

Micellization studied by small-angle neutron scattering

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1 Introduction

Neutron scattering is next to X-ray scattering and light scattering one of the widely used scattering techniques to investigate the structure and dynamics of a wide range of materials. As with X-rays, neutron radiation can give access to the structure of a material from the atomic scale up to sizes of about 150 nm, which roughly corresponds to the smallest size that can be probed with light scattering. The interaction of neutron radiation with matter differs fundamentally from that of photons, which mainly interact with the electrons in a material. Neutrons are uncharged but carry a magnetic moment and interact via the strong nuclear force with the atomic nuclei in a material. The magnetic moment makes neutrons a direct probe for magnetic properties. The magnetic scattering of neutrons has an intensity on the same order of magnitude as the nuclear scattering. Due to their interaction with matter, neutron scattering is complementary to X-ray scattering and has its largest advantages in the investigation of magnetic structures and magnetic excitations as well as the study of materials containing light chemical elements such as hydrogen which are often not easy to detect by X-rays in the presence of heavier elements.

Small angle neutron scattering (SANS) [1] allows to gain access to structures much larger than the neutron wavelength, which typically lies in the range from 1 Å up to 20 Å. Therefore, SANS is used to probe features with a typical size in the range from 1 nm up to 150 nm in all kinds of materials. As for neutron scattering in general, the main applications of SANS are the investigation of magnetic structures and materials containing a large ratio of relatively light elements.

The properties of the neutron that must be taken into account for the study of neutron scattering from condensed matter are:

$$m_n = 1.67410^{-27} \text{kg} \quad (1)$$

$$E = \frac{m_n v^2}{2} = \frac{m_n}{2} \left(\frac{h}{\lambda} \right)^2 \quad (2)$$

$$C = 0e \text{ (no charge)} \quad (3)$$

$$\mu = -1.913 \mu_N \quad (4)$$

$$\tau = 881.5 \text{ s (free neutron life time)} \quad (5)$$

The energy of a neutron with wavelength $\lambda = 1.5 \text{ \AA}$ is 36.4 meV, while a photon with the same wavelength has an energy of 8.2 keV. So, an important difference between neutron radiation and X-rays is that neutrons have lower energy and do not damage the sample as much as X-rays. Thermal neutrons are a non-destructive probe. Furthermore, the electromagnetic neutrality allows neutrons to penetrate deep into sample materials, while X-rays are absorbed and scattered pretty close to the surface of the sample. Neutron radiation allows to work with thick samples, while X-ray scattering is done with thin samples.

2 Neutron sources

Neutron radiation is produced in nuclear research reactors or in spallation sources. Thermal neutrons with a Maxwellian energy spectrum around 320 K ($\lambda \sim 1.7 \text{ \AA}$) are produced in the moderator kept at normal temperature, while cooled moderators with temperatures in the range from 20 K to 40 K are used to generate neutrons with a Maxwellian spectrum around $\lambda \sim 6 \text{ \AA}$. Research reactors work in the same way as nuclear power stations but are designed to yield a high neutron flux leaving the moderator system. Large research reactors near Switzerland are located in Grenoble, France, at the Institut Laue-Langevin (the most powerful neutron source in Europe), in Garching near Munich, Germany, or in Saclay near Paris, France.

Neutron spallation sources use a beam of accelerated protons to bring the nuclei in a target to an excited state, such that neutrons “evaporate” from the target. These neutrons are moderated in the same way as in a reactor to obtain a thermal or cold spectrum of neutrons for scattering experiments. Most spallation sources are pulsed sources, delivering intense pulses of neutron radiation. The Swiss spallation source, SINQ, at Paul Scherrer Institute is an exception from this rule. It delivers neutrons continuously, as the proton pulses hitting the target follow each other rapidly and generate a continuous output. Other spallation sources are ISIS near Oxford, UK, or the Spallation Neutron Source, Oakridge

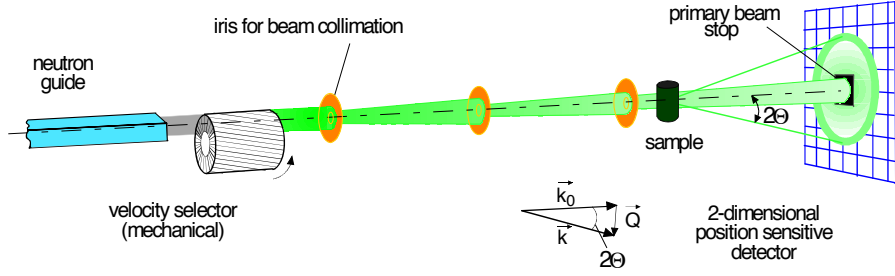


Figure 1: Sketch of a classical SANS instrument. See text for details.

National Laboratory, USA. A new European spallation source is being built in Lund, Sweden. It will become operational in 2018 and will be the new European high intensity neutron source.

Neutron sources are not as brilliant as advanced X-ray sources (synchrotrons). The neutron yield per rad^2 and second is orders of magnitudes lower than that of X-rays from a synchrotron. The intensity of neutron sources can be compared to that of bench-top X-ray sources with rotating anode X-ray generator.

3 SANS instruments

A classical SANS instrument has a pinhole geometry, as shown in Fig. 1. A polychromatic, “white” neutron beam is guided to the instrument from the neutron source, and a monochromatic beam is generated by selecting a narrow range of wavelengths with a mechanical neutron velocity selector. Typically, the FWHM of the wavelength distribution of the monochromatic beam is 10% of its peak position. The beam is then collimated using pinholes placed in the collimation section of the instrument before the beam hits the sample. Scattered neutrons are counted with an area sensitive detector located at some variable distance from the sample. Usually, the flight path from sample to detector has the same length as the collimation section, as this configuration gives the optimal compromise for beam intensity and resolution. A typical SANS detector is a ^3He detector with an area $\sim 1 \text{ m}^2$ and 128×128 pixels. The spatial resolution of the detector allows to determine the scattering angle θ of the counted neutrons and the corresponding momentum transfer $q = \frac{4\pi}{\lambda} \sin(\theta/2)$, where θ is the scattering angle. A beamstop protects the detector from the intense direct beam penetrating the sample. The SANS setup outlined above is typical for continuous neutron sources. SANS instruments at pulsed sources use a white beam and work in a time-of-flight mode; the flight time from sample to detector is registered to determine the wavelength of each detected neutron. Modern SANS instruments offer different sample environments

for experiments under tailored conditions with e.g. controlled temperature, applied pressure, electric or magnetic fields, or controlled humidity.

4 SANS experimental procedure

As the sample holder and sample environment also give rise to some small-angle scattering, the proper measurement and subtraction of the scattering background is essential in SANS. For proper data analysis, the neutron transmission is measured for the empty sample container + sample environment, t_B , and the sample container with sample, t_S . The scattering from sample + container and from the container alone are determined in separate measurements, see Fig. ???. The background is then subtracted:

$$I = \frac{S}{t_S} - \frac{B}{t_B}, \quad (6)$$

where S and B represent the scattering measured with sample + container and empty container, respectively. The measured scattering intensity, I , can be brought to absolute unites by calibrating with a standard sample. A good standard for SANS is H_2O , which scatters neutrons mainly due to the incoherent scattering of the hydrogen nuclei, the two protons contained in each H_2O molecule. Such a calibration allows to determine the scattering cross section

$$\frac{d\sigma}{d\Omega} = k \frac{I}{C}, \quad (7)$$

where k is a factor depending on the instrument and the neutron wavelength, and the calibration measurement, C , is obtained as explained above:

$$C = \frac{W}{t_W} - \frac{B_W}{t_{B_W}} \quad (8)$$

from the measurements of the water standard, W , the corresponding background, B_W , and the corresponding transmissions of water, t_W , and the background, t_{B_W} .

The procedure outlined above gives a $2d$ image of the scattering cross section $\frac{d\sigma}{d\Omega}$. With samples giving isotropic scattering, this image is radially averaged; i.e. all the pixels with the same q are averaged to obtain the q -dependent $\frac{d\sigma}{d\Omega}(q)$, see Fig. ???. In the case of anisotropic scattering, the ϕ -dependence of the scattering signal is analyzed by averaging sectors at different azimuthal angles ϕ .

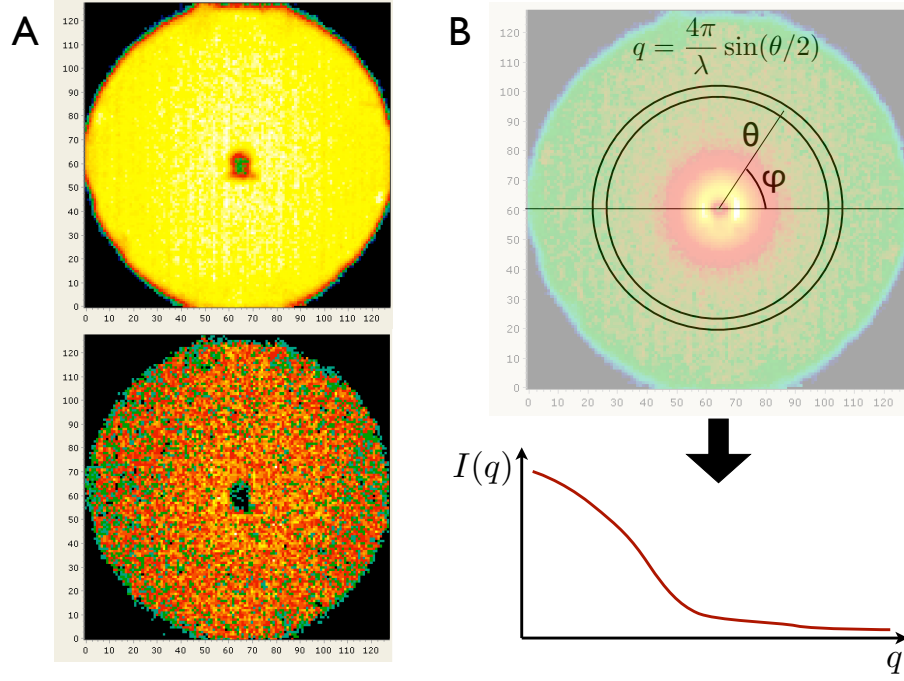


Figure 2: (A) Measurement of a H₂O sample (top) and the corresponding background obtained with the empty sample cell (bottom). The darker spot in the center is due to the beam stop, the edge of the circular detector does not count with the same efficiency as the central part and is excluded for data analysis. (B) Illustration of the procedure for radially averaging the measured data. The 2d detector image is split up into “rings” with constant scattering angle θ , which corresponds to constant q , and the data is averaged over the azimuthal angle ϕ .

5 Neutron cross section

As neutrons interact with the atomic nuclei of the sample via the strong nuclear force, the scattering of thermal neutrons is due to point-scatterers: The nuclei are 10^4 to 10^6 times smaller than the wavelength of neutron radiation. Therefore, the interaction of thermal neutrons with a nucleus can be described by the Fermi pseudo potential

$$V(\mathbf{r}) = \frac{2\pi\hbar^2}{m_n} b \delta(\mathbf{r}), \quad (9)$$

where b is the scattering length of the nucleus, a constant giving the strength of the scattering which depends not only on the chemical element but also on the isotope. The scattering lengths of all elements and isotopes can be found in the literature [2, 3]. In general, a nucleus gives rise to coherent and incoherent scattering. Therefore, coherent (*coh*) and incoherent (*inc*) scattering cross sections have been determined for all isotopes. Furthermore, a nucleus may absorb neutron with a certain cross section (*abs*). E.g. the scattering from ^1H and ^2D (deuterium nucleus) is rather different:

^1H : $b_{coh} = -3.741 \text{ fm}$, $\sigma_{coh} = 1.8 \text{ barns}$, $\sigma_{inc} = 80.3 \text{ barns}$, $\sigma_{abs} = 0.3 \text{ barns}$

^2D : $b_{coh} = +6.671 \text{ fm}$, $\sigma_{coh} = 5.6 \text{ barns}$, $\sigma_{inc} = 2.1 \text{ barns}$, $\sigma_{abs} = 0.0 \text{ barns}$

As a consequence of the small nucleus size compared to the neutron wavelength, the scattering from a nucleus is isotropic and given by a spherical wave:

$$-\frac{b}{r}e^{ikr}. \quad (10)$$

In general, the neutron scattering cross section can be given as

$$\frac{d\sigma}{d\Omega}(q) = \frac{1}{V} \left| \sum_{i=1}^N f_i(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}_i} \right|^2, \quad (11)$$

where $f_i(\mathbf{q})$ gives the nuclear and magnetic scattering strength of nucleus i in the sample. Here, we do not consider magnetic scattering, which is described in detail in Ref. [4], but restrict ourselves to nuclear scattering and have $f_i(\mathbf{q}) = b_i$.

6 SANS cross section

In a small angle scattering experiment, a collimated beam with I_0 neutrons per solid angle and second hits the sample. The illuminated volume V of the sample scatters or absorbs part of the neutrons, the other part of the incident beam passes the sample without interaction. The scattered neutrons are detected with

an efficiency $\eta(\lambda)$ by the detector. The scattering intensity per second and solid angle at wavelength λ and momentum transfer q is, therefore, given by

$$I(\lambda, q) = I_0 \Delta\Omega \eta(\lambda) t V \frac{d\sigma}{d\Omega}(q), \quad (12)$$

where $\Delta\Omega$ is the solid angle covered by the detector counting the scattered neutrons, t is the transmission of the sample, and $\frac{d\sigma}{d\Omega}(q)$ is the differential scattering cross section per unit volume of sample.

We are interested in the cross section $\frac{d\sigma}{d\Omega}(q)$, which carries all the information about the structure of the sample. As SANS does not have atomic resolution, $2\pi/q_{max} \approx 1$ nm, the scattering lengths of all the individual atoms or isotopes in the sample are not considered, but a coarser distribution of scattering lengths per volume is used: the scattering length density $\rho(\mathbf{r})$. Therefore, we can write the scattering cross section as

$$\frac{d\sigma}{d\Omega}(q) = \frac{1}{V} \left| \int_V d^3r \rho_{coh}(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} \right|^2 + B_{inc} \quad (13)$$

B_{inc} represents the incoherent scattering of all scattering centers in the sample. This is an isotropic background carrying no structural information about the sample. Therefore, we are interested in the coherent part, and the incoherent part is neglected in the following. Also, the subscript *coh* is omitted in the following.

Now, we assume that the sample consists of N particles (or other entities) with positions $\mathbf{r}_i$ in a solvent. As the solvent is homogenous and has a constant scattering length density ρ_0 , it does not contribute to variations of $\rho(\mathbf{r})$. As a consequence, neutrons are mainly coherently scattered due to the variations in $\rho(\mathbf{r})$ caused by the N particles. Therefore, we write the scattering length density as $\rho(\mathbf{r}) = \sum_{i=1}^N \Delta\rho_i(\mathbf{r} - \mathbf{r}_i) + \rho_0$, where $\Delta\rho_i(\mathbf{r})$ is the scattering contrast of particle i with the solvent. Now, we rewrite the expression for the coherent scattering cross section:

$$\frac{d\sigma}{d\Omega}(\mathbf{q}) = \frac{1}{V} \left| \sum_{i=1}^N F_i(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{r}_i} \right|^2 \quad (14)$$

$$F_i(\mathbf{q}) = \int_{V_i} d^3r \Delta\rho_i(\mathbf{r}) e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}_i)}. \quad (15)$$

$F_i(\mathbf{q})$ is the scattering amplitude of particle i . We separate the information about the single particles and about the correlation between separate particles by replac-

ing $|\dots|^2$ with a double sum and restructuring the summation:

$$\frac{d\sigma}{d\Omega}(\mathbf{q}) = \frac{1}{V} \sum_{i,k} F_i(\mathbf{q}) F_k^*(\mathbf{q}) e^{-i\mathbf{q}\cdot(\mathbf{r}_i - \mathbf{r}_k)} \quad (16)$$

$$= \frac{1}{V} \left(\sum_i |F_i(\mathbf{q})|^2 + \sum_{i \neq k} F_i(\mathbf{q}) F_k^*(\mathbf{q}) e^{-i\mathbf{q}\cdot(\mathbf{r}_i - \mathbf{r}_k)} \right). \quad (17)$$

Assuming that all particles are identical, we obtain the simpler expression

$$\frac{d\sigma}{d\Omega}(\mathbf{q}) = \frac{N}{V} |F(\mathbf{q})|^2 \underbrace{\left(1 + \frac{1}{N} \sum_{i \neq k} e^{-i\mathbf{q}\cdot(\mathbf{r}_i - \mathbf{r}_k)} \right)}_{S(\mathbf{q})}, \quad (18)$$

where $S(\mathbf{q})$ is the structure factor containing the information about the arrangement of the particles in space. The internal structure of the particles and their sizes enter in the factor $|F(\mathbf{q})|^2$. Furthermore, we assume that the particles have a constant scattering length density $\Delta\rho$. This allows to rewrite the scattering amplitude and the cross section:

$$F(\mathbf{q}) = \Delta\rho \int_{V_p} d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} \quad (19)$$

$$= \Delta\rho V_p \frac{\int_{V_p} d^3r e^{-i\mathbf{q}\cdot\mathbf{r}}}{V_p} \quad (20)$$

$$= \Delta\rho V_p P(\mathbf{q}) \quad (21)$$

$$\frac{d\sigma}{d\Omega}(\mathbf{q}) = \frac{N \Delta\rho^2 V_p^2}{V} P(\mathbf{q}) S(\mathbf{q}) \quad (22)$$

$$\text{with } P(\mathbf{q}) = \left| \frac{\int_{V_p} d^3r e^{-i\mathbf{q}\cdot\mathbf{r}}}{V_p} \right|^2. \quad (23)$$

V_p is the particle volume and $P(\mathbf{q})$ is the particle form factor normalized to $P(\mathbf{0}) = 1$. It is dimensionless and carries the information about the internal structure of the particles. The form factor is known for many relevant particle shapes. For a uniform sphere it is given by

$$P_{\text{sphere}}(q) = \left(\frac{3[\sin(qr) - qr \cos(qr)]}{(qr)^3} \right)^2, \quad (24)$$

where r is the sphere radius. It plays an important role for scattering from colloidal particles in suspension, which can often be modeled as compact spheres. For the

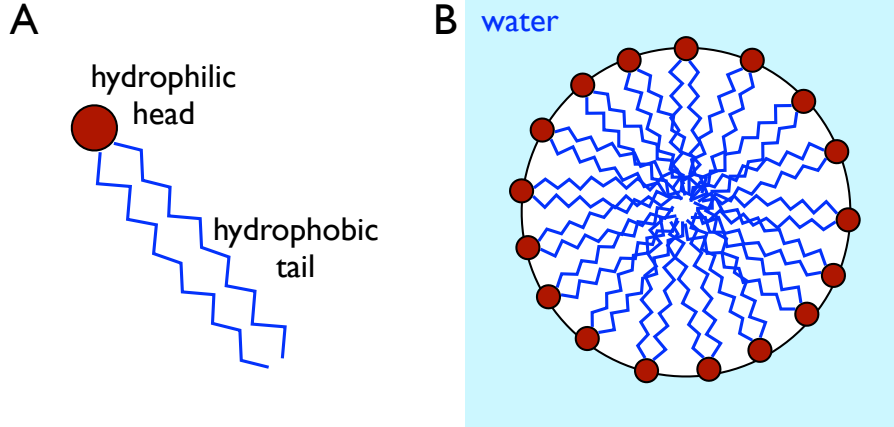


Figure 3: (A) Sketch of a surfactant with hydrophilic head group and hydrophobic tail. (B) Sketch of a micelle formed by a surfactant in water.

scattering from long polymer strands in suspension, the form factor of a random walk chain is given by the Debye function

$$P_{\text{random walk}}(q) = 2 \frac{e^{-q^2 R_g^2} - 1 + q^2 R_g^2}{q^4 R_g^4}, \quad (25)$$

where R_g is the radius of gyration of the polymer chain.

The structure factor is related to the pair distribution function, $g(r)$, of the particles:

$$S(q) = 1 + \frac{4\pi N}{qV} \int_0^\infty dr r [g(r) - 1] \sin(qr). \quad (26)$$

$g(r)$ gives the probability to find a particle at a distance r from a particle that is fixed at $r = 0$. $S(q)$ and $g(r)$ depend on the concentration of the sample and the interaction between the particles.

7 Surfactants and micelles

Surfactants are materials that lower the surface tension between a liquid and another phase that is either a gas, a liquid, or a solid. Surfactants usually consist of organic molecules containing both a hydrophobic and a hydrophilic group such that they adsorb at interfaces between e.g. water and oil. Surfactants are used in a wide range of applications such as detergents, dispersants, or emulsifiers e.g. in food- or cosmetics products.

A sketch of a surfactant is given in Fig. 3, where the hydrophilic head and the hydrophobic tail of a surfactant molecule is shown. A surfactant is soluble in water, but the surfactant molecules arrange in groups called micelles above a critical concentration such that the hydrophobic tails are inside the micelle and the hydrophilic heads are located at the water interface. Therefore, the surfactants spontaneously form particles, micelles, when the critical micellization concentration (CMC) is reached.

In the following, we consider Pluronic F88 (BASF), which is a hydrophilic triblock copolymer that undergoes micellization as a function of concentration and temperature. At a concentration of 5 wt% in D₂O, micellization can be observed with increasing temperature between 30 K and 70 K, as the solubility of F88 in water decreases with temperature [5].

The chemical composition of Pluronic F88 is C₅H₁₀O₂, its molecular weight is 11.4 g/mol, and its mass density is 1.06 times that of H₂O.

SANS experiment:

- Estimate the optimal sample thickness for a SANS experiment with F88 in D₂O. Use the scattering length density calculator [3] to determine the coherent, incoherent, and absorption cross section of F88.
- Below the CMC, the pluronic polymer is dissolved in water. Individual F88 molecules give rise to a SANS signal. Prepare a sample of 5 wt% F88 in D₂O and determine the SANS cross section, $\frac{d\sigma}{d\Omega}(q)$ in the q -range from $0.02 \text{ \AA}^{-1}$ to $0.2 \text{ \AA}^{-1}$ at ambient temperature. The scattering signal can be interpreted using the Debye function. Determine the radius of gyration, R_g .
- Increase the temperature to $T = 50^\circ\text{C}$, $T = 60^\circ\text{C}$, and $T = 70^\circ\text{C}$ and explain the observed change in the scattering signal in terms of micellization. Micelles scatter like spherical particles; the form factor of a homogenous sphere can be used as an approximation. Determine the average size of the micelles.

References

- [1] C. G. Windsor. An introduction to small-angle neutron scattering. *J. Appl. Cryst.*, 21:582–588, 1988.
- [2] F. Sears. Neutron scattering lengths and cross sections. *Neutron News*, 3(3):26–37, 1992.

- [3] A. Munter. Scattering length density calculator, 2012.
- [4] G. L. Squires. *Introduction to the theory of thermal neutron scattering*. Cambridge University Press, Cambridge, 1978.
- [5] N. J. Jain, V. K. Aswal, P. S. Goyal, and P. Bahadur. Micellar structure of an ethylene oxide propylene oxide block copolymer: A small-angle neutron scattering study. *Journal of Physical Chemistry B*, 102(43):8452–8458, 1998.