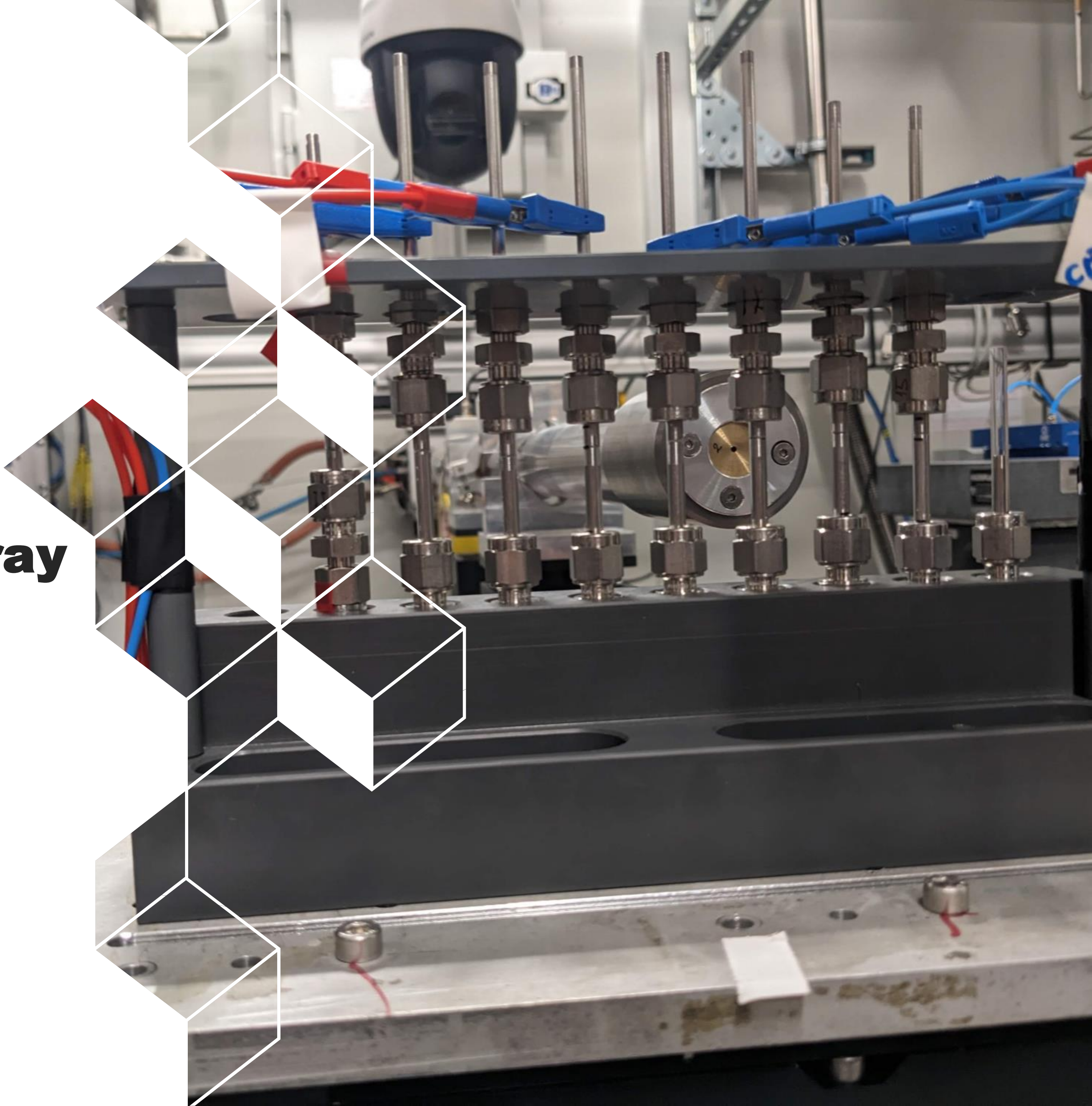


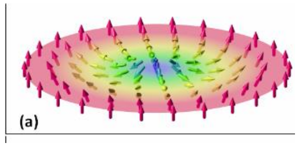
Small Angle Neutron and X-ray Scattering: Leaving Atoms Behind and Going Big

Xaver S. Brems

www.europeanbatteryhub.eu

My Journey to SAXS and SANS

B. Sc. Physics (TUM)
TISANE: AC Coil Setup for Time Resolved Kinetic Neutron Scattering

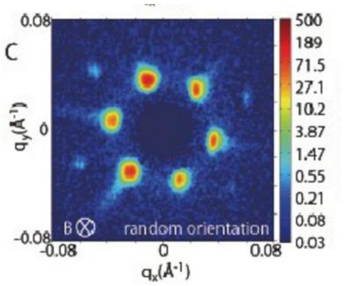


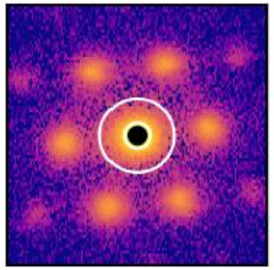
M. Sc. Condensed Matter Physics (TUM)
Current-induced Self-organization of Mixed Superconducting States

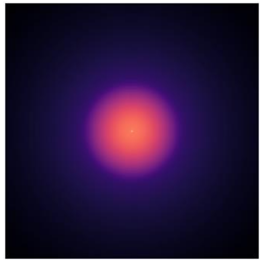
PhD Experimental Physics (TUM/ILL)
Vortex Matter Transport Phenomena of the Intertype Superconductor Niobium
Bob Cubitt (ILL), Sebastian Mühlbauer (TUM)

Postdoctoral Researcher at CEA
Project Manager of the European Battery Hub
operando SAXS/SANS on battery materials

Bragg peaks in my scattering patterns





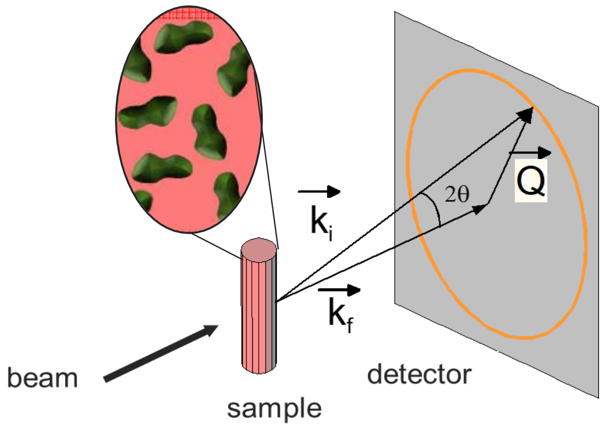


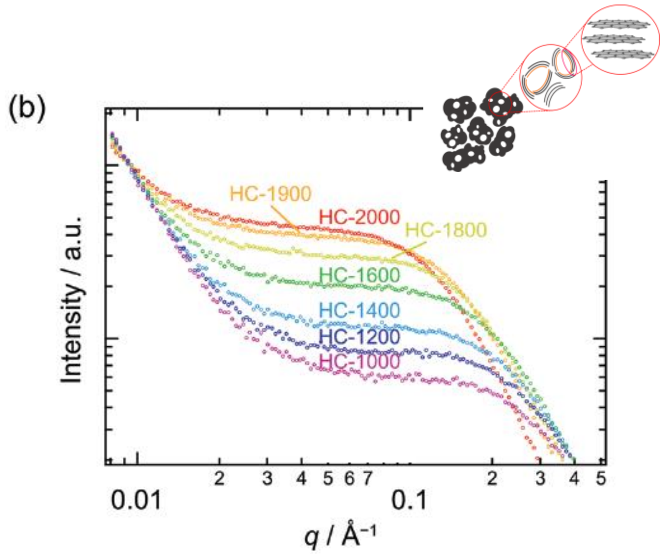
Excitement when seeing small bumps / slope changes in my curve

Outline

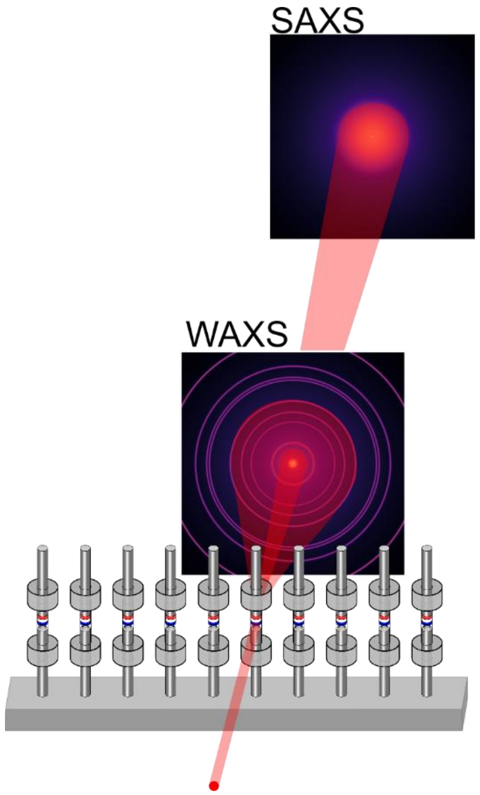
- **I – SAXS/SANS TUTORIAL**
  Basic principle of Small Angle Scattering techniques (SAXS, SANS)

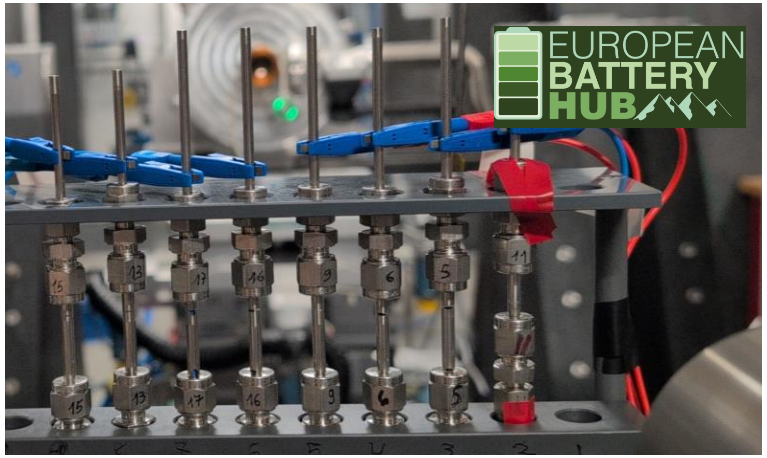
- **II – APPLICATION to battery research**
  Operando SAXS/SANS study of HC electrodes for Na-ion batteries





Morikawa et al, Adv. Energy. Materials

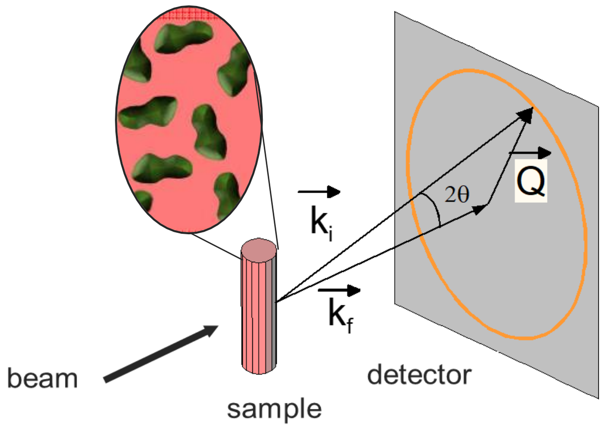




Outline

❖ **I – SAXS/SANS TUTORIAL**

Basic principle of Small Angle Scattering techniques (SAXS, SANS)



https://www-ssrl.slac.stanford.edu/~saxs

https://www.fhi.mpg.de/1075129/armin_hoell__anomalous_small-angle_x-ray_scattering__150116.pdf

https://www.diamond.ac.uk/Instruments/Soft-Condensed-Matter/small-angle.html

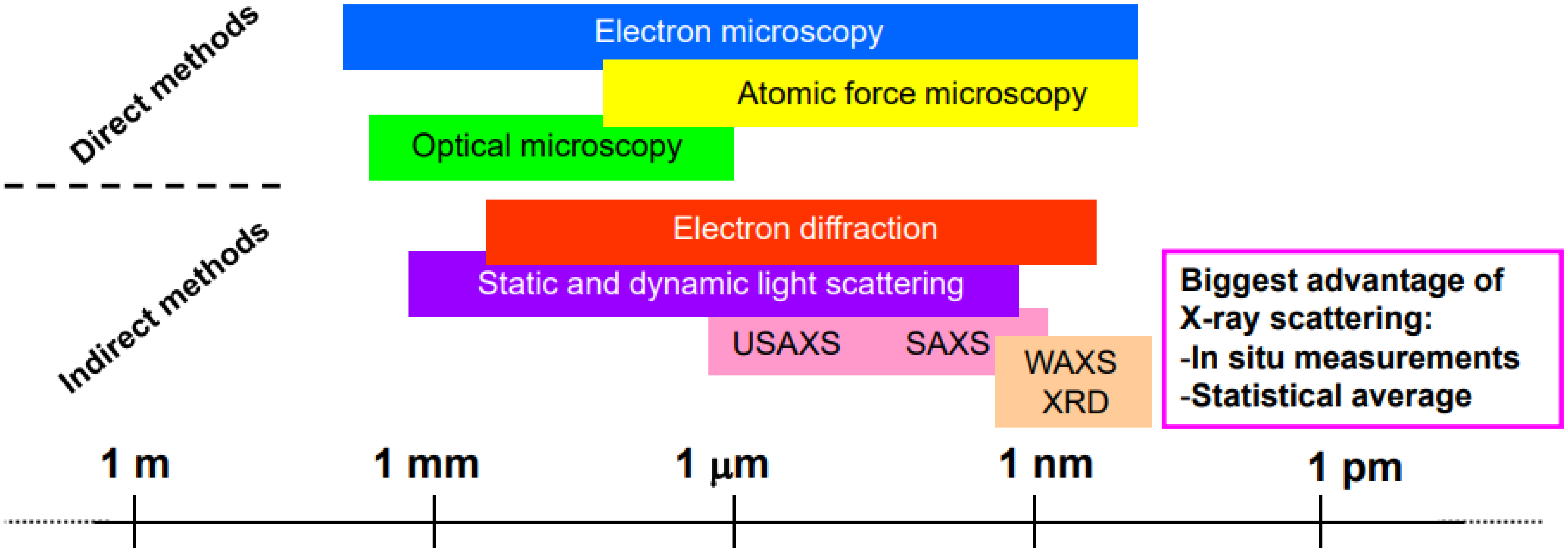
https://brockhouse.lightsource.ca/documents/1/240620_xrd_school_saxs_al.pdf

https://www.eng.uc.edu/~beaucag/Classes/Properties/the_SANS_toolbox.pdf

R. Heenan, ISIS Neutron Training Course Introduction to SANS

F. Cousin, Small Angle Neutron Scattering, EPJ Web of Conferences 104, 01004 (2015)
DOI: 10.1051/epjconf/201510401004

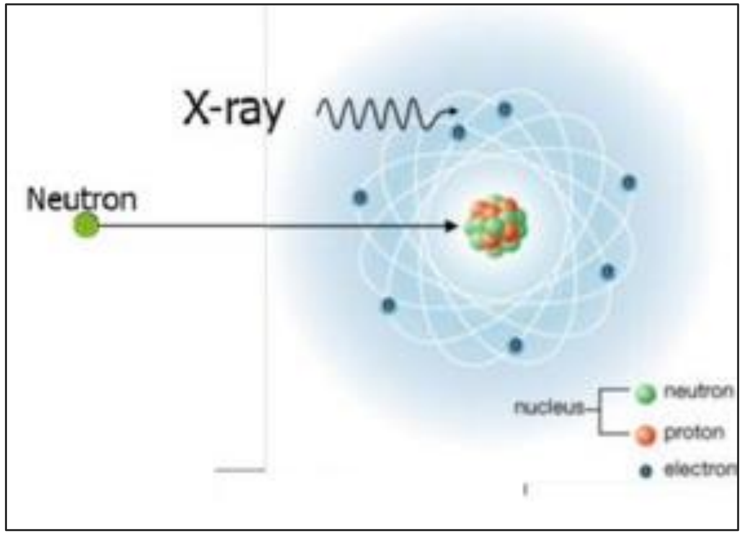
S. Lyonnard, *SAXS/WAXS Techniques for 1D, 2D, and 3D Mapping of Structural Changes in Battery Materials*; Battery2030+/OPINCHARGE/UltraBat seminar series


Direct methods
Electron microscopy
Atomic force microscopy
Optical microscopy
Indirect methods
Electron diffraction
Static and dynamic light scattering
USAXS
SAXS
WAXS
XRD
Biggest advantage of
X-ray scattering:
-In situ measurements
-Statistical average
1 m
1 mm
1 µm
1 nm
1 pm

Basic principles of SAXS/SANS

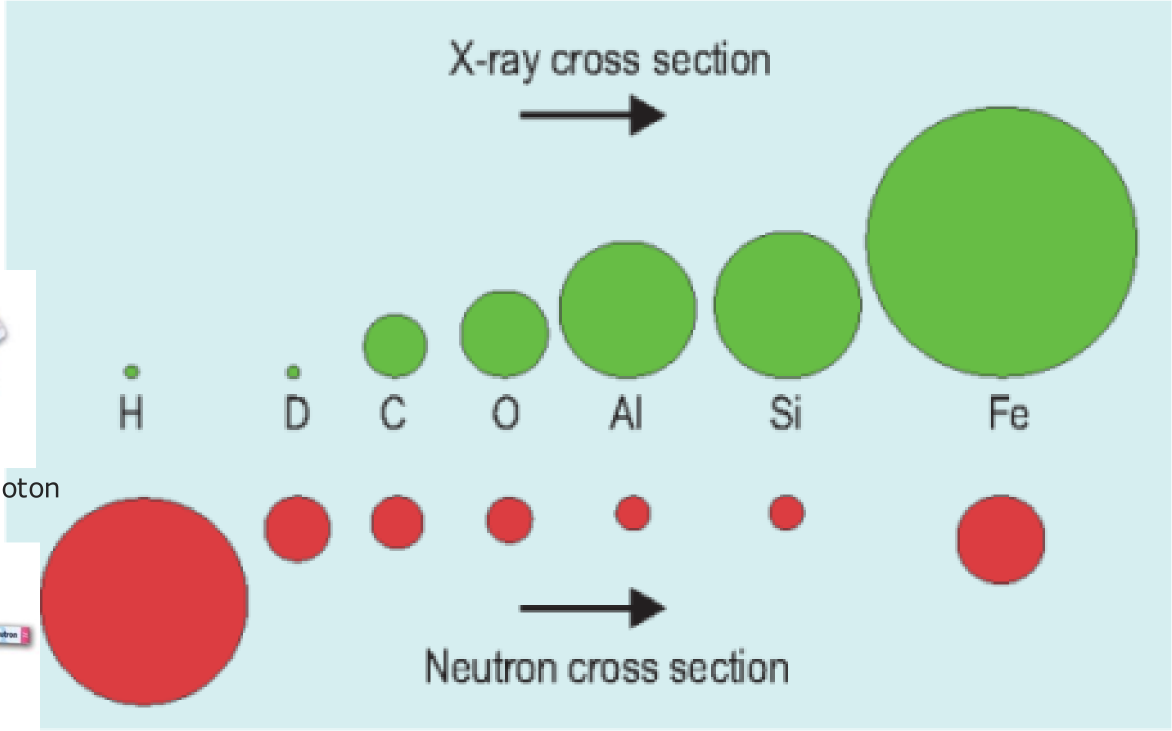
neutrons interact with nuclei while X-rays interact with e-

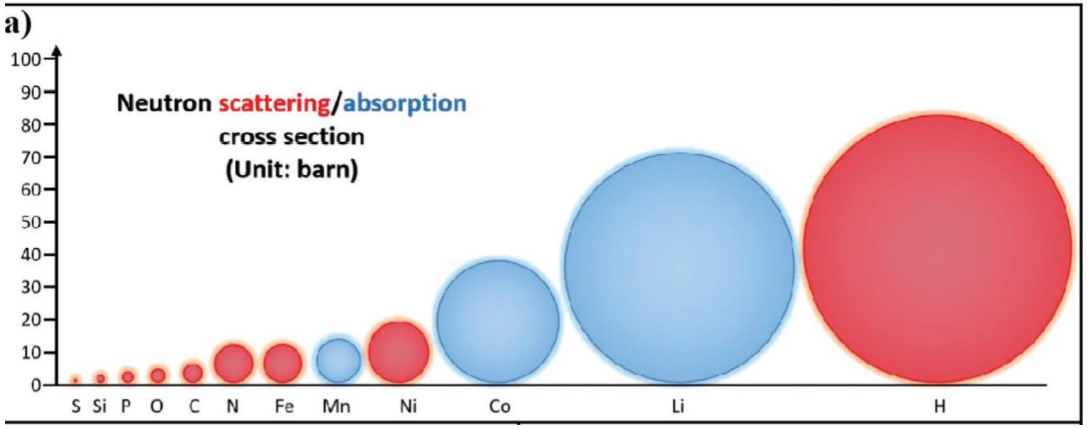
Scattering cross sections & absorption cross sections



X-Ray / photon

neutron

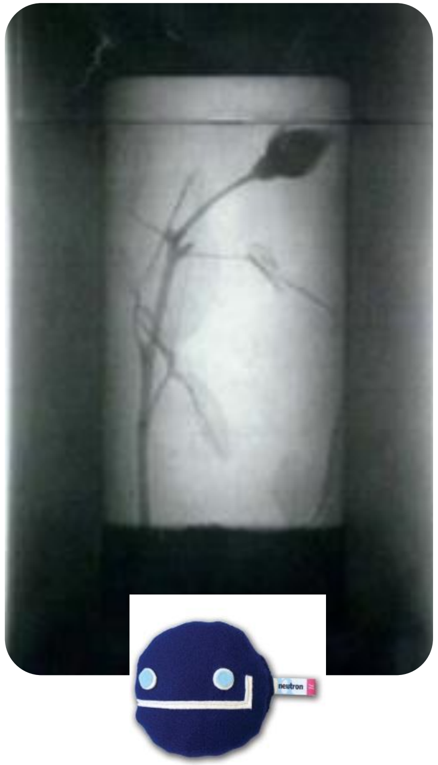




Adv. Energy Mater. 2020, 2000806

Basic principles of SAXS/SANS

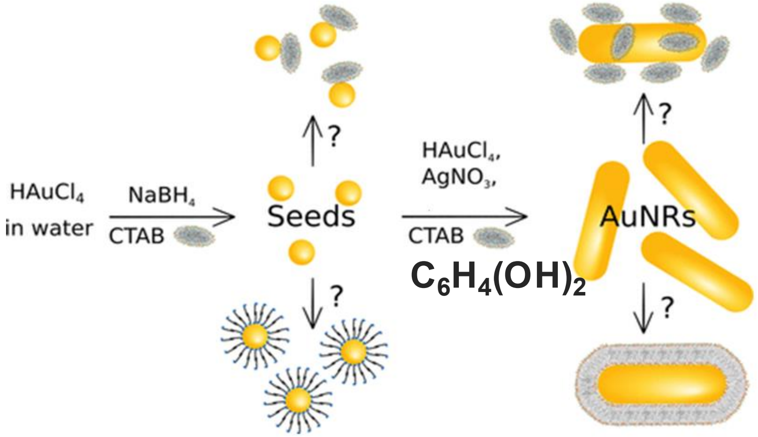
Human hand with ring and bracelet



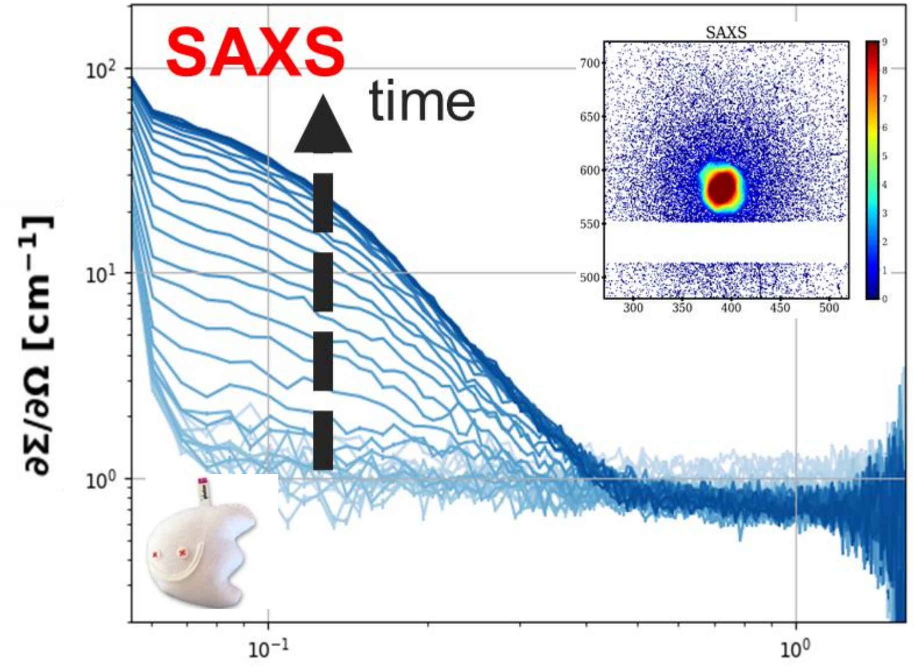
Rose in lead container

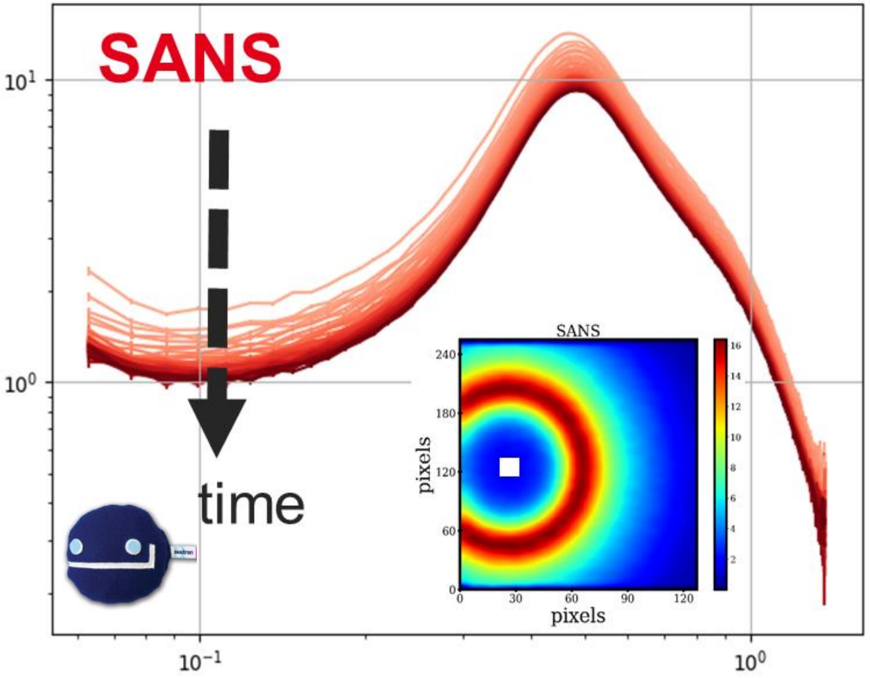
Basic principles of SAXS/SANS

Hydroquinone synthesis of Au NPs:
Gold nanoparticles (Au NPs) synthesis begins with the gold precursor (HAuCl4) which forms small seeds after reduction with the reducing agent NaBH4 in the presence of cetyltrimethylammonium bromide (CTAB). The subsequent reduction of HAuCl4 using Hydroquinone (C6H6(OH)2) in the presence of AgNO3, CTAB, and the seed particles leads to the formation of single crystalline Au NPs.



Temporal structural cross-correlation between organic stabilizing agent (CTAB micelles) and gold seeds ? How do they cooperate in the formation of different size/shape of large stabilized gold nanoparticles ?





SAXS+SANS = Complementary nanoscale structural information at two different contrast situations

Time evolution of both SAXS and SANS 1d profiles during the in-situ reduction process of gold solution at 35°C.

FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

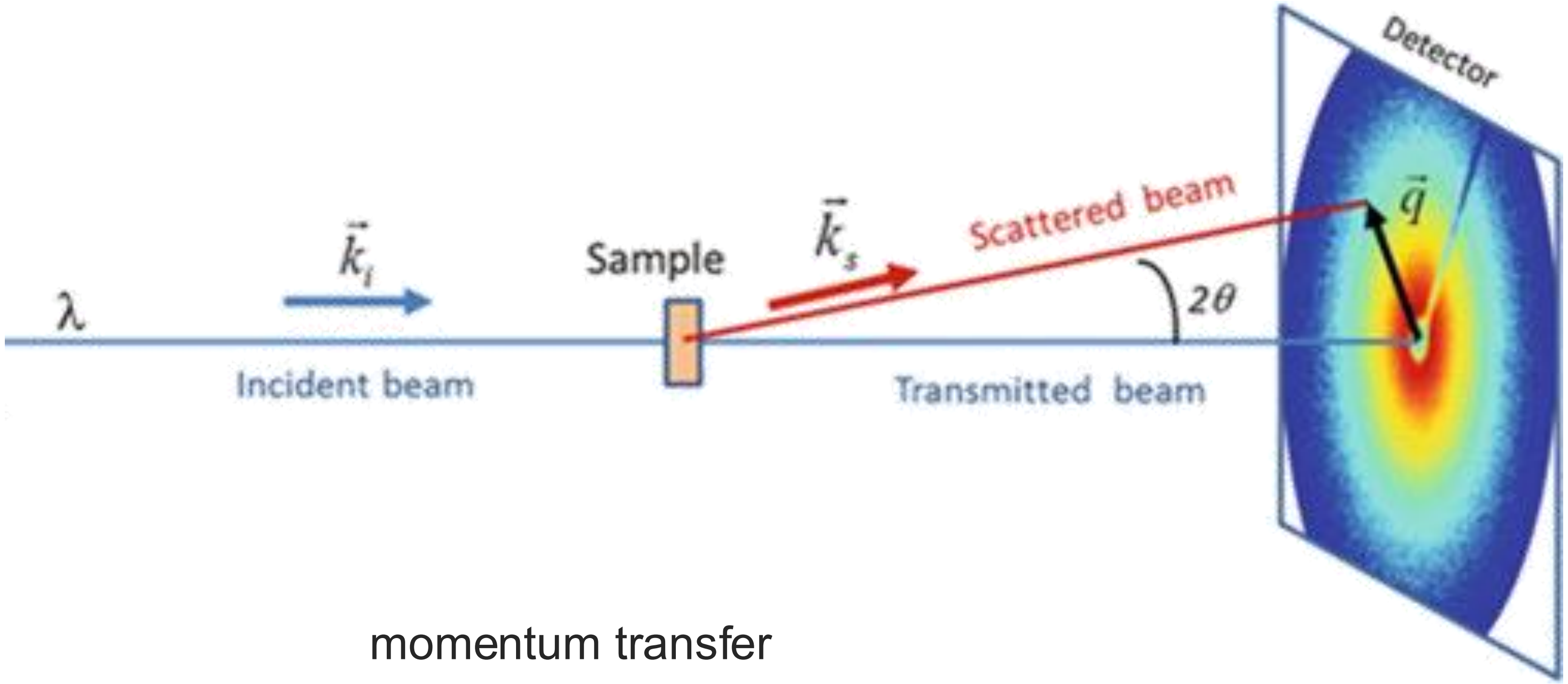
NEUTRONS FOR SOCIETY

Metwalli, E.; Gotz, K.; Lages, S.; Bar, C.; Zech, T.; Noll, D. M.; Schuldes, I.; Schindler, T.; Prihoda, A.; Lang, H.; Grasser, J.; Jacques, M.; Didier, L.; Cyril, A.; Martel, A.; Porcar, L.; Unruh, T. *A novel experimental approach for nanostructure analysis: simultaneous small-angle X-ray and neutron scattering. Journal of Applied Crystallography* **2020**, *53* (3) 722-733.

Basic principles of SAXS/SANS

The typical scattering setup

X-ray or neutron



elastic process

$$\vec{k}_2 - \vec{k}_1 = \vec{Q} \quad , \quad \left|\vec{k}_1\right| = \left|\vec{k}_2\right|$$

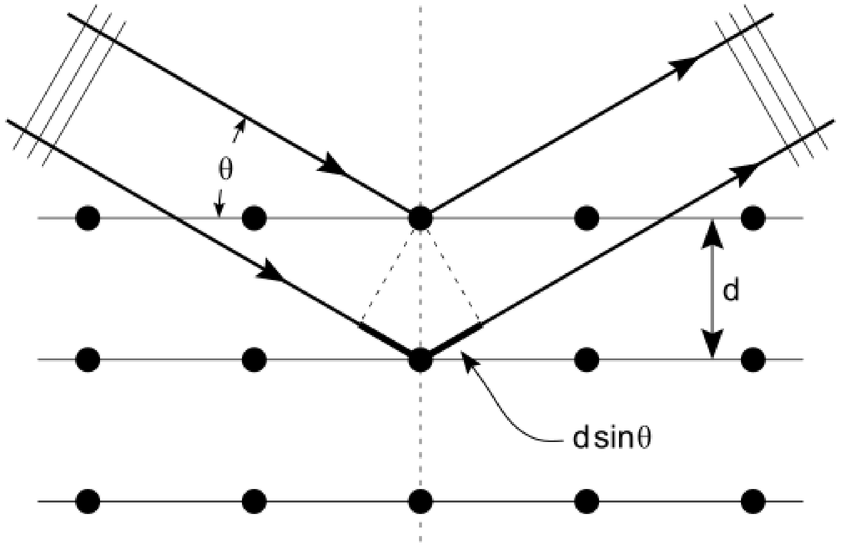
$$k = \frac{2\pi}{\lambda}$$

momentum transfer

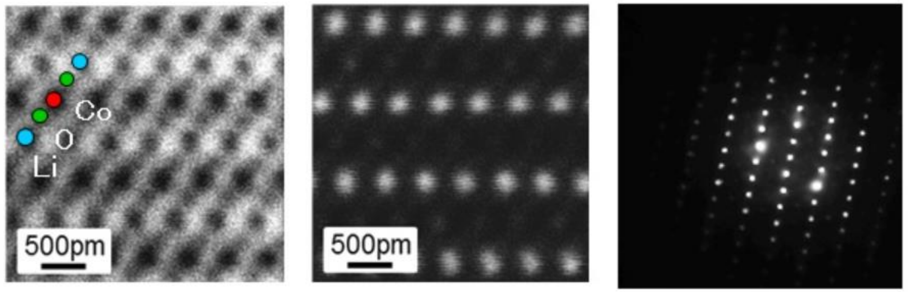
$$\left|\vec{Q}\right| = 2\left|k\right| \sin(\theta) = 4\pi \sin(\theta)/\lambda$$

Basic principles of SAXS/SANS

Note 1. Small Angle scattering is somehow a diffraction technique probing the wave interferences from nanoscale scattering objects ! Think about Bragg's law, not on atomic planes but at larger scales, e.g. atoms are replaced by colloids/particles/nanosized areas of the sample !

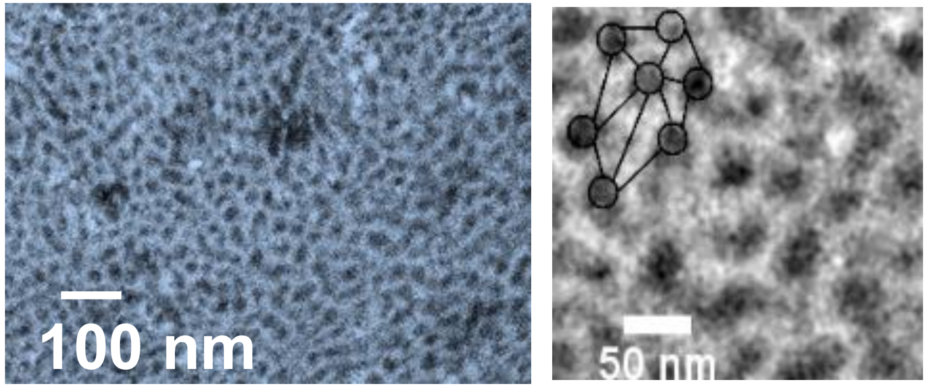


TEM image of a battery LCO cathode



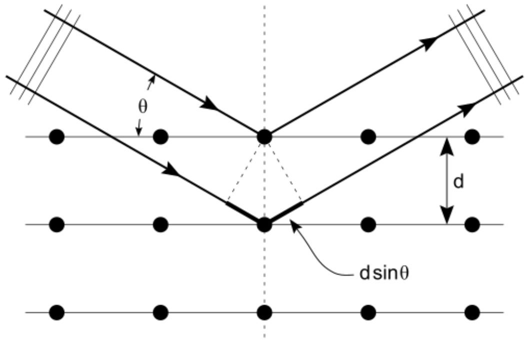
ABF-STEM image | HAADF-STEM image | Electronic Diffraction Pattern

MEB image on a nanostructured polymer



Basic principles of SAXS/SANS

Small Angle Scattering: The Big Picture



$$2\,\mathrm{d}\sin\theta = n\lambda$$

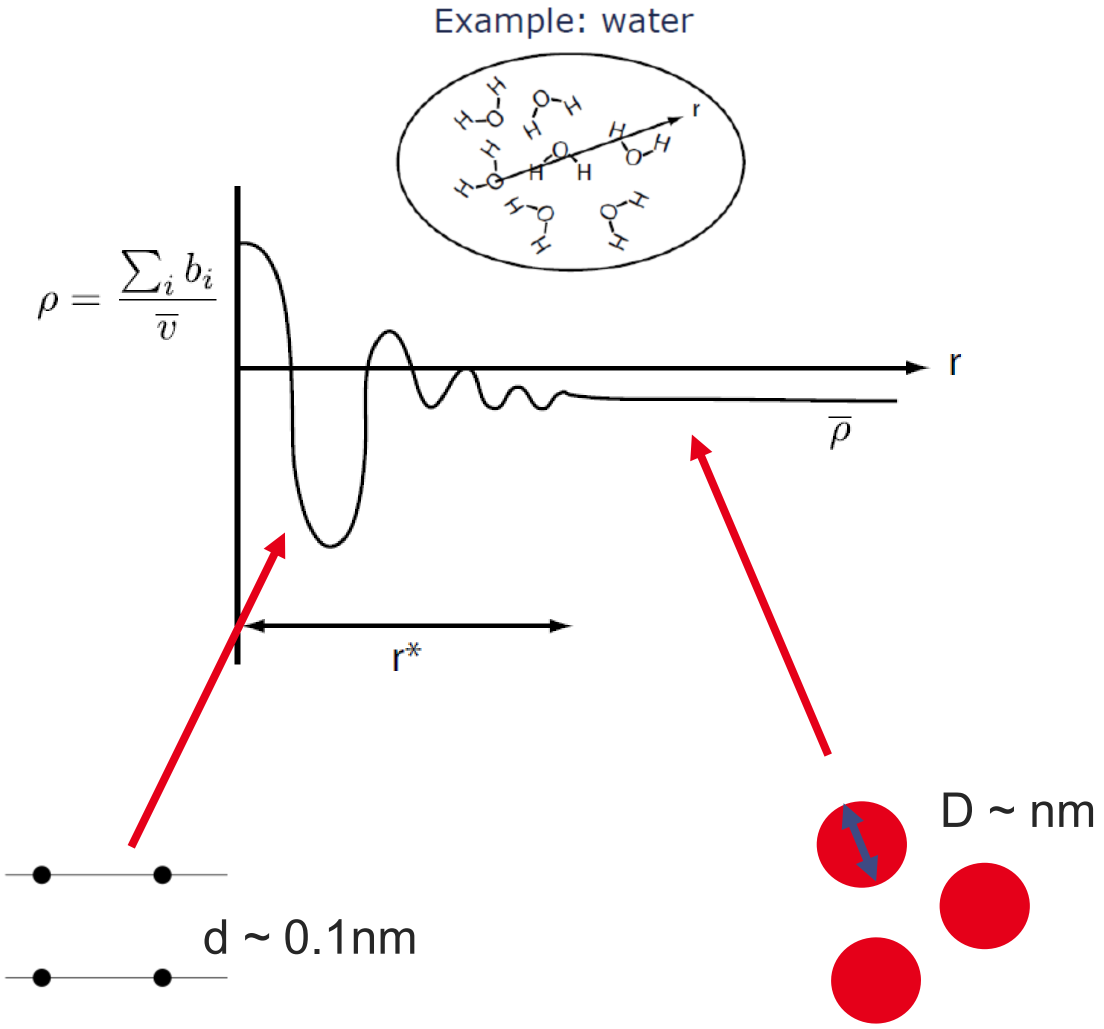
d, distance probed, 1 – 1000 nm
large compared to λ

Wavelengths of Probe, of the order of 0.1 - 2 nm. Of the order of atomic spacing. FIXED

λ fixed, d large:
θ must be small!

Basic principles of SAXS/SANS

SAXS/SANS = Fourier transform of the scattering length density (SLD)

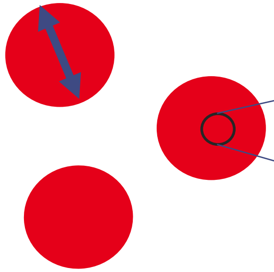


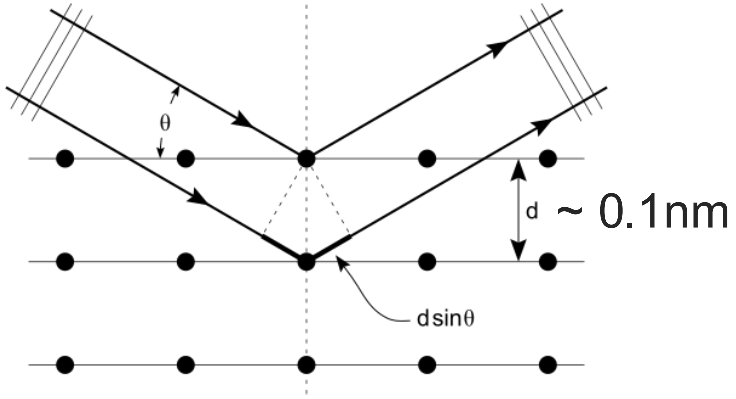
- Individual atoms (characterized by b) looses relevance
- Scattering determined by variations in the scattering length density $\rho = \frac{\sum_i b_i}{V}$

$$I(\vec{Q}) \propto \left| \int_V \rho(x) e^{-i\vec{Q}\vec{x}} \, dx \right|^2$$

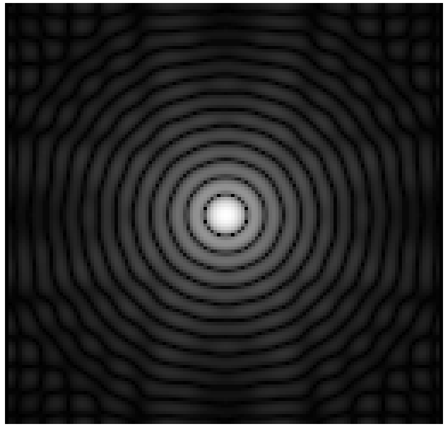
Basic principles of SAXS/SANS

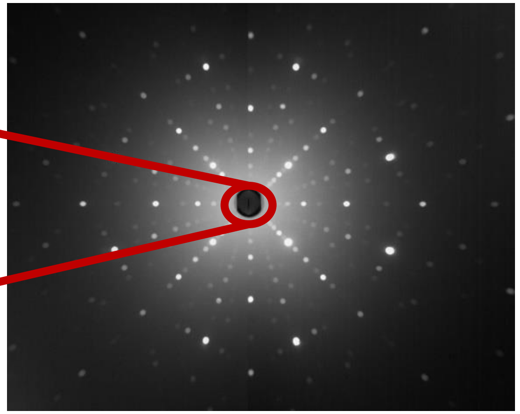
Real space image





Scattering image

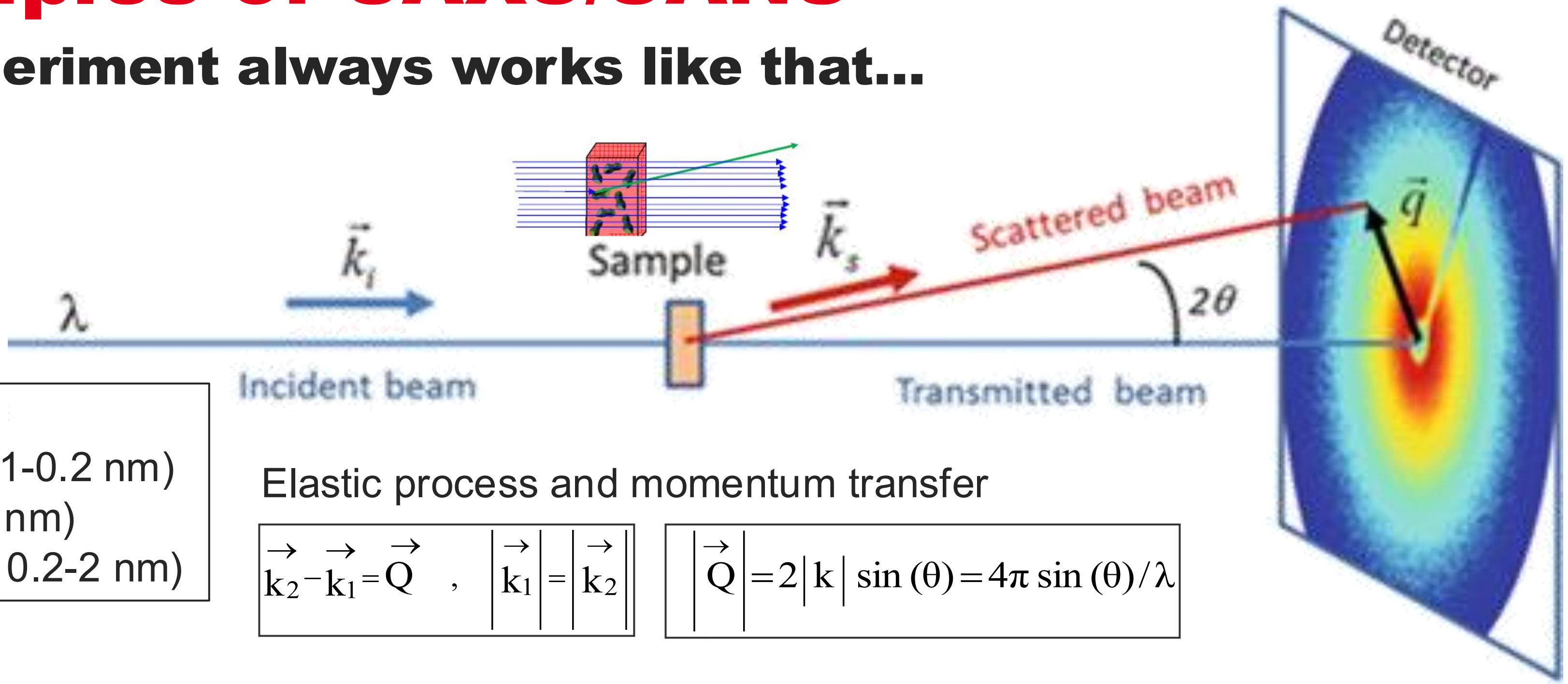




Basic principles of SAXS/SANS

A small angle experiment always works like that…

X-ray or neutron



Radiation sources
Lab X-ray generator (λ = 0.1-0.2 nm)
Synchrotron (λ = 0.03-0.35 nm)
Thermal/cold neutrons (λ = 0.2-2 nm)

Elastic process and momentum transfer

$$\vec{k}_2 - \vec{k}_1 = \vec{Q} \quad , \quad |\vec{k}_1| = |\vec{k}_2|$$

$$|\vec{Q}| = 2|k|\sin(\theta) = 4\pi\sin(\theta)/\lambda$$

Magnitude of the scattering vector

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

Bragg-equation

$$2d\sin(\theta) = \lambda$$

$$|\vec{q}| = \frac{2\pi}{d}$$

Threshold value: $|\vec{q}| \to 0 \qquad d \to \infty$

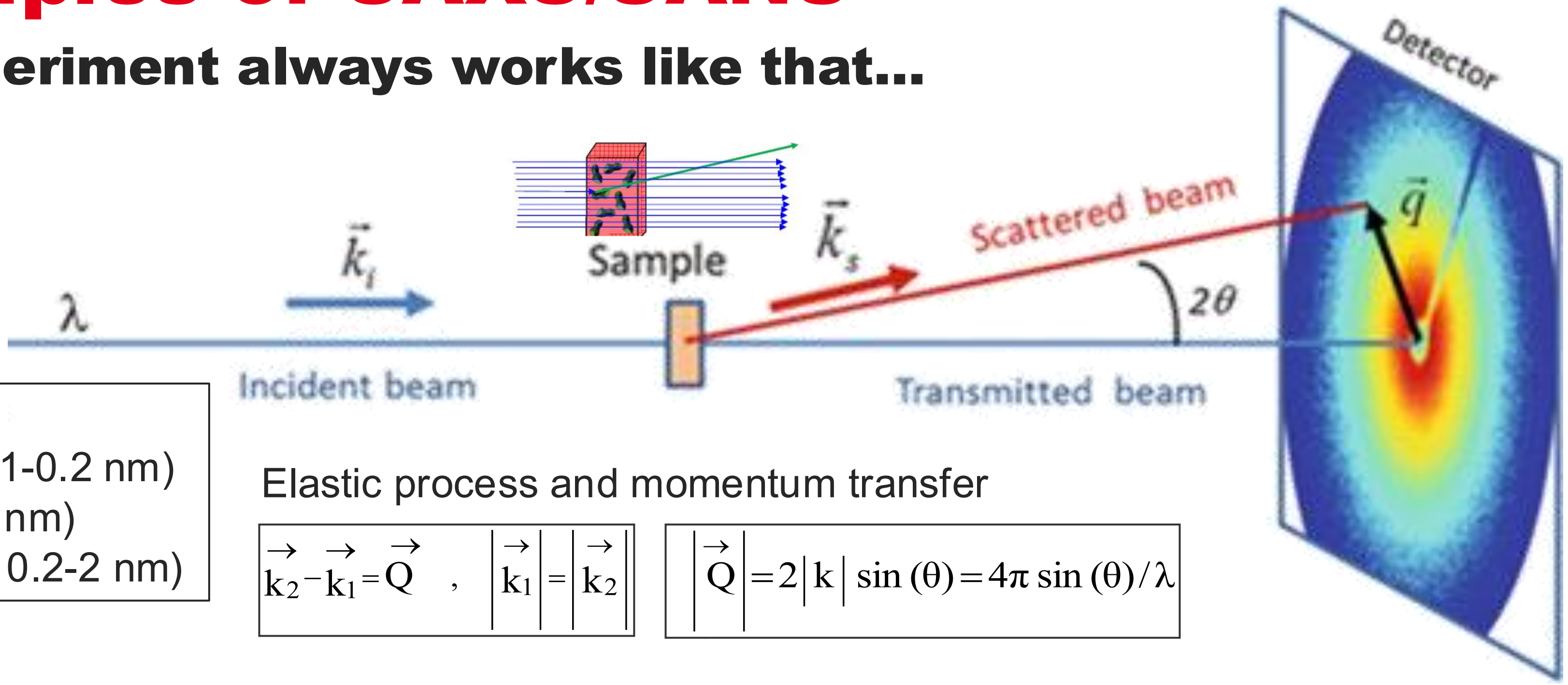
Scattering also allows to investigate structures in the nm- and µm- range.
→ Small-Angle Scattering (SAXS, SANS, USAXS, USANS) ←

Small angles θ < 5° Q typically [0.001 – 1 $Å^{-1}$]

$$d = \frac{2\pi}{Q}$$ [6000 – 6 Å]

Basic principles of SAXS/SANS

A small angle experiment always works like that…



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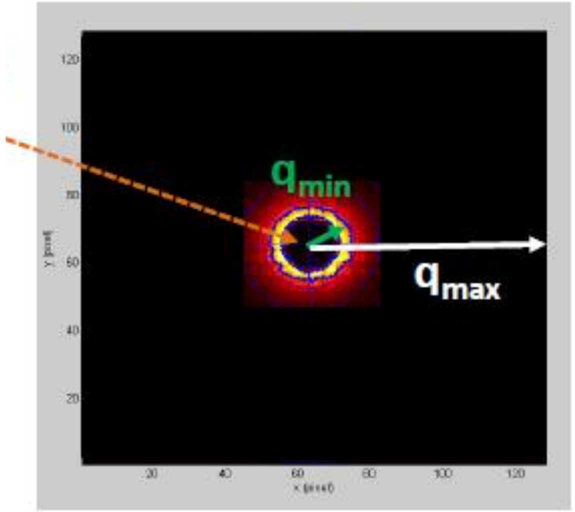
The sample-detector distance L defines the smallest accessible q_{min}
The detector size defines the maximum qmax accessible
Q-range is (L, λ) dependent

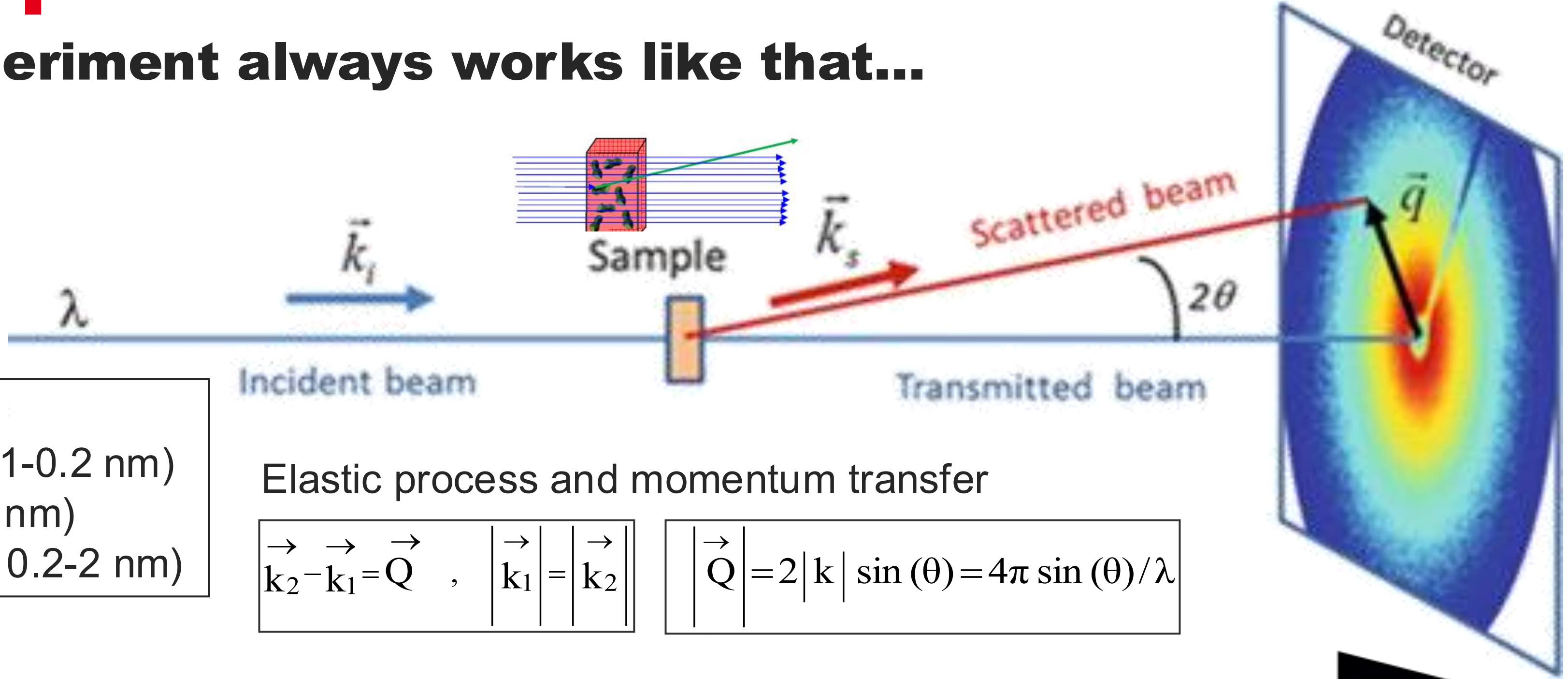
Beamstop



Basic principles of SAXS/SANS

A small angle experiment always works like that…

X-ray or neutron



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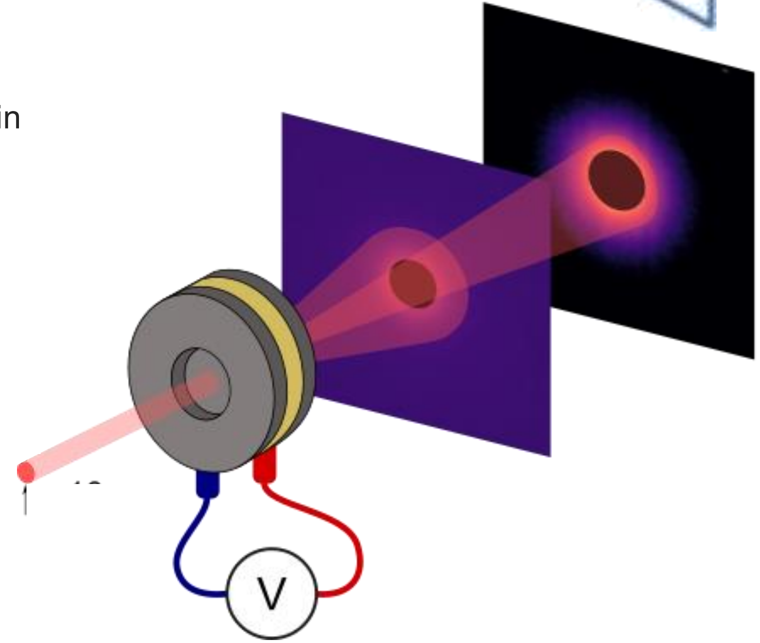
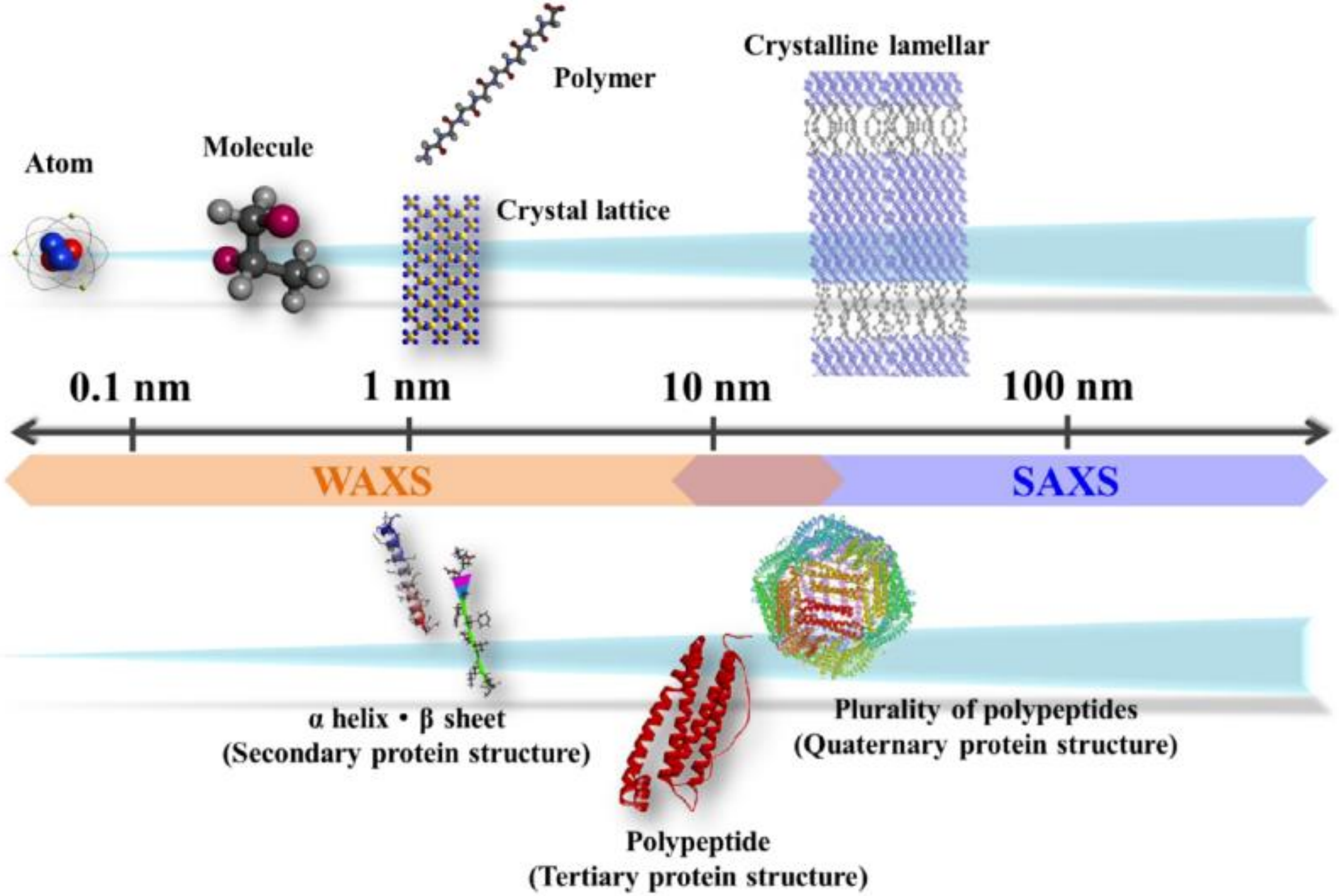
The detector size defines the maximum qmax accessible
Q-range is (L, λ) dependent

To obtain an extended Q-range, detector is moved !



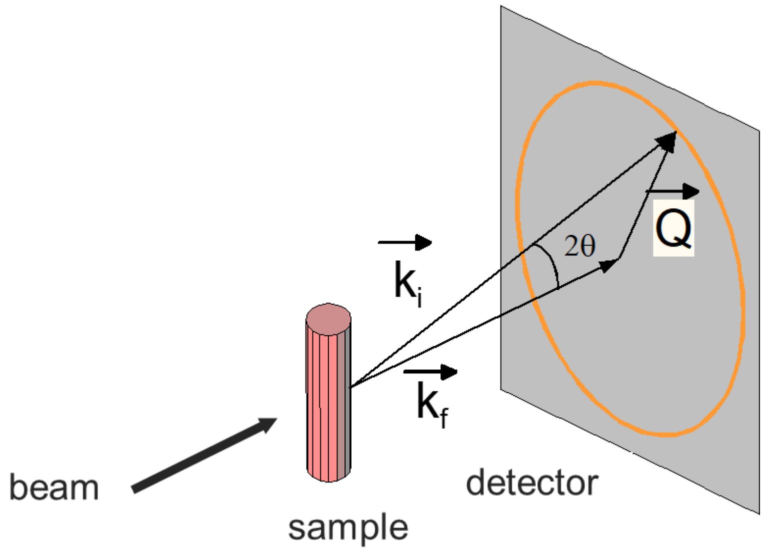
Basic principles of SAXS/SANS

Looking at matter / materials across extended nano-microscales

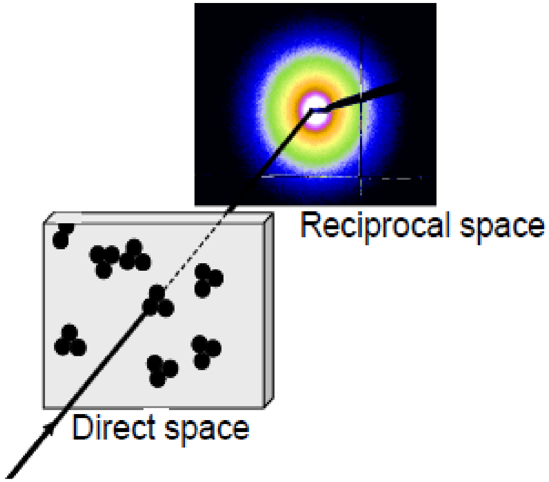


Basic principles of SAXS/SANS

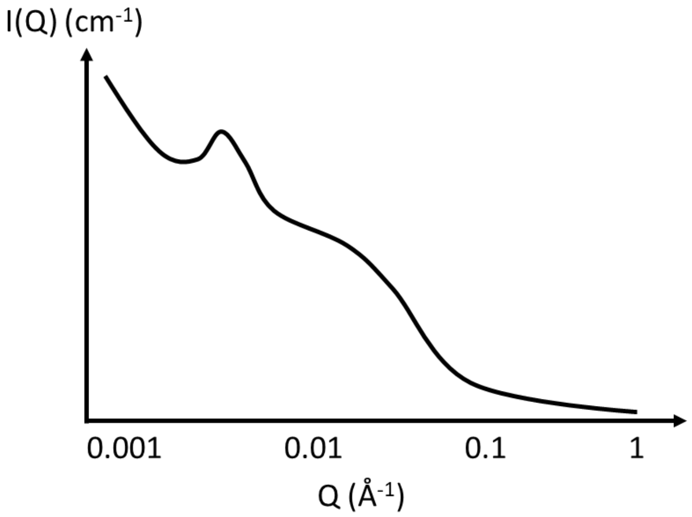
Note 2. Small Angle scattering measures a 2D intensity pattern vs Q

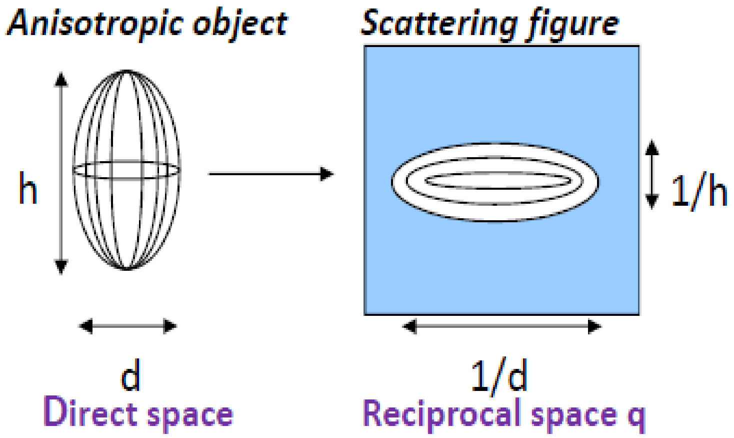


Isotropic sample

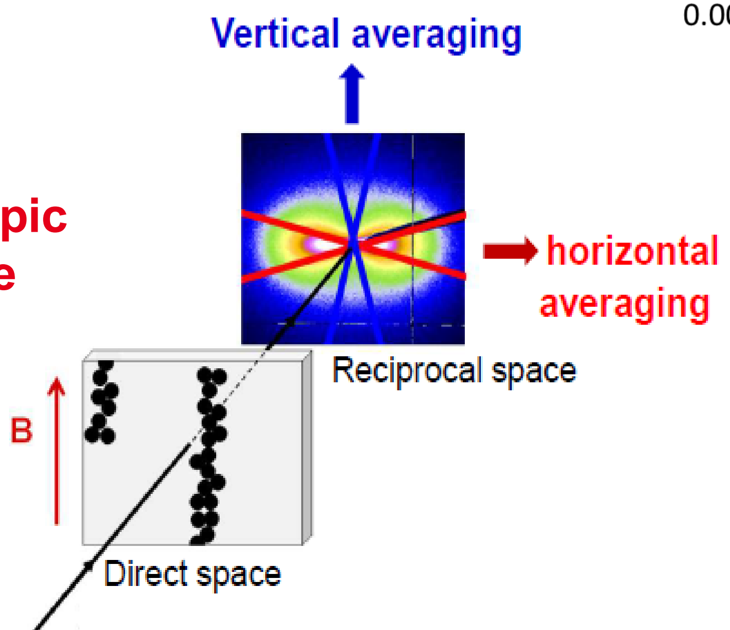


radial averaged intensity I (Q)





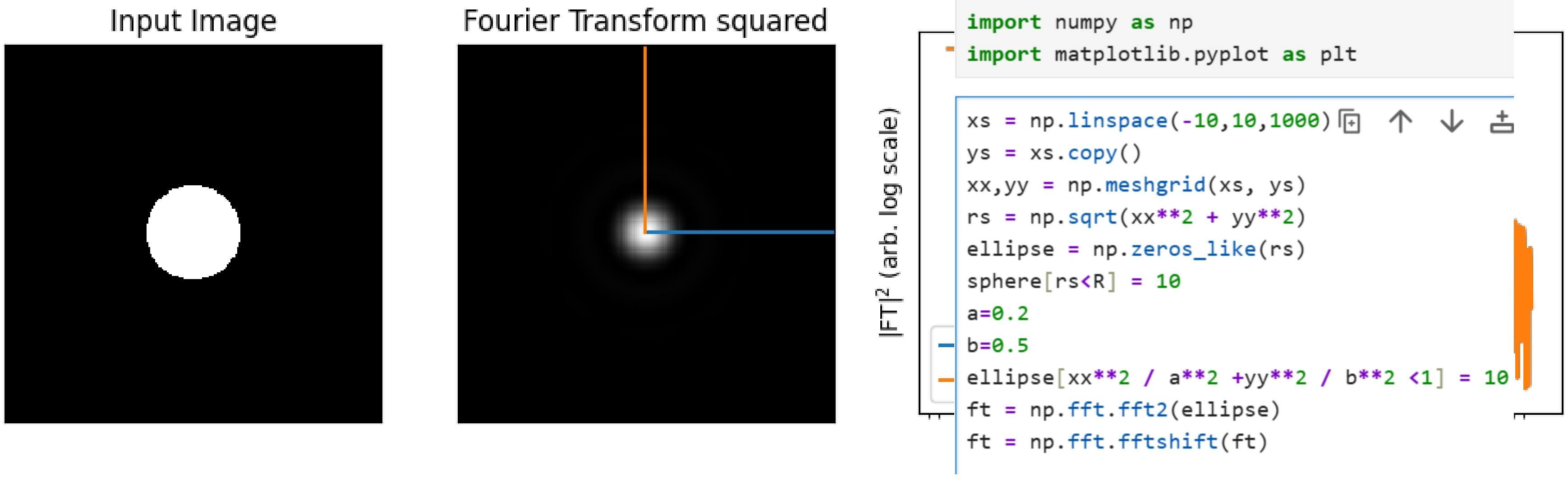
Anisotropic sample



Basic principles of SAXS/SANS

Try it out yourself: Do some 2D Fourier Transforms (using for example python)

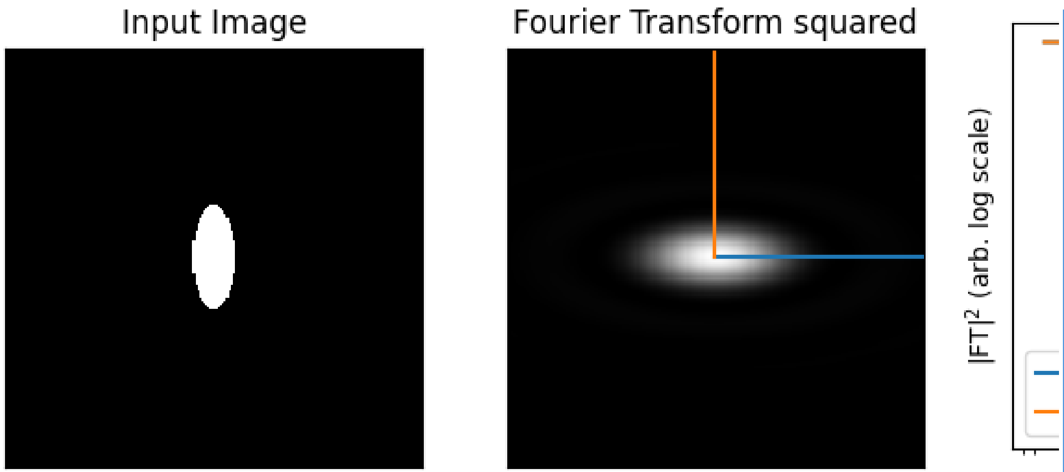
$$I(\vec{Q}) \propto \left| \int_V \rho(x) e^{-i\vec{Q}\vec{x}}\, dx \right|^2$$




```
import numpy as np
import matplotlib.pyplot as plt
```

```
xs = np.linspace(-10,10,1000)
ys = xs.copy()
xx,yy = np.meshgrid(xs, ys)
rs = np.sqrt(xx**2 + yy**2)
ellipse = np.zeros_like(rs)
sphere[rs<R] = 10
a=0.2
b=0.5
ellipse[xx**2 / a**2 +yy**2 / b**2 <1] = 10
ft = np.fft.fft2(ellipse)
ft = np.fft.fftshift(ft)
```

Horizontal and vertical cut identical



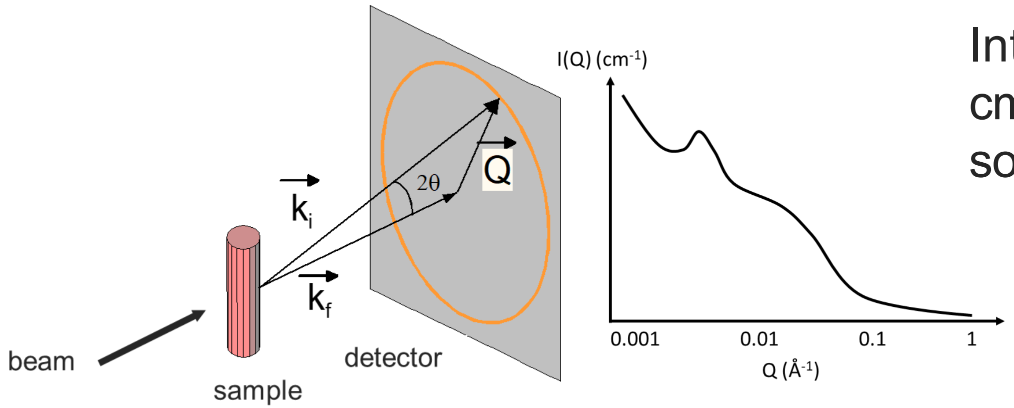

```
fig,axes = plt.subplots(1,2)
ax=axes[0]
ax.pcolormesh(xs, ys, ellipse, cmap=plt.cm.grey)
ax.set_xlim([-2,2])#
ax.set_ylim([-2,2])
ax.set_aspect('equal')
ax.set_title('Input Image')

ax=axes[1]
ax.pcolormesh((np.abs(ft)**2)[400:600,400:600], cmap=plt.cm.grey)
ax.set_aspect('equal')
ax.set_title('Fourier Transform squared')
for ax in axes:
    ax.set_yticks([])
    ax.set_xticks([])
ax.plot([100,200],[100,100])
ax.plot([100,100],[100,200])
```

›tropic scattering

Basic principles of SAXS/SANS

Note 3. SAXS is analytical (sometimes)



Intensity I(Q) is the absolute scattering cross section dσ(Q)/dω in units of cm^{-1} = probability of a neutron of wavelength λ being scattered, per unit solid angle, at that Q.

Differential cross-section
= scattered intensity I (Q)

$$\frac{d\sigma}{d\Omega}(Q) = \frac{1}{N}\left|\int_{V_S} dr\, \rho(r)\, e^{i\mathbf{Qr}}\right|^2 = \frac{1}{N} I(Q)$$

$$I(Q) = N\Delta\rho(r)^2 F(Q, r)^2 S(Q)$$

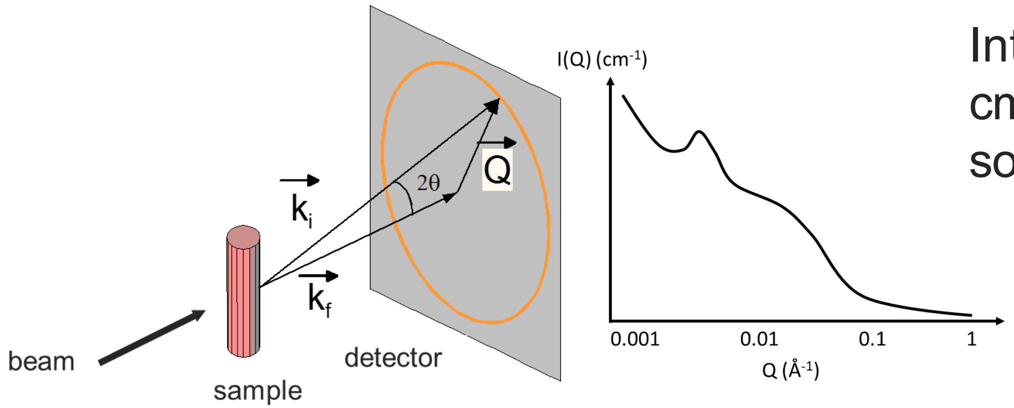
Scattering contrast Δρ
Scattering length b of element i
concentration c_i, density ρ_i

$$\Delta\rho(r) = \sum_i (b_i c_i \rho_i)_{Phase1} - \sum_j (b_j c_j \rho_j)_{Phase2}$$

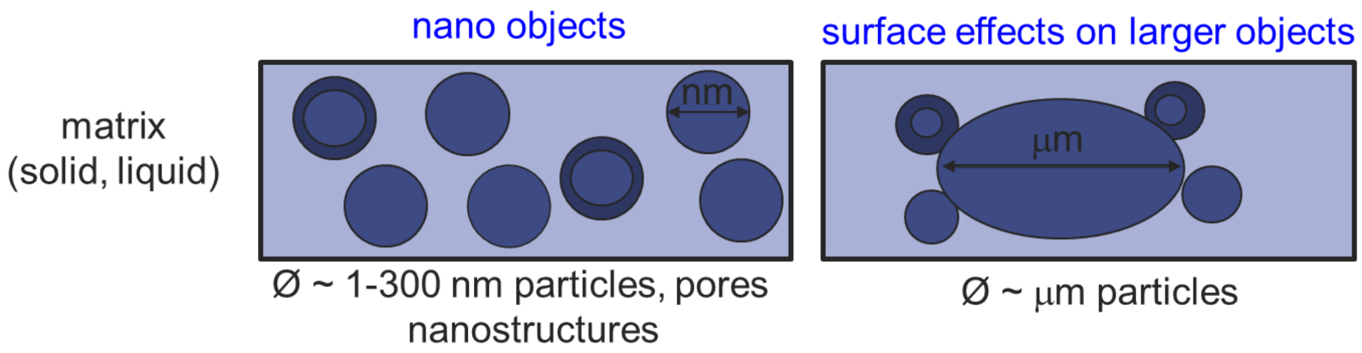
Form factor P(Q) size, shape of particle (we note $P(Q)=F(Q)^2$)
Structure factor S(Q) arrangement of particles

Basic principles of SAXS/SANS

Note 3. SAXS is analytical (sometimes)



Intensity I(Q) is the absolute scattering cross section $d\sigma(Q)/d\omega$ in units of cm^{-1} = probability of a neuton of wavelength λ being scattered, per unit solid angle, at that Q.



$$I(Q) = N\Delta\rho(r)^2 F(Q, r)^2 S(Q)$$

Scattering contrast $\Delta\rho$
Scattering length b of element i
concentration c_i, density ρ_i

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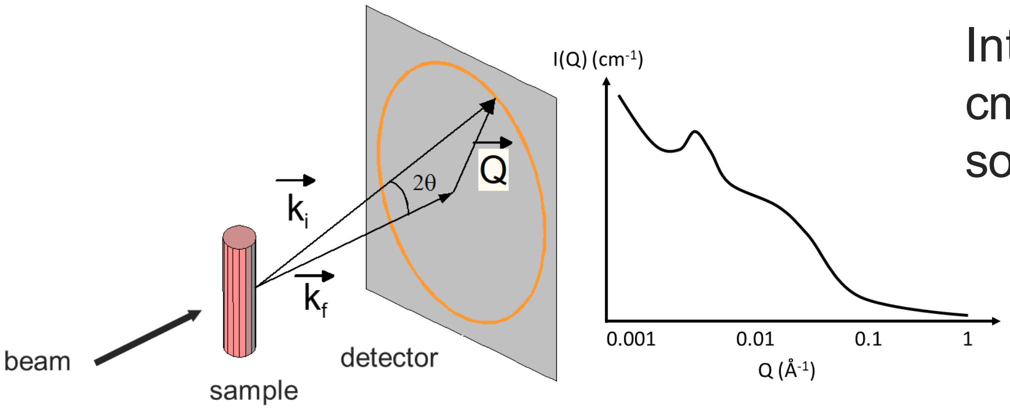
Basic principles of SAXS/SANS

Note 3. SAXS is analytical (sometimes)



Intensity I(Q) is the absolute scattering cross section $d\sigma(Q)/d\omega$ in units of cm^{-1} = probability of a neuton of wavelength λ being scattered, per unit solid angle, at that Q.

What do we measure experimentally ?

Counts in detector of area A at radius R and distance L from sample

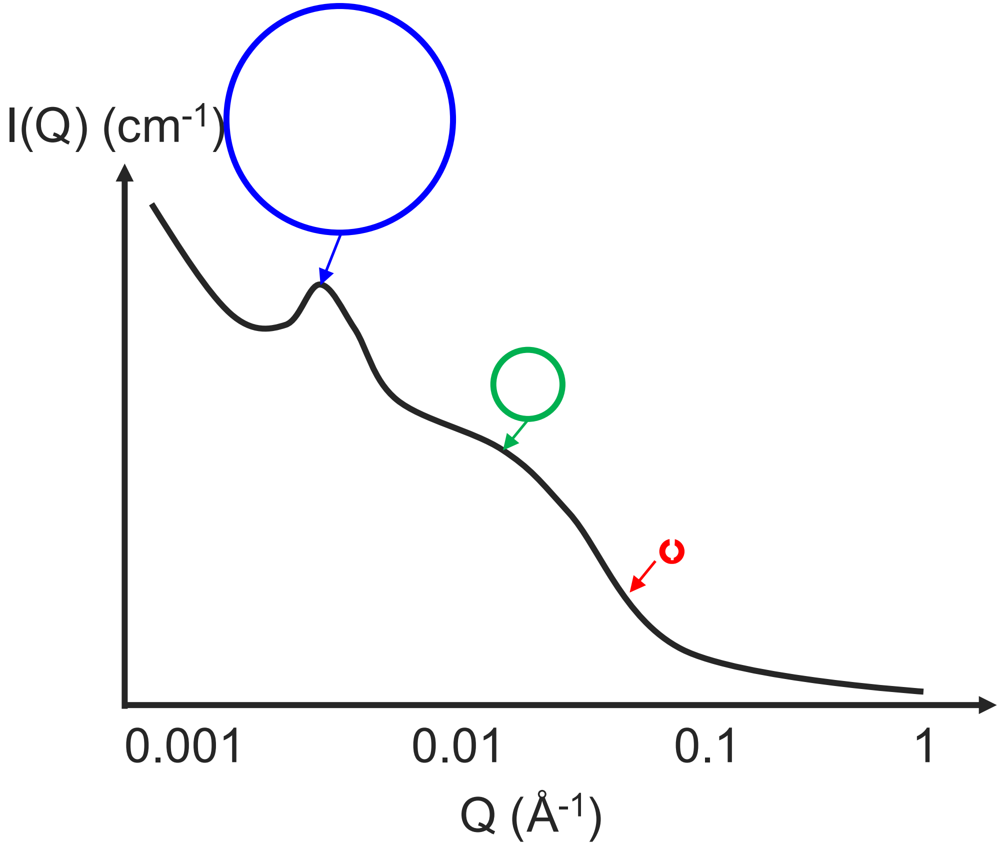
$$I(R,\lambda)=I_0(\lambda).\frac{\partial \Sigma(Q)}{\partial \Omega}.\Delta\Omega(R).t.T(\lambda).\eta(\lambda)$$

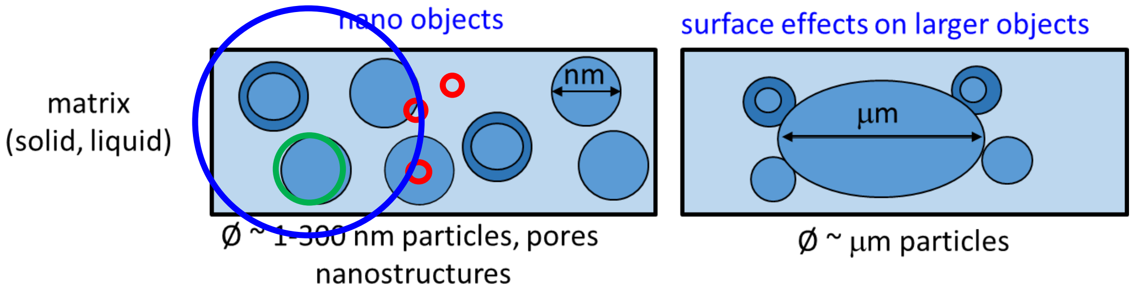
Solid Angle $\Delta\omega = A/L^2$
t = sample thickness
T = transmission
η = detector efficiency
$\mathrm{Tan}(\theta) = R/L$

Basic principles of SAXS/SANS

Note 4. SANS is like having a microscope with a magnifying glass of diameter $2\pi/Q$

You get a signal when you have a contrast !





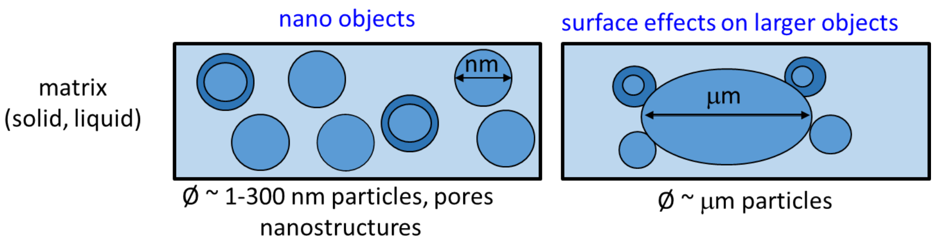
Interface (Porod's limit)

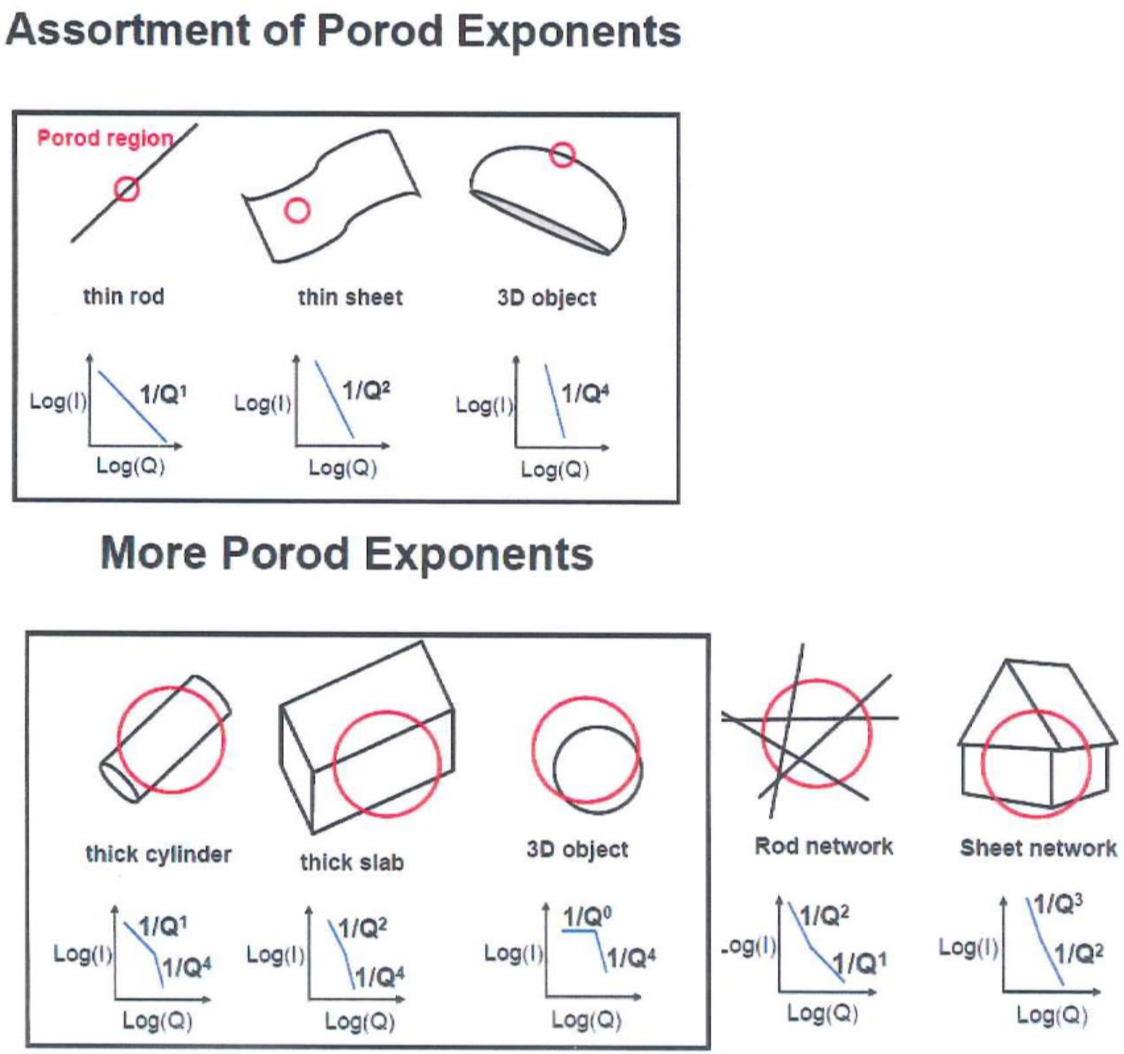
Particle size and shape (form factor)

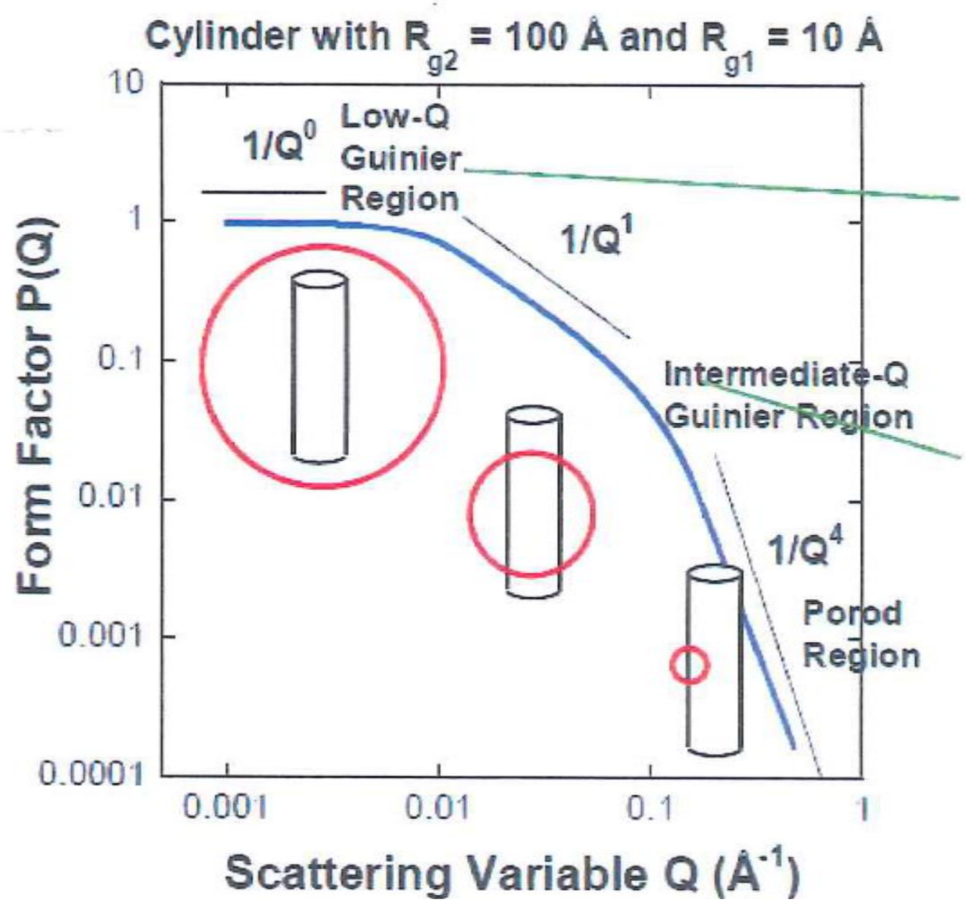
Particles's organization (structure factor)

Interfaces

SANS/SAXS from disperse particles

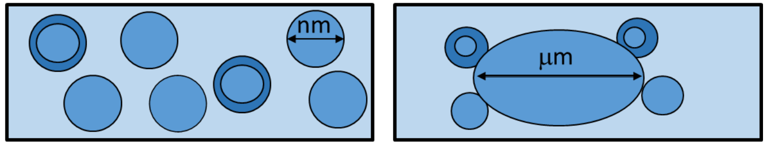






Courtesy of Boualem Hammouda

Interfaces



Fractal aggregates or pores

I(Q) from fractals give straight line regions on log-log plots
Ex : rocks, coals, cement, zeolites, silicas, battery electrodes !

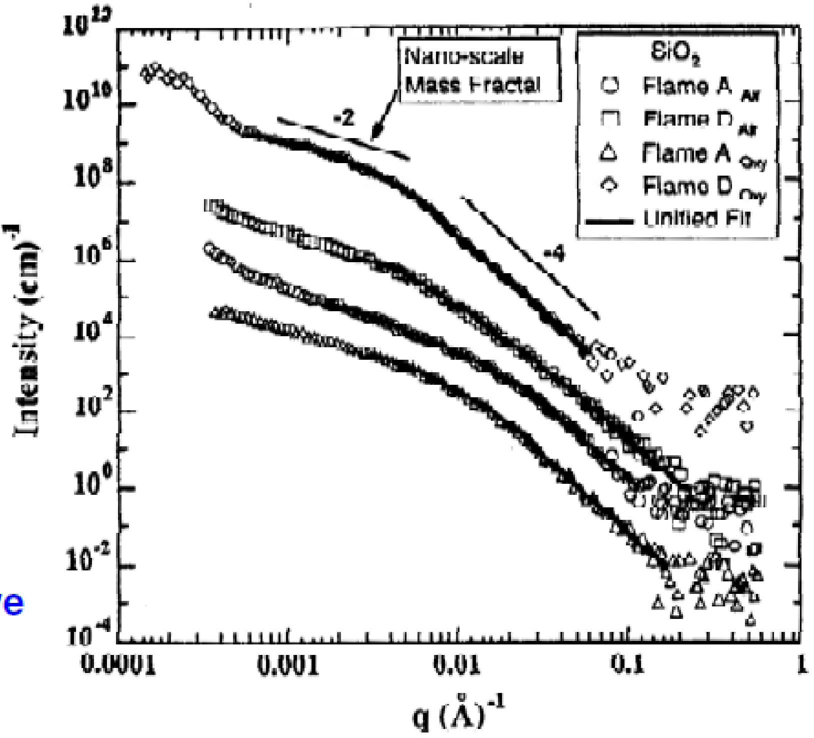
Slopes are meaningful !

Volume or Mass Fractals give Q^{-d} where d ranges:
d = 1 – thin rods,
d ~ 1.8 diffusion limited aggregation (particles stick on first contact)
d ~ 2.1 reaction limited aggregation (some relaxation after sticking)
d = 3 perfectly rough,

Surface fractals give $Q^{-(6-d)}$ where
d = 2 - smooth i.e. Q^{-4} Porod law
up to d = 3 - perfectly rough.

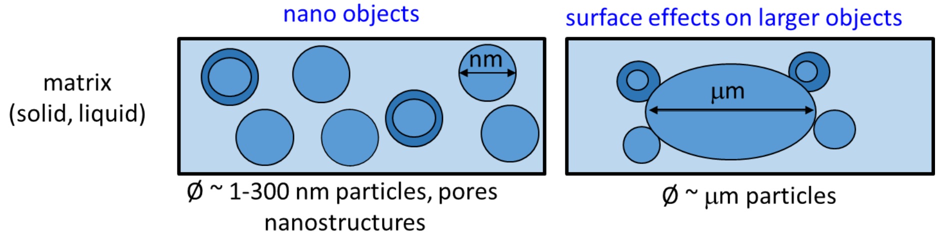
Other scattering laws also give power laws in Q !!! Diffuse interfaces can give steeper than Q^{-4}, to Q^{-6}

Fumed silica aggregates

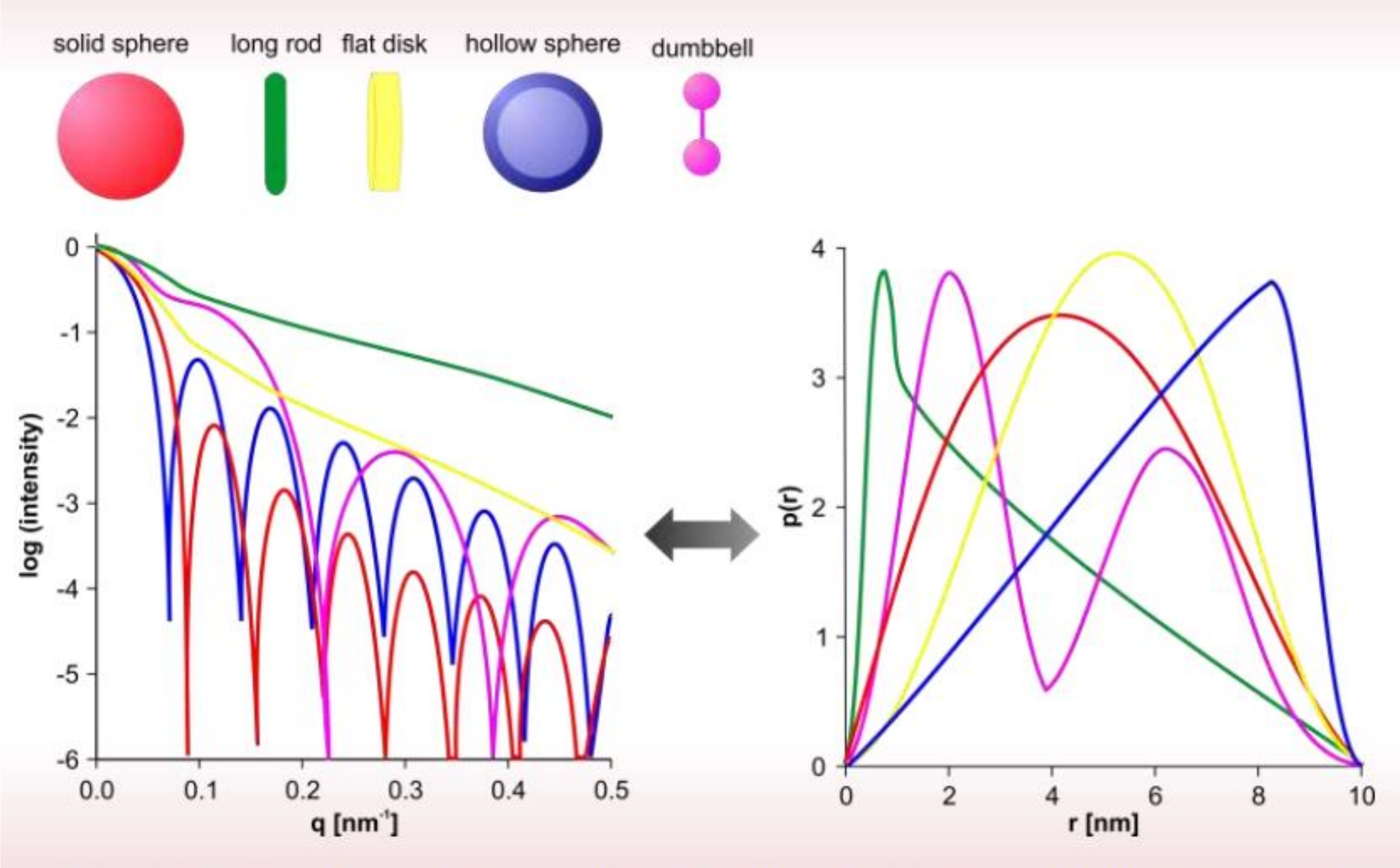


J. Hyeon-Lee, Langmuir 14 (1998) 5751-5756

Form Factors P(Q)

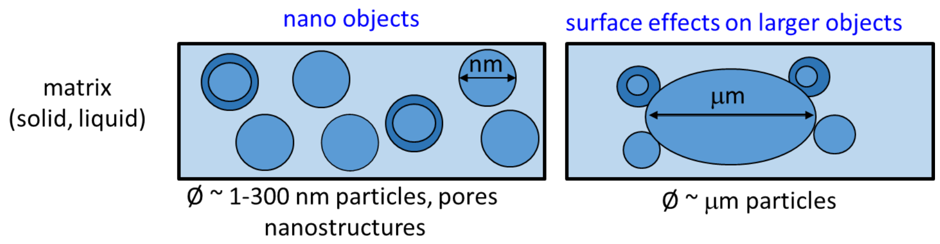


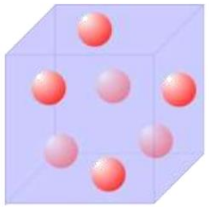
Single objects (diluted suspensions / solutions) have very different SAXS fingerprints

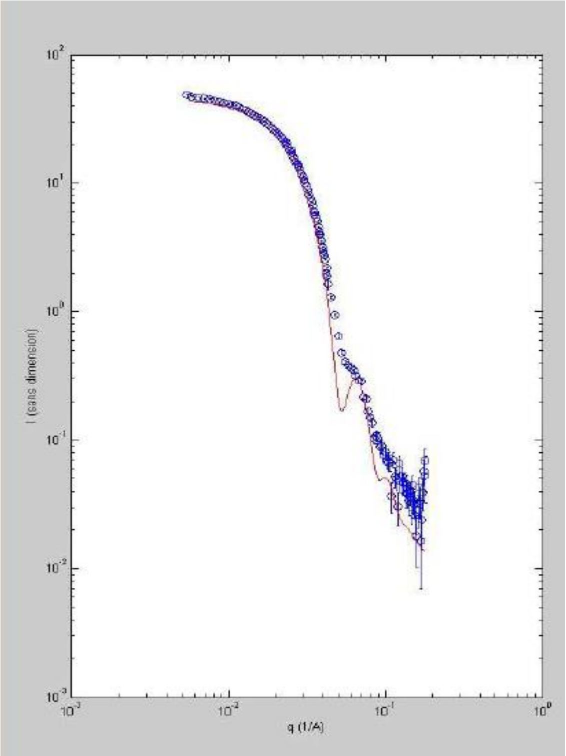


Adopted from Svergun & Koch, "SAS studies of biological macromolecules in solution", Rep. Prog. Phys. 66 (2003) 1735-1782, Fig. 5 (c)l

Form Factors P(Q)







Dilute sample

Modelling : Form factor of sphere 

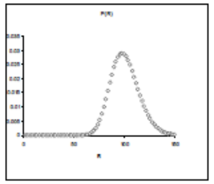
$$P_{sphere}(q, \boldsymbol{R}) = \left[3\,\frac{(\sin(qR) - qR.\cos(qR))}{(qR)^3}\right]^2$$

Calculation of form factor with R ~ 86 Å

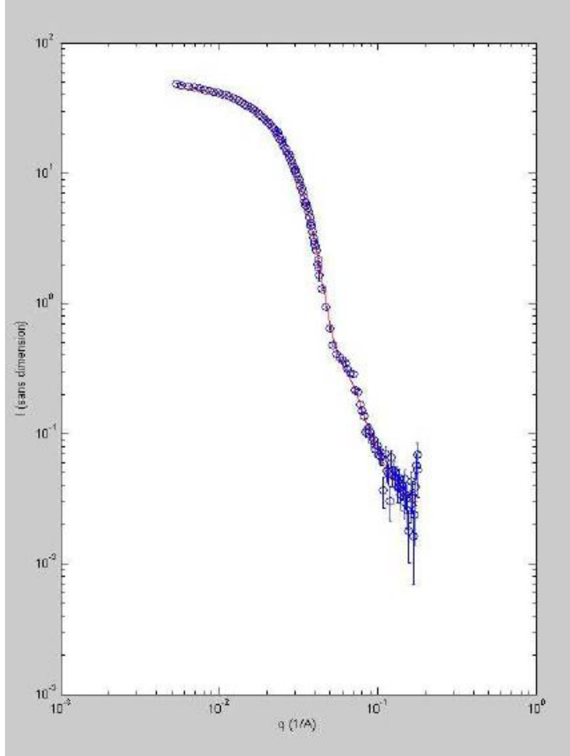
Why oscillations are not reproduced ?

- **Polydispersity**

$$P(R, R_0, \sigma) = \frac{1}{\sqrt{2\pi}R\sigma}\exp\left[\frac{-\ln\left(\frac{R}{R_0}\right)^2}{2\sigma^2}\right]$$



Log normal



Dilute sample

Modelling : Form factor of sphere 

$$P_{sphere}(q, \boldsymbol{R}) = \left[3\,\frac{(\sin(qR) - qR.\cos(qR))}{(qR)^3}\right]^2$$

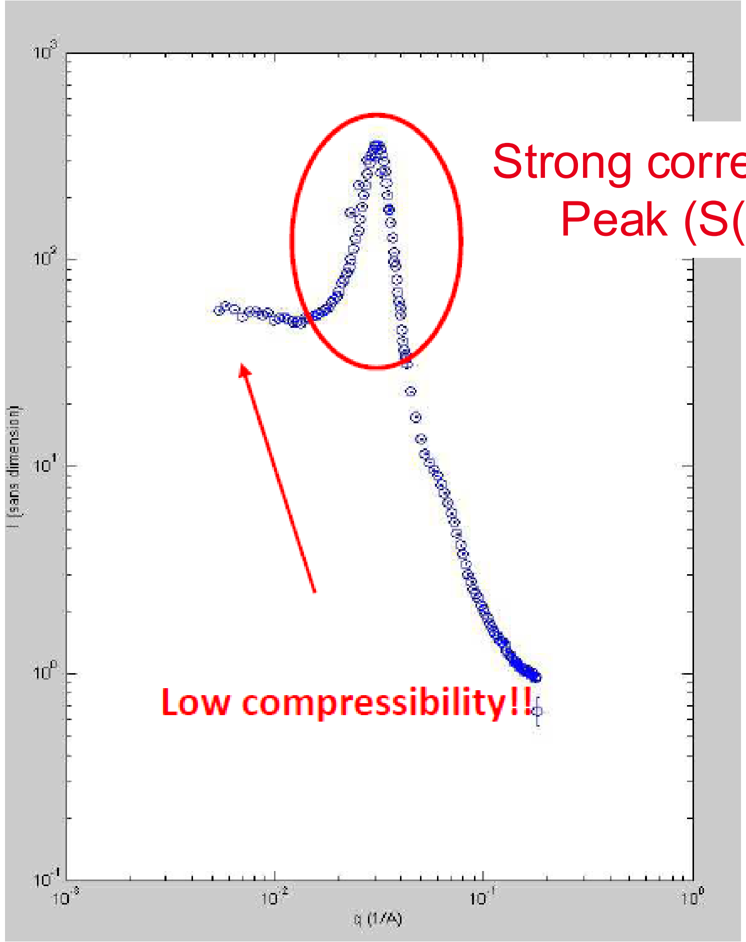
$$P(R, R_0, \sigma) = \frac{1}{\sqrt{2\pi}R\sigma}\exp\left[\frac{-\ln\left(\frac{R}{R_0}\right)^2}{2\sigma^2}\right]$$

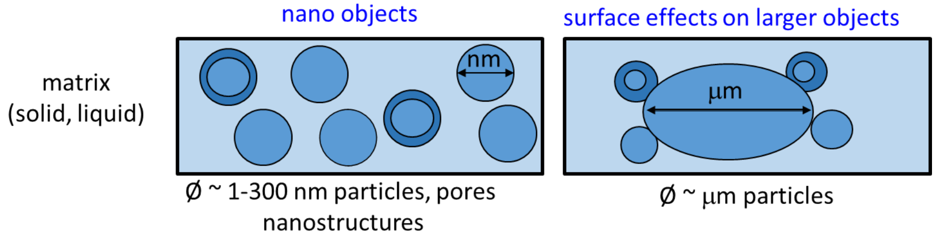
R = 72 Å, σ = 0.23

Courtesy of Fabrice Cousin

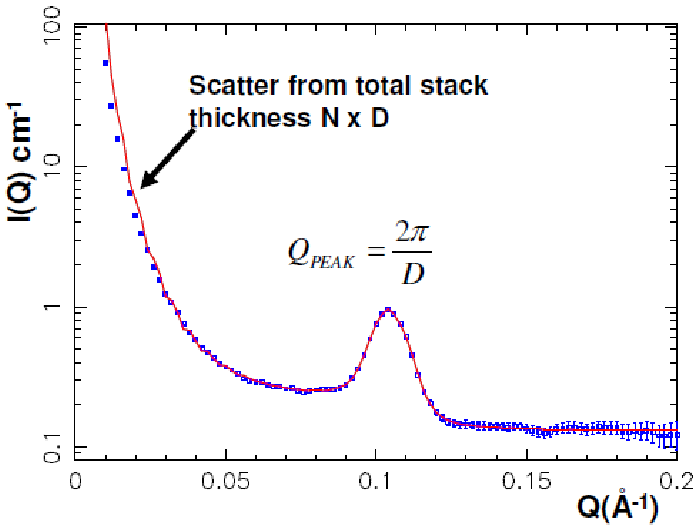
Form Factor P(Q) + Structure Factor S(Q)

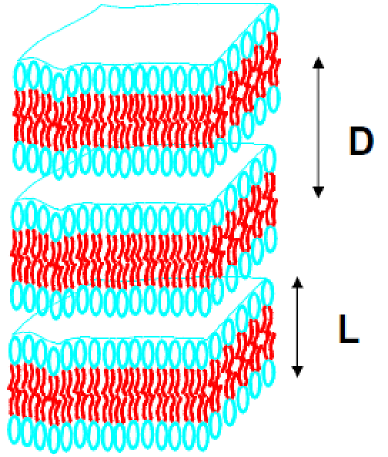
Concentrated solution





Lamellar assemblies
Ex : 3% DPPC lipid in D2O





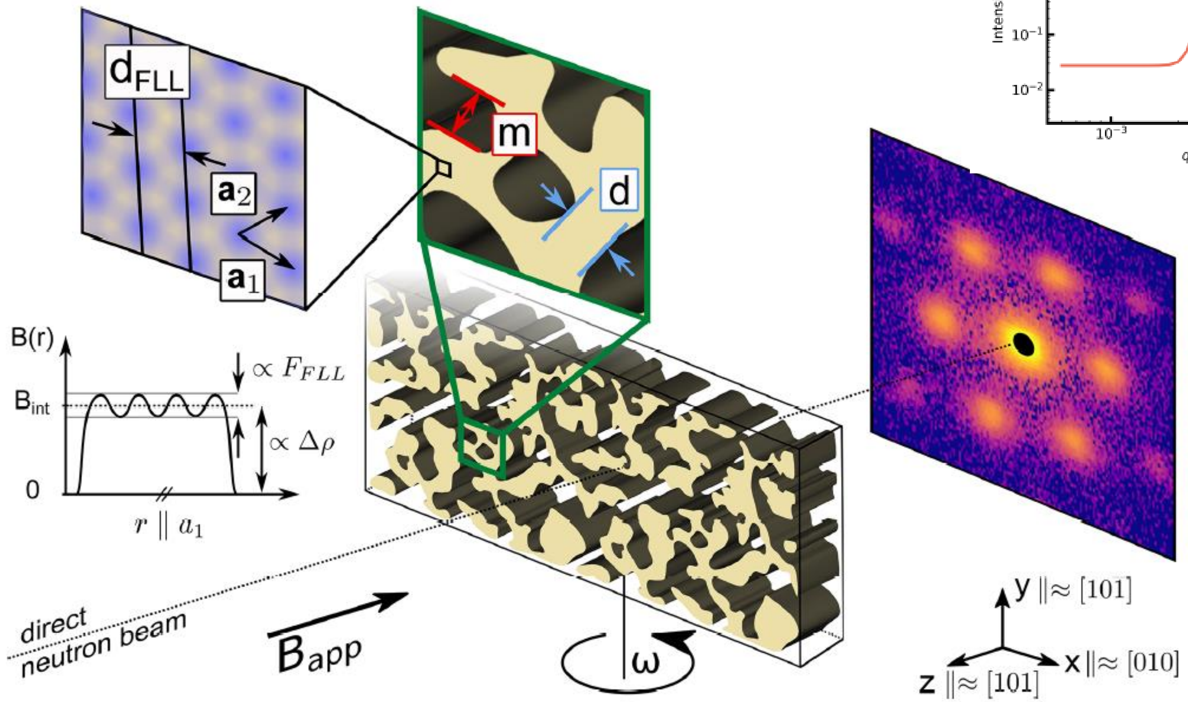
Fit has 18 layers of (L = 4.64nm lipid +1.32nm water) D = 5.96 nm

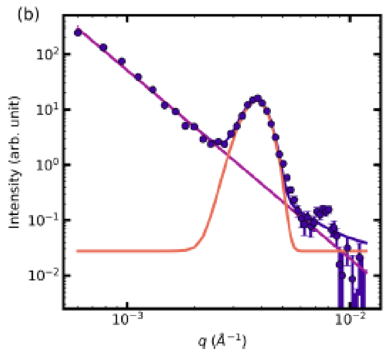
σ_D/D = 7%, σ_L/L = 10% (fixed)

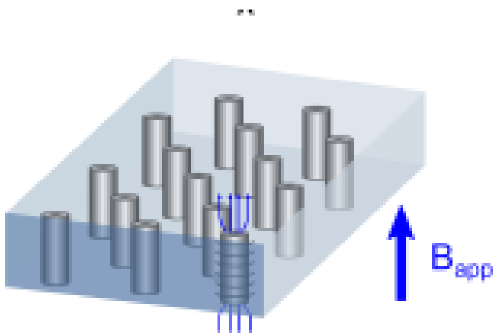
Courtesy of Fabrice Cousin

Form Factor P(Q) + Structure Factor S(Q)

Side note: SANS crystallography. Bragg peaks, but not just :)







d~100-200 nm → SANS

Tunable crystal structure (T, B)
Extract Vortex Lattice structure
Extract size of well-ordered domains

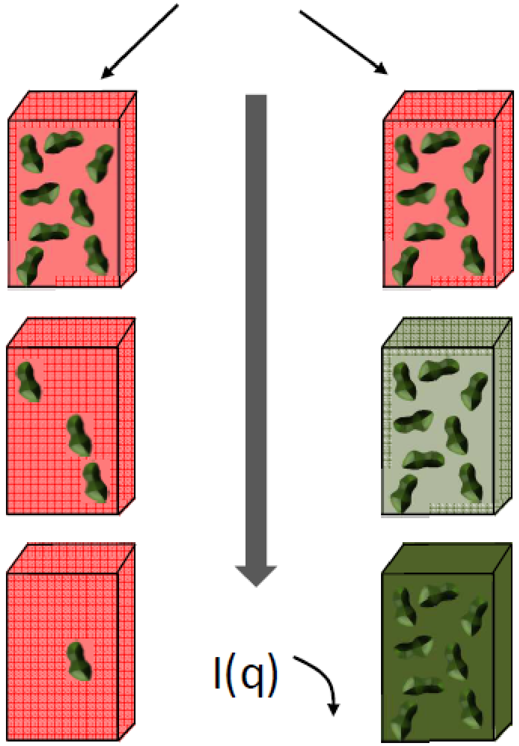
Track for different T, B, and also current

X.S. Brems et al. J. Appl. Cryst. (2024). 57, 1358–1372

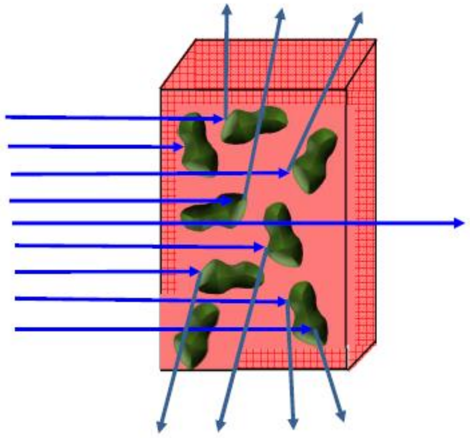
Practicalities

Samples must be concentrated enough (but not too much)
with a sufficient contrast

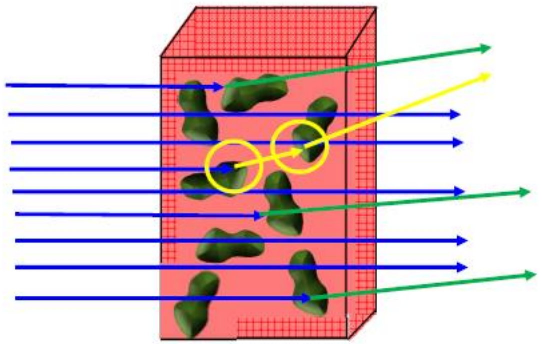
$I(Q) \sim n.\Delta\rho^2.P(Q).S(Q)$



Incoherent scattering ?

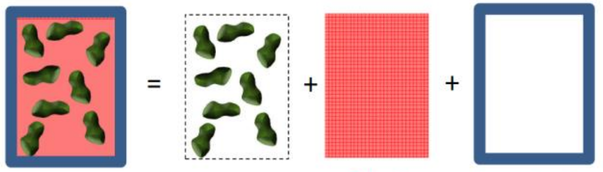


Multiple scattering ?



Adapt sample thickness

1) Choose X vs N
2) Choose set-up
3) Choose sample environment



Calculate SLD prior to experiment

$$\rho_i = \sum_i \frac{b_i}{V} \qquad V = \frac{d.N_A}{M} \qquad V_{H_2O} = \frac{M_{H_2O}\bar{v}_{H_2O}}{N_A}$$

b_H=-0.374 10^{-12} cm; b_D=0.667 10^{-12} cm; b_O=0.580 10^{-12} cm

H_2O

$$\rho_{H_2O} = \frac{2b_H + b_O}{V_{H_2O}} = \frac{(5.81 - 3.74 \cdot 2)\,fm}{30\,\AA^3}$$

$$\rho_{H_2O} = -0.56 \cdot 10^{10}\,cm^{-2}$$

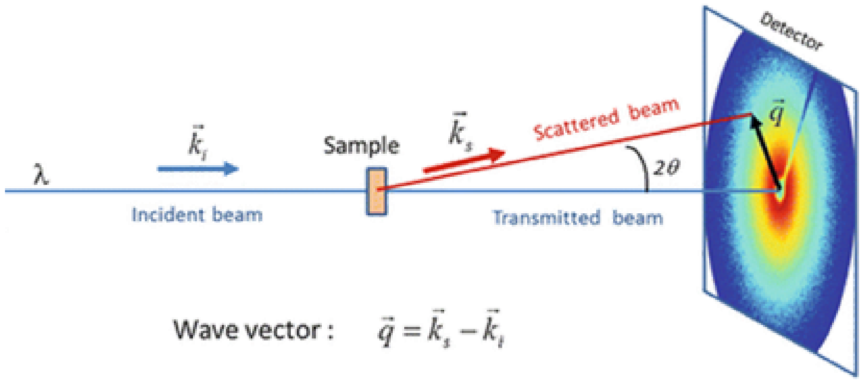
D_2O

$$\rho_{D_2O} = \frac{2b_D + b_O}{V_{H_2O}} = \frac{(6.67 \cdot 2 + 5.81)\,fm}{30\,\AA^3}$$

$$\rho_{H_2O} = 6.38 \cdot 10^{10}\,cm^{-2}$$

Courtesy of Fabrice Cousin

Practicalities

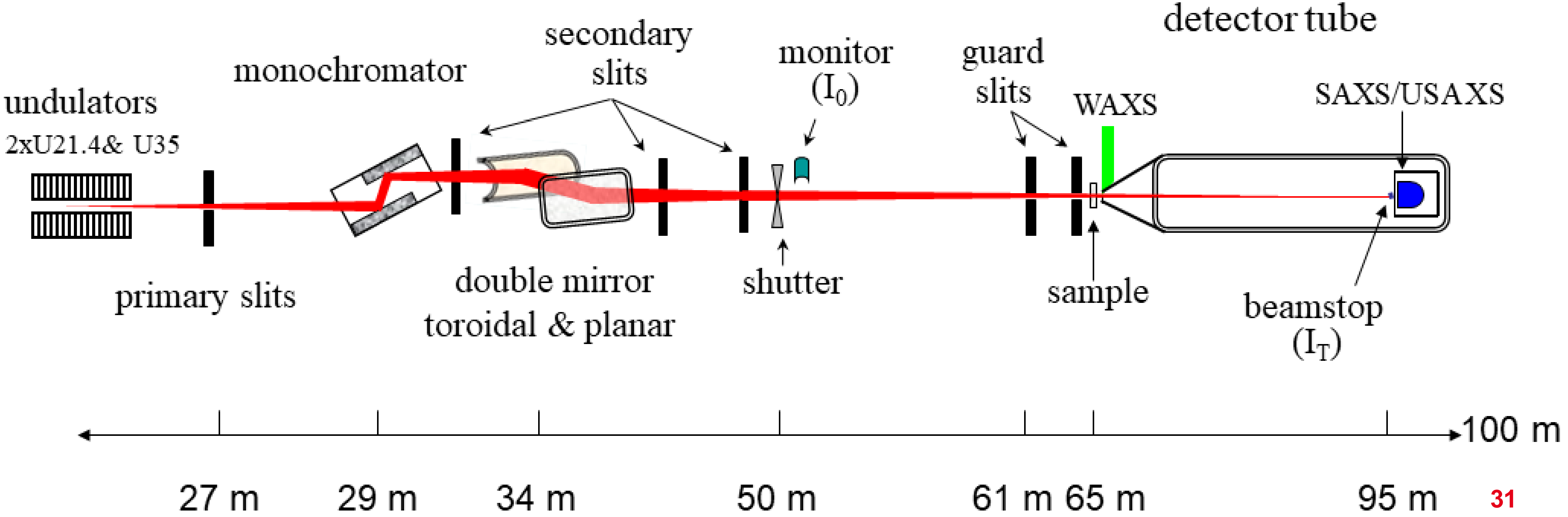


Lab-SAXS

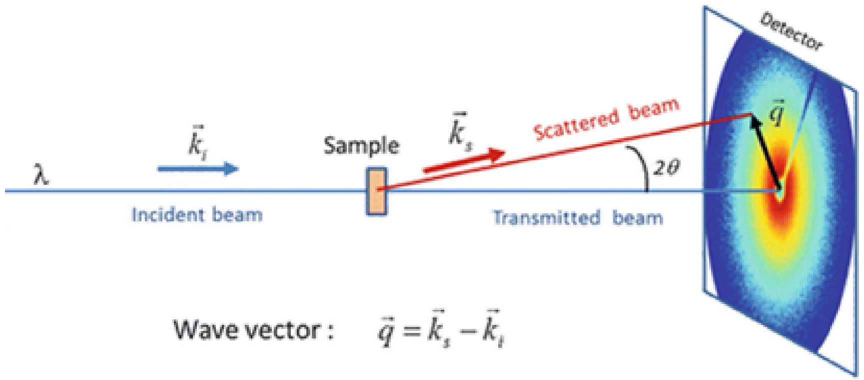
Synchrotron SAXS

ID02

ESRF
The European Synchrotron



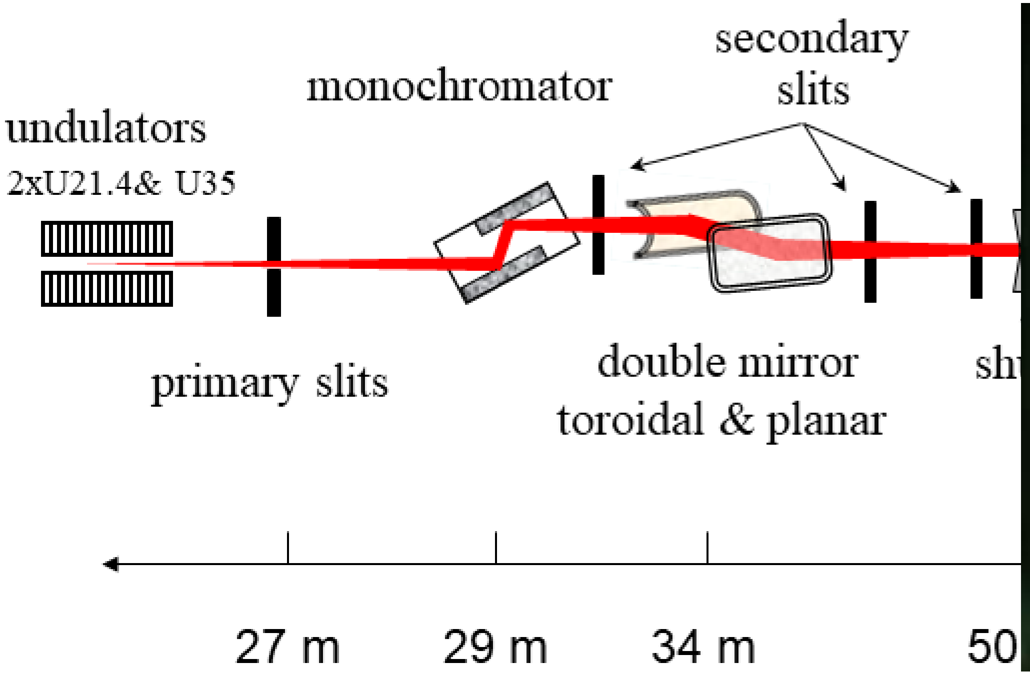
Practicalities



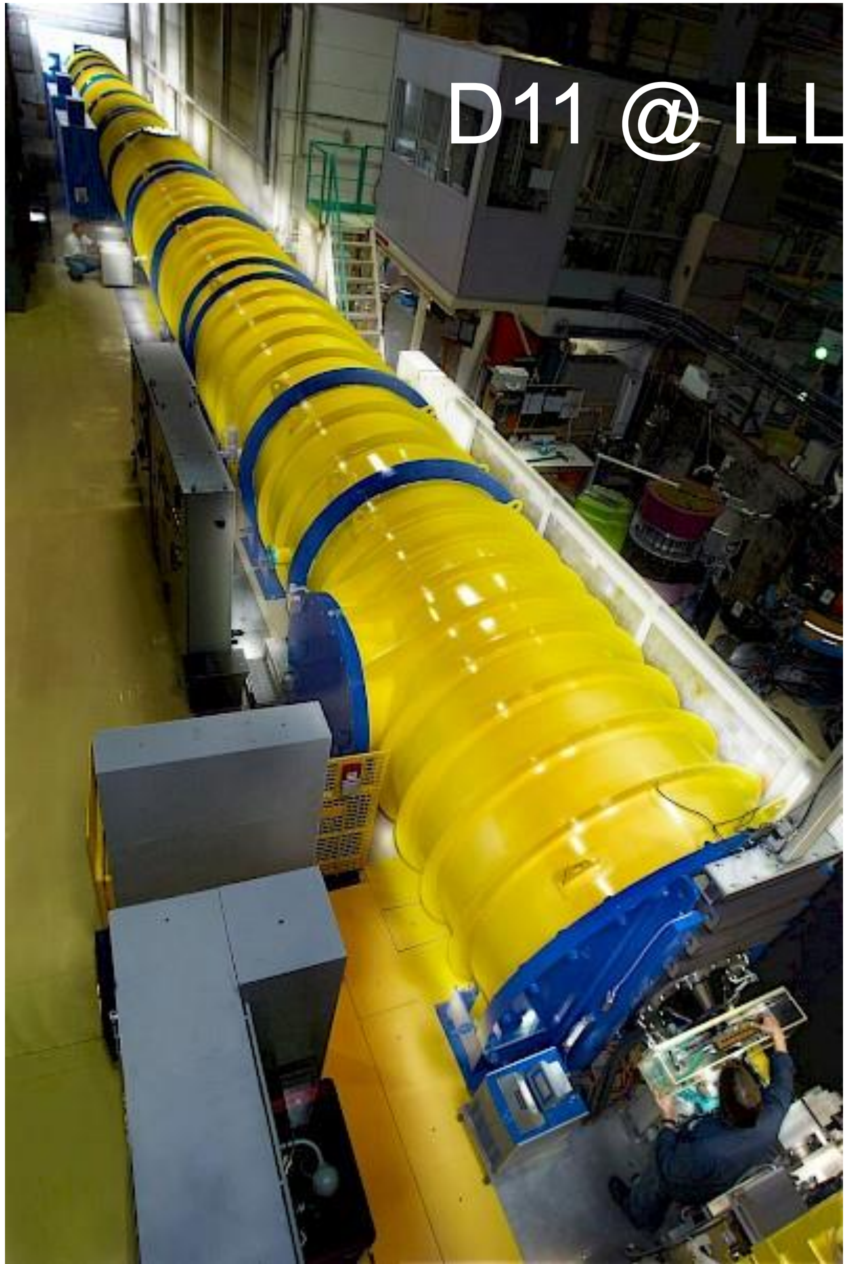
Lab-SAXS

Synchrotron SAXS

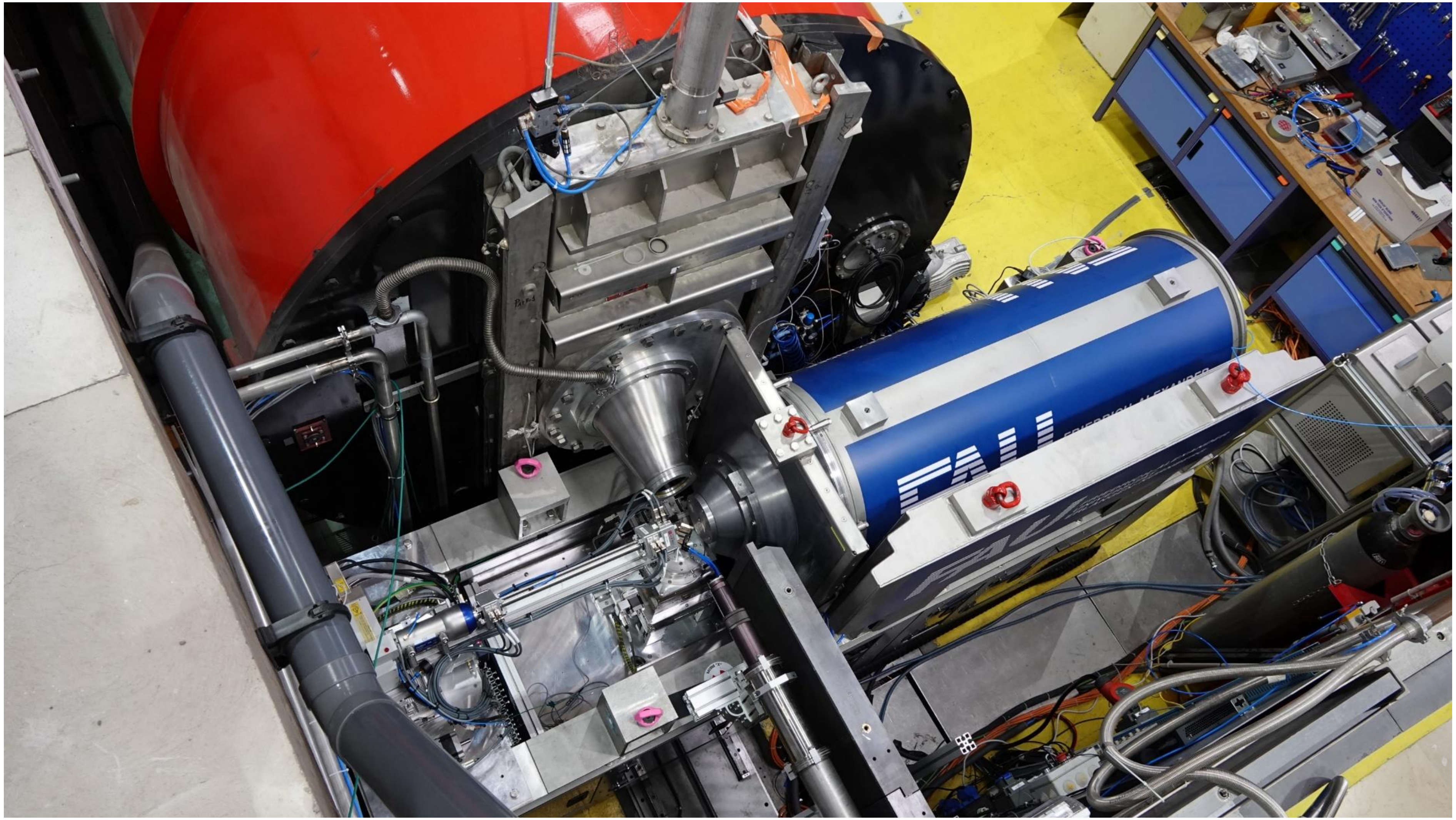
ID02



Practicalities



Coupled SAXS/SANS



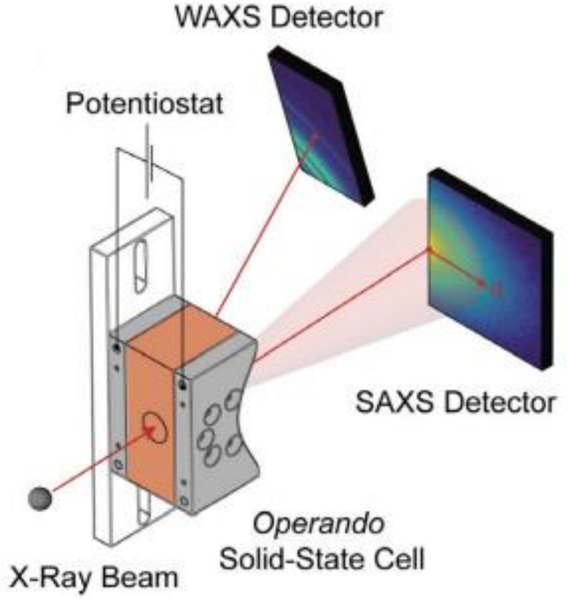
D22 spectrometer

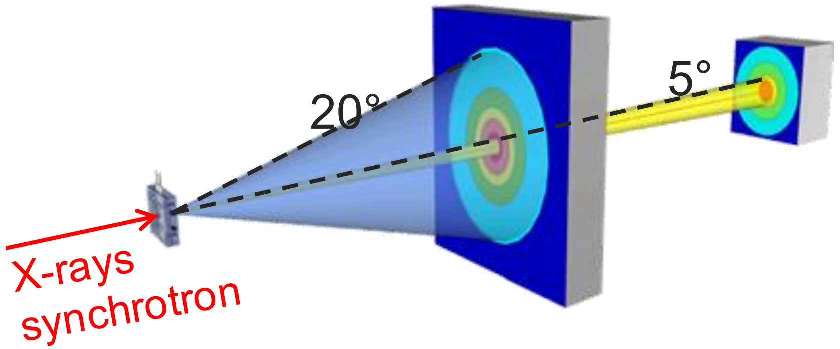
NEUTRONS FOR SOCIETY

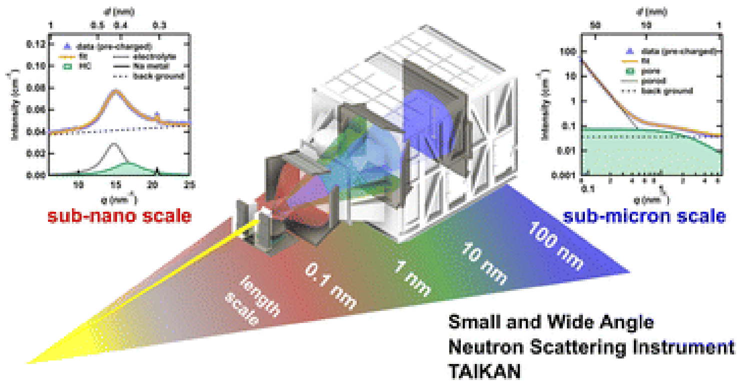
FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

E. Metwalli, .., T. Unruh, *J. Appl. Cryst.* **53**, *722* (2020)

Coupled SAXS/WAXS and SANS/WANS





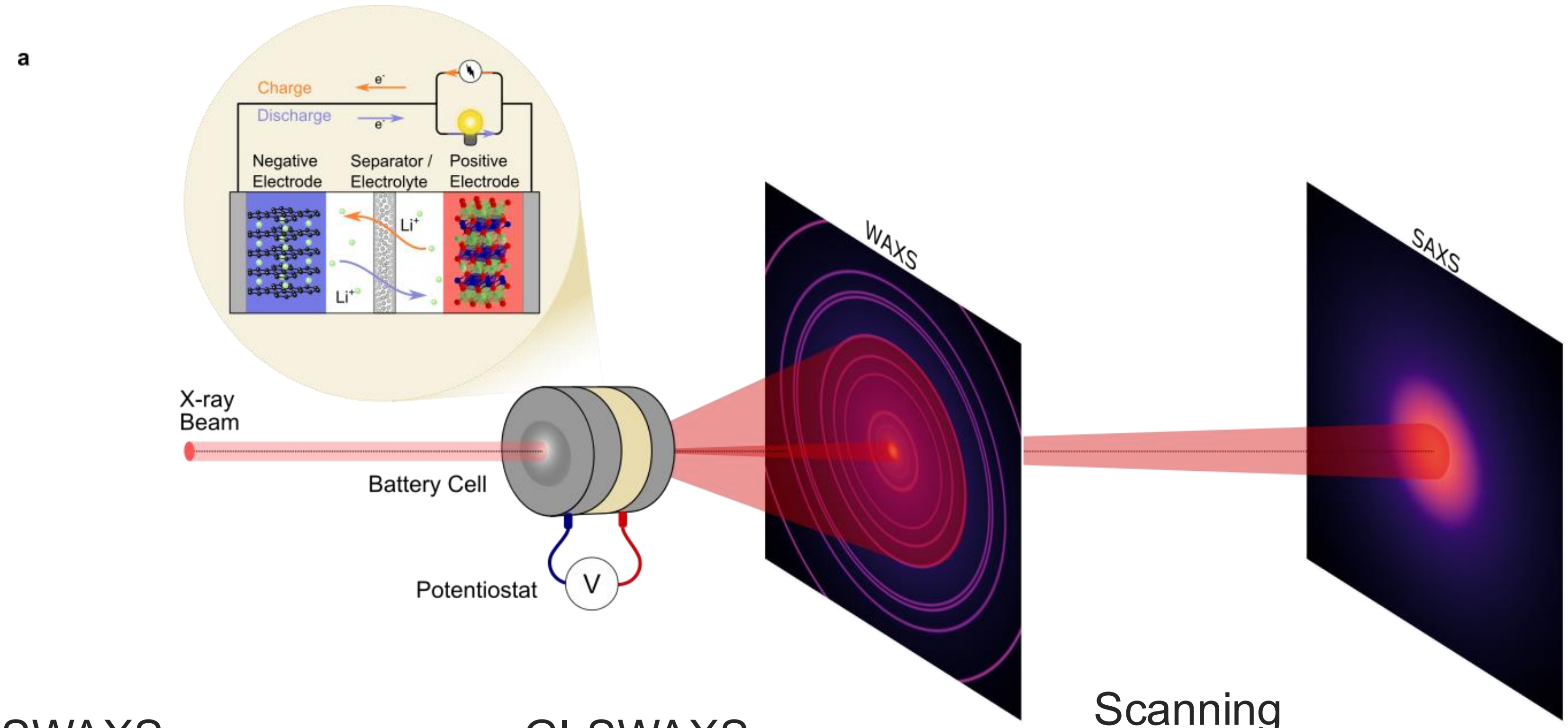


J-M. Von Mentlen et al, Batteries and supercaps, 2025, e202500428

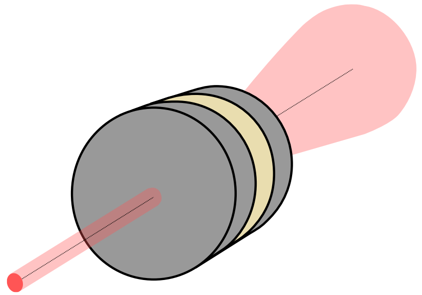
C. Berhaut *et al*, ACS Nano (2019), 13, 10, 11538-11551

Y. Umemoto *et al*, Chem. Sci., 2026, Advance Article, 10.1039/d5sc09600f

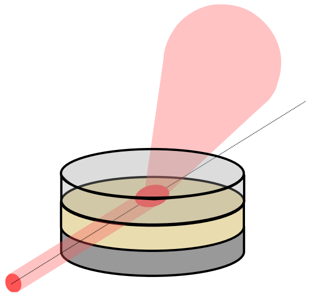
Measurement Modalities



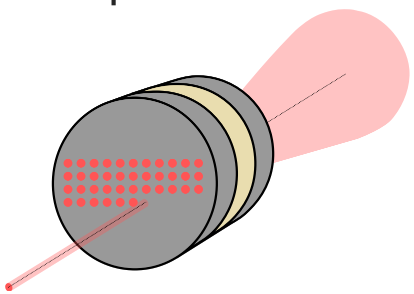
SWAXS



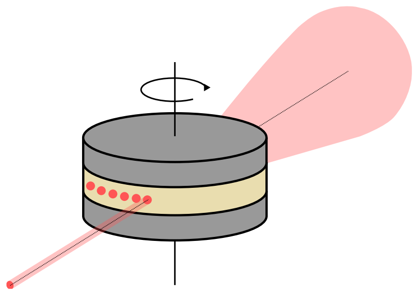
GI-SWAXS



Scanning µSWAXS



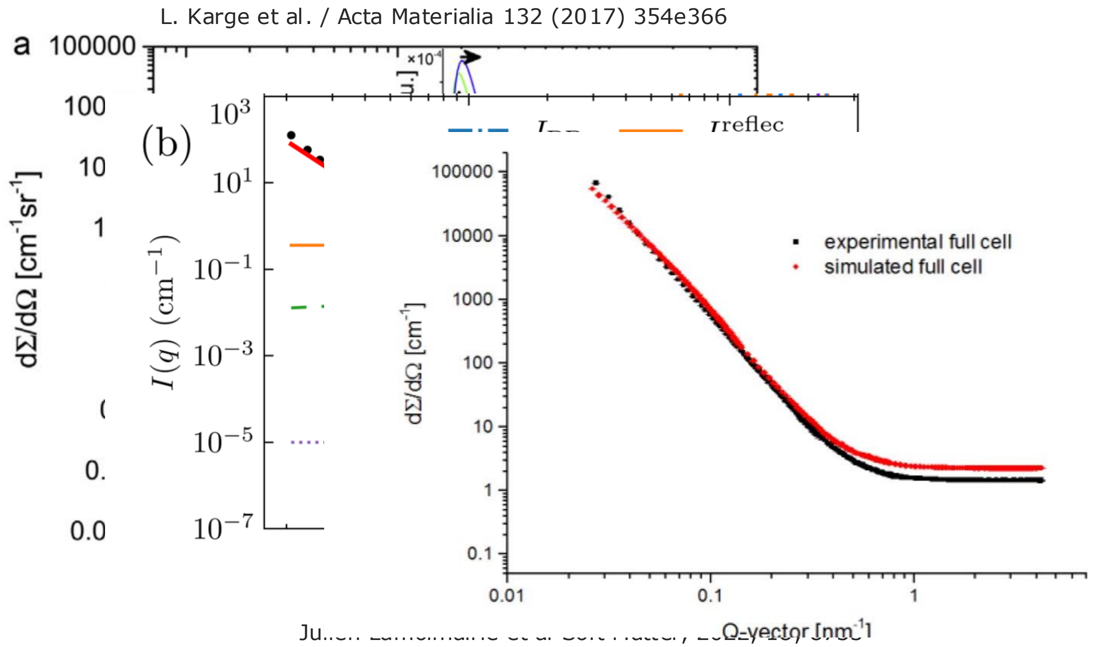
Tomography SWAXS-CT



Need small beams, so mostly limited to X-Rays

X. S. Brems, M. Olsson, A. Matic, S. Lyonnard, Operando SWAXS for batteries, JPhys Energy, in revision

SAXS/SANS in batteries...not always easy !



Stefan Seidlmayer et al 2015 J. Electrochem. Soc. 162 A3116

sans
/sanz/
preposition LITERARY • HUMOROUS
without.

SANS and SAXS features are subtle
Need complementary / background info
Analysis is not always straightforward

BUT SANS/SAXS can give acces to:

- Nanostructural changes
- Particle morphology (size, shape, layers, etc)
- Chemical information (SLD variation)
- Sample average: statistically relevant

Few reviews

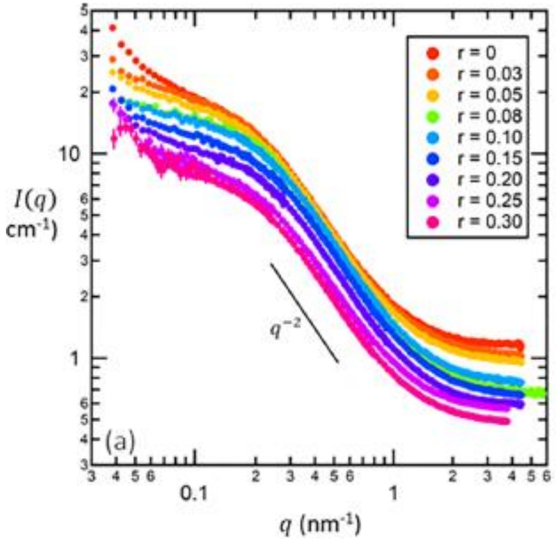
A. Black et al, Synchrotron radiation based operando characterization of battery materials, Chem. Sci., 2023, 14, 1641

L. Fang et al, Synchrotron small-angle X-ray scattering technique for battery electrode study, Nano Energy, 2024, 121, 109255

W. Cheng et al, Recent advances in battery characterization using in situ XAFS, SAXS, XRD, and their combining techniques: From single scale to multiscale structure detection, Exploration, 2023, DOI: 10.1002/EXP.20230056

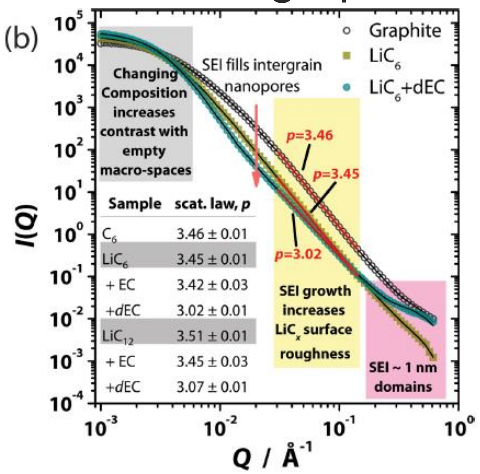
Main applications of SAXS/SANS in batteries

Polymer (blends, composites)



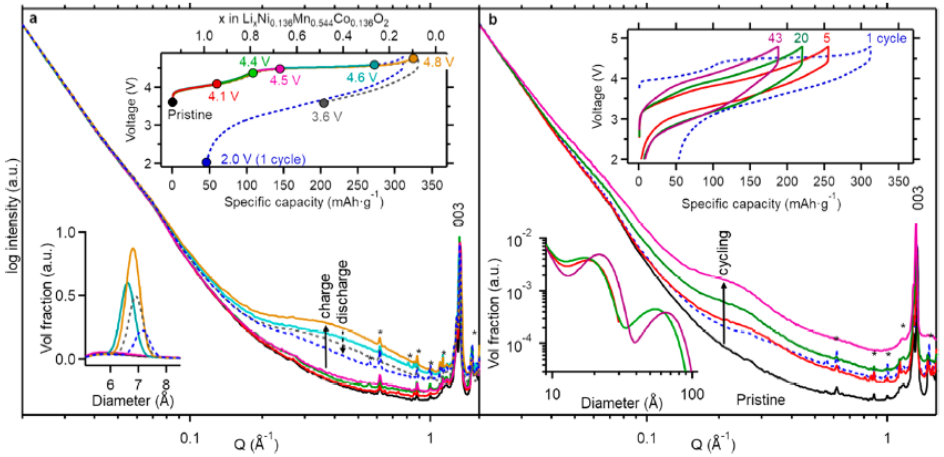
W.S. Loo et al, Macromolecules 2019, 52, 8724−8732

SEI on graphite



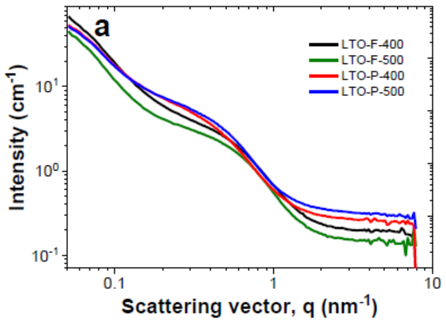
R.L. Sacci et al, J. Phys. Chem. C 2015, 119, 9816−9823

LNMO



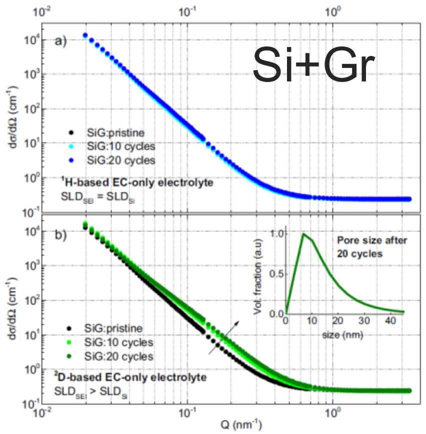
Grenier et al, https://doi.org/10.1021/jacs.1c00497

LTO interfaces



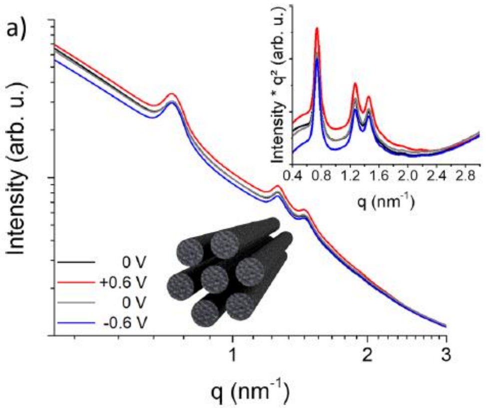
C.J. Jafta et al, 10.1002/cssc.202000802

Si+Gr



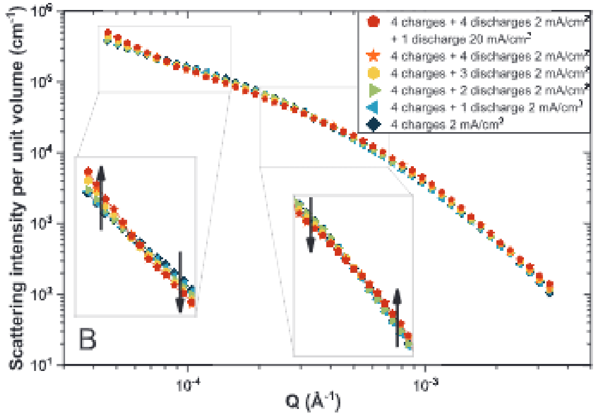
N. Paul et al, Journal of The Electrochemical Society, 166 (6) A1051-A1054 (2019)

Porous Carbon



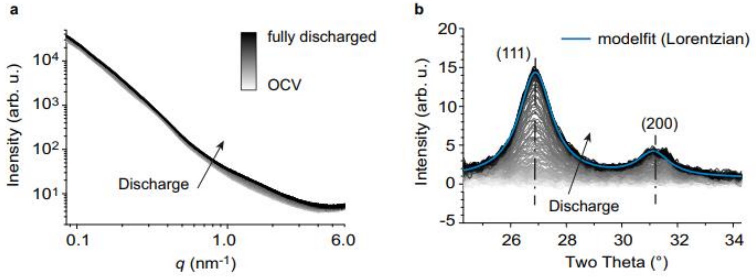
C. Kocswara et al, ACS Appl. Mater. Interfaces 2019, 11, 42214−42220

Lithium metal batteries



C. Didier et al, Adv. Energy Mater. 2023, 13, 2301266

Lithium sulphur batteries



C. Prehal et al, Nature Communications | (2022) 13:6326

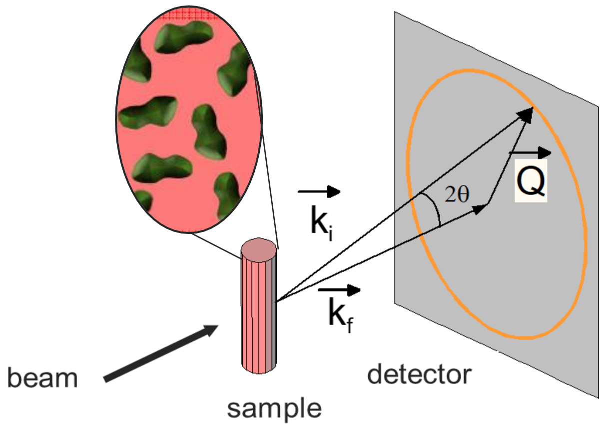
Outline

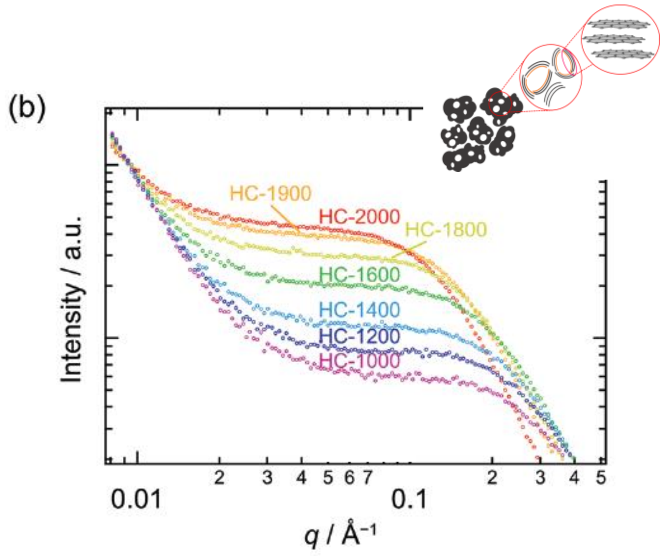
❖ **I – SAS TUTORIAL**

Basic principle of Small Angle Scattering techniques (SAXS, SANS)

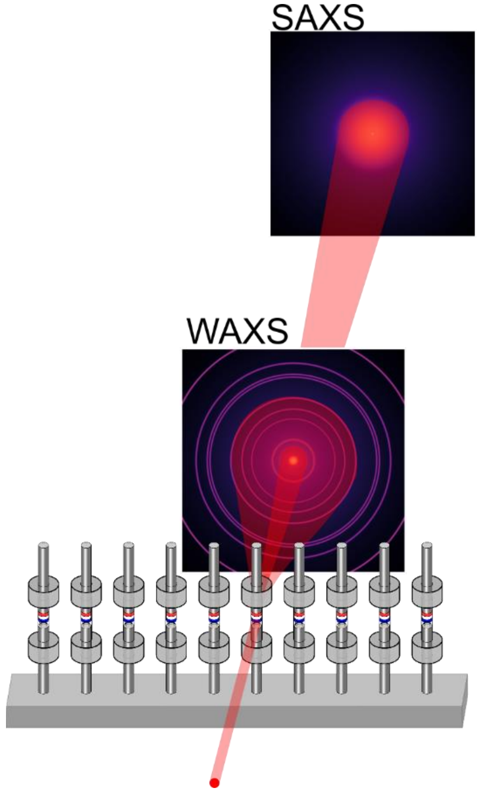
❖ **II – APPLICATION to battery research**

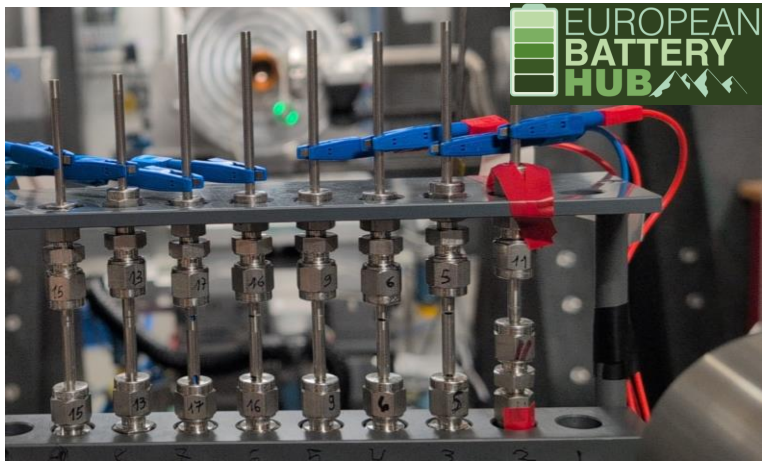
Operando SAXS study of HC electrodes for Na-ion batteries





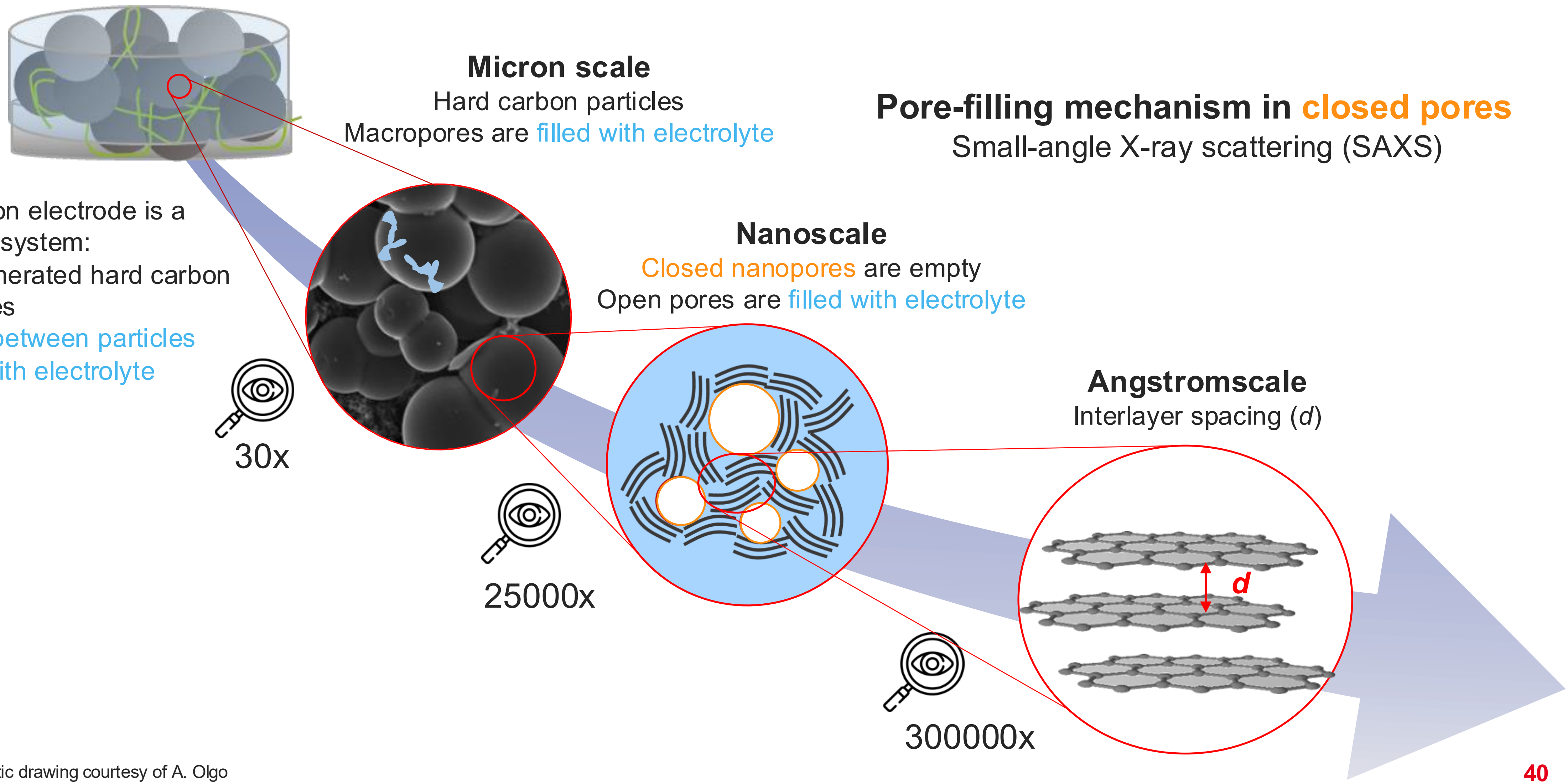
Morikawa et al, Adv. Energy. Materials





Hard Carbon as negative electrodes for Na-ion Batteries

(100 µm)

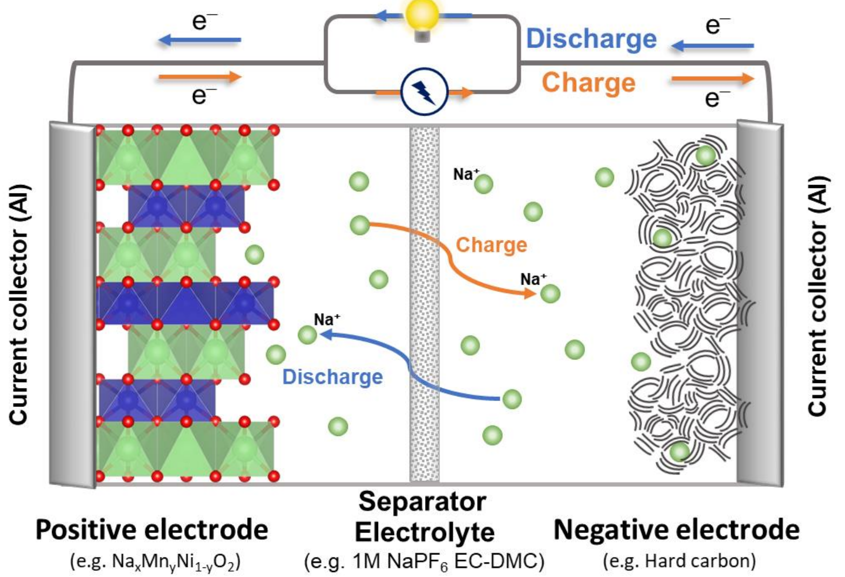


Hard carbon electrode is a multiscale system:

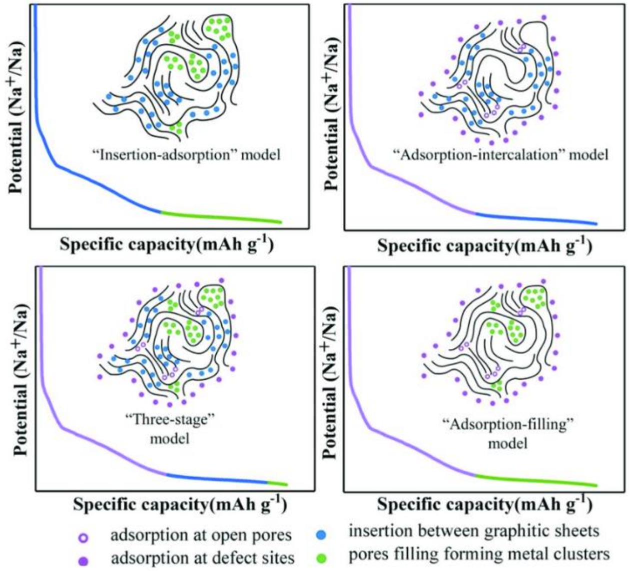
- Agglomerated hard carbon particles
- Voids between particles filled with electrolyte
- Binder

Schematic drawing courtesy of A. Olgo

Hard Carbon as negative electrodes for Na-ion Batteries



Hard Carbons:
- Hierarchical structure
- Several Na mechanisms proposed
- Depend on the HC type
- No true consensus in litterature



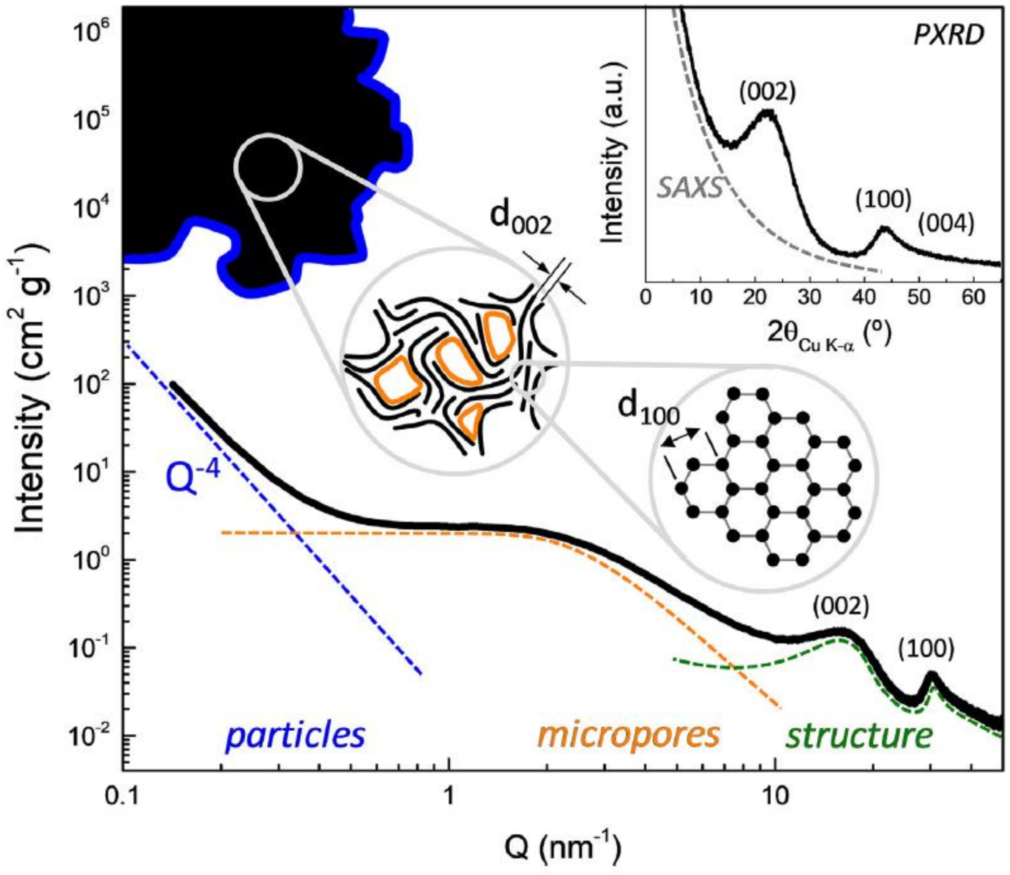
Key Topics / interests:
- HC structure-performance relationship
- Sodiation mechanims of different HC / HC composites
- Influence of different electrolyte formulations
- Influence of different C-rates

Common Hub Workflow to tackle these questions

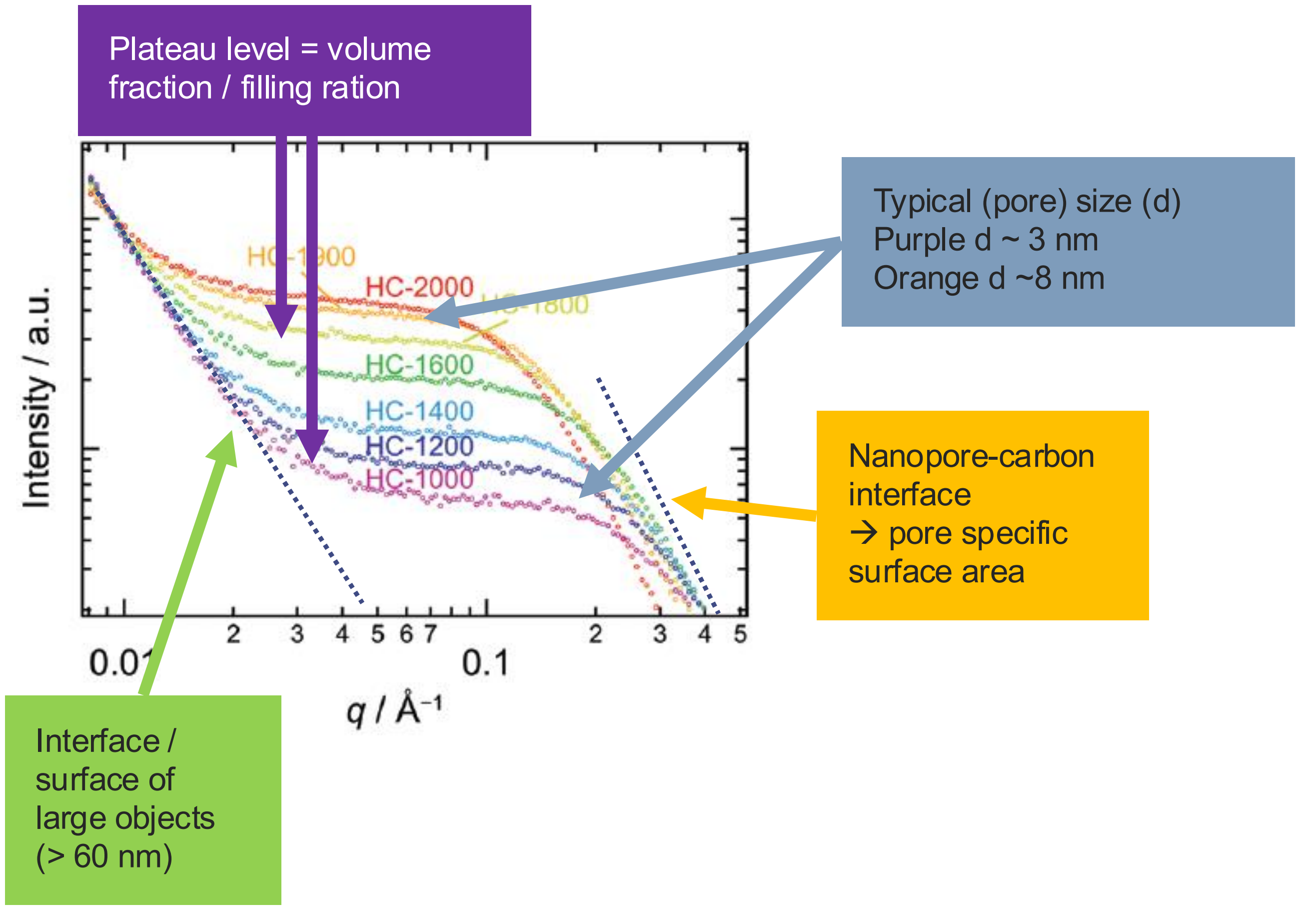
EUROPEAN BATTERY HUB

Tool:
SAXS → HC pores (nm)
WAXS → crystalline changes

Hard Carbon SAXS Pattern

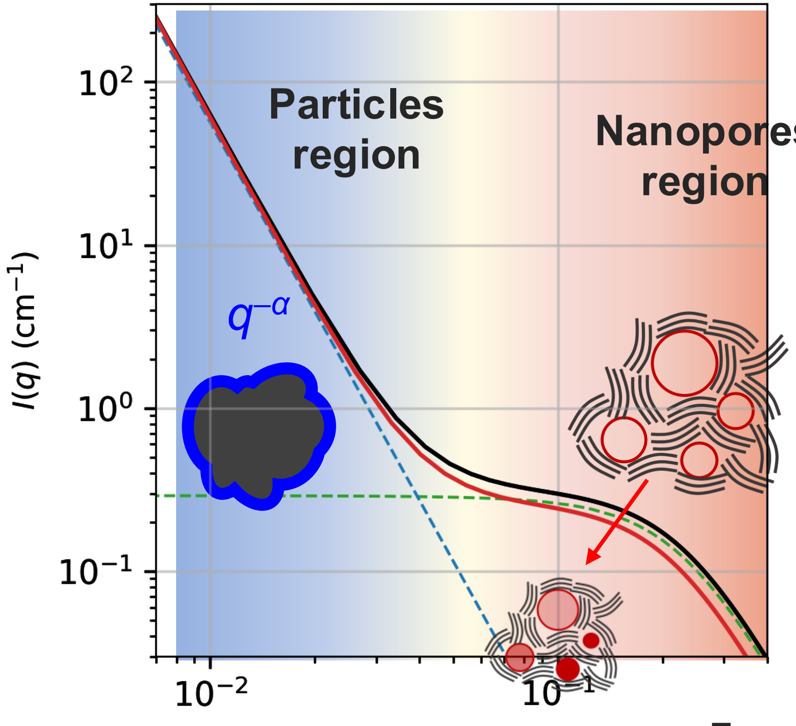


D. Saurel et al. Energy Storage Materials 21 (2019) 162–173



Morikawa et al., *Adv. Energy Mater.* **2020**, *10*, 1903176

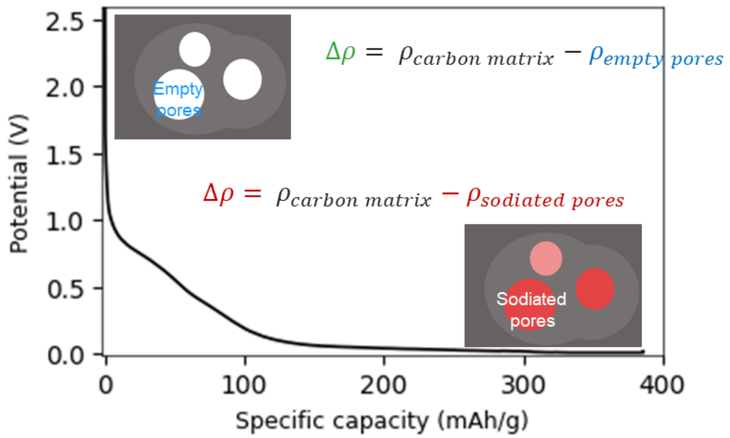
What happens during the charge/discharge?



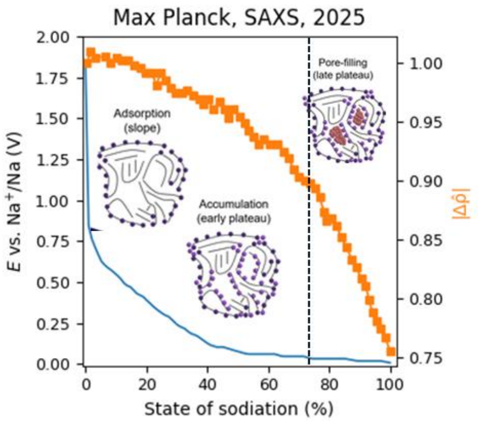
Two-phase system in nanopores region

$\Delta\rho_{pristine\ HC} = \rho_{carbon\ matrix} - \rho_{empty\ pores}$

$$I(q) \propto \Delta\bar{\rho}^2$$

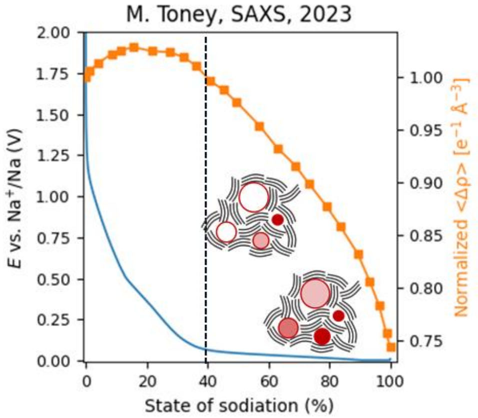


Track pore filling via SLD contrast Δρ



Spatial in plane heterogeneities

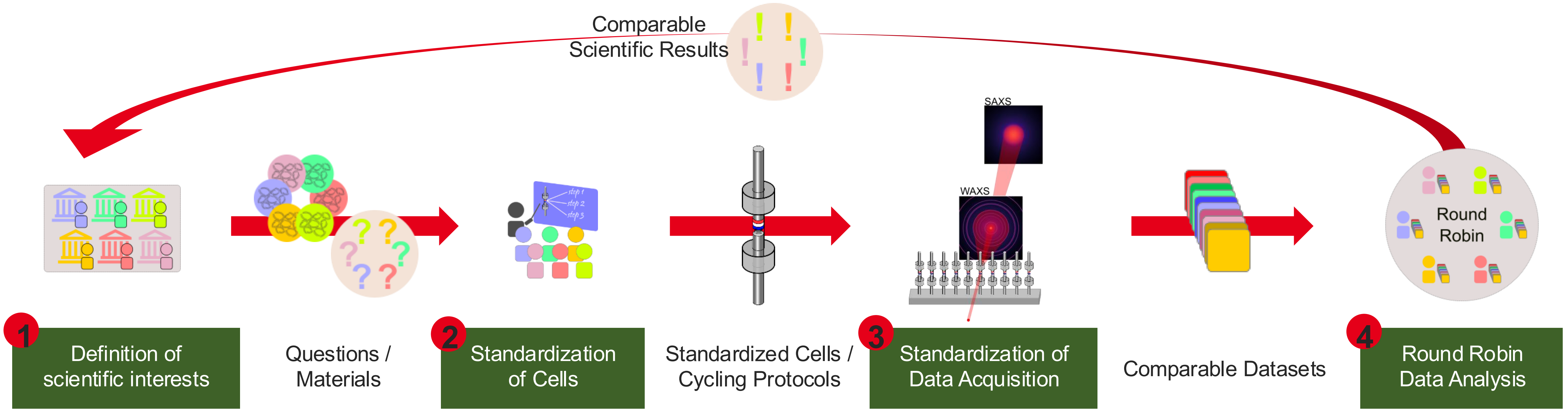
Eren et al., Energy Environ. Sci., 2025, 18, 7859–7868



Pore-size dependent pore filling

Iglesias et al., Adv. Energy Mater. 2023, 13, 2302171

operando Scanning SAXS/WAXS Workflow of Hard Carbons and Hard Carbon Composites



Fall 2024: Start of Hub / Begining of Discussions

March 2025: SAXS/WAXS Proposal

Aug. / Sept 2025: Tutorial & Workshop

Oct. 2025: *operando* scanning SAXS/WAXS experiment

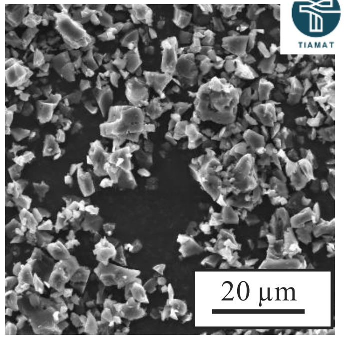
Since Fall 2025: Ongoing collaborative data analysis

X. S. Brems, G. Navallon, A. Olgo, J. Togonon. G. Gammaitoni, I. Drevander, S. Dovren, S. Zhang, Y. Zoizou, V. Vinci, J. Ruellou, A. Matic, J. Maibach, M. Bianchini, L. Daniel, L. Simonin, M. Zarrabeitia, J. Drnec, S. Lyonnard; operando scanning SWAXS workflow of hard carbon based electrodes for Na-ion batteries; in preparation.

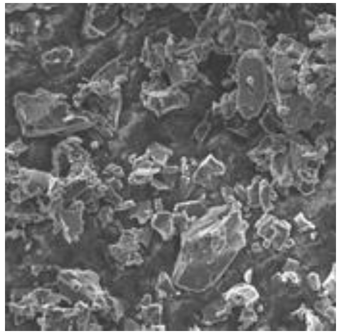
operando Scanning SAXS/WAXS Workflow of Hard Carbons and Hard Carbon Composites

Hard Carbons

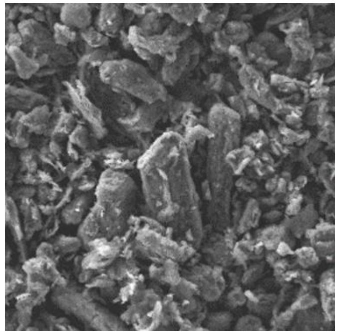
IRIG (Tiamat)



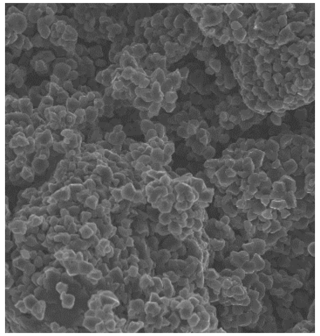
CTH



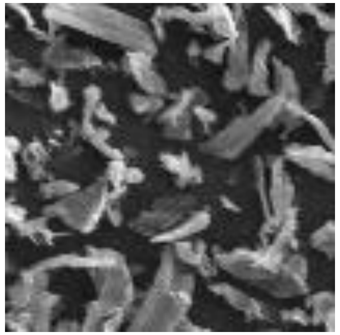
HIU



LITEN

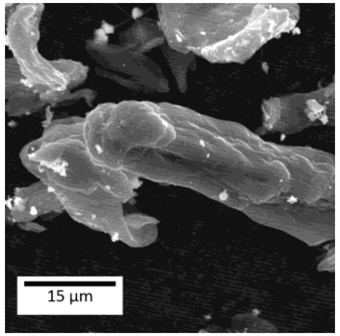


UBT

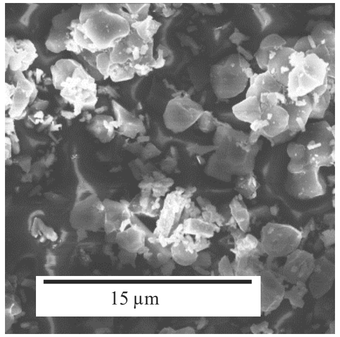


Composites

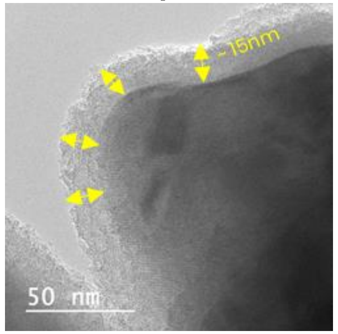
UBT HC+Sn



LITEN HC+NTO



LITEN pure NTO



Electrolytes

- Carbonate
- Diglyme
- Monoglyme
- Carb. + additives

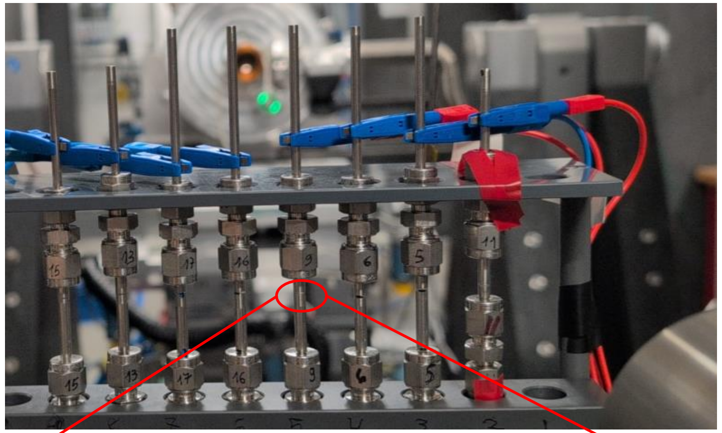
Counter electrode

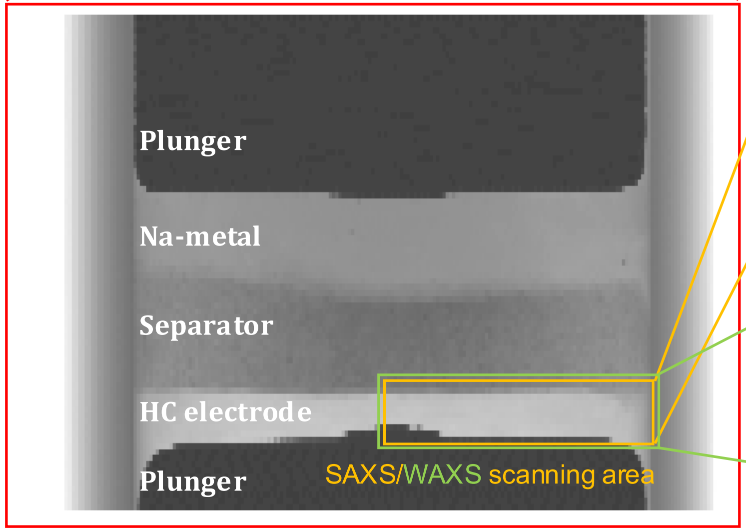
- Na metal

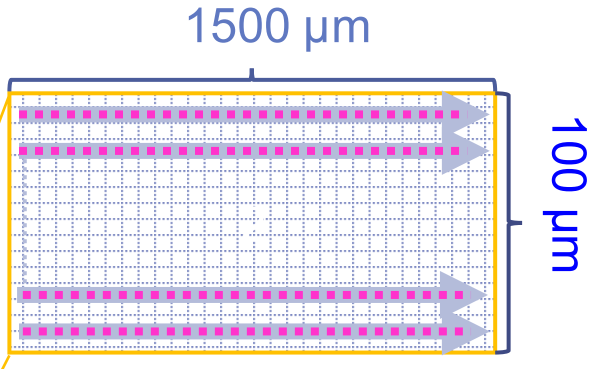
Other

- Beam damage

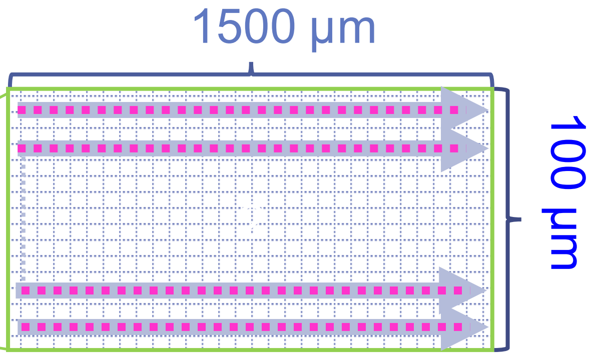
operando Scanning SAXS/WAXS Workflow of Hard Carbons and Hard Carbon Composites



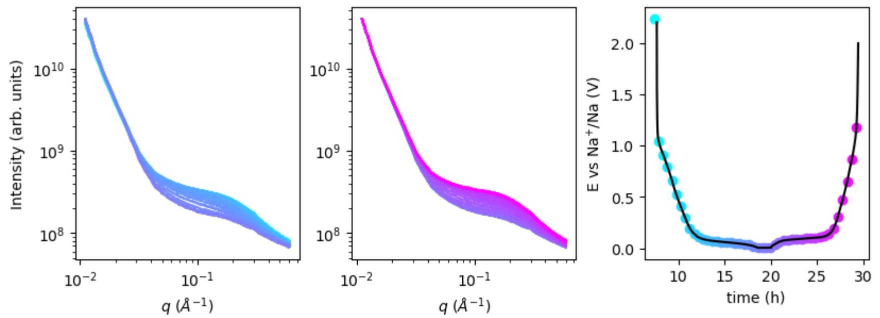




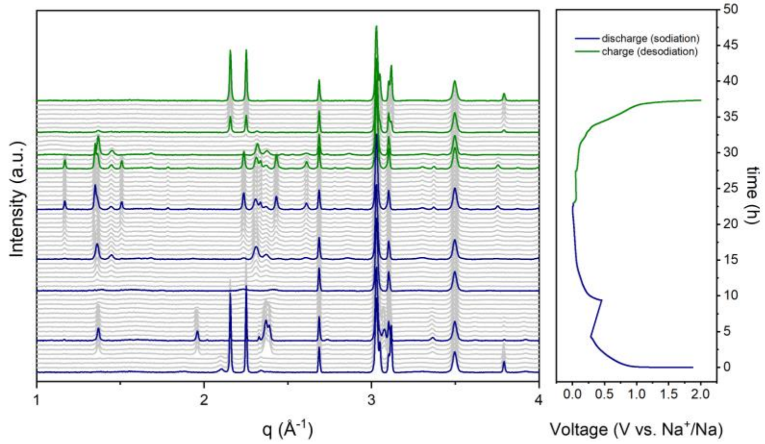
E = 75 keV
Beam size: 20 x 8 μm^2
(y,z) map of 225 pixels
Pixel size : 60 x 8 μm^2
1 map in 1 minute



SAXS (for pure HC)

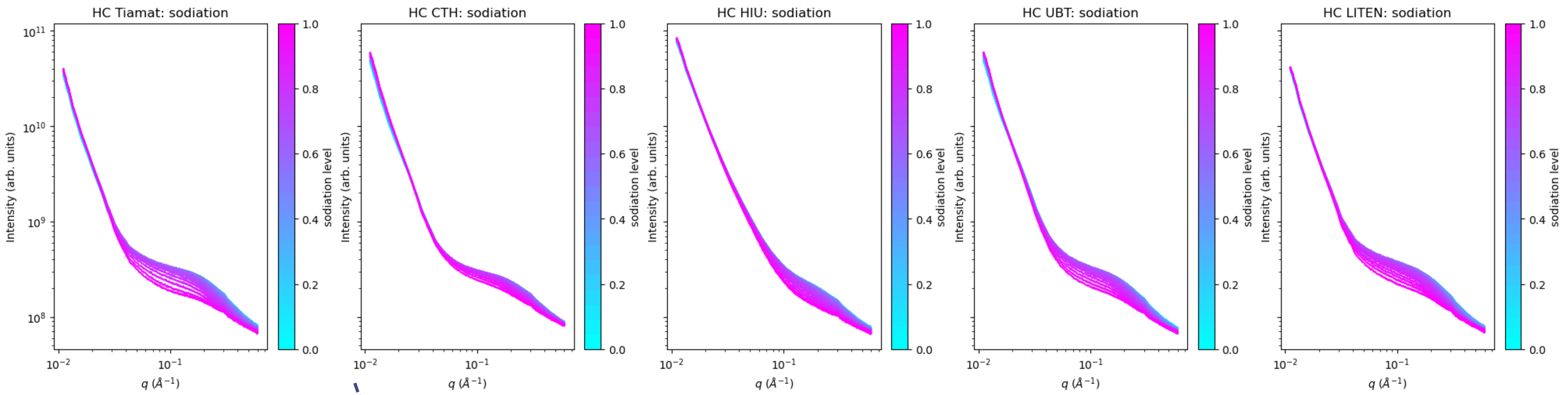


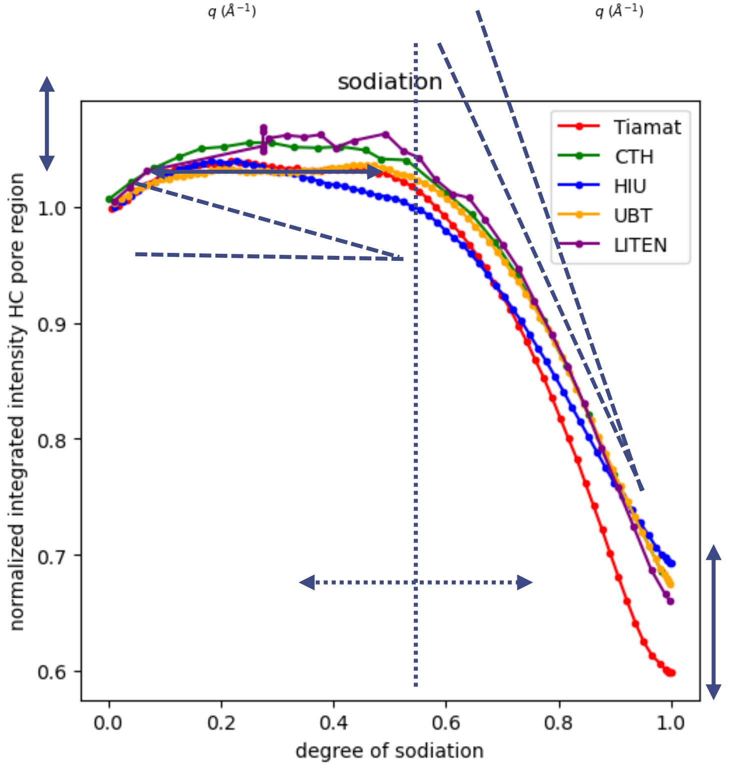
+ WAXS (HC composites)

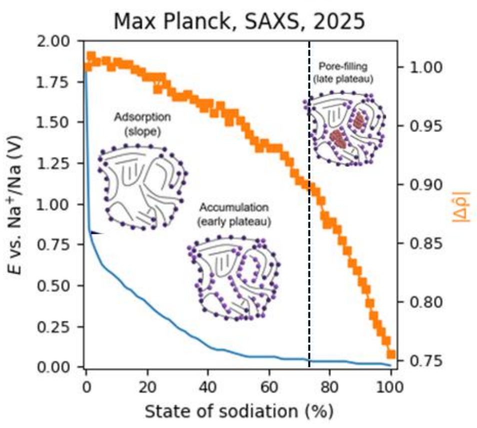


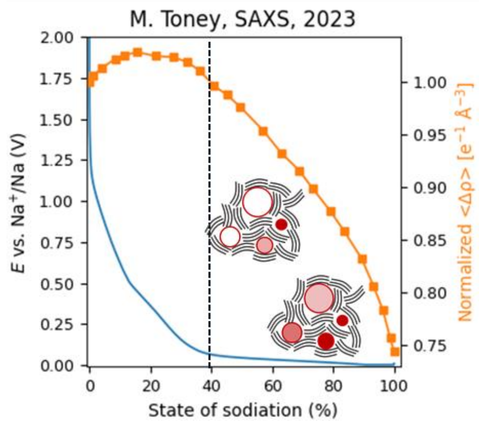
ID13: Transmission image

Beamtime at the ESRF was granted within the European Battery Hub MA-6230



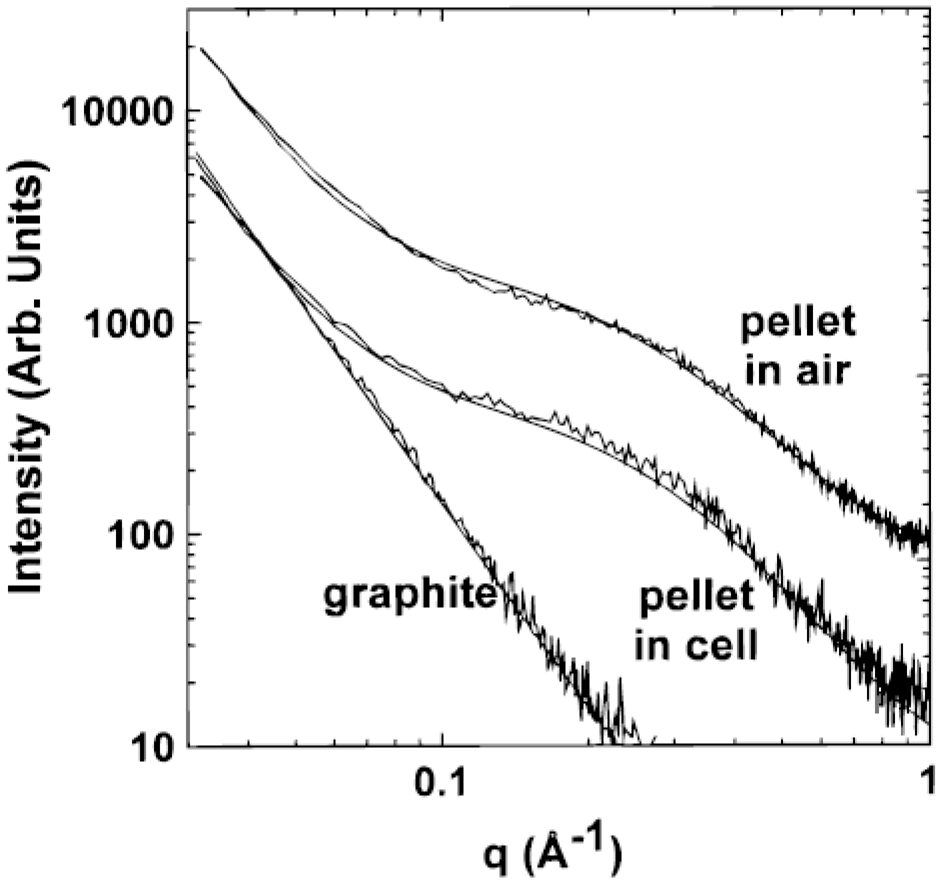






Beamtime at the ESRF was granted within the European Battery Hub MA-6230

How do you fit/model this?

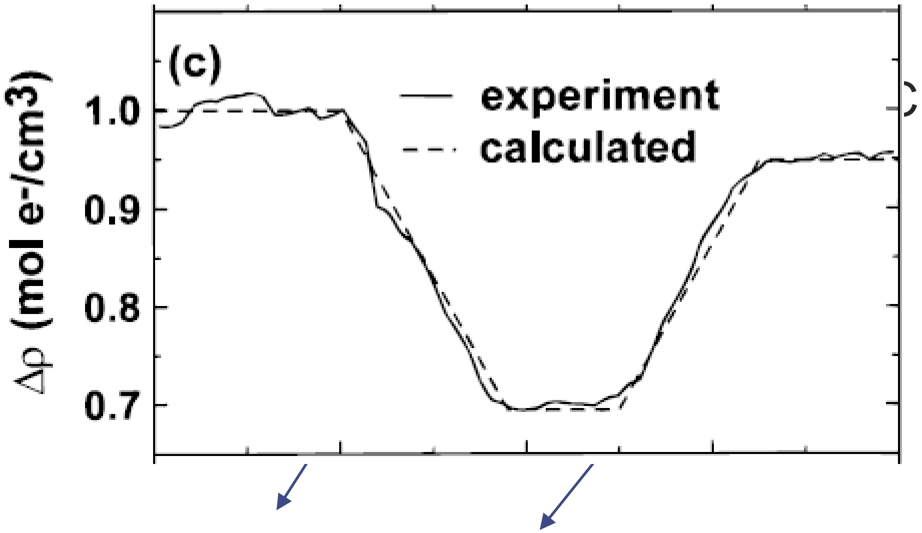


D. A. Stevens and J. Dahn 147 (12) 4428-4431 (2000)

General Form:

$$I(q) = \frac{A}{q^n} + Ipor_{es}(q) + const$$

Debye Büche Model

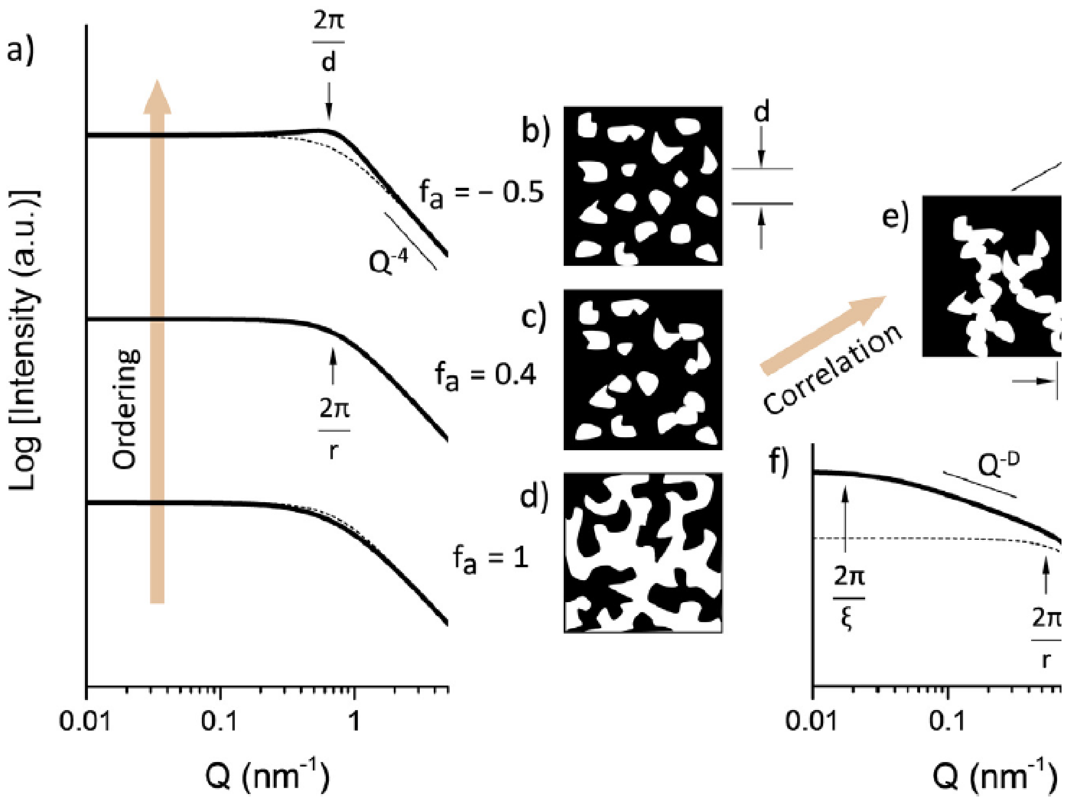


C matrix

a1/2: characteristic size of pores

For spherical pores: R=$a_1\sqrt{10}$

How do you fit/model this?



D. Saurel et al. Energy Storage Materials 21 (2019) 162–173

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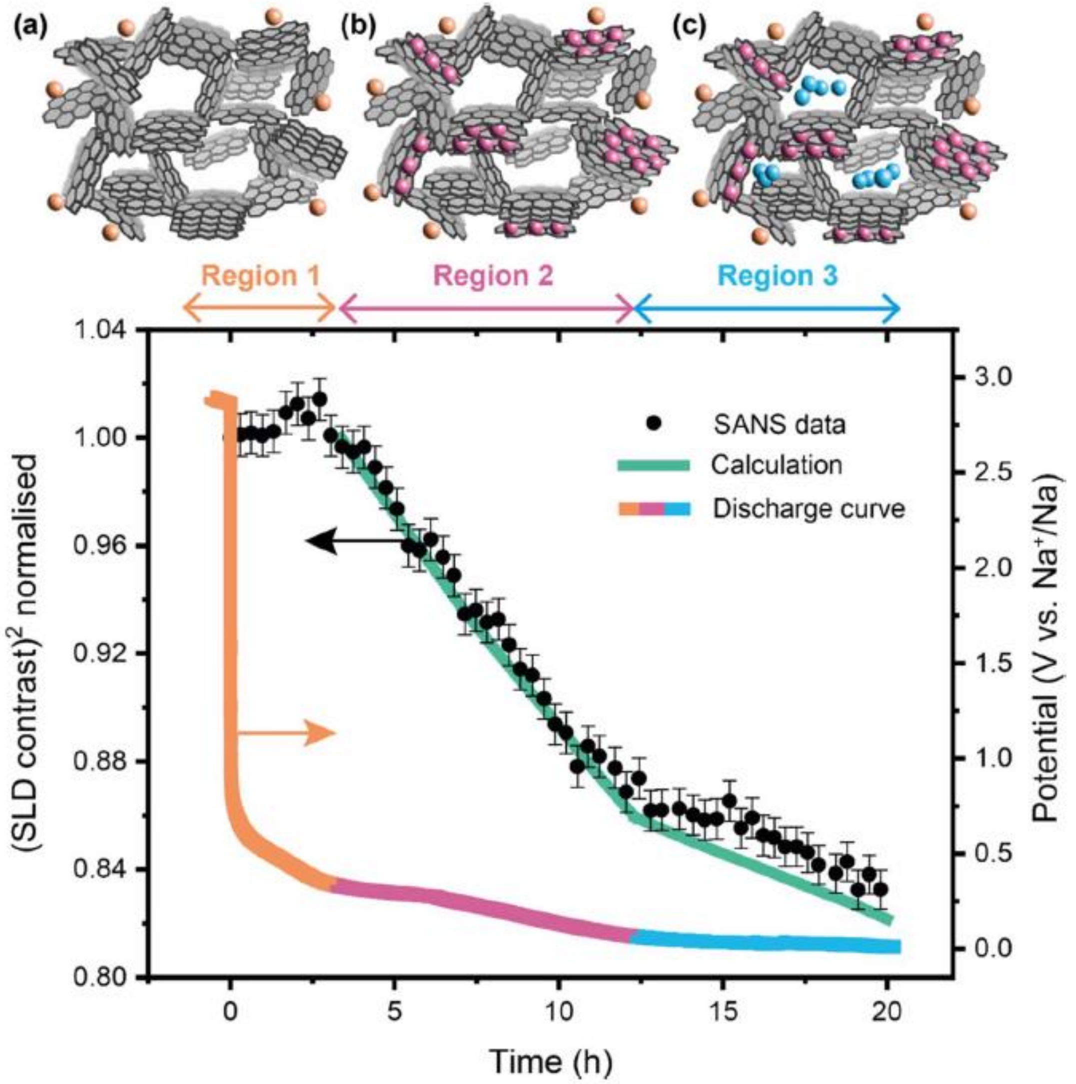

E. Reynolds et al. J. Mater. Chem. A, 2024, 12, 18469–18475

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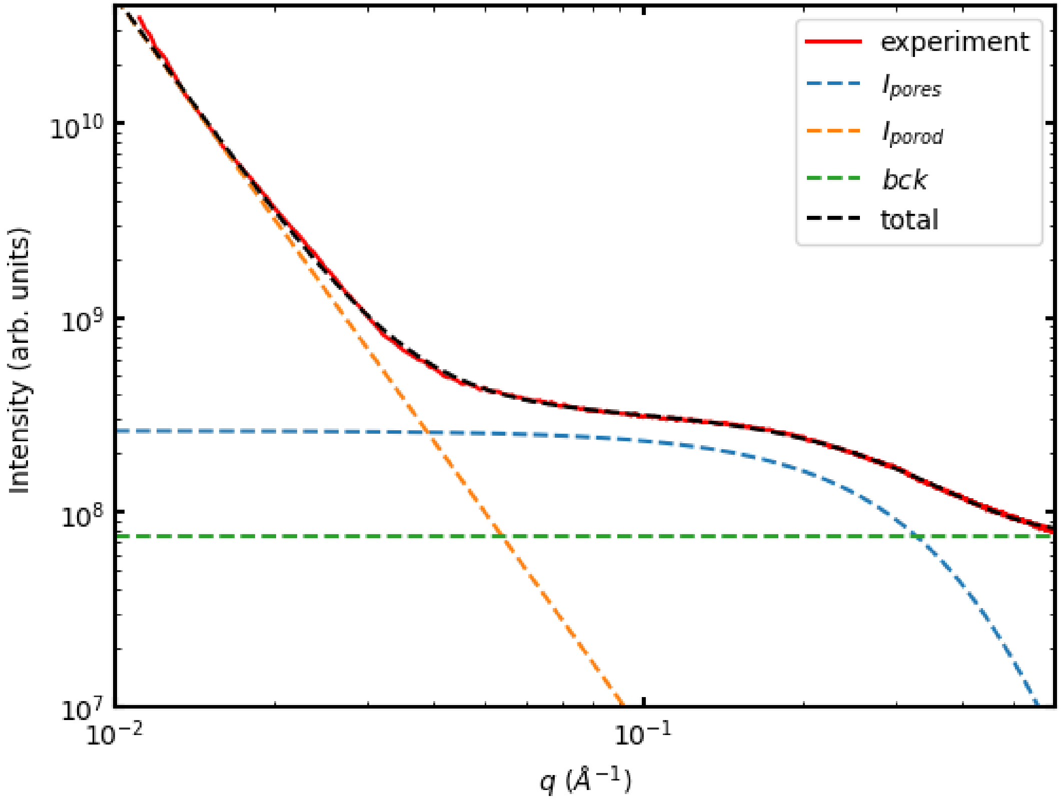


General Form:

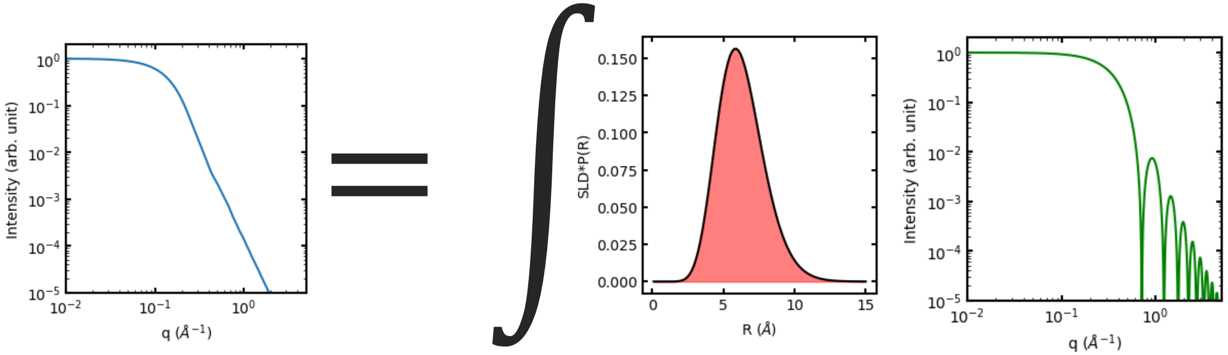
$$I(q) = \frac{A}{q^n} + Ipor_{es}(q) + const$$

Spheres + Size Distribution
+ Size dependent Pore filling. More realistic?

$$I_{\text{pores}}(Q) = scale(\rho_{\text{pore}} - \rho_{\text{HC}})^2 b^2 \int_0^\infty \frac{P(R)}{\frac{4}{3}\pi R^3}(F(Q,R))^2 dR \quad (4)$$

$$F(Q,R) = \int_0^R e^{iQr} d^3r = \frac{4}{3}\pi R^3 \left(3\frac{sin(QR) - QRcos(QR)}{(QR)^3}\right) (5)$$

$$P(R) = \left(\frac{z+1}{R_{\text{avg}}}\right)^{z+1} \frac{R^z}{\Gamma(z+1)} e^{\left(-(z+1)\frac{R}{R_{\text{avg}}}\right)} \quad (6)$$



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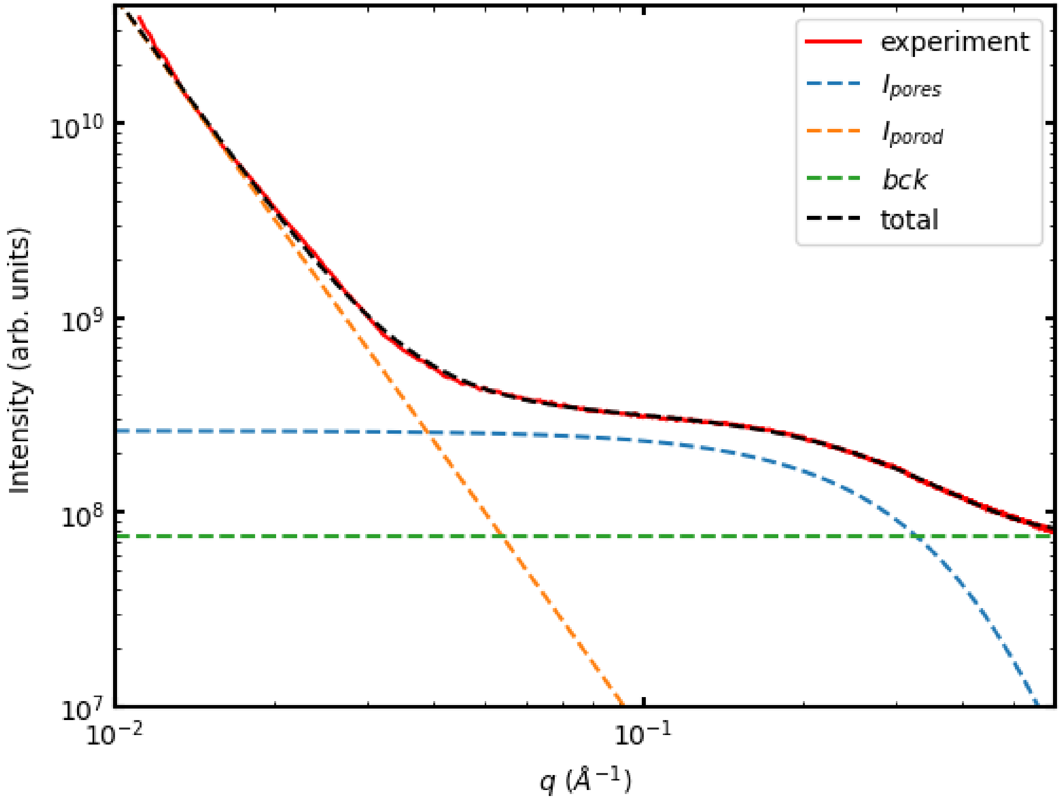

General Form:

$$I(q) = \frac{A}{q^n} + Ipor_{es}(q) + const$$

Spheres + Size Distribution
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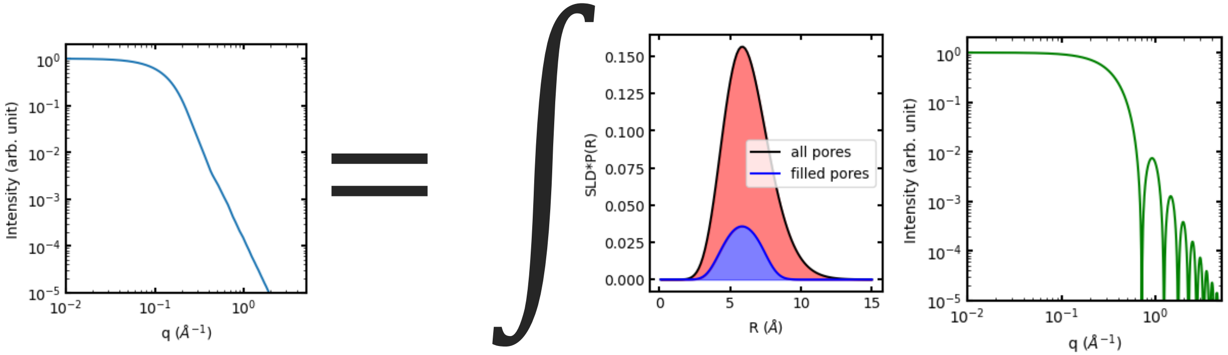
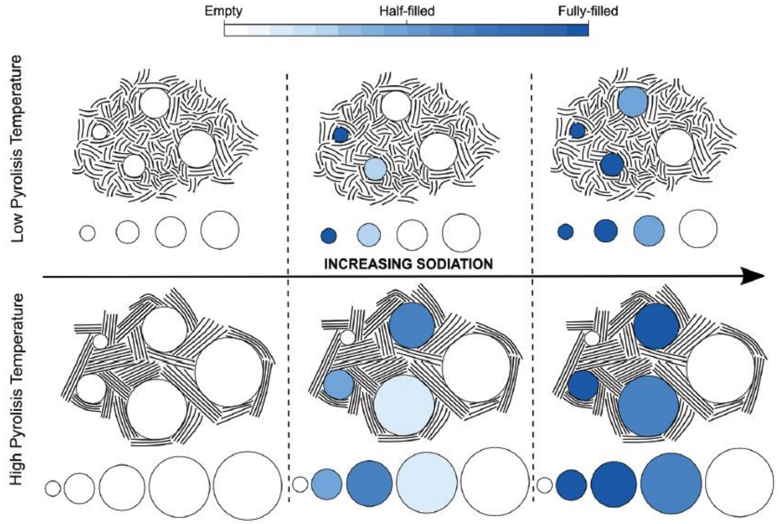
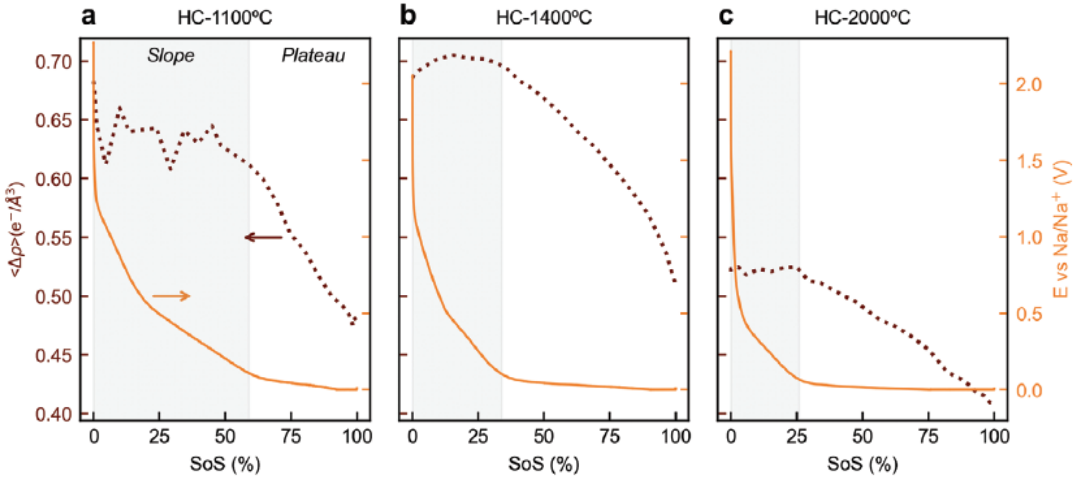
$$I^{\mathrm{plateau}}_{\mathrm{pores}}(Q) = scale \cdot b^2 \int_0^\infty \left(\rho_{\mathrm{pore}} - \rho_{\mathrm{HC}}\right)^2 \frac{P(R)}{\frac{4}{3}\pi R^3} \left(F(Q,R)\right)^2 dR \quad (8)$$

$$\rho_{\mathrm{pore}} = \frac{\rho_{\mathrm{scale}}}{2} \left[erf\left(\frac{R - R_{\mathrm{i}}}{\sigma_{\mathrm{r}}}\right) - erf\left(\frac{R - R_{\mathrm{ii}}}{\sigma_{\mathrm{r}}}\right) \right] \quad (9)$$



How do you fit/model this?





Iglesias et al., Adv. Energy Mater. 2023, 13, 2302171

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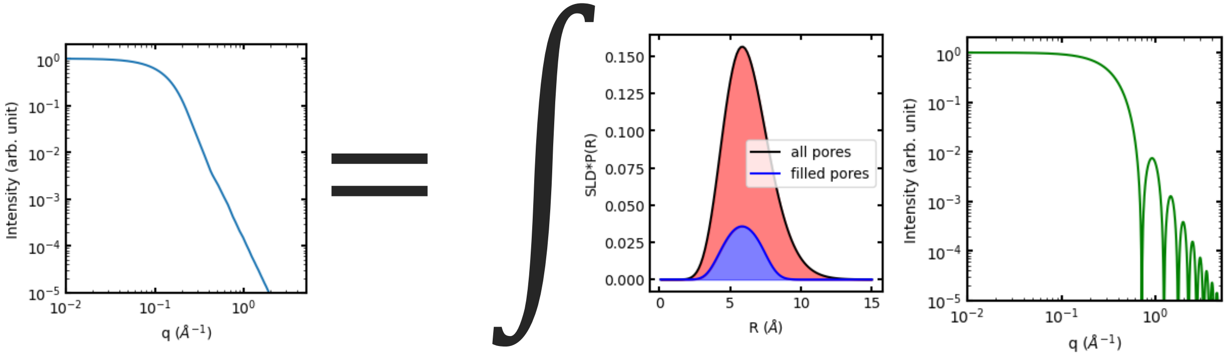
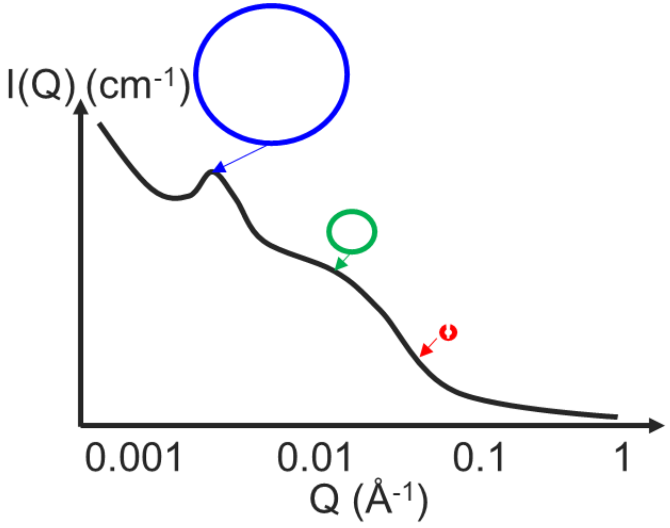


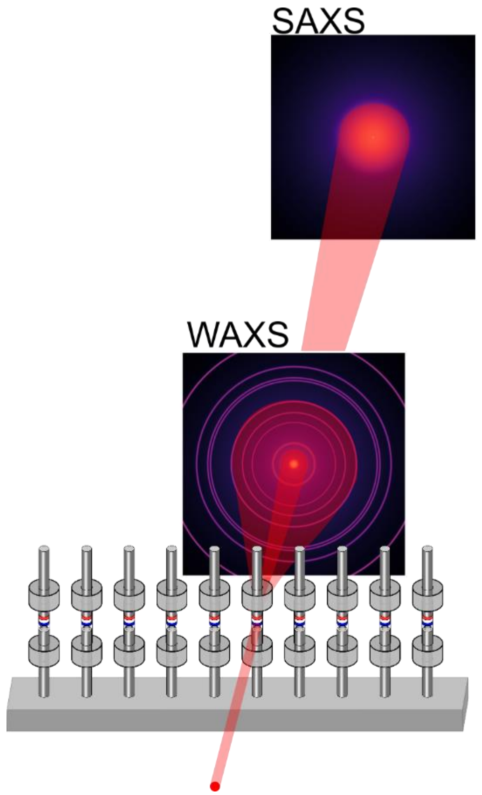
Conclusions and take-home message



Slopes and Bumps are meaningful!

SAXS/SANS is powerful to look at:

- **Sizes and shapes of objects**
- **Nanoscale Organizations**
- **Porous materials**
- **Interfaces**



Quantitative analysis is possible (but often difficult)

Nevertheless:
SAXS/SANS often times the only way to study certain phenomena

Conclusions and take-home message