SCATTERING [100 points total]

Please use separate pieces of paper for EM and Scattering.
Don't forget to write down your name on every piece of paper!
For scattering you can write your answers either in English or in Dutch.

1. Explain the idea of contrast variation using the H/D substitution. Is it used in light, x-ray or neutron scattering? Why is it useful? [10 points]

Hydrogen/deuterium substitution is used in neutron scattering.
Since both H and D have relatively large scattering length with different sign, the scattering length density ζ can be varied in a wide range. One can vary ζ of the solvent; one can also (partially) deuterate a part of your macromolecule, (nano)particles, etc. This allows one revealing fine details of the structure of the scattering objects.

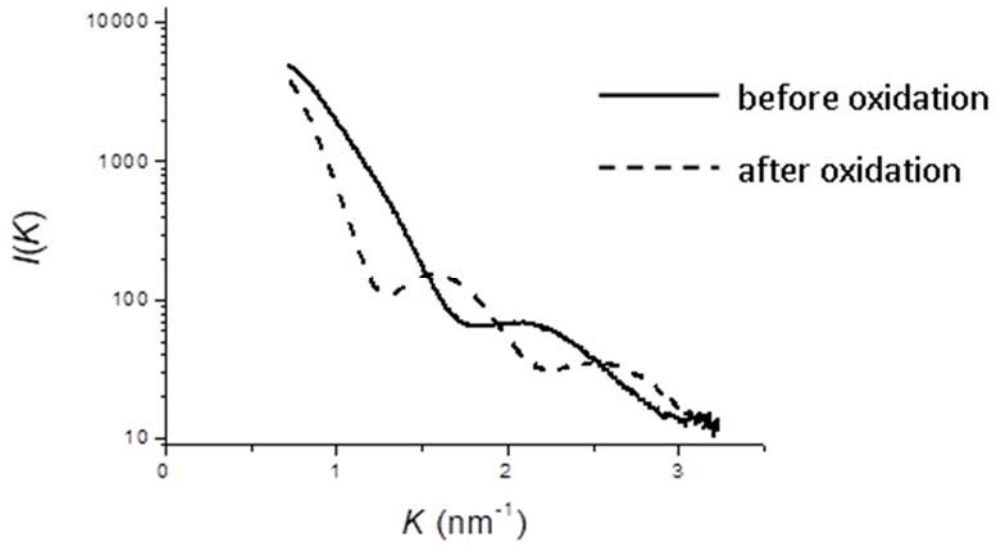
2. What is the difference between the Guinier range and the Porod range? What type of information can be obtained from the measurements in these two cases? [10 points]

Guinier range is the range of small K-values, $Ka < 1$, where a is the characteristic size of the scattering objects. Porod range is in another extreme, $Ka >> 1$.
From the Guinier range the radius of gyration can be determined in dilute suspensions.
From the Porod law the total surface area can be estimated.

3. What is the radius of gyration? How can it be determined from the scattering data? [10 points]

The radius of gyration R_g is a measure of the typical size of a scattering object. It equals to the mean-square distance from the centre of the objected weighted with the scattering length.
The radius of gyration R_g can be determined by fitting a straight line to the dependence of the logarithm of the scattering intensity versus K^2 for the smallest K-values. The fit must be performed in the Guinier range, $KR_g < 1$, at low concentration of the scattering objects so that there is negligible correlation between their positions.

4. The figure below displays the intensity of the small-angle x-ray scattering $I(K)$ as a function of the scattering wavevector K for iron nanoparticles before (solid line) and after (dashed line) oxidation.



a). The data is taken between K_{min} = 0.8 nm^{-1} and K_{max} = 3.2 nm^{-1}. What range of scattering angles θ was used in this experiment? The x-ray wavelength was λ = 0.1 nm. [15 points]

Using $K = \frac{4\pi}{\lambda} n \sin\frac{\theta}{2}$, with $n = 1$ for x-rays, one can easily get $\theta_{\min} = 12\ \text{mrad} = 0.73°$ and $\theta_{\max} = 51\ \text{mrad} = 2.9°$.

b) Do the particles become larger or smaller after the oxidation? Clearly motivate your answer! [10 points]

After oxidation the minima in the scattering profile shift to the left and the distance between them reduces. Since the minima occur at fixed values of $K\sigma$, where σ is the diameter, smaller values of K at the minima suggest that the diameter is larger.

c) Give a rough estimate of the particle diameter <u>*after*</u> oxidation. [15 points]

The positions of the minima are about 1.3 nm^{-1} and 2.2 nm^{-1}.
From the first minimum position σ = 2a = 4.49 * **2** / 1.3 = 6.9 nm. [Do not forget **2**!]
From the second minimum position σ = 2a =7.72 * **2** / 2.2 = 7.0 nm.
From the distance between minima σ = 2π / 0.9 = 7.0 nm.

d) Explain why the minima in the curve are not very deep. Give two possible reasons [10 points]

The minima are not very deep due to effects such as **particle polydispersity** and **finite resolution** of the experimental setup.

As an additional reason, background scattering could also be mentioned. We always attempt to measure the background signal as good as possible. However, its subtraction could be incomplete in some cases thus making minima less deep.

5. Imagine that one studies the same system (as above) using light scattering.
   a) What range of K can be reached with light having the wavelength of $\lambda = 628$ nm? Assume that the average refractive index in the sample is n = 1.5 and that the scattering angle can be varied between 5 and 180 degrees. [10 points]

For light one needs to account for the refractive index n of the sample: $K = (4\pi/\lambda)n\,sin(\theta/2)$. By plugging in the numbers one gets $0.0013 < K < 0.03$ nm^{-1}.

   b) Can light scattering supplement the x-ray data shown above? Are there advantages/disadvantages in using light? Describe at least 3 advantages and/or disadvantages of using light in this case. [10 points]

Possible answers (list is not exhausted) are given below. You get 3 points for each correct answer with a maximum of 10 points. I can, however, subtract some points for nonsense answers.
[+] One could complement the x-ray data with light scattering, which can reach much smaller K values (compare numbers given in 4a with the answer in 5a). Here one could attempt determination of R_g.
[+] With smaller K values one could also see whether particles aggregate and form much larger objects.
[+] Light scattering is advantageous since it is simple, fast and (relatively) cheap.
[-] However, one has to take care of careful index matching, which is difficult to achieve in many cases. One can, for example, easily get too much multiple scattering if the sample is too turbid.
[-] Another problem of light scattering, which especially harmful in this case, is that iron oxide nanoparticles strongly adsorb light.

Possibly useful relations

$$2d \sin\frac{\theta}{2} = n\lambda$$

$$K = \frac{4\pi}{\lambda} n \sin\frac{\theta}{2}$$

$P(K) = \left(3\frac{\sin Ka - Ka\cos Ka}{(Ka)^3}\right)^2$, minima at *Ka* = 4.49, 7.72, 10.90, …

$$R_g{}^2 = \frac{\sum_i b_i(\mathbf{r_i} - \mathbf{R_b})^2}{\sum_i b_i}$$

$$I_{\mathrm{sc}}(K) \cong I_{\mathrm{sc}}(K \to 0) \exp\left(-\frac{1}{3}K^2 R_g{}^2\right)$$

$$I_{\mathrm{sc}}(K) \cong \frac{A}{K^4}$$

$$I_{\mathrm{sc}}(K) \cong \frac{A}{K^n}$$