MSE-238
Structure of Materials

Week 11 - Scattering

Spring 2025

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Overview

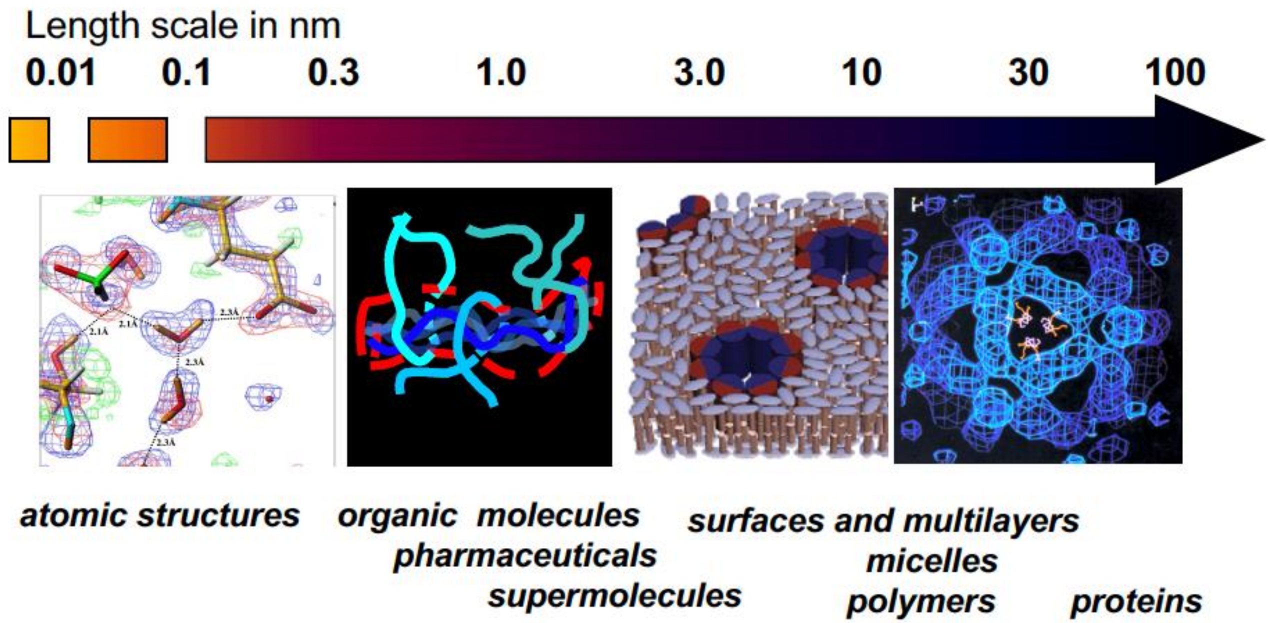
- SAXS vs XRD and length scales
- Labsource and large scale facilities
- Scattering as Fourier transform
- model indpendent analysis:
    - diffraction peaks,
    - Guinier approximation,
    - Power law
    - Porod regime
    - orientated particles
- mathematical modelling
    - SAXS vs XRD
    - particle form factor and structure factor
- Material science application example

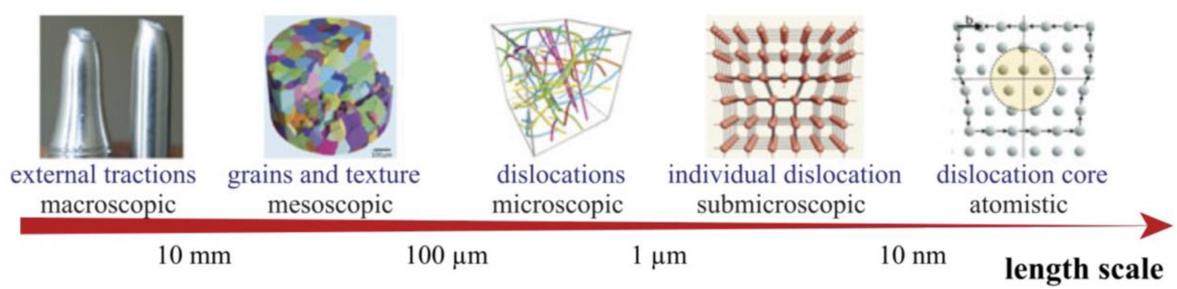
Additional reading

- Fundamentals of Materials Science, Mittemeijer
  - Chapter 4.7 Determination of Crystal structure; X-ray diffraction
  - Chapter 6.9 X-ray Diffraction Analysis of the Imperfect Microstructure
- Introduction to Synchrotron Radiation (Willmott)
  - Chapter 6 Scattering Techniques

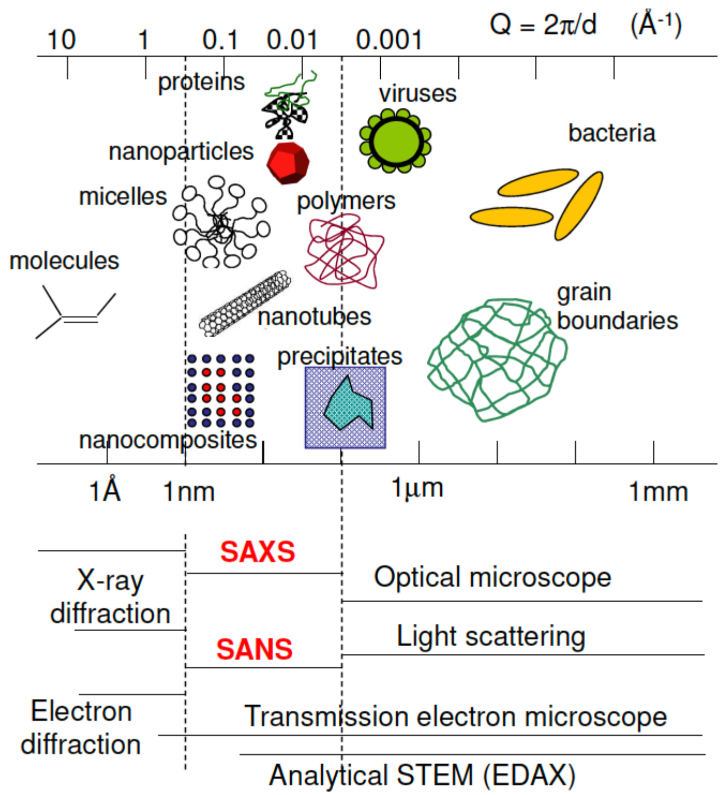
- see also the open online course from EPFL on EDX from Phil Willmott on "Synchrotrons and X-Ray Free Electron Lasers" part 2, in week 2: small-angle scattering

Length scales





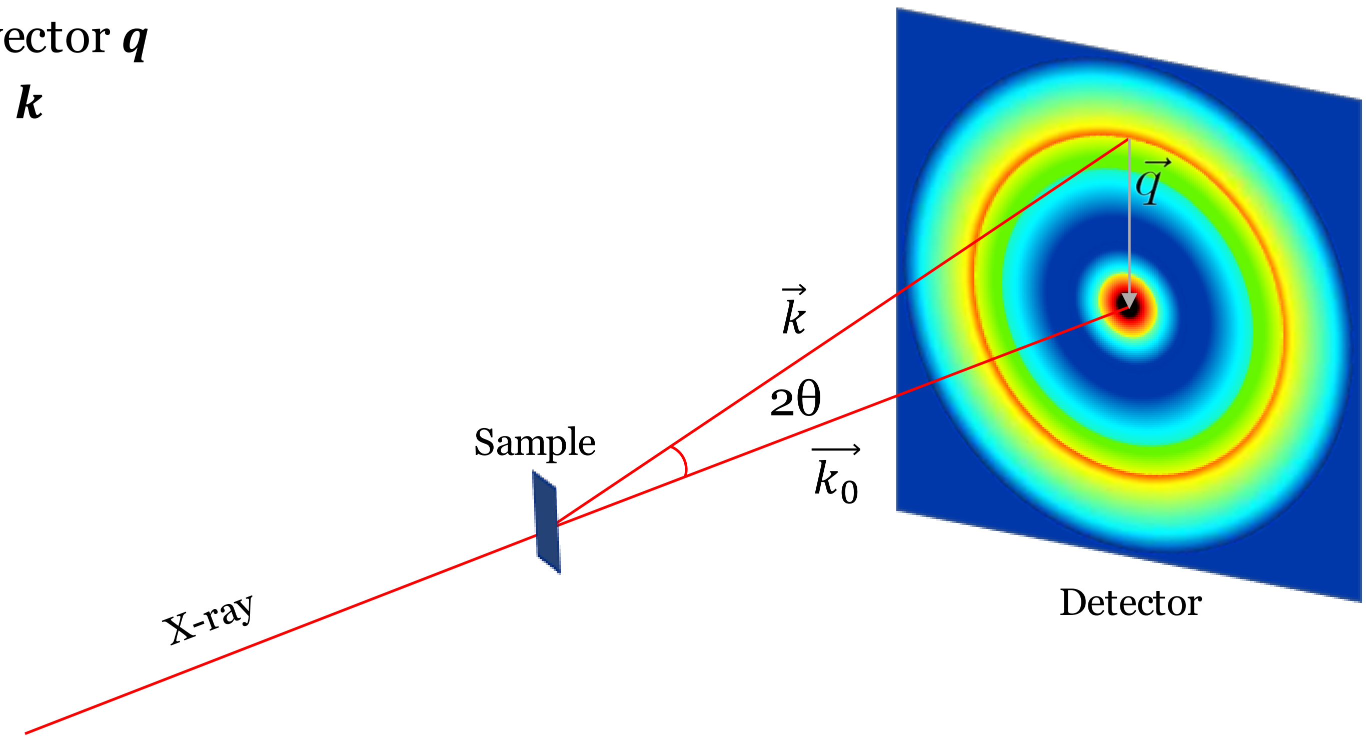
Length-scales and characterization techniques



Scattering/Diffraction: the scattering vector

scattering vector $\boldsymbol{q}$

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



Scattering/Diffraction

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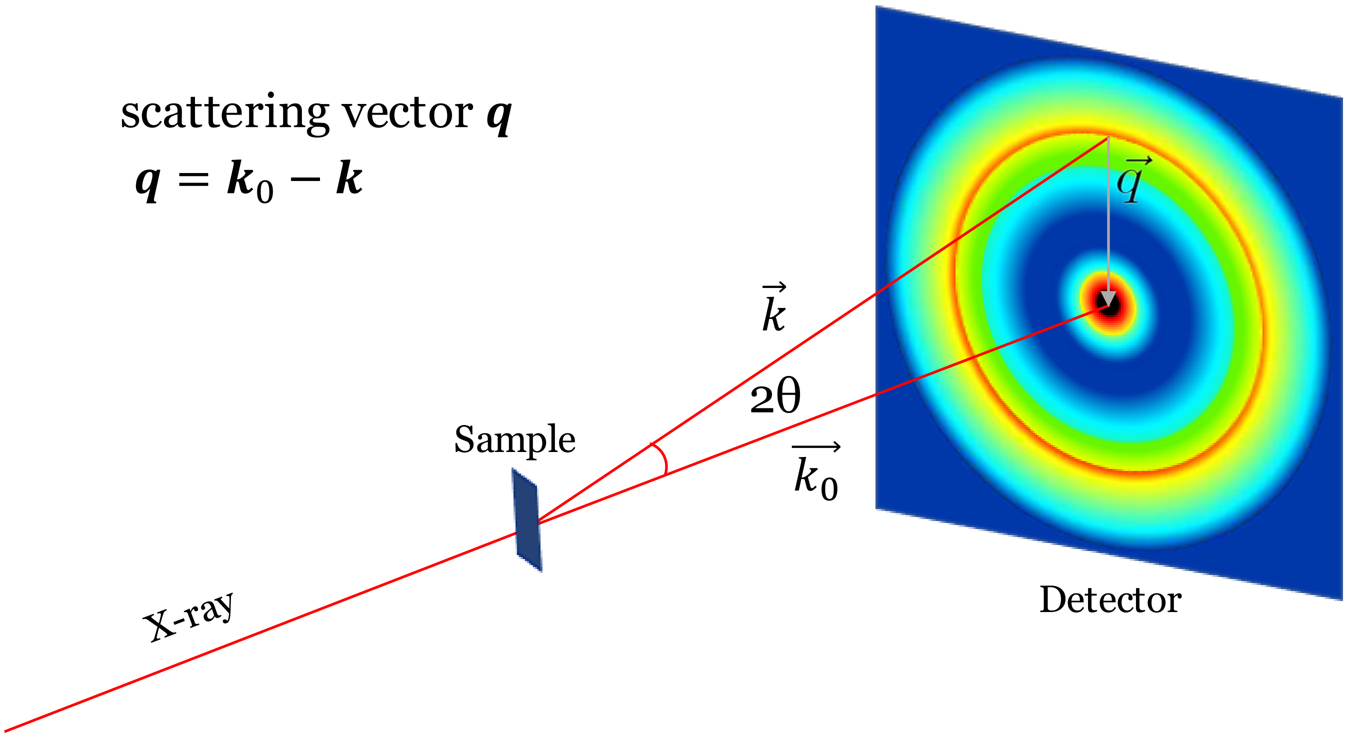


$$|\vec{q}| = q = \frac{4\pi \sin(\theta)}{\lambda}$$

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

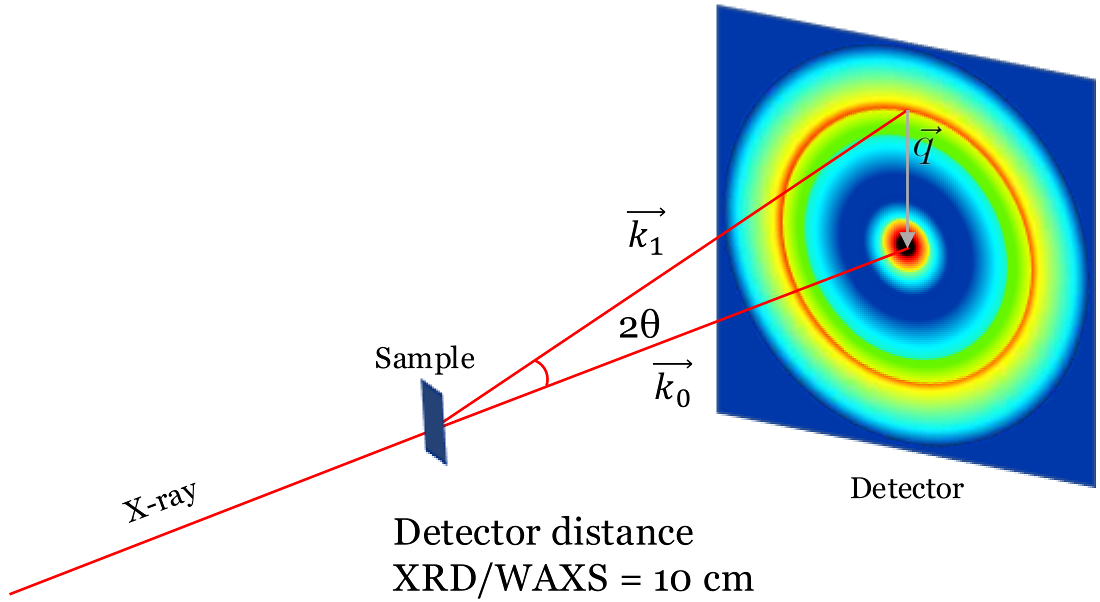
Bragg's law

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

SAXS: scattering from variation in electron density distribution, NOT from single atoms as in XRD

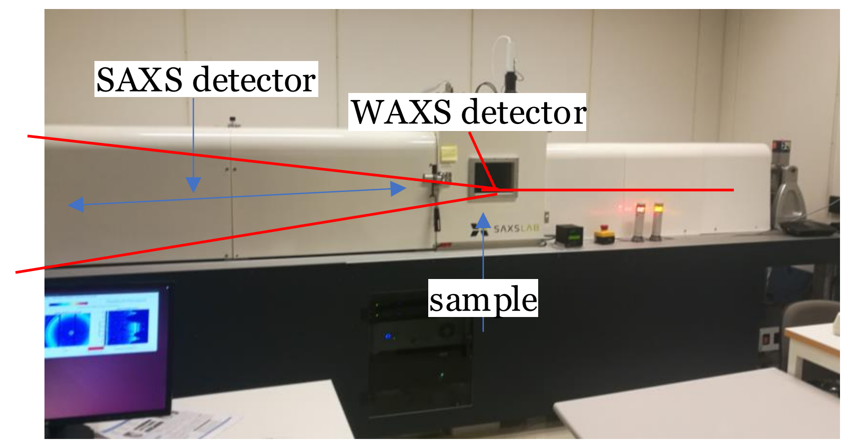
larger structures → smaller angles
XRD/WAXS: 10 cm detector distance
SAXS: several m detector distance

SAXS/WAXS at a labsource

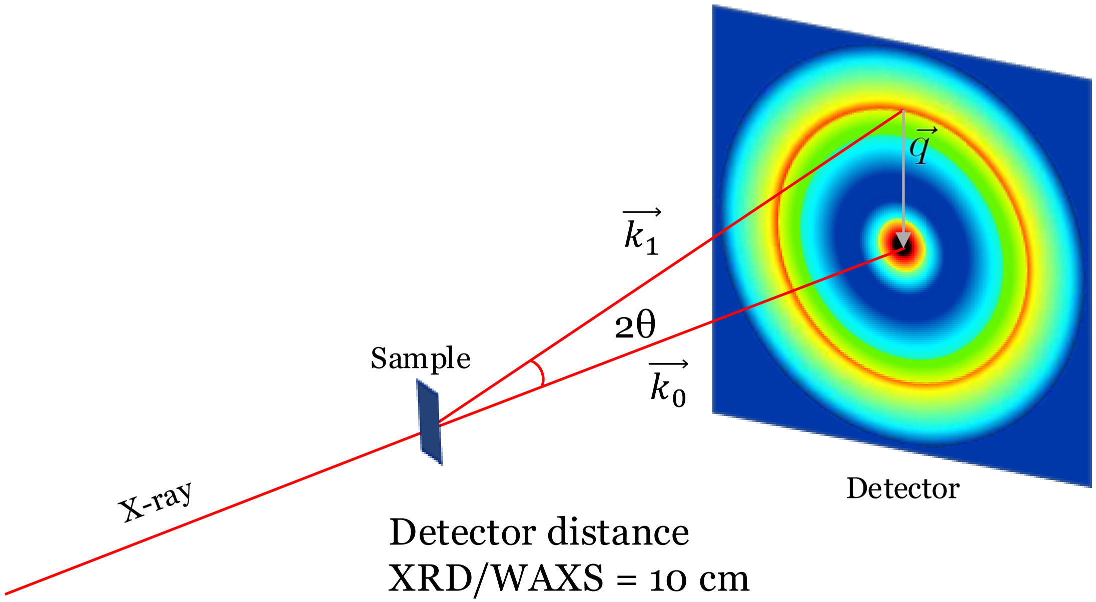


Detector distance
XRD/WAXS = 10 cm
SAXS = several m

Labsource SAXS instrument



SAXS/WAXS
at a synchrotron beamline



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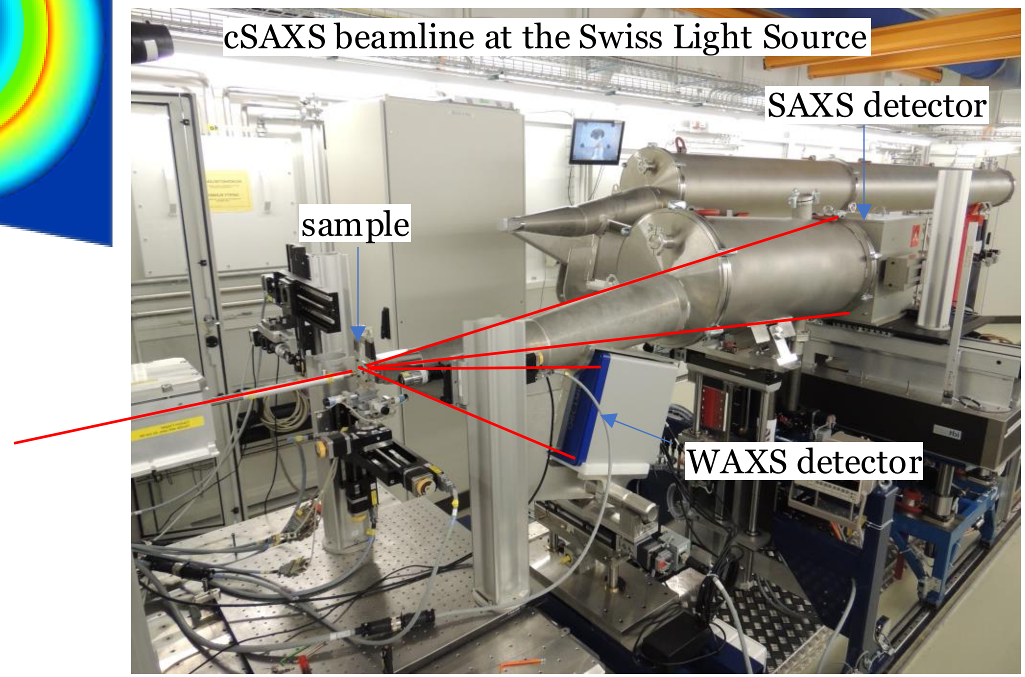
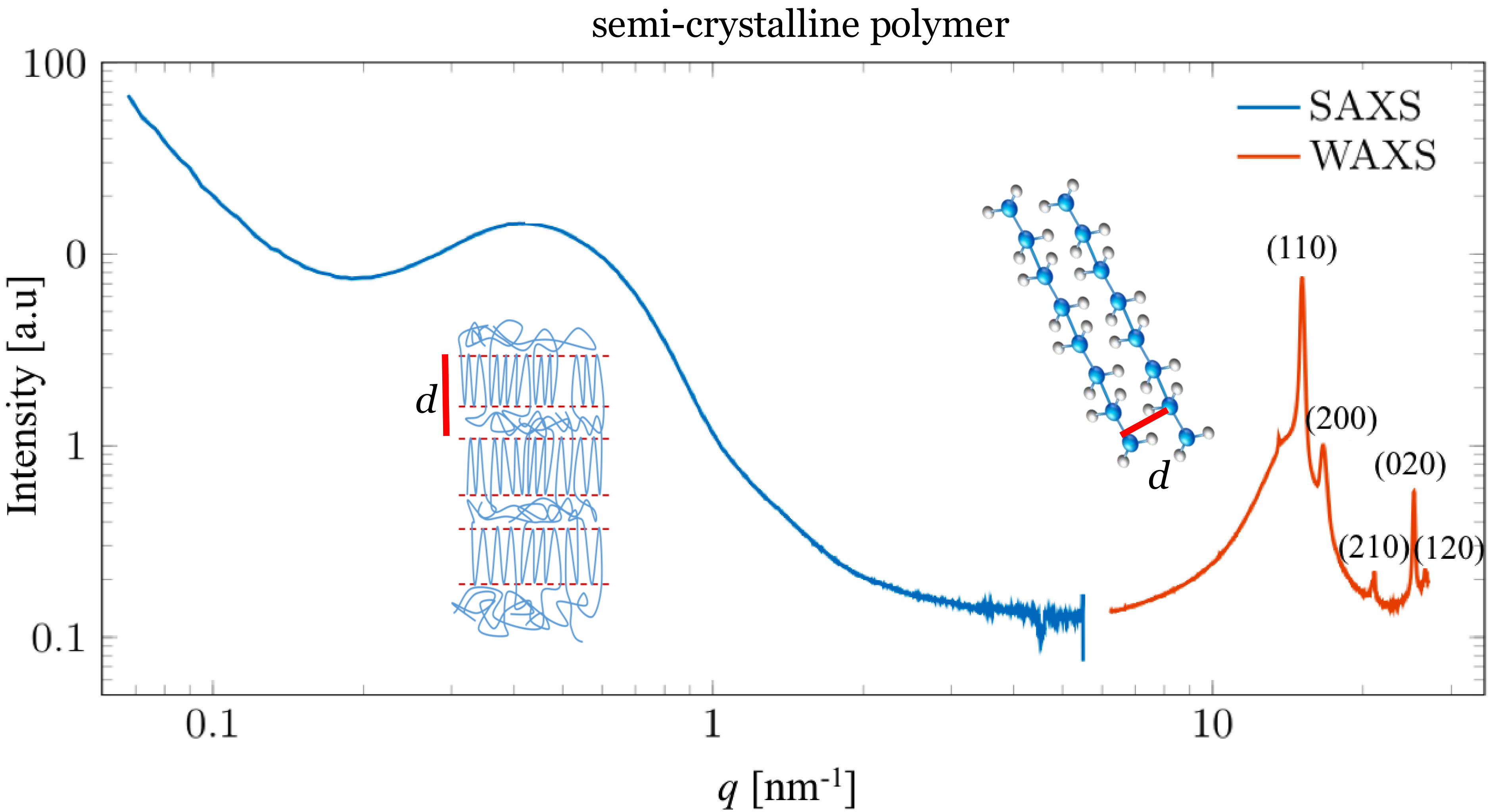
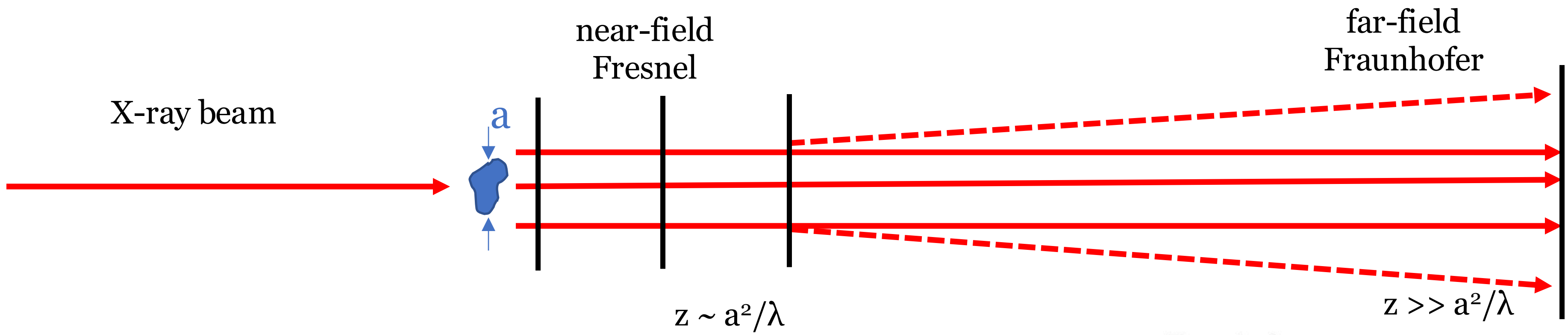


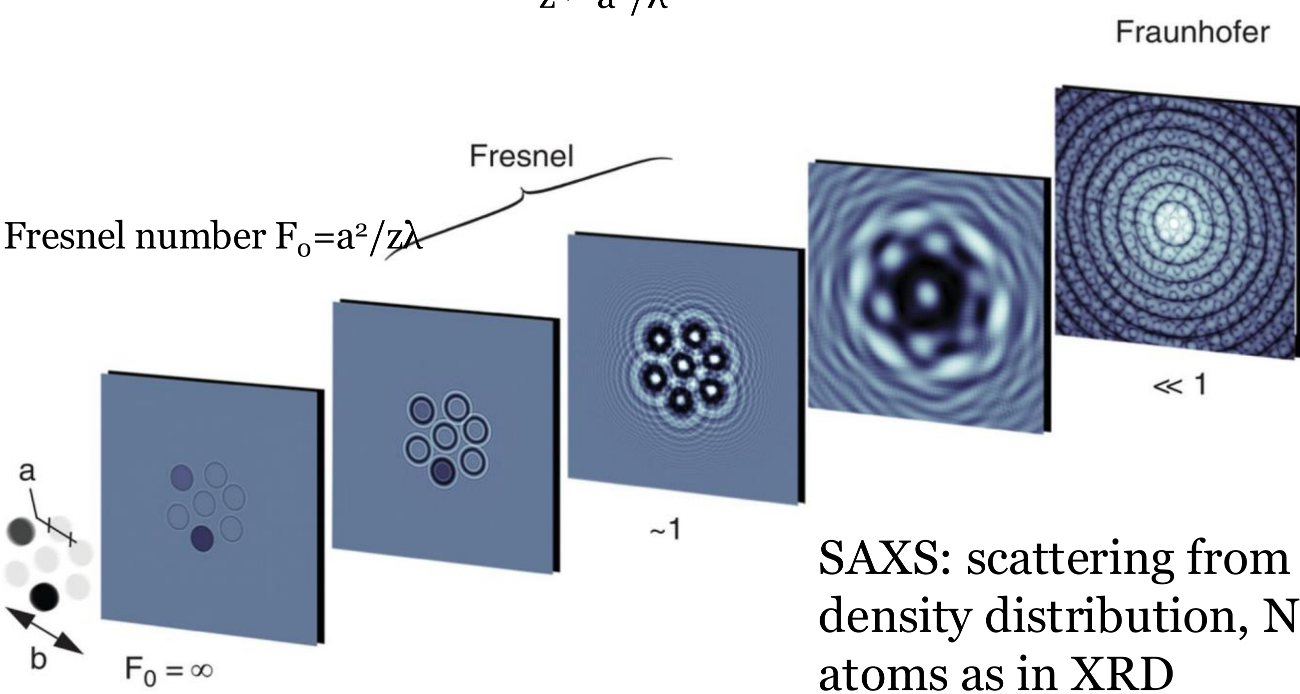
Neutron detectors have large pixels, even larger distances are needed to resolve the small-angles

SAXS and WAXS=XRD



Far-field





dimensionless Fresnel number $F_o = a^2/z\lambda$

SAXS: scattering from variation in electron density distribution, NOT from single atoms as in XRD

Willmott, P., John Wiley & Sons, Ltd: 2019 (2nd Edition).

Small-angle scattering

- Fraunhofer approx. Fourier theorem:

the field distribution at a distant detector is the Fourier transform of the electric field distribution in the exit plane of a sample

Demonstration: Fourier-Transform

Initial Python coding and refactoring:
Brian R. Pauw
http://www.lookingatnothing.com
With input from:
Samuel Tardif

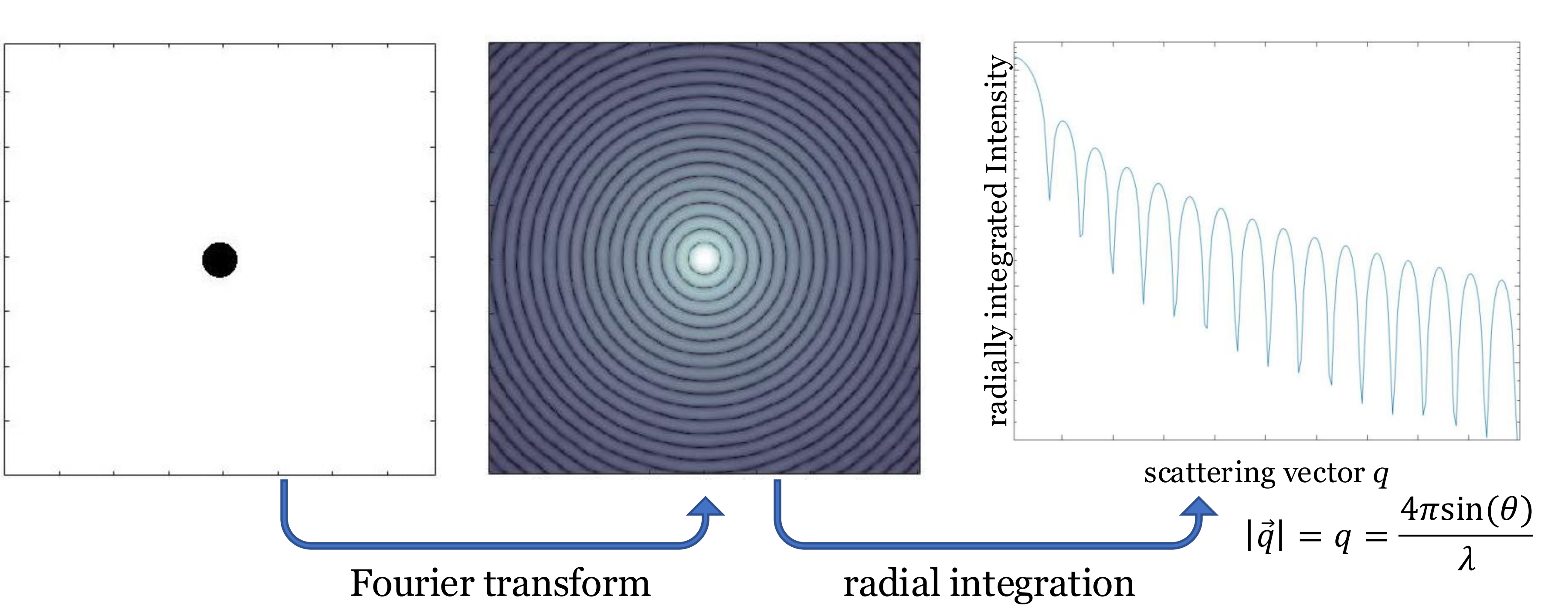
Windows compatibility resolution:
David Mannicke
Chris Garvey

Windows compiled version:
Joachim Kohlbrecher

Sample images:
Joachim Kohlbrecher
Brian R. Pauw.

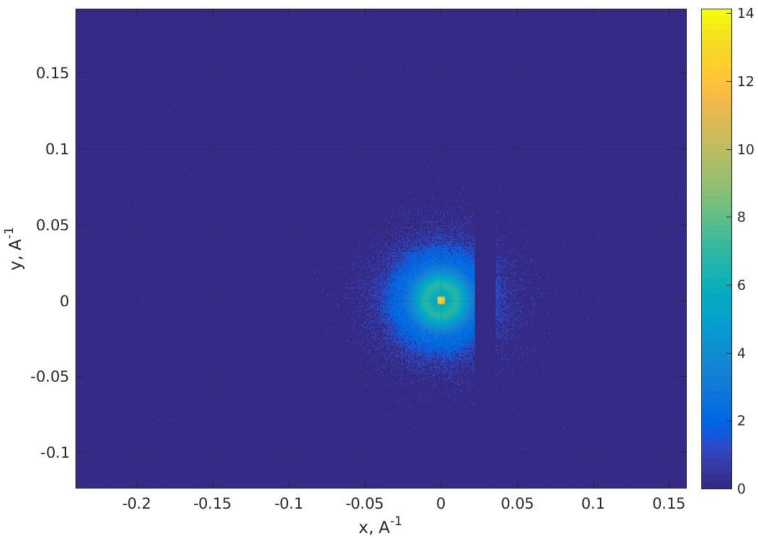
simulation
https://phet.colorado.edu/sims/html/wave-interference/latest/wave-interference_en.html

Scattering/Diffraction

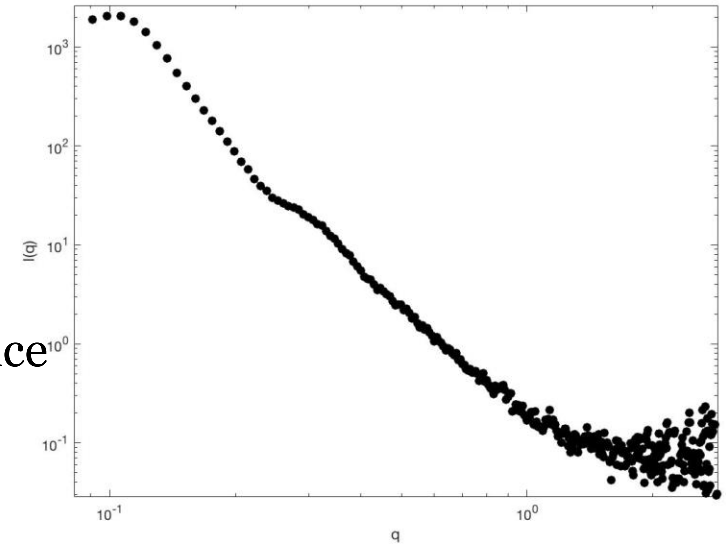


$$|\vec{q}| = q = \frac{4\pi \sin(\theta)}{\lambda}$$

Scattering/Diffraction: data treatment



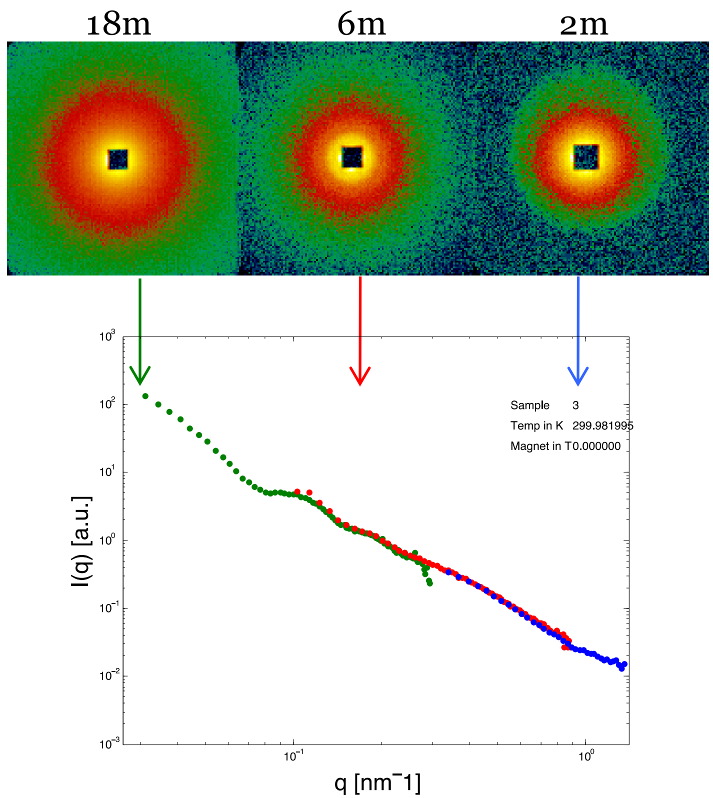
beam center
detector distance
wavelength λ
mask



raw data: 2D scattering pattern
(example measured at SAXSLAB in CMAL)

average scattering profile I(q)

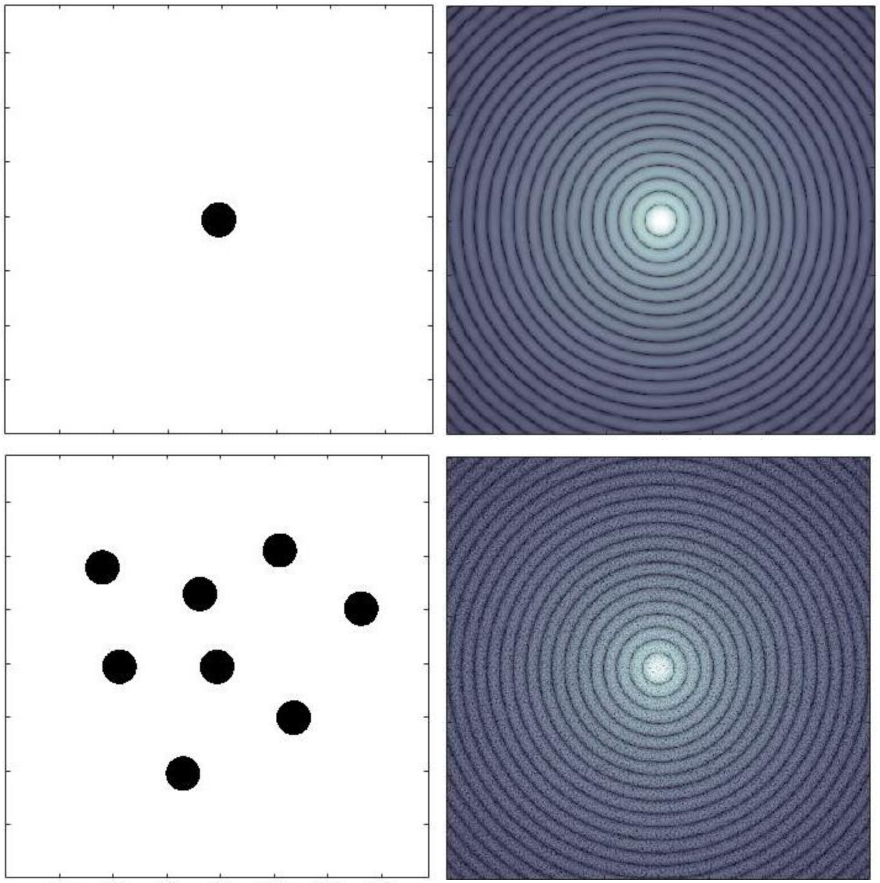
SANS



vesicles July 2010

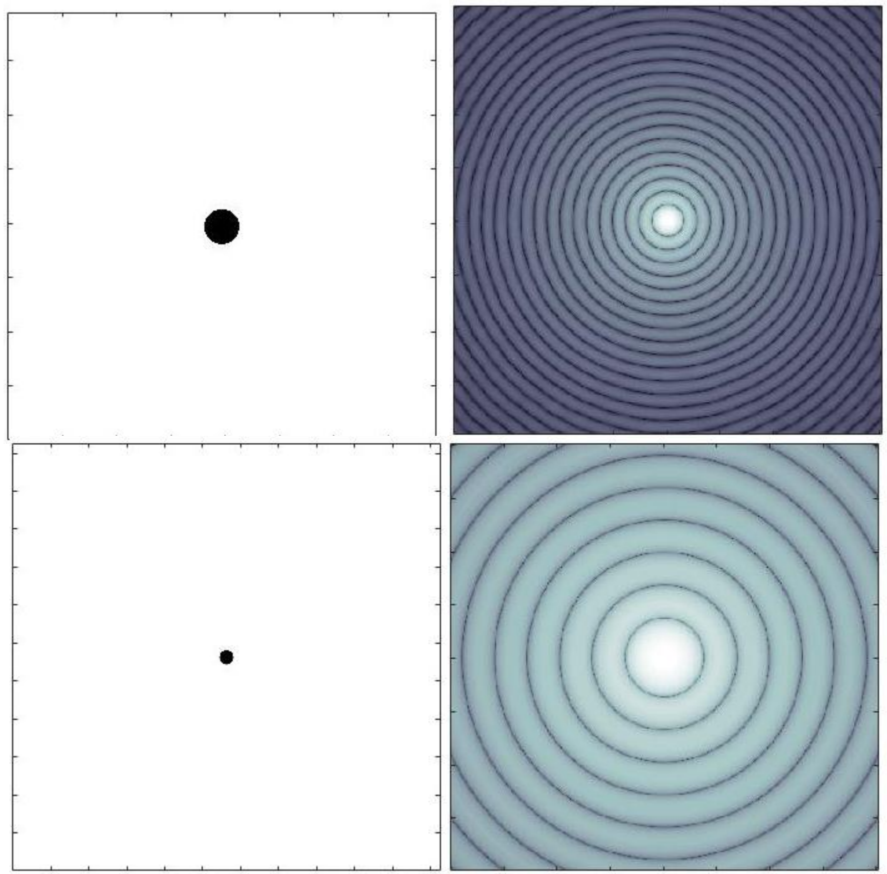
SANS instruments at SINQ

small-angle X-ray scattering



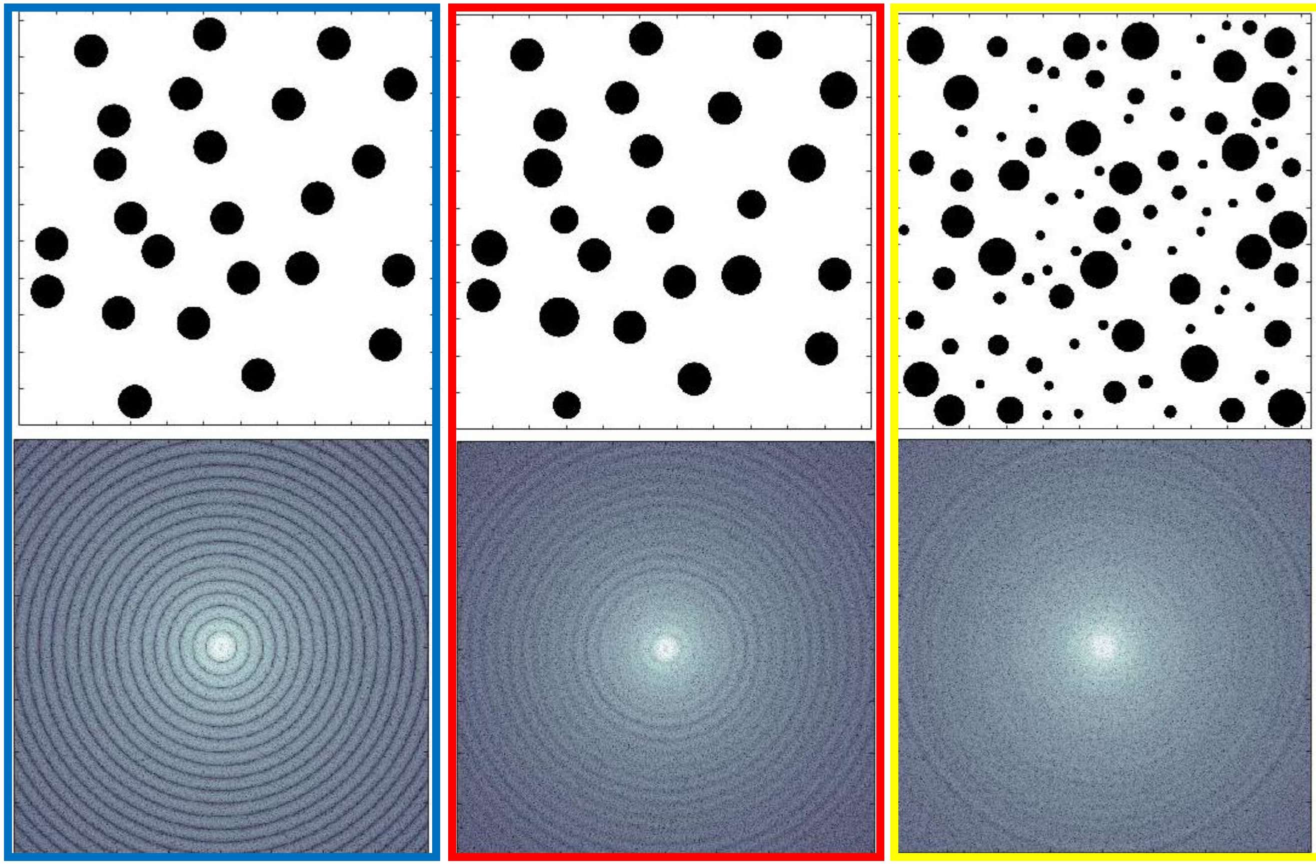
scattering pattern shows
average over particle ensemble

small-angle X-ray scattering
size

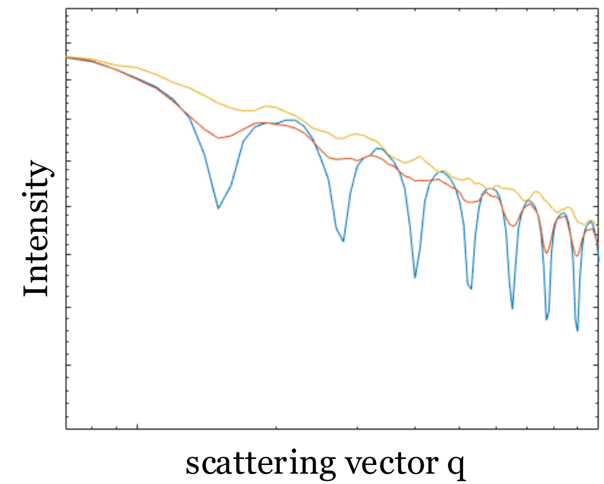


smaller structures scatter
at larger angles

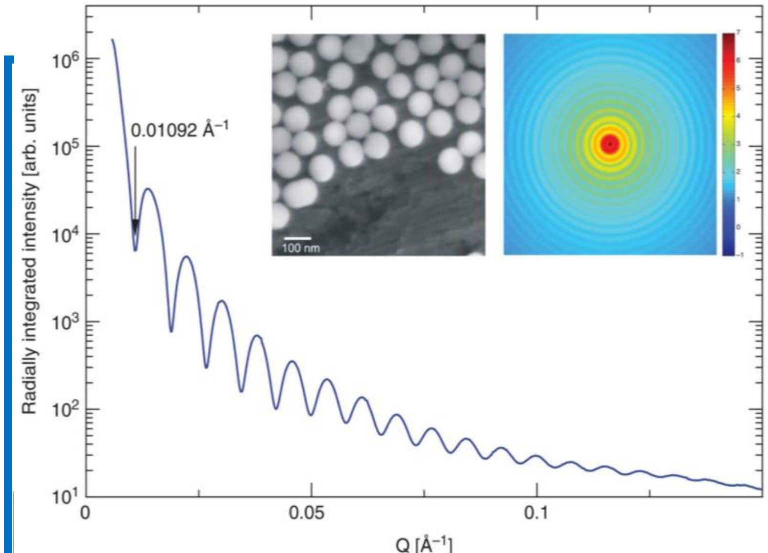
small-angle X-ray scattering
polydispersity



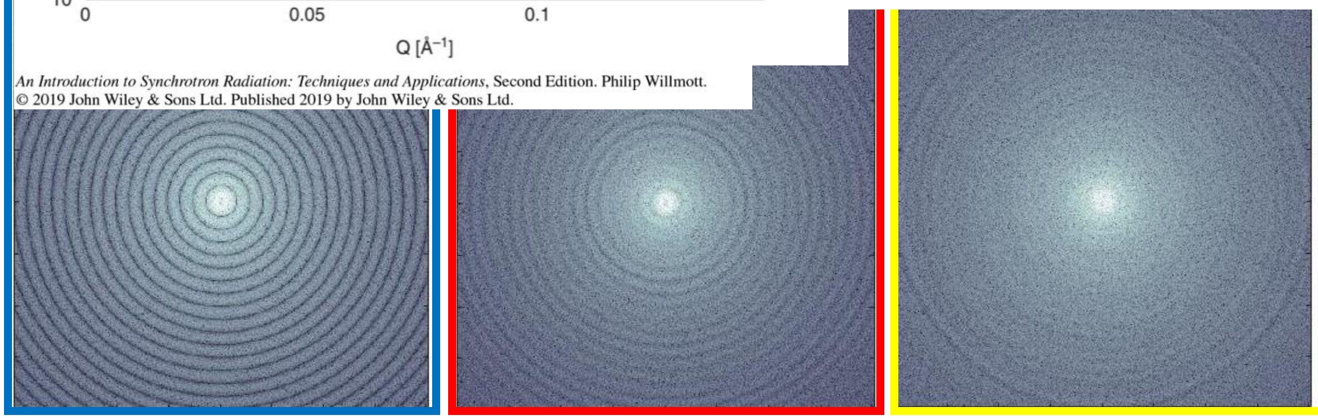
effect of polydispersity

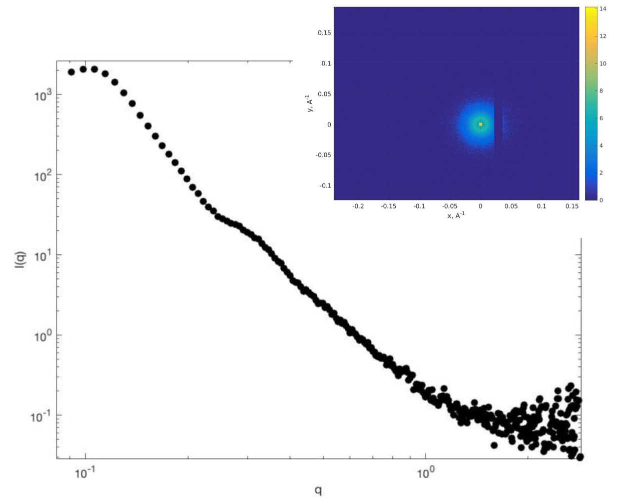


small-angle X-ray scattering
polydispersity

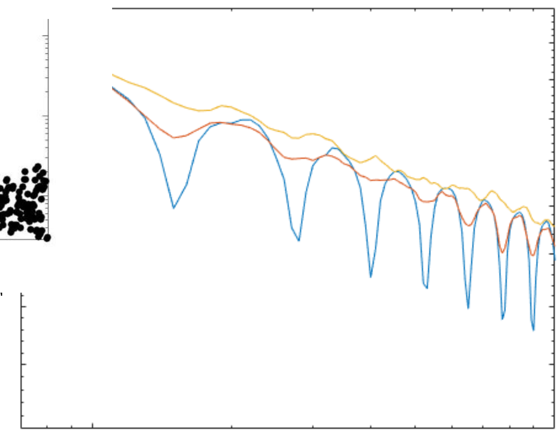


An Introduction to Synchrotron Radiation: Techniques and Applications, Second Edition. Philip Willmott.





polydispersity



scattering vector q

Small-angle scattering

- Fraunhofer approx. Fourier theorem:

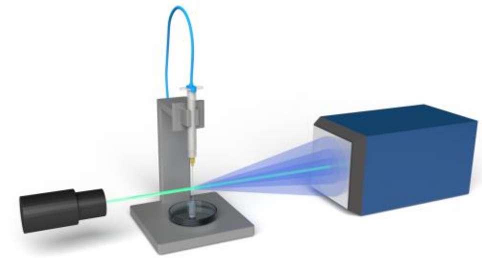
the field distribution at a distant detector is the Fourier transform of the electric field distribution in the exit plane of a sample

BUT we don't measure field but the intensity, which is the squared field: complex quantity: complex part (the phase) get lost → **the phase problem**

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

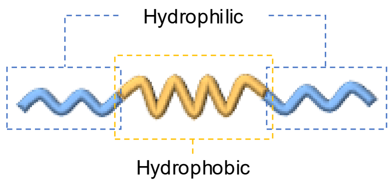
- **model independent**
- mathematically model the SAXS curve
- iterative phase retrival
- pair distance distribution function (PDDF)

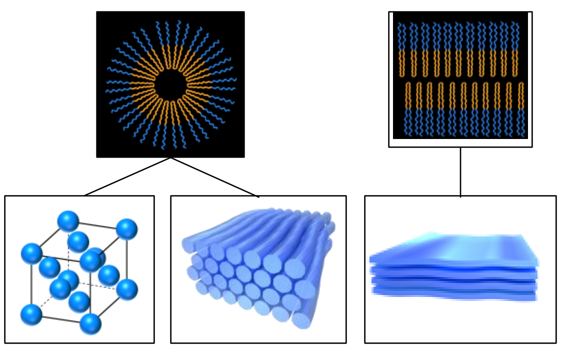
Small-angle scattering: any peaks?

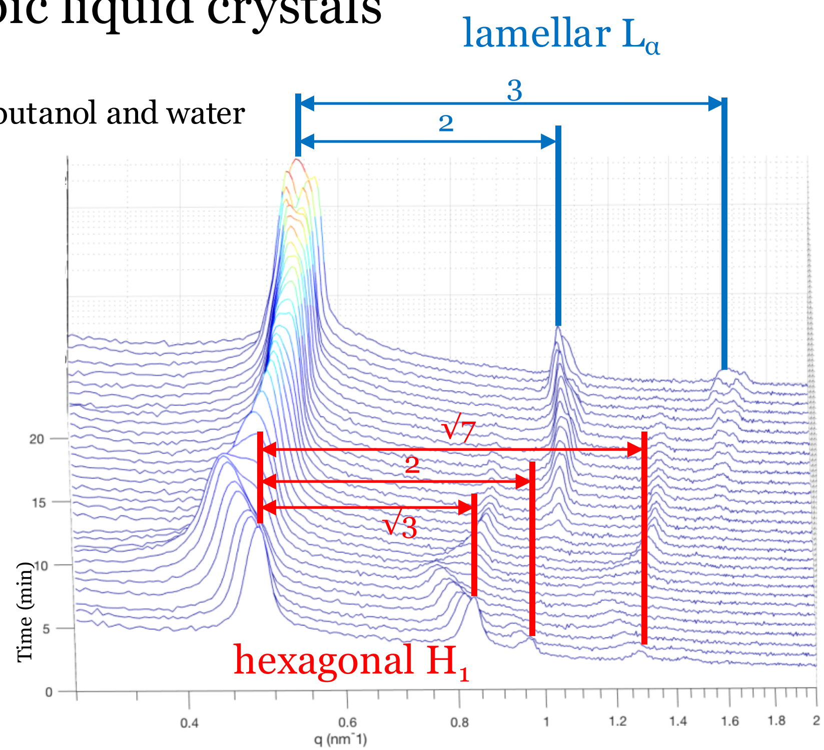


3D printing of lyotropic liquid crystals

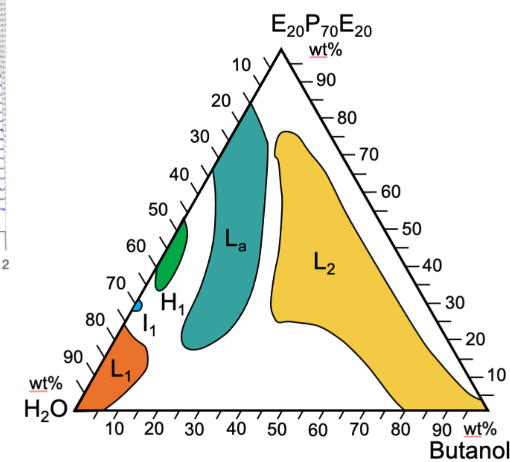
Pluronic F-127 ($EO_{100}PO_{70}EO_{100}$), 1-butanol and water







time-resolved measurements of phase changes after 3D printing



Small-angle scattering

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

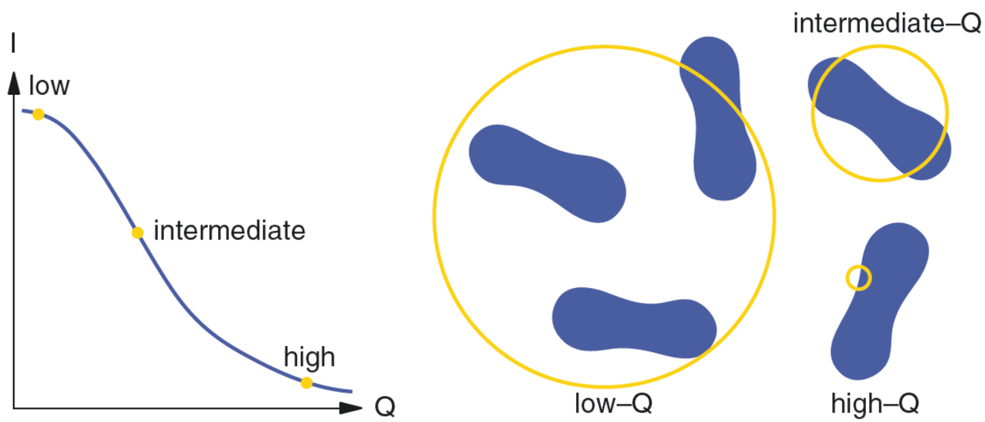
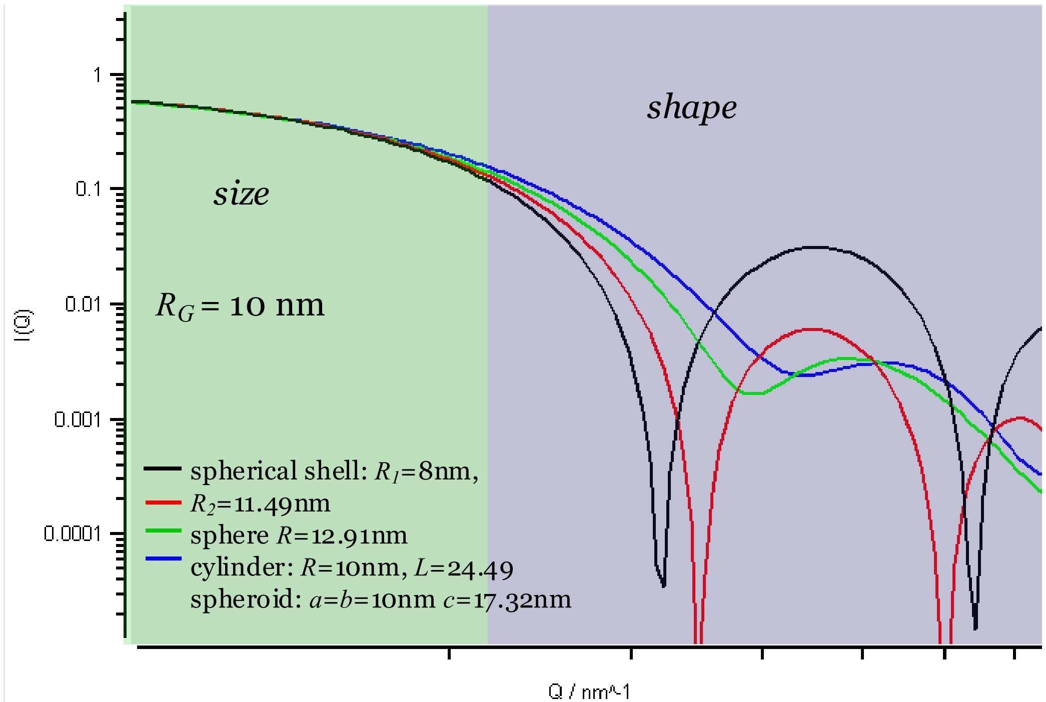


Figure 5.67 *The three Q-domains of SAXS.*

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

Low q: Size information

simulated SAS curve of different shapes but the same radius of gyration



First part of the scattering curve tells object's size, second part object's shape

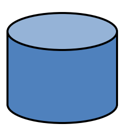
Guinier approximation

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

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

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

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



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

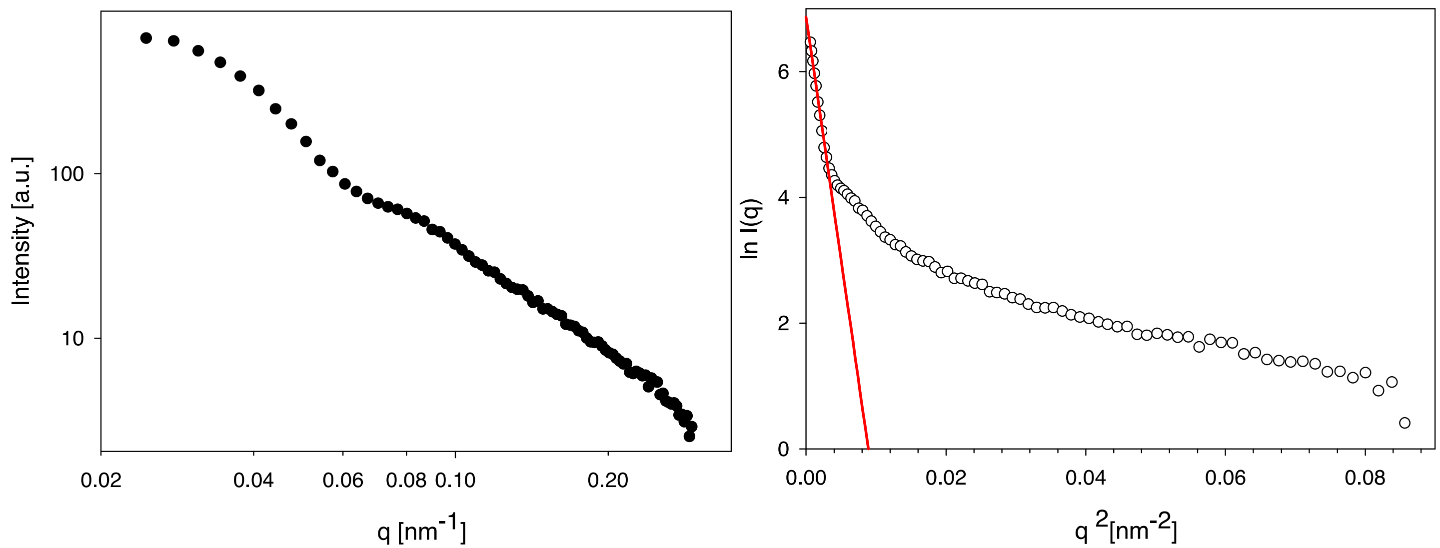
For a polymer coil with end to end distance R

$$R_G = R\left(\frac{1}{6}\right)^{1/2} = a\left(\frac{1}{6}N\right)^{1/2}$$

Guinier approximation

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

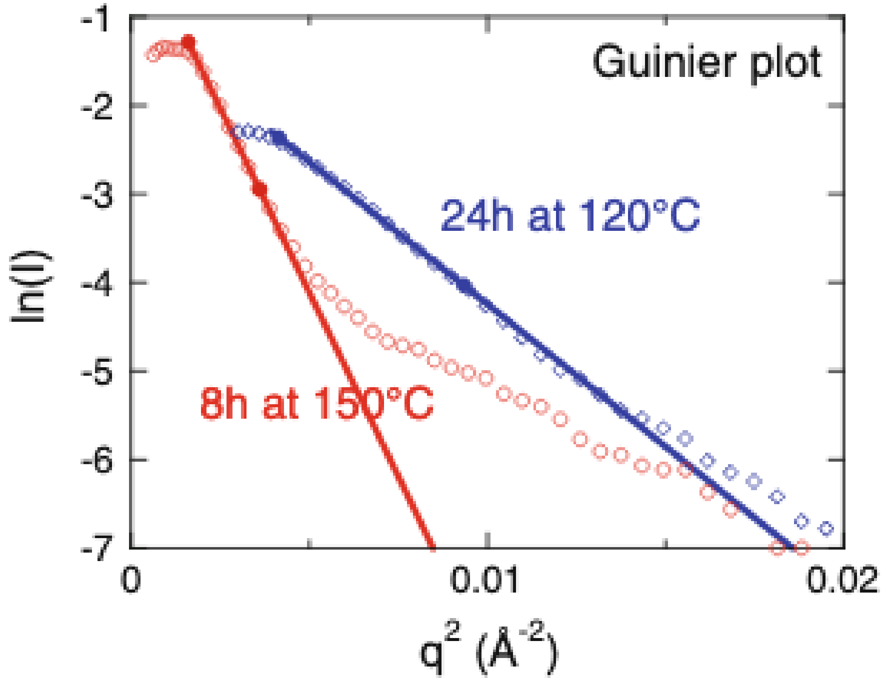
$$I(q) \approx I(0)e^{-(1/3)q^2R_G^2}$$



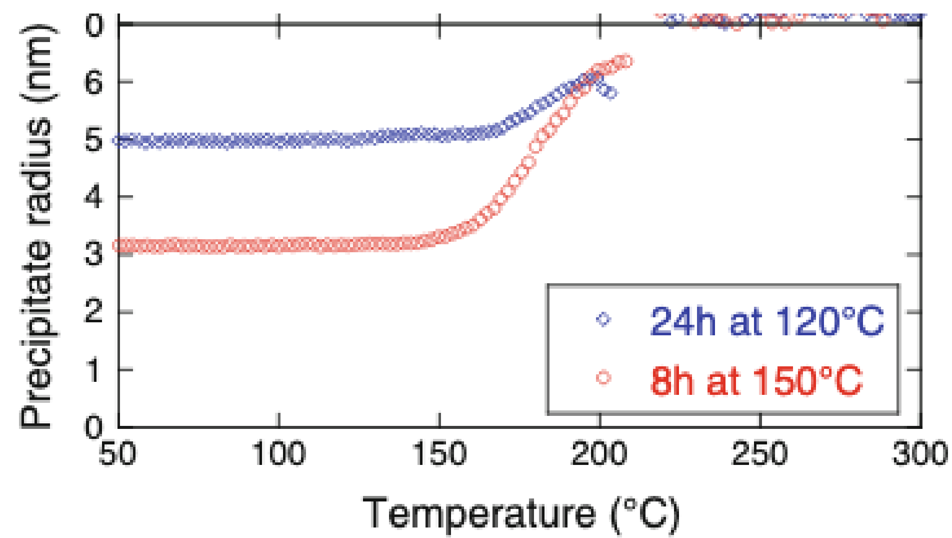
A not existing linear range indicates the presence of very large structures which scatter at low q, perhaps outside the accessible q range → change detector distance, change λ, check with SLS

SAXS on metal alloys

SAXS measurements on Al-Mg-Li alloy for two aging conditions



Evolution of precipitate radius during ramp heating experiments on these two initial aging conditions



Deschamps A. and De Geuser F. Metallurgical and Materials Transactions A, 44, 2013, 77-86

Small-angle scattering: Power law

Slope of the scattering curve: power law behavior

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

How does the mass changes as a function of the size

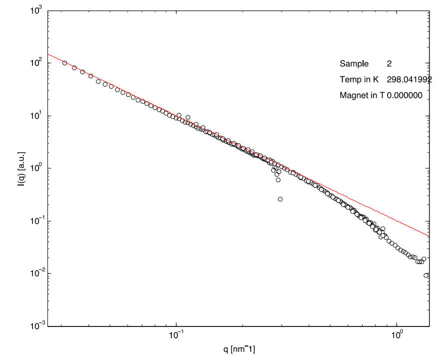
rod-like D=1

disk-like D=2

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

D=4 Porod scattering

→ sharp interphase of two phases, information about surface area



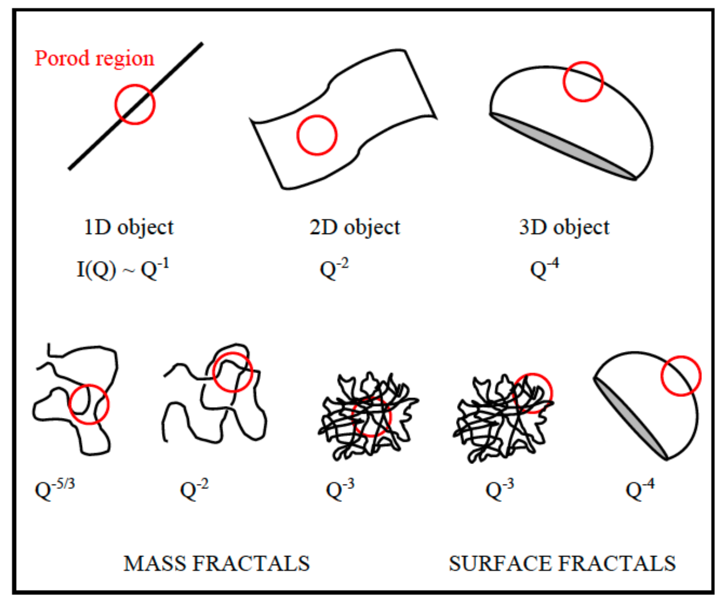
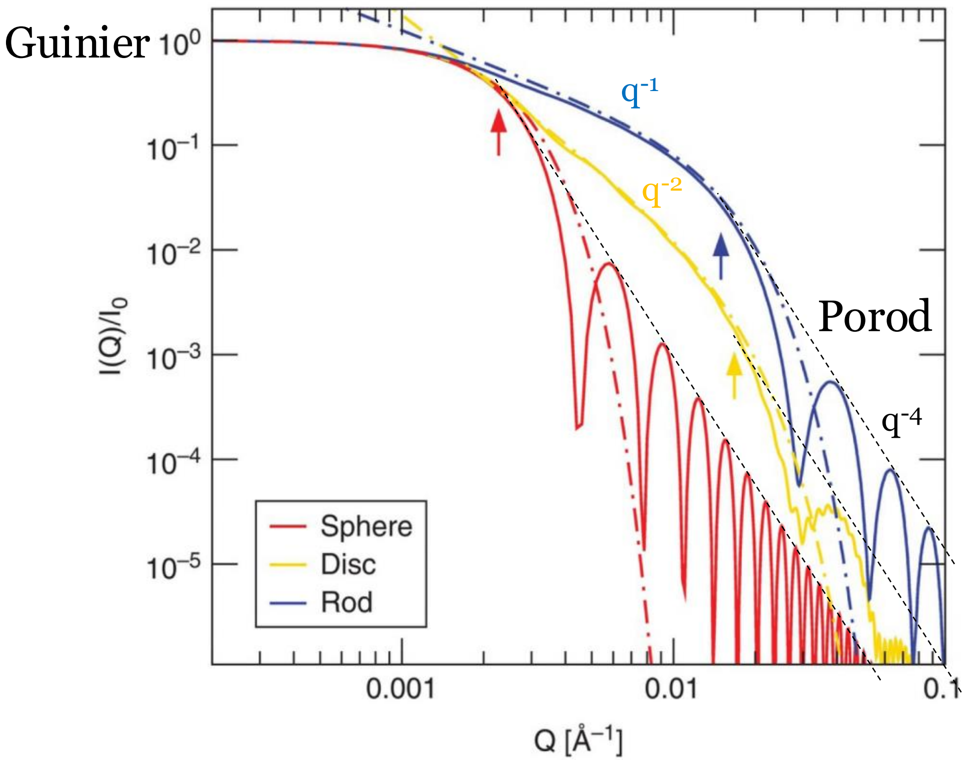


Figure 7: Assortment of Porod law behaviors for different shape objects.

small-angle X-ray scattering size & shape



An Introduction to Synchrotron Radiation: Techniques and Applications, Second Edition. Philip Willmott.

sphere, disc and rod with the same characteristic length (radius of gyration) → same scattering at low *q* (Guinier regime)

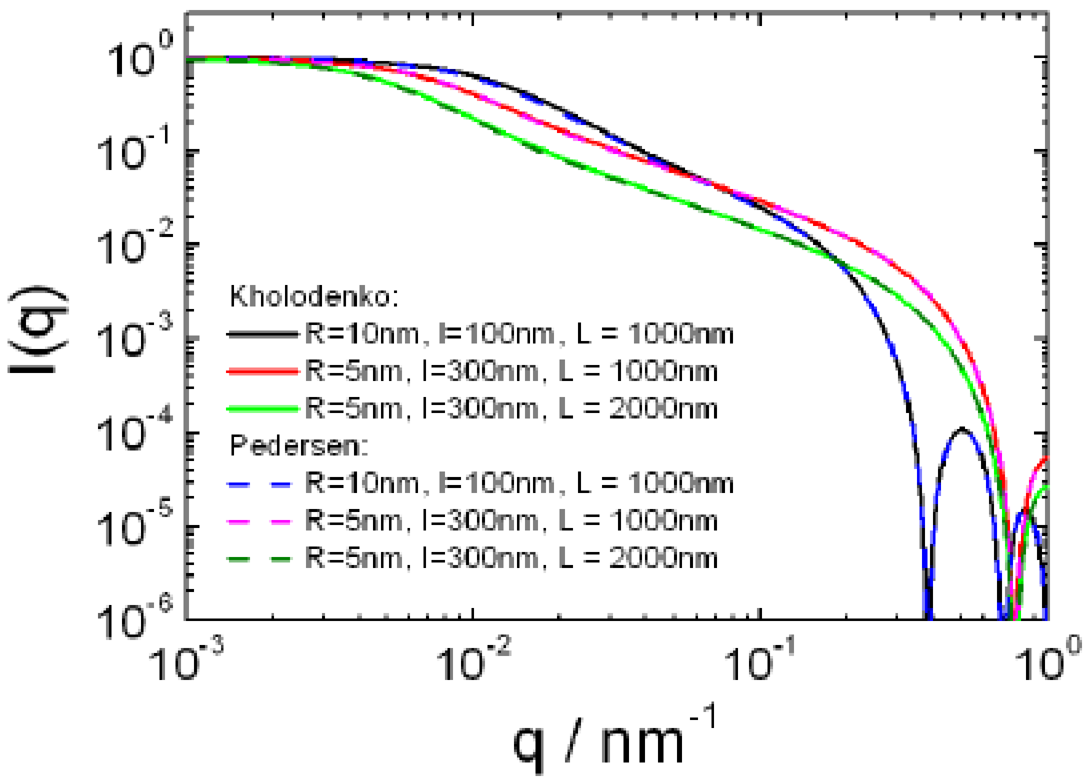
intermediate region depends on fractal dimension

q^{-1}: rod

q^{-2}: disk

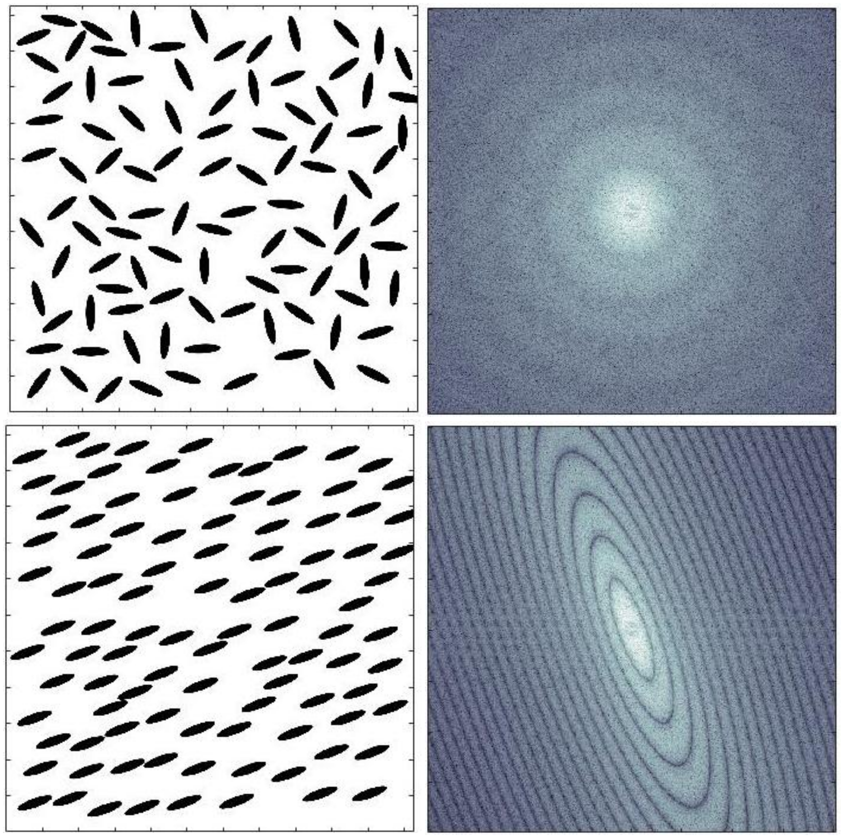
at high *q*: Porod regime q^{-4}

Measuring persistence length: small-angle scattering



semi-flexible worm-like structure
l: Kuhn length (= $2l_p$ persistence length)
L: contour length

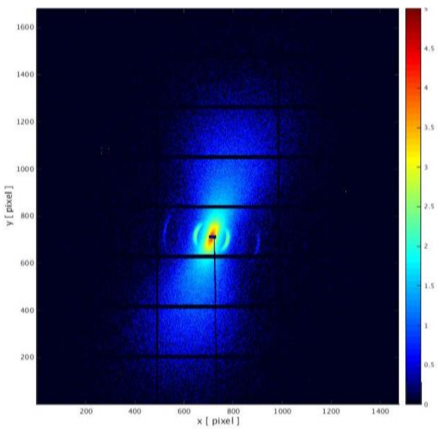
small-angle X-ray scattering: anisotropic particles



anisotropic and aligned particles produce anisotropic scattering

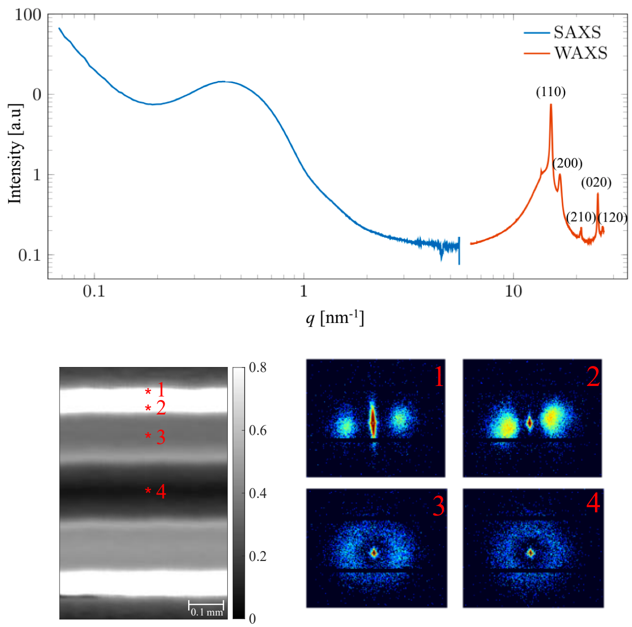
→ direct determination of orientation of nanoparticles!

SAXS of anisotropic materials

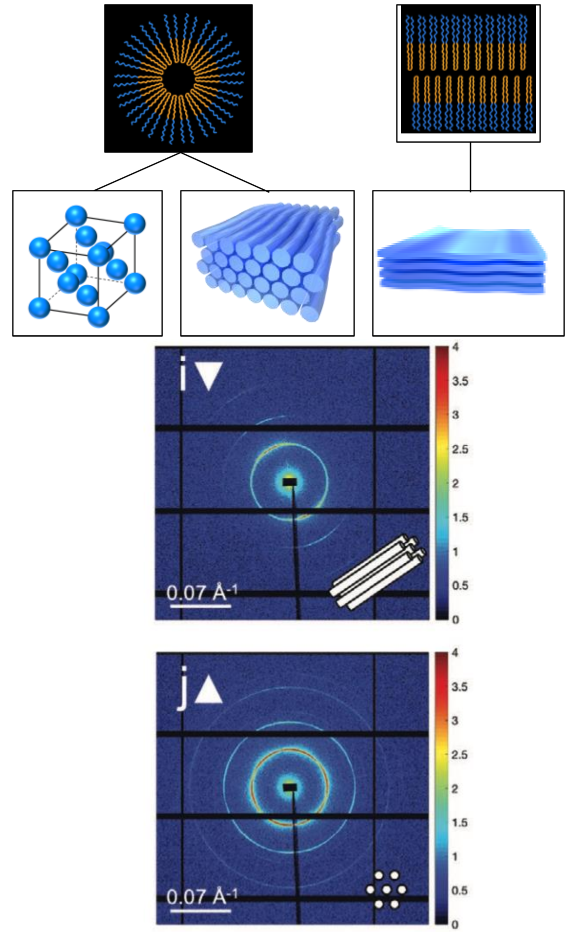


SAXS signal from mineralized collagen in human bone

CHALMERS

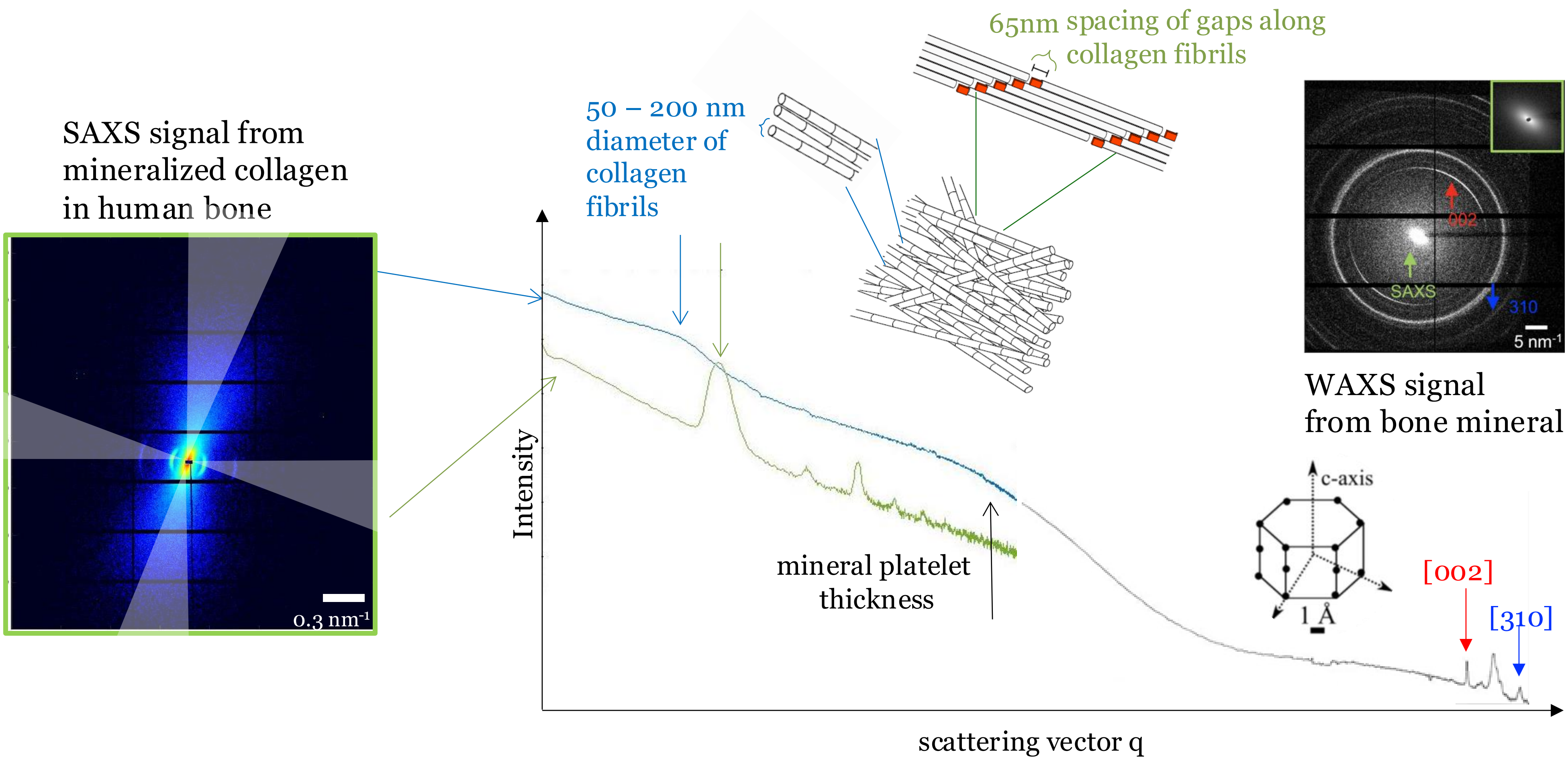


SAXS signal from different layers in injection-molded polymers



SAXS signal from liquid crystals oriented in flow

Small-and wide- angle x-ray scattering: Bone



Small-angle scattering

- Fraunhofer approx. Fourier theorem:

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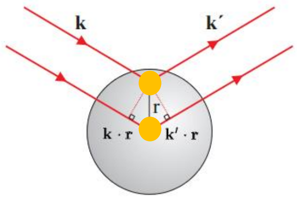
BUT we don't measure field but the intensity, which is the squared field: complex quantity: complex part (the phase) get lost → **the phase problem**

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

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

Scattering and Fourier Transform

2 electrons



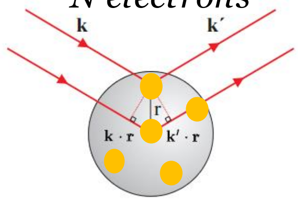
Phase difference of electron placed at position $\vec{r}$:
$\Delta\varphi(\boldsymbol{r}) = (\boldsymbol{k} - \boldsymbol{k}') \cdot \boldsymbol{r} = \boldsymbol{q} \cdot \boldsymbol{r}$

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

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

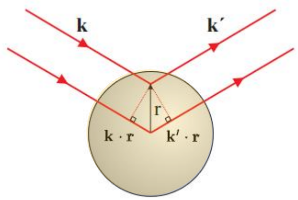
→ *contribution of electron placed at origin* ($\boldsymbol{r} = \vec{0}$)

N electrons



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

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



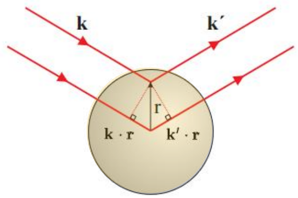
atomic form factor: $f^0(\boldsymbol{q}) = \int \rho(\boldsymbol{r}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}} d\boldsymbol{r}$

Fourier Transform of electron density distribution !

Scattering amplitude: $A(\boldsymbol{q}) = -r_0 f^0(\boldsymbol{q}) = -r_0 \int \rho(\boldsymbol{r}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}} d\boldsymbol{r}$

Atomic form factor and structure factor → scattering from unit cell

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

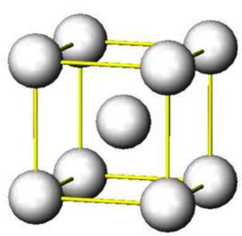


at large **Q**: small structure
atomic scales

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

Fourier Transform of electron density distribution !

→atomic form factor f



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

Scattering amplitude: $A(\boldsymbol{q}) = \sum_n e^{i\boldsymbol{q}\cdot\boldsymbol{R}n} \sum_j f_l(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}j}$

lattice

unit cell structure factor

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

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

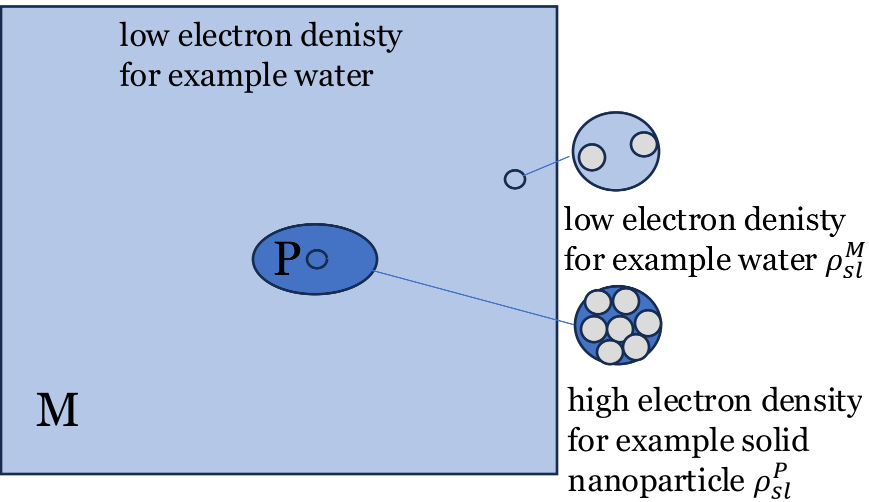
we measure intensity $I(\boldsymbol{q}) = |A(\boldsymbol{q})|^2$

WAXS/XRD and SAXS

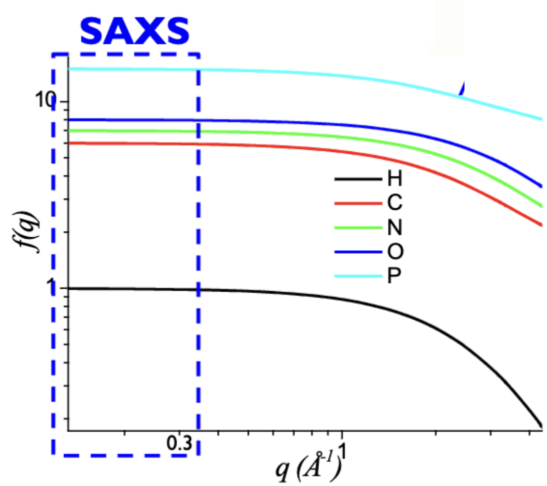
scattering length density, proportional to average electron density

$$A(\boldsymbol{q}) = \int \rho_{sl}\, e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\, dV$$

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



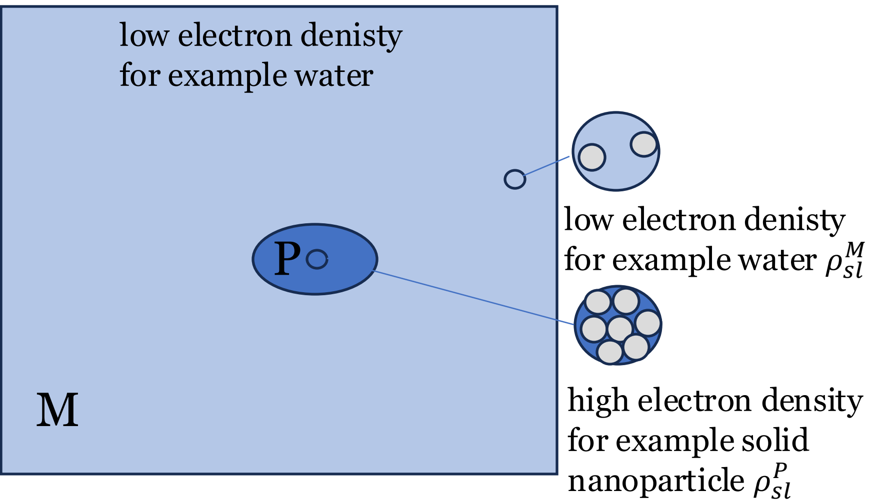
at small **Q**: larger structures nanometer scales



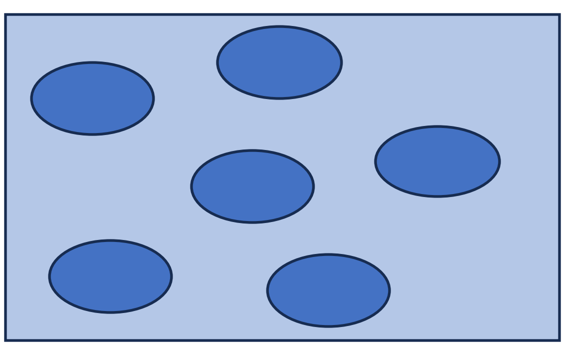
Data taken from International Tables for Crystallography, Vol. C, Table 6.1.1.1

note that the <u>atomic</u> form factor in the SAXS regime is a constant

WAXS/XRD and SAXS



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



scattering length density, proportional to average electron density

$$A(\boldsymbol{q}) = \int \rho_{sl}\, e^{i\boldsymbol{q}\cdot\boldsymbol{r}} dV$$

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

$$I^{SAXS}(\boldsymbol{q}) = (\rho_{sl,P} - \rho_{sl,M})^2 \left| \int e^{i\boldsymbol{q}\cdot\boldsymbol{r}} dV_P \right|^2$$

$$P(\boldsymbol{q}) = \left| \frac{1}{V_P} \int e^{i\boldsymbol{q}\cdot\boldsymbol{r}} dV_P \right|^2$$

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

$$I^{SAXS}(\boldsymbol{q}) = \Delta\rho^2 N_P\, V_P^2 P(\boldsymbol{q})$$

non-dilute system: inter-particle interaction

$$I^{SAXS}(\boldsymbol{q}) = \Delta\rho^2 N_P\, V_P^2 P(\boldsymbol{q})\ \mathrm{S}(\boldsymbol{q})$$

$S(\boldsymbol{q})$ = particle structure factor

Mathematical modelling of Small-angle scattering

$$I(q) = (\rho_{\mathrm{P}} - \rho_M)^2 N_P V_P^2 P(q) S(q)$$

$\rho_{\mathrm{P}} - \rho_M$: contrast in scattering length density between particle and matrix

for X-rays: electron density difference
for neutrons: neutron scattering length density difference

also referred to as η

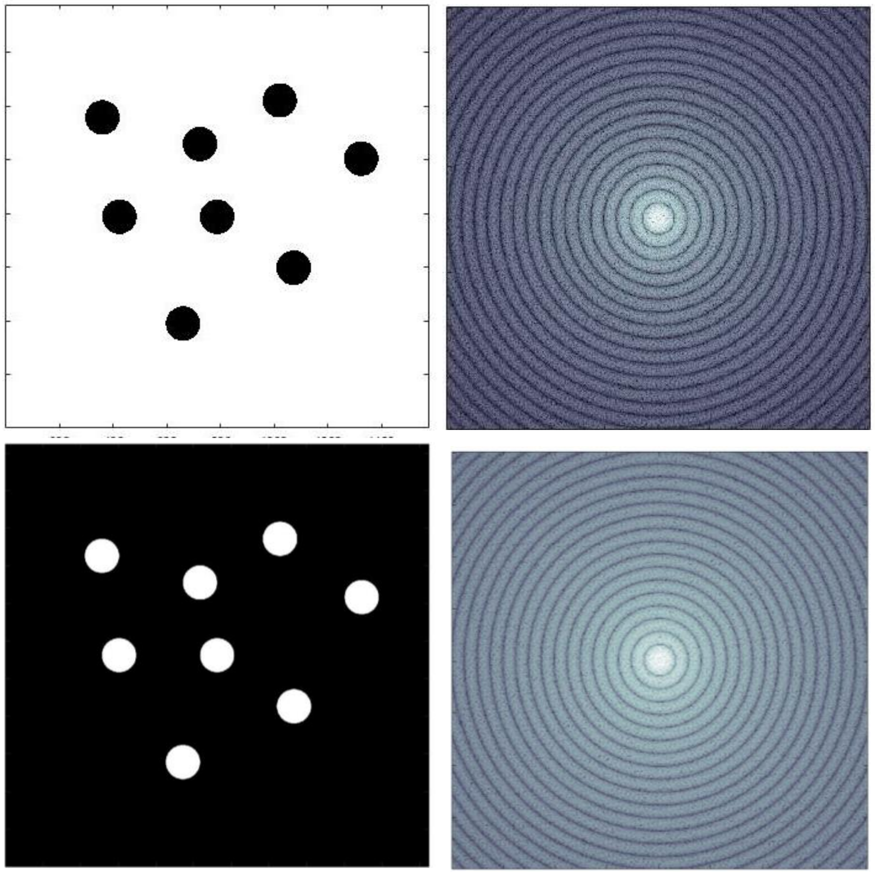
N_P: number of particles
V_P: volume of particles

Formfactor P(q)
Intra-particle interference
shape, size

Structure factor S(q)
Inter-particle interference
spacing, interactions

small-angle X-ray scattering

$$I(q) = (\rho_P - \rho_M)^2 N_P V_P^2 P(q) S(q)$$



Babinet's principle:

particle vs. pores

same diffraction pattern apart from overall intensity

only sensitive to electron density difference!

Model dependent fitting: Formfactor

$$I(q) = (\rho_P - \rho_M)^2 N_P V_P^2 P(q) S(q)$$

3.1. Spheres & Shells

3.1.1. Sphere.

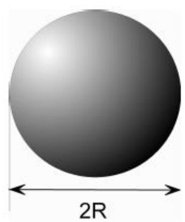


FIGURE 3.1. Sphere with diameter $2R$

$$I_{\text{Sphere}}(Q,R) = K^2(Q,R,\Delta\eta) \quad (3.1a)$$

with

$$K(Q,R,\Delta\eta) = \frac{4}{3}\pi R^3 \Delta\eta \, 3\frac{\sin QR - QR\cos QR}{(QR)^3} \quad (3.1b)$$

The forward scattering for $Q = 0$ is given by

$$\lim_{Q=0} I_{\text{Sphere}}(Q,R) = \left(\frac{4}{3}\pi R^3 \Delta\eta\right)^2$$

Input Parameters for model `Sphere`:

- `R`: radius of sphere R
- `---`: not used
- `---`: not used
- `eta`: scattering length density difference between particle and matrix $\Delta\eta$

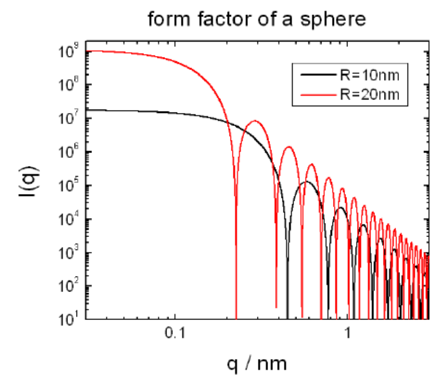


FIGURE 3.2. Scattering intensity of spheres with radii $R = 10\text{nm}$ and $R = 20\text{nm}$. The scattering length density contrast is set to 1.

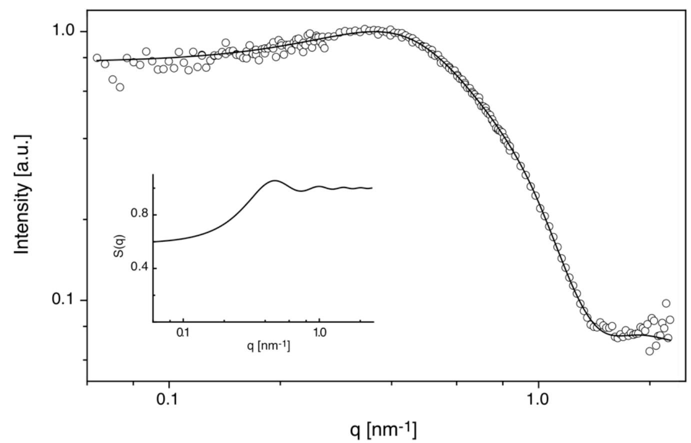
sasfit manual: https://kur.web.psi.ch/sans1/SANSSoft/sasfit.pdf

Model dependent fitting: Structure factor

$$I(q) = (\rho_P - \rho_M)^2 N_P V_P^2 P(q) S(q)$$

Formfactor P(q)

Structure factor S(q)
Interacting particles
→Measure different concentrations



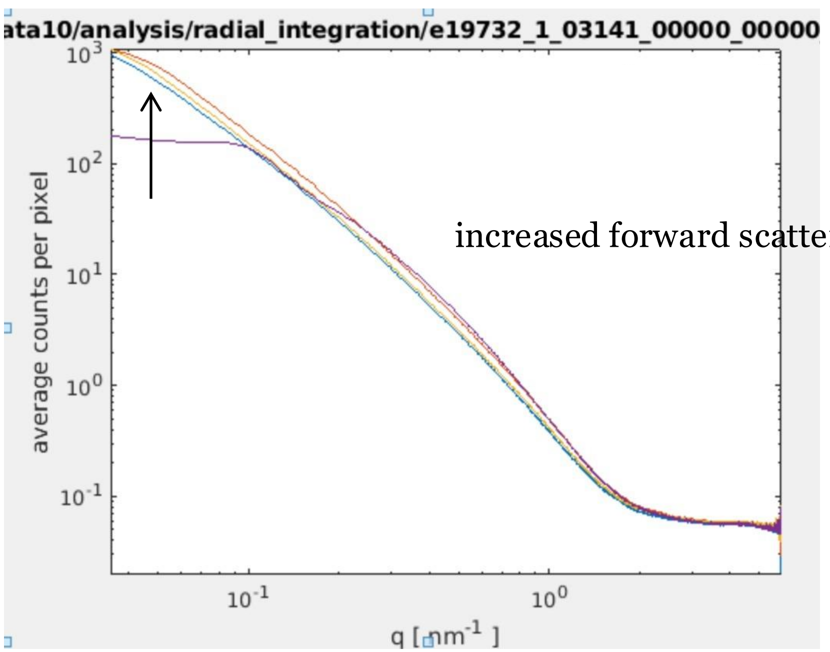
example: Phospholipid micelle
ellipsoidal form factor
hard sphere structure factor (hard sphere radius larger than radius of micelles)

Beck, P., et al. (2010). Langmuir **26**(8): 5382-5387.

Model dependent fitting: Structure factor

$$I(q) = (\rho_P - \rho_M)^2 N_P V_P^2 P(q) S(q)$$

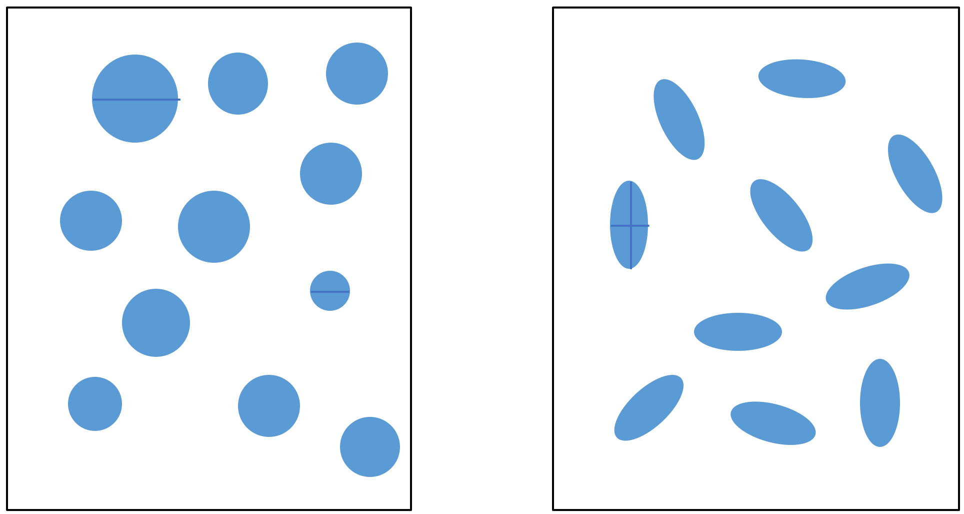
Structure factor S(q)
Interacting particles



increased forward scattering: typical sign of aggregation

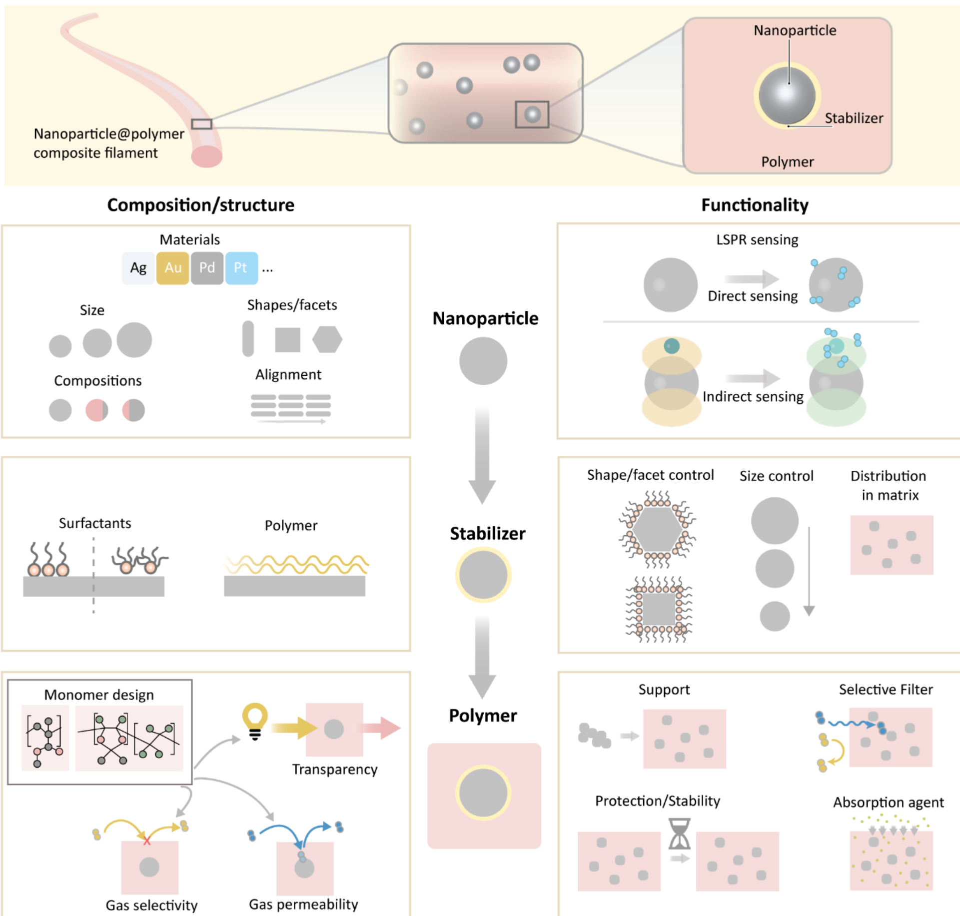
Polydispersity is the devil…

Small-angle scattering is a statistical method of all length scales in a sample
particle polydispersity or particle shape?



Application example from material science

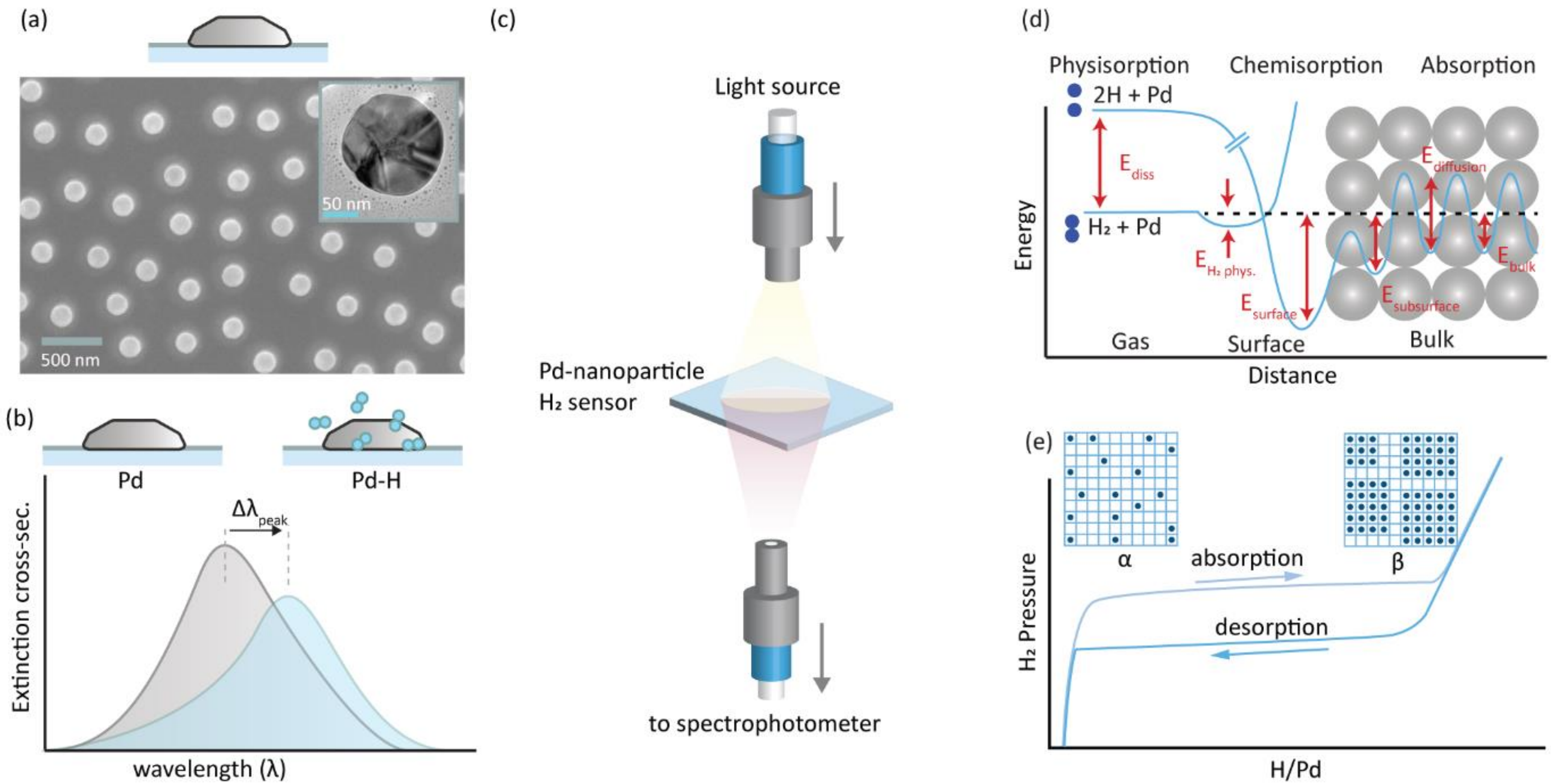
Hydrogen gas sensors:
Plasmonic plastic Nanocomposites



Plasmonic plastics comprise three key components:

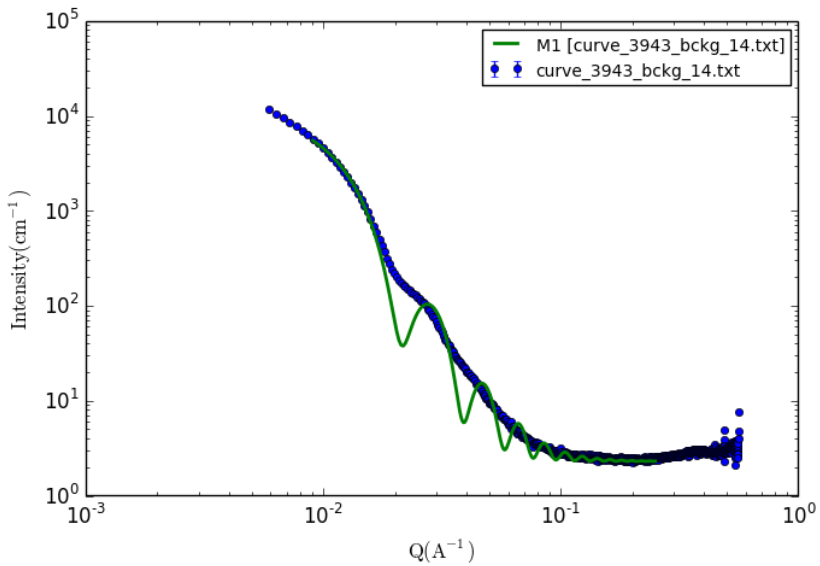
(i) plasmonic metal nanoparticles
(ii) surfactant/stabilizer molecules on the nanoparticle surface
(iii) polymer matrix, and how they can be tailored from a composition/structure and functionality perspective.

Hydrogen gas sensors: Plasmonic plastic Nanocomposites

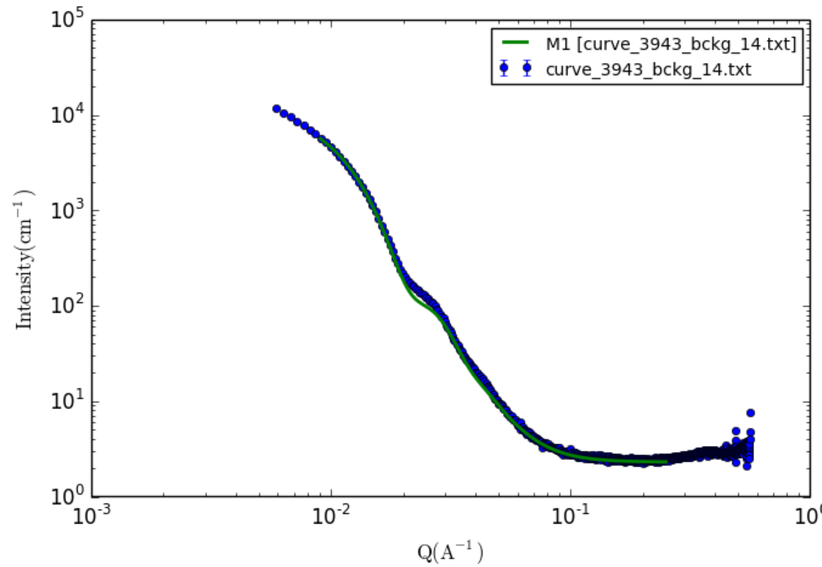


Plastic-Plasmonic composites

Plasmonic nanoparticle for hydrogen sensing



Fitted curve of monodisperse cubes

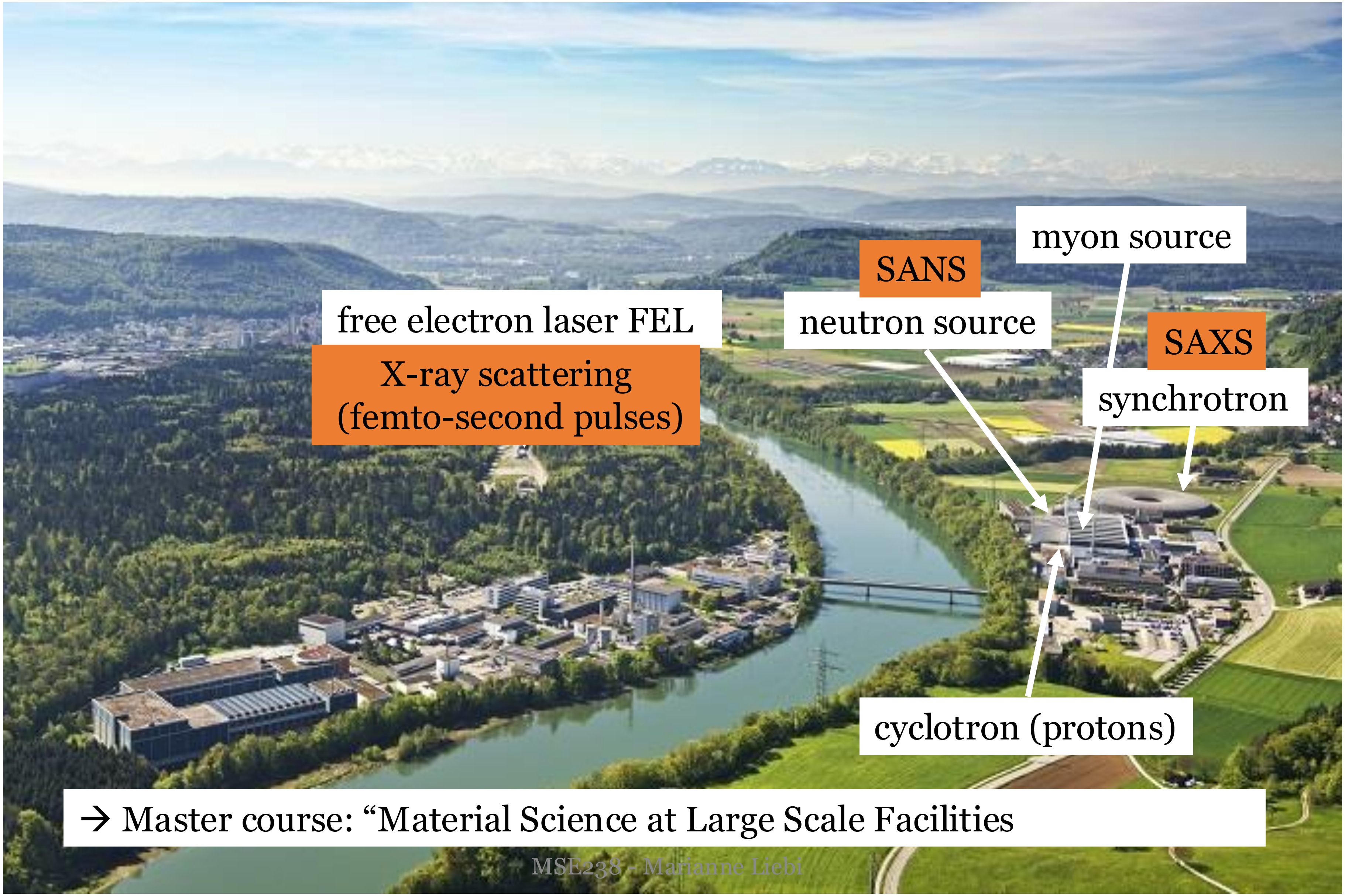


Fitted curve of polydisperse cubes

Form factor for a rectangular prism

$$P(q) = \frac{2}{\pi} \times \int_0^{\frac{\pi}{2}} \int_0^{\frac{\pi}{2}} A_P^2(q) \ \sin\theta \, d\theta \, d\phi$$

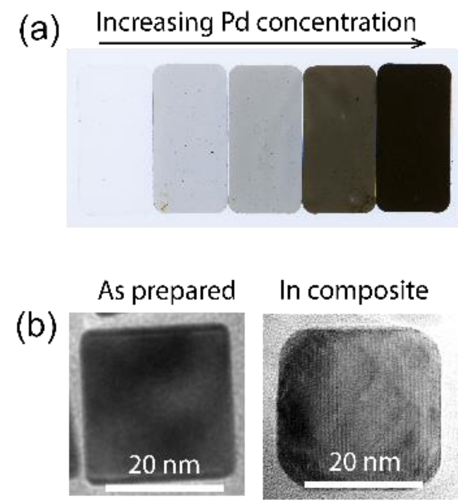
size of cube: 26.8 nm ± 2.2 nm



→ Master course: "Material Science at Large Scale Facilities

Plastic-Plasmonic composites

Plasmonic nanoparticle for hydrogen sensing



- The nanoparticles are protected inside the polymer matrix, while still able to perform the efficient hydrogen sensing.
- SAXS with a highly focused X-ray beam in a synchrotron was used to study the spatial distribution of nanoparticles, and determine their size.

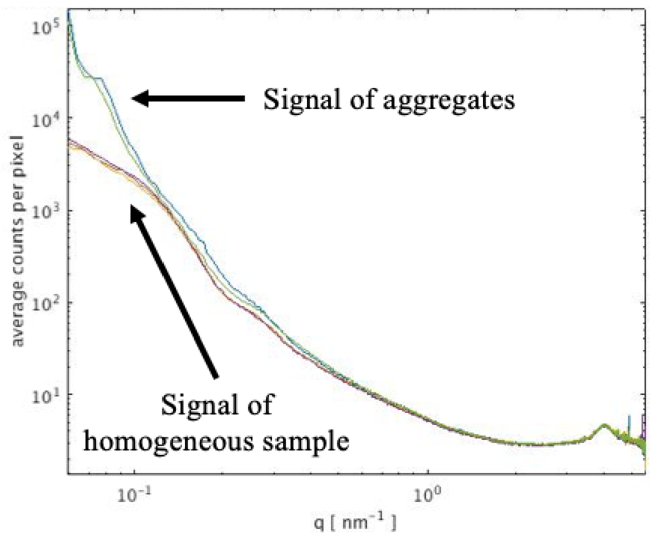
TEM
direct image of nanoparticle!
small field of view

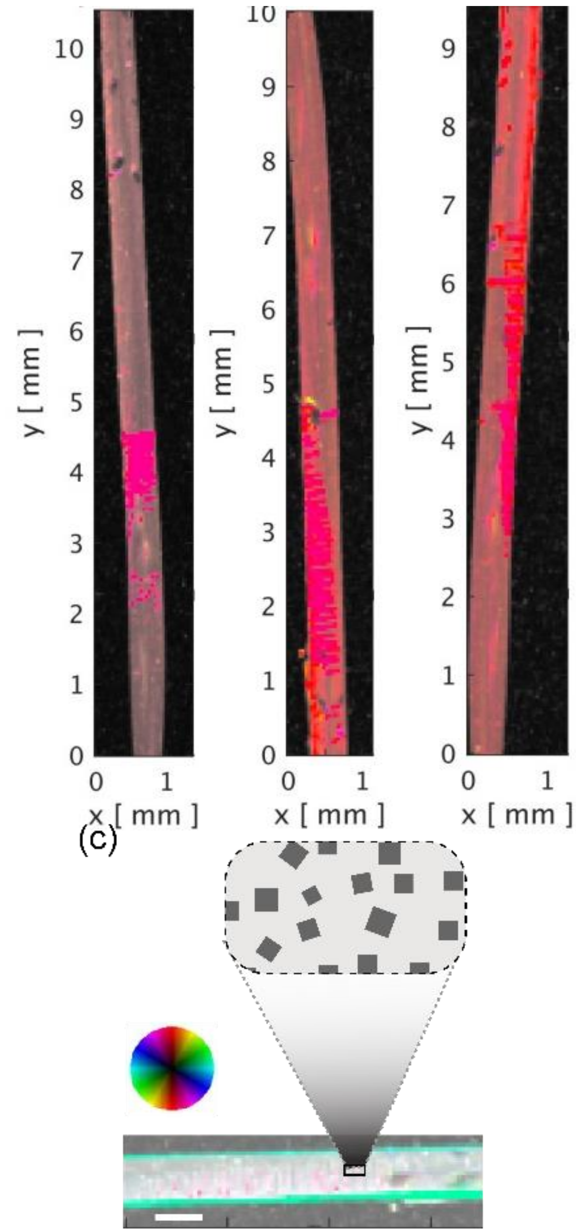
SAXS
indirect measurement, model fitting

Plastic-Plasmonic composites

Plasmonic nanoparticle for hydrogen sensing

- 3 slices of the same sample show inhomogeneities
- Scattering pattern shows the presence of aggregates





Summary

- SAXS probes electron density differences in the nanometer scale
- Scattering as the Fourier transform of the real structure, no direct solution because only the intensity can be measured
- model indpendent analysis:
  - diffraction peaks → Bragg law
  - Guinier approximation → size
  - Power law → fractal dimension, shape
  - Porod regime → surface
  - orientated particles
- mathematical modelling
  - SAXS vs XRD
  - particle form factor and structure factor
- Material science application example