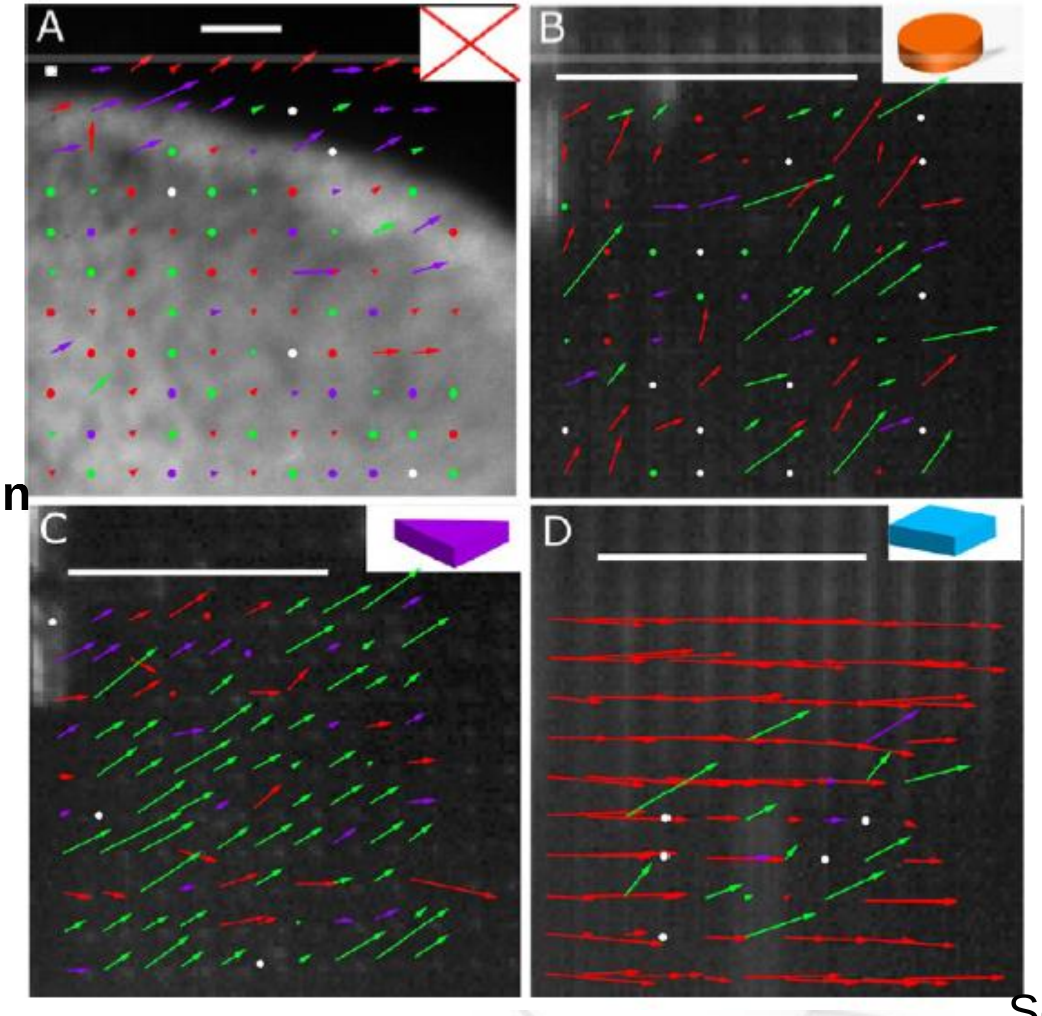
µSAXS analysis



Orientation of the 1st domain



Extension of the domains



$\frac{\pi}{2} = 90\,°$

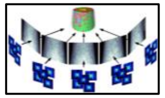
$\frac{\pi}{3} = 60\,°$

$\frac{\pi}{5} = 36\,°$

Scale bar is 200 µm on all images

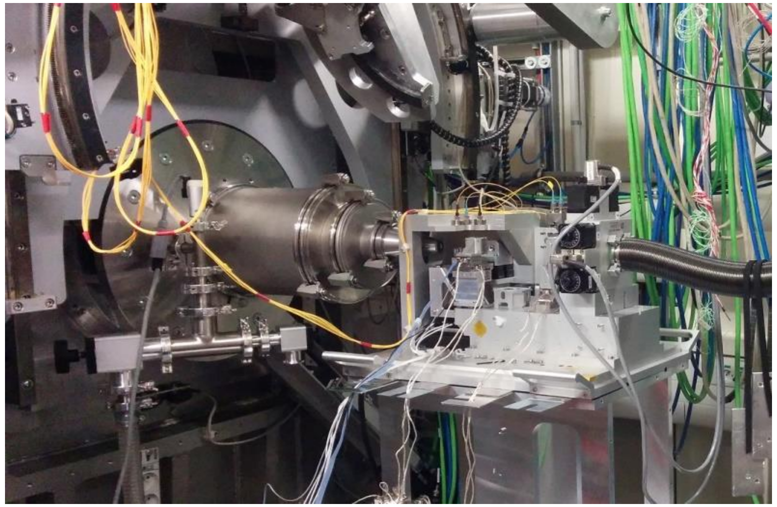
W. Chaâbani, J. Lyu, et al. *ACS Nano* **2024**

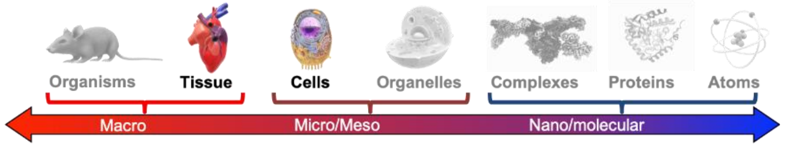
Ptychography X-rays computed Tomography



Ptychography **X**-rays **C**omputed **T**omography
Based on coherent beam diffraction, it gives 3D volume of the electronic density à high spatial resolution
3D resolution <30 nm

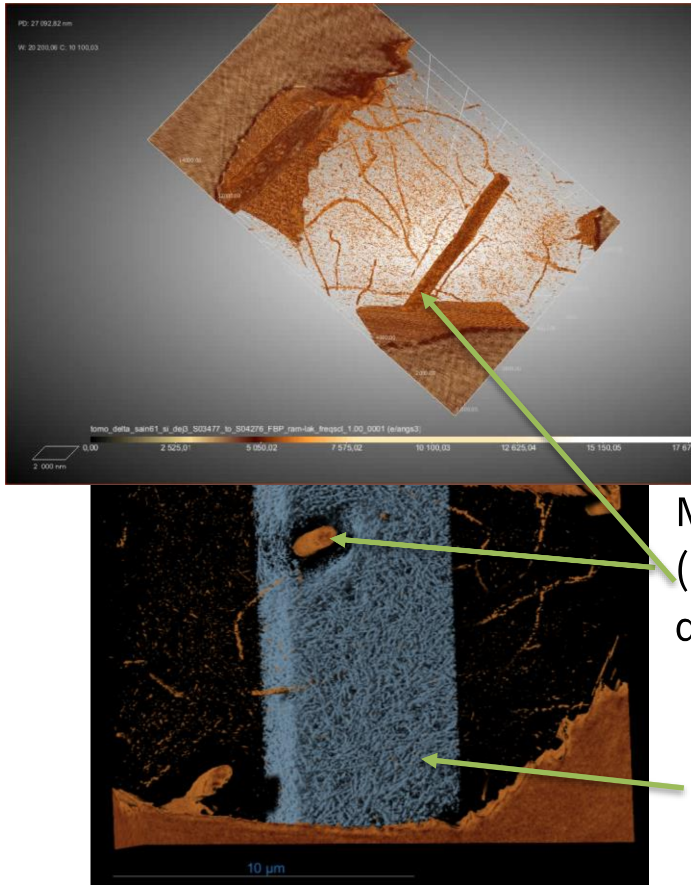
Sample size : 10 – 30 µm





High resolution volume of dentine electronic density

Dentinogenesis Imperfecta study (cyl. Ø 15 µm)



Microtubule (brown) diam ~ 1 µm

Collagen network (blue)

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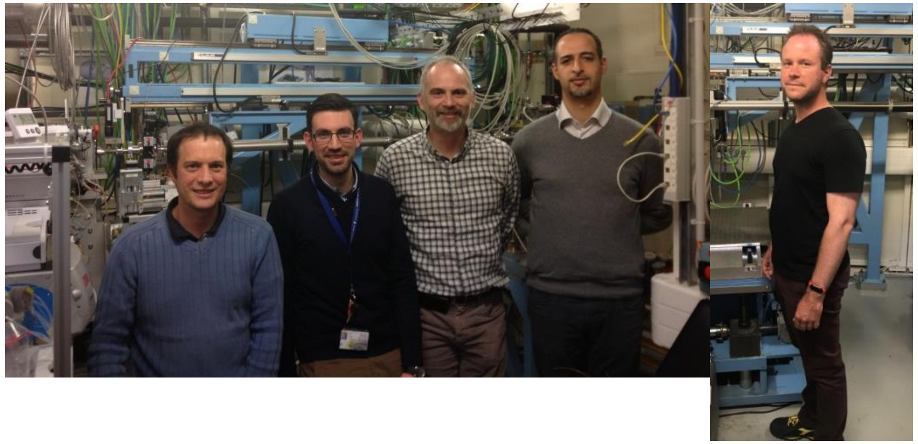

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