Week 11

Characterization of Materials: Scattering

Exercise 1
Answer these questions by true or false:

1. SAXS signal derives from the electron-density contrast of the sample
   True/false

2. The Guinier regime operates at scattering-vector values for which $q > 2\pi/d$, whereby d is the characteristic size of the scattering elements
   True/false
   Operates at scattering-values where $q<2\pi/d$

3. In SAXS the field distribution measured is the Fourier transform of the electric field distribution in the exit plane of a sample
   True/false

4. A diffraction peak appears in powder diffraction measurements but never in a small-angle X-ray scattering experiment
   True/false
   Diffraction peaks can also be found in SAXS experiments, if a well defined repetitive length scale is found in the sample, in the range of a few nm to a few 100 nm, examples for that are lyotropic liquid crystals

Exercise 2:
Select the correct answer(s) (more than one answer can be correct)

1. SAXS …
   a. Is used in determining atomic positions in crystals
   b. Involves elastic scattering processes
   c. Is used in determining general sizes and shapes of objects in the few nanometer-to-micron range
   d. Can only be applied for crystalline samples
   e. Can only be applied for amorphous samples

2. What is a structure factor in small-angle scattering
   a. the interparticle interference
   b. the intra-particle interference
   c. provides information on the spacing between scattering objects and their interaction

3. The Porod regime…
   a. Provides information on the shape of the scattering particles
      This is in the intermediate q-regime between Guinier and Porod regime, the slope and change of slope.
   b. Provides information on the roughness of the interface of the scattering particles in their surrounding medium
   c. Provides information on the overall size of the scattering particles
      That is provided in the Guinier regime

4. Two samples are investigated at the same beamline using identical incident radiation. Sample A consists of an ensemble of particles with a difference in electron density relative to the medium in which they sit of = 0.2 e/Åand a number density of particles of = 1000/mm. Sample B on the other hand contains identically shaped particles, but with = 0.1 e/Å and = 4000/mm. Which sample produces a stronger SAXS pattern?
   a. Sample A
   b. Sample B
   c. Both exhibit the same intensity

Exercise 3: Experimental setup

1. You want to measure bone using small-angle X-ray scattering with an energy of 12.4 keV, the interesting features you expect to be the spacing along the collagen fiber with a d-period of 67 nm, what is the minimum distance you need to place your detector at for measuring the collagen peak when you have a 1mm beamstop blocking the direct beam mounted 1cm in front of the detector?
   Using $q = 4\pi\sin(\theta)/\lambda$ and $d = 2\pi/q$, calculate the scattering angle $2\theta \approx 0.0855°$ The horizontal distance needed between sample and detector can be calculated from $dist = \frac{r}{\tan(2\theta)} + 10mm$, with $r = 0.5mm$ for the beamstop radius. This gives $dist \approx 345mm$.
2. If you want to also measure the diameter of the collagen fiber which you expect to be in the range of 150 – 200 nm, do you need to move the detector closer or further away?
   Larger structures scatter at smaller angle, thus the detector needs to be moved further away
3. How large do you need the detector area to be, to also measure the (002) peak of the hydroxy-apatite (hexagonal crystal structure) and a lattice parameter c = 6.88 Å?
   The interplanar distance of the (002) planes in the hexagonal structure are calculated by d = c/2. Using $q = 4\pi\sin(\theta)/\lambda$ and $d = 2\pi/q$, calculate the scattering angle $2\theta \approx 16.7°$. The detector size can be calculated from $l = \tan(2\theta) * dist$ using dist calculated in (1), we have $l = 103.5mm$. Then $area = (2l)^2 \approx 428cm^2$

Exercise 4: Scattering of nanoparticles and Guinier law

In Figure 1 you see the small-angle neutron scattering (SANS) curve of a colloidal dispersion consisting of silica spheres coated with octadecane in toluene.

The Guinier approximation is given by the equation: $I(q) \approx I(0)e^{-(1/3)q^2R_G^2}$

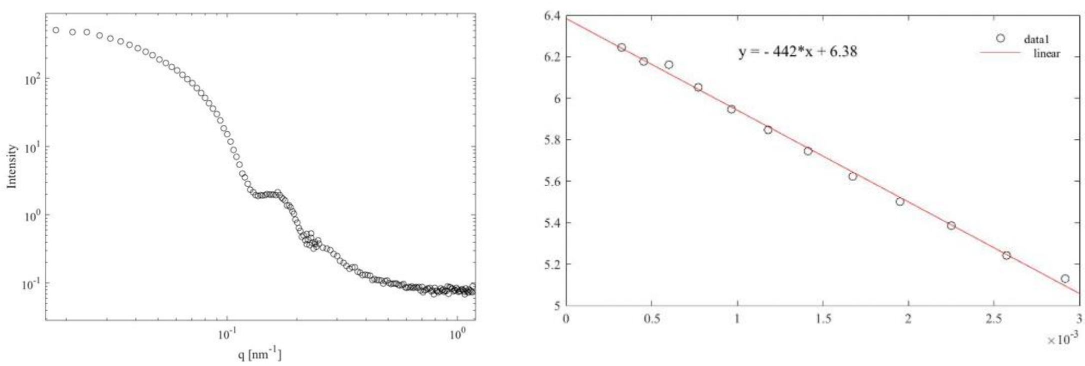


Figure 1. a) SANS curve of colloidal dispersion b) corresponding Guinier plot

a. Label the x and y axis of Figure 1b, assuming that it is a standard Guinier plot.
x-axis: q^2 y-axis: ln(I(q))

b. Determine the radius of gyration using the Guinier approximation

$$R_G = \sqrt{3 * 442} = 36.4 \text{ nm}$$

c. Determine the radius of the colloidal particle

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

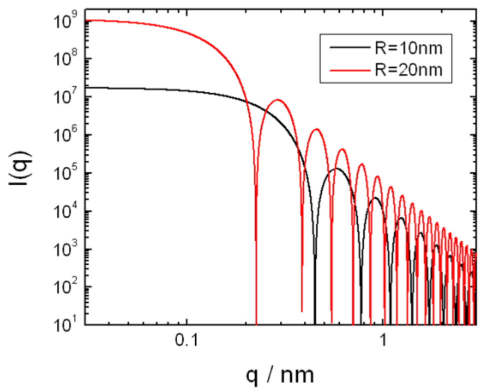
$$R = \sqrt{5/3\, R_G} = 47 \text{ nm}$$

d. The colloidal particles have been stored for a long time and they started to agglomerate, which part of the scattering curve would you expect to change and why?
The first part (low-q regime) will change, interaction between particles: structure factor, at low q, other argument: structures are getting larger with agglomeration, thus larger structure: lower scattering angle, the low-q part will change (increase)

e. Consider Exercise 4 of week 10 where you calculated the expected end to end distance of a polyethyleneoxide assuming random walk. How can you measure this value with scattering?
A SAXS experiment which includes the Guinier regime, with the Guinier approximation the Radius of Gyration can be calculated, which relates to the end to end distance R with the formula $R_G = R\left(\frac{1}{6}\right)^{1/2}$

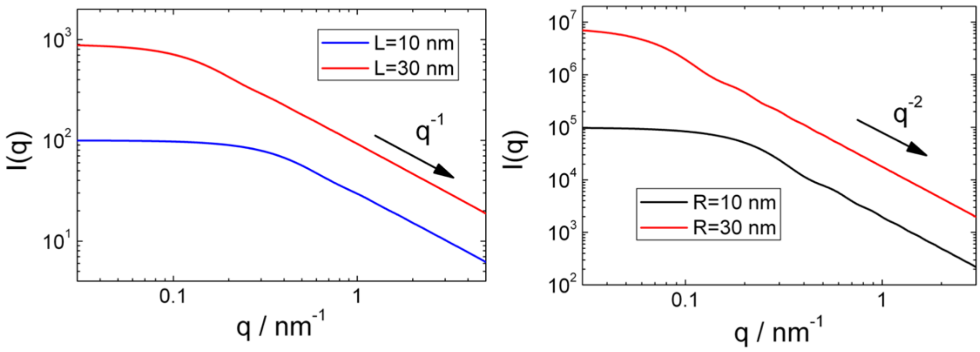
Exercise 5: Scattering of nanoparticles and form factor

a. The following figure shows the simulated scattering of spheres. Which of the curves revers to the larger spheres? Justify your answer



The Guinier regime, i.e. the plateau at small q-values for the red curves stopps at smaller q-values compared to the black curve, and the Guinier regime relates to the size of the particle. The smaller q-values refer to larger sizes (reciprocal space!) thus the red curve is from larger spheres.

b. Which curves belong to a long cylinder and which belong to a flat disk. Justify your answer



The slope of the scattering in the intermediate q-range (larger q-range than the Guinier plateau) relates to the shape of particles and their fractal dimension, i.e. how the characteristic size (radius R for a disk, length L for a long cylinder) relates to their volume.
Long cylinders V= $\pi R^2 L$, characteristic length is length of cylinder L, does fractal dimension is 1 thus the scattering curves on the left with slope in double log-plot -1
Flat disk V= $\pi R^2 L$, characteristic length is the radius R of the cylinder, does fractal dimension is 2, thus the scattering curve on the right with slope in double log-plot -2

c. Are the red curves in b. characteristic for the larger or smaller nanoparticles compared to black/blue? Justify your answer
With the same argumentation as in a. The red curve transitions at lower q from the Guinier plateau into the slope characteristic for the shape of the particle, does the red curves relate to larger particles.

Exercise 6: Synchrotron scattering/ diffraction experiments
List three advantages of performing scattering/diffraction experiments at synchrotrons rather than using a lab source

1. Much larger flux of synchrotrons compared to lab-based sources (allowing for example much faster measurements, time resolution)
2. The very small divergence of synchrotron radiation allows to resolve diffraction peak better (advantage for crystal size, strain analysis, or for resolving partially overlapping signals which would not be resolved in lab sources
3. The large working volume (sample space) in typical beamlines that allows more complex sample environments to be installed, allowing for example in-operando experiments of 3D printing of metals
4. The ability to focus down to sub-micron dimensions, allowing the investigation of extremely small samples, plus possibility of scanning across heterogenous samples
5. The possibility at some synchrotrons to access very high photon energies, above 100 keV, allows to probe deeply into samples (for example larger metal samples)
6. Detectors with small pixels and long beamlines where the detector can be placed many meters after the sample allow to reach smaller scattering angles, thus larger structures can be probed