Chapter 5

Small angle neutron scattering, SANS

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Elastic neutron scattering, or *neutron diffraction* was first used to reveal the crystal structure of materials, as will be presented in chapter 6. Here, we consider the conceptually simpler - but historically later developed - field of (elastic) small angle neutron scattering (SANS), which provides information on the size and shape of nanometer-sized objects. The SANS technique is particularly useful within biological and other organic systems, where the difference in scattering length between hydrogen (H) and deuterium (D) can be utilized to enhance domains of specific interest in the system under investigation.

5.1 The cross section for neutron diffraction

Our starting point is the elastic scattering cross section, (2.44).

$$\frac{d\sigma}{d\Omega} = \frac{k_{\mathrm{f}}}{k_{\mathrm{i}}} \left(\frac{m_{\mathrm{n}}}{2\pi\hbar^2} \right)^2 \left| \left\langle \psi_{\mathrm{i}} \left| \hat{V} \right| \psi_{\mathrm{f}} \right\rangle \right|^2 . \tag{5.1}$$

We now consider the scattering from a system of nuclei. In analogy with (2.48), the scattering potential can be considered as the sum of the single nuclear potentials,

$$\hat{V} = \frac{2\pi\hbar^2}{m_{\mathrm{n}}} \sum_j b_j \delta(\mathbf{r} - \mathbf{r}_j), \tag{5.2}$$

By insertion, the scattering cross section becomes

$$\left. \frac{d\sigma}{d\Omega} \right|_{\text{nucl. el.}} = \left| \sum_j b_j \exp(iq \cdot \mathbf{r}_j) \right|^2 . \tag{5.3}$$

We here consider the nuclei as being fixed in position, *i.e.* we take $\mathbf{r}_j$ as constants. This is for small-angle scattering a very good approximation. For technical details on this approximation, see chapter 7 on the effect of (lattice) vibrations.

5.2 The SANS cross section

We will here consider only scattering vectors of sufficiently small length, q, so that the phase of the exponential, $\mathbf{q} \cdot \mathbf{r}_j$, does not vary significantly between neighbouring atoms. The condition for this is

$$qa \ll 1, \tag{5.4}$$

where a is a typical interatomic distance. For larger values of q, we are in a regime where the crystalline structure of the material is responsible for the scattering. This is explained in detail in chapter 6.

In a typical SANS experiment $q \leq 0.5$ Å^{-1} and only structures larger than $2\pi/q_{max} \approx 12$ Å are resolved. This implies that the scattering from the single atoms can not be distinguished and that it becomes valid to transform the sum in (5.3) into an integral

$$\sum_j b_j \exp(i\mathbf{q} \cdot \mathbf{r}_j) \longrightarrow \int_V \rho_b \exp(i\mathbf{q} \cdot \mathbf{r}) dV, \tag{5.5}$$

where ρ_b is the effective scattering length density for the material. For one formula unit of the material, this equals

$$\rho_b = \frac{1}{V_0} \sum_{\mathbf{d}} b_{\mathbf{d}}, \tag{5.6}$$

where V_0 here is the corresponding volume of one formula unit. After the transformation, the SANS cross section reads

$$\left.\frac{d\sigma}{d\Omega}\right|_{\text{SANS}} = \left| \int \rho_b(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) dV \right|^2. \tag{5.7}$$

5.3 SANS from particles in solution

We now consider one single nano-sized object suspended in a solution. (In practice this solvent could be water or an organic liquid). For the combined system, it is convenient to separate the volume integration into an integral over the object and an integral over the solvent.

$$\left.\frac{d\sigma}{d\Omega}\right|_{\text{SANS, 1}} = \left| \int_{\text{object}} \rho_b(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) dV + \rho_s \int_{\text{solvent}} \exp(i\mathbf{q} \cdot \mathbf{r}) dV \right|^2. \tag{5.8}$$

By using the *contrast* in scattering length density, $\Delta\rho(\mathbf{r}) = \rho_b(\mathbf{r}) - \rho_s$, the solvent integration can be turned into an integration over the entire volume, V:

$$\left.\frac{d\sigma}{d\Omega}\right|_{\text{SANS, 1}} = \left|\int_{\text{object}} \Delta\rho_b(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r}) dV + \rho_s \int_V \exp(i\mathbf{q}\cdot\mathbf{r}) dV\right|^2 . \quad (5.9)$$

For typical samples the total solvent volume is on the order of mm^3. This is roughly 5 orders of magnitude larger than the length scale of a typical nano-sized object. This implies that the small-angle scattering from the solvent in practice falls at such low q-values, that it is not at all visible in the studied q-range where typically $(q_{min}, q_{max}) = (0.001\text{Å}^{-1}, 0.5\text{Å}^{-1})$. We therefore can neglect this term altogether, leaving

$$\left.\frac{d\sigma}{d\Omega}\right|_{\text{SANS, 1}} = \left|\int_{\text{object}} \Delta\rho_b(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r}) dV\right|^2 . \quad (5.10)$$

Notice that the scattering cross section depends on the square of the contrast in scattering length density. Hence, the scattered intensity can be changed strongly by, *e.g.*, varying the scattering length density of the solvent. This is typically done by deuteration, as illustrated in Fig. 1.2.

We describe a realistic sample with a certain particle density $n = N/V$. We assume the density is sufficiently small to neglect interactions between particles. The total cross section per unit volume then becomes

$$\left.\frac{d\Sigma}{d\Omega}\right|_{\text{SANS, } n} = n\left|\int_{\text{object}} \Delta\rho_b(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r}) dV\right|^2 . \quad (5.11)$$

In real systems, the interference between particles must also be accounted for. This results in a term, the *inter-particle structure factor*, $S(\mathbf{q})$, which is multiplied onto the right hand side of (5.11) to yield the correct result. In the dilute limit, $S(\mathbf{q}) \to 1$. We will not go deeper into this here.

5.3.1 The particle form factor

For monodisperse, homogeneous particles, the cross section (5.11) simplifies to

$$\begin{aligned} \left.\frac{d\Sigma}{d\Omega}\right|_{\text{SANS, part.}} &= n\Delta\rho_b^2 \left|\int_{\text{object}} \exp(i\mathbf{q}\cdot\mathbf{r}) dV\right|^2 . \quad (5.12) \\ &\equiv n\Delta\rho_b^2 V^2 P(\mathbf{q}), \end{aligned}$$

where V is the particle volume and $P(\mathbf{q})$ is known as *the particle form factor*.

$$P(\mathbf{q}) = \left|\frac{1}{V}\int dV e^{-i\mathbf{q}\cdot\mathbf{r}}\right|^2 \quad (5.13)$$

For a solid sphere of radius R, the form factor is isotropic and is easily calculated (see problem 5.6.1). The result is

$$P_{\text{sphere}}(q) = \left(3\,\frac{\sin(qR) - qR\cos(qR)}{(qR)^3}\right)^2 . \quad (5.14)$$

5.3.2 The limits of small and large q

We will here present two very important approximations for particle structure factors in small-angle scattering: The *Guinier approximation* for small values of q and the *Porod law*, which is valid for large q values.

The Guinier approximation Let us first study the hard-sphere form factor (5.14) for small values of q, *e.g.* $qR \ll 1$. We expand the trigonometric functions to 5'th(!) order in qR, reaching

$$P_{\text{sphere}}(q) \approx 1 - \frac{1}{5}(qR)^2. \tag{5.15}$$

This function has the same second order series expansion as the expression $\exp(-(qR)^2/5)$, which is the Guinier approximation for the sphere form factor.

To generalize from this example, let us first define the radius of gyration of an object, R_{g}, by

$$R_{\text{g}}^2 \equiv \frac{\int_0^R \gamma(r) r^4 dr}{2\int_0^R \gamma(r) r^2 dr}, \tag{5.16}$$

where r is the distance from the particel centre-of-mass, R the maximum extension of the particle, and $\gamma(r)$ is the average "filling" of the particle at this distance. (This definition bears some resemblance to the definition of moment of inertia in classical mechanics.) For a sphere, $\gamma(r) = 1$ for $0 \leq r \leq R$, and 0 elsewhere. The sphere radius of gyration is easily calculated from (5.16), $R_{\text{g}}^2 = 3R^2/5$, leading to

$$P(q) \approx \exp\left(-\frac{1}{3}(qR_{\text{g}})^2\right). \tag{5.17}$$

In fact, this is the general Guinier approximation valid for any particle shape. We will, however, not show it in the general case.

The Porod law We now consider the sphere form factor (5.14) for large values of q, *e.g.* $qR \gg 2\pi$. To leading value of qR, this becomes

$$P_{\text{spheres}}(q) \approx 9\cos^2(qR)/(qR)^4. \tag{5.18}$$

Now, for large q, even very small polydispersities (variations in the particle size, R) will lead to a variation of the cosine argument (qR) by a substantial amount, larger than 2π. For such a sample, we will observe approximately the average value of the cosine, *i.e.*, $\langle\cos^2(qR)\rangle = 1/2$, leading to

$$P(q) \propto q^{-4}. \tag{5.19}$$

This is, in fact, the generally valid Porod law for small-angle scattering. We will not show it directly here. Intuitively, however, it is reasonable to generalize from the example of the spheres. Here, the real-space structures (the particle

radius) probed at a scattering vector of q is of the order $2\pi/q$. At large values of q, the measurement is sensitive to small real-space structures. However, the only real-space structure visible at this scale is a sharp surface: The boundary between two different scattering length densities. And the reflectivity from a surface is in fact proportional to q^{-4}. (the chapter on reflectivity is not yet written).

5.4 Applications of SANS in nanoscience

We had no time to write about this important topic. In stead, we refer to a recent review article by one of us [27]. Here, chapter 1 gives an overview of the topic, while chapters 2 and 3 overlaps strongly with these notes (but you should browse through them anyway). Then, study chapter 4 on data analysis, and some of the science sections 5-9 (to be specified at the class).

5.5 SANS instrumentation

The principle of an ordinary SANS instrument is rather simple. We will here present a continuous source SANS instrument, although a generalization to time-of-flight instrument is straightforward. A sketch of a SANS instrument is shown in Fig. 5.1.

A SANS instrument uses neutrons from a cold moderator and is situated at the end of a guide. The neutrons are being monochromatized by a rotating velocity selector made from spinning absorbing blades, that will let through neutrons of velocities close to a particular value (see problem). The monochromatization is coarse; typically of the order of $\Delta\lambda/\lambda \approx 10\%$.

The divergence of the incident neutrons is limited by a pair of pinholes, that act as a collimator. Often, one can control the pinhole diameter and their distance, the *collimation length* by inserting different pinholes at a number of fixed positions. The collimation length is typically of the order 1-10 m.

The sample is often flat and mounted perpendicular to the beam direction, so that all neutrons scattered at small angles will penetrate the full sample thickness. Hence, samples are often thin to limit absorption and multiple scattering.

The neutrons are detected by a position-sensitive detector (PSD), which can determine the position of an incident neutron, typically to a few millimeters precision. The PSD is placed within an evacuated tank to avoid air scattering (mainly due to nitrogen), and the sample-detector distance can be varied by moving the PSD within the tank. The minimum PSD distance is around 1 m, while the maximum distance varies in the range 5-20 m determined by the length of the tank. Typically, one would match the sample-detector distance to the collimation length.

An absorbing beam stop is placed in the direct beam just before the detector to limit the number of neutrons from the direct beam. This strong beam could

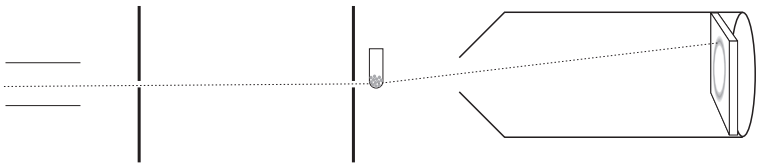

Figure 5.1: The principles of a SANS instrument. The pinholes (left) limit the beam divergence, while a position sensitive detector inside the vacuum tank (right) detects all neutrons scattered at small angles from the sample (middle).

otherwise saturate the detector.

5.6 Problems

5.6.1 Scattering form factor for spheres

A sample of identical spheres with radius R dispersed in a solvent will scatter uniformly with the form factor given by (5.14). Show by direct integrations that this form is correct. Hint: Use spherical coordinates.

5.6.2 Calculating the SANS and SAXS from spherical surfactant micelles

The experimental setup of a Small-angle X-ray scattering (SAXS) instrument is in principle very similar to that of the SANS instrument. The main difference between the two methods is that in SANS, the incoming neutrons are scattered by the nuclei of the studied sample, whereas in SAXS the incoming photons are scattered by the electrons of the studied sample.

The scattering length of an electron, b_e is given by the classical electron radius (also known as the Compton radius or the Thompson scattering length). It is calculated from $b_\mathrm{e} = e^2/(4\pi\varepsilon_0 m_\mathrm{e} c^2) = 2.82$ fm, where ε_0 is the vacuum permittivity, e and m_e are the charge and mass of the electron and c is the speed of light. Thus the scattering length of an atom with atomic number n is simply nb_e.

The anionic surfactant Sodium Dodecyl Sulphate (SDS) (see Fig. 5.2, left) is one of the main active components in ordinary dishwasher detergent. When dissolved in water, the SDS molecules self-organize into small spherical micelles, with the hydrophobic alkyl chains in the core of the micelles and the hydrophilic sodium sulphate head-groups surrounding the micelles (see Fig. 5.2, right). Assume that the aggregation number of the micelles, *i.e.* the average number of surfactant molecules per micelle, is 55 and that the micelles are perfectly monodisperse.

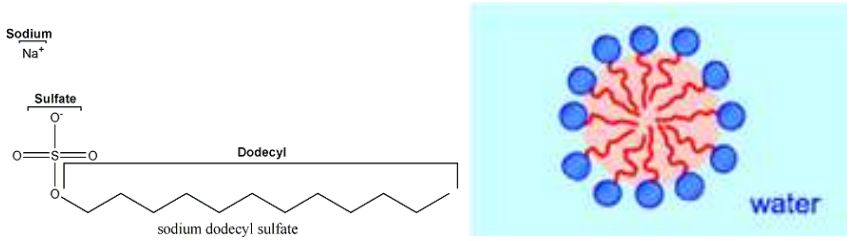

Figure 5.2: (left) Molecular structure of the surfactant Sodium Dodecyl Sulphate (SDS). (right) Illustration of the cross-section of a spherical micelle.

The partial specific mass density of SDS in water is 1.03 g/cm^3. The maximal extension, $l_{\max}$, and partial specific molecular volume, ν, of alkyl chains with n carbon atoms can be estimated from the so-called Tanford's formulas:

$$\begin{aligned} l_{\max} &= (1.54 + 1.265 \times n)\text{Å} \\ \nu &= (27.4 + 26.9 \times n)\text{Å}^3. \end{aligned} \tag{5.20}$$

A combined SANS and SAXS experiment on SDS micelles in deuterated water (D_2O) is being planned. Use the above information to calculate and sketch the excess scattering length density profiles, $\rho(r)$ of the micelles in water for neutrons and for X-rays (hint: See Fig. 5.3 for an example of an excess scattering length density profile from another surfactant micelle system.).

With the aid of MatLab, Excel or similar, calculate and plot the expected SAXS and SANS scattering intensity curves, i.e. the particle form factor in a q-range from 0.001 Å^{-1} to 0.5 Å^{-1}.

Estimate how a spread of the wavelength of the incoming beam, $\Delta\lambda/\lambda$ of 10% FWHM will affect the SAXS and SANS intensity curves.

In practice the micelles are polydisperse and can be described by a Gauss distribution with a reduced standard deviation $\sigma(R)/\overline{R}$ of 20%. Discuss how this polydispersity affects the SAXS and SANS intensity curves.

5.6.3 Neutron velocity selector

A neutron velocity selector is a drum that spins around an axis parallel to the beam. This axis lies below the guide. From the drum, a series of absorbing neutron blades sticks out radially. The ends of the drum are twisted with respect to each other, as illustrated in Fig. 5.1. This effect of the selector is that only neutrons around a certain velocity (or wavelength) can pass through.

Assume $n = 68$ blades and a twisting angle of 48.3°, as for the selector at the SANS-2 instrument at PSI. Calculate the rotation speed you should use to select 10 Å neutrons.

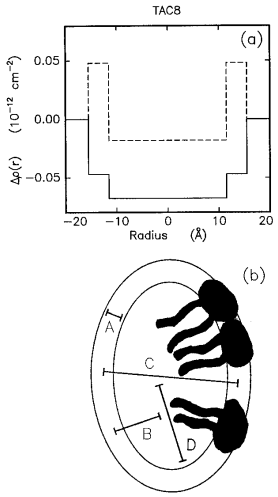

Figure 5.3: (top) Excess scattering length density profiles corresponding to a simple model of the TAC8 micelles assuming no hydration of the hydrophilic shell. The continuous line is for neutrons, and the broken line is for X-rays. (bottom) Cross-section of the prolate ellipsoidal TAC8 micelles. From Ref. [28].

5.6.4 Pinhole collimation

The collimation in a typical SANS instrument is performed by two pinholes separated by a distance. Consider a circular pinhole (made from an absorbing material), $d = 8$ mm, placed in the centre of a neutron beam and an identical circular pinhole a distance $L = 6$ m further down the beam. Calculate the maximal divergence in the x and y direction.

5.6.5 The effect of gravity

Until now, the effect of gravity has been neglected. Estimate the effect of gravity on neutrons in a SANS instrument with $L_{\mathrm{c}} = L_{\mathrm{d}} = 10$ m for neutrons of 4 Å and 20 Å.

5.6.6 Simulation of SANS scattering

Calculate an equation for the Monte Carlo weight factor adjustment, w, in a sample component for spheres, where all neutrons are scattered, $f_{\mathrm{MC}} = 1$. The form factor for spheres is discussed in problem 5.6.1.

5.7 Simulation project: SANS-2

SANS-2 is a small-angle neutron scattering instrument situated at the neutron source SINQ, PSI, Switzerland. SANS-2 is placed at the SINQ cold source.

In this project, you should construct a model of SANS-2, program a SANS sample component modelling nano-sized objects, perform a virtual SANS experiment, and analyze the data. You will also study the q resolution of the spectrometer.

5.7.1 The source-guide system

The SINQ cold source is made from liquid deuterium, D_2. The outgoing neutrons are not brought into complete thermal equilibrium with the cold source, so the energy/wavelength spectrum is not completely Maxwellian. However, it can be described as a sum of three Maxwellians. This is implemented in the source component `source_maxwell_3`. The correct parameters for this component are `width=0.085, height=0.16, T1=150.42, T2=38.74, T3=14.84, I1=3.67E11, I2=3.64E11, I3=0.95E11`.

The opening in the biological shielding, that we use for the SANS-2 beam port, is 0.050 m high and 0.050 m wide and starts 1.5 m from the cold source, which is 0.08 m wide and 0.16 m tall.

The SANS-2 guide system first has a 4.5 m long straight section. Then follows a 20 m curved section made from 40 0.5 m straight pieces, placed so that the radius-of-curvature is 2.4 km, then a 10 m long straight guide. However, here we make the simplification that the guide is straight and is in one piece.

The guide material has $m = 2$ with same parameters as in project 4.5. The guide has measures 0.05 m times 0.05 m along its whole length.

Update your simulation of the guide system and measure the wavelength and energy spectrum at the end of the guide. You can neglect neutrons with a wavelength below 1 Å (corresponding to an energy above 82 meV).

5.7.2 Velocity selector

Insert a velocity selector, centered 0.2 m after the guide. Use the default parameters, except for the aperture size (which you adjust to be "large enough"). Another exception is the number of blades which is 68, and the rotation, which you use as an input parameter of the instrument.

Adjust the rotation speed to select neutrons of $\lambda = 10$ Å. Perform the simulation and verify that the correct wavelength is chosen. Measure the wavelength spread, $\Delta\lambda/\lambda$.

McStas hint: the wavelength monitor performs simple statistics when you perform a single plot from the plot menu. The width it calculates is the statistical (or Gaussian) variance. To convert to FWHM, multiply by $2\sqrt{2\ln(2)}$.

5.7.3 Pinhole collimation

Place one pinhole (circular slit), 8 mm diameter, right after the exit of the velocity selector, and place an identical one at a distance of $L_c = 6$ m. Simulate the divergence of the beam after the second slit. Compare to the calculated values.

Perform the same task for the case of $L_c = 3$ m. (move the first slit 3 m further downstream. (Does it make a difference to place a 3 m guide piece after the velocity selector? Why?).

McStas hint: You may like to store the results of your two simulations by `virtual_output` to ease the simulations in the problems below. You will probably need $1 \cdot 10^8$ rays or more to reach a reasonable statistics.

5.7.4 Detector

The detector is a circular PSD, diameter 60 cm, with a pixel size of 8×8 mm^2, placed in an evacuated tank that begins 0.5 m after the second slit. The distance between the second slit and the detector is either $L_d = 3$ m or $L_d = 6$ m. Calculate and simulate the size of the direct beam for $L_c = L_d = 3$ m and $L_c = L_d = 6$ m.

Place a circular beamstop of diameter 40 mm just before the detector to avoid the direct beam. Control whether this beamstop blocks the whole of the direct beam.

McStas hint: As preliminary treatment of isotropic SANS data, one would normally perform an average of the measured $d\sigma/d\Omega(\mathbf{q})$ for positions of the detector with equal value of $|\mathbf{q}|$. This corresponds to a radial average of the pixels in concentric circles. The monitor component `PSD_monitor_rad` performs this radial average. Perform the simulation with this component at the detector position.

5.7.5 A full virtual experiment

The component `Sans_spheres` uses the equations derived in the previous problems. Use this sample and the simulated set-up to make a full virtual SANS experiment. Insert a `Sans_spheres` sample 0.05 m from the last slit and perform a simulation. Use the particle size $R = 50$ Å. Try a few settings of collimation length and detector length to simulate the result in various ranges of q. Try also particles of sizes $R = 200$ Å and 500 Å .

McStas hint: Use if possible similar collimation length and detector distance. Convert position at the radially averaging detector to q for each detector distance.

5.7.6 Data analysis

Fit the 1-dimensional data from `PSD_monitor_rad`. Determine the particle size from the virtual data using the Guinier approximation. Compare the obtained radius of gyration, R_g, with the particle radius R.

For the largest particles, try to fit the data to the Porod law. Comment on the results.

5.7.7 Resolution of the SANS instrument

Write an infinitely thin sample that scatters the beam with a fixed value of q; a ring. Insert this component and simulate the result of this sample for $L_c = L_d = 6$ m for two values of q. Perform the same simulations for $L_c = L_d = 3$ m. Comment on the results.

McStas hint: In the weight transformation, you could simply keep the weight of the neutron ray. For the programming, see component `SANS-spheres` for inspiration.