# SANS-1

## Small-angle neutron scattering on magnetic nanoparticles

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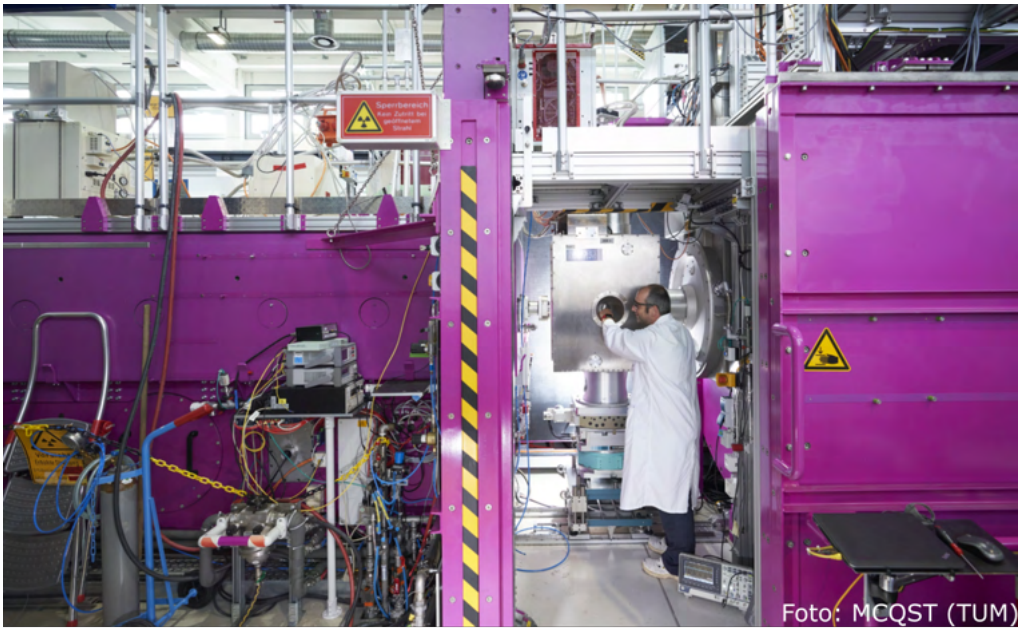


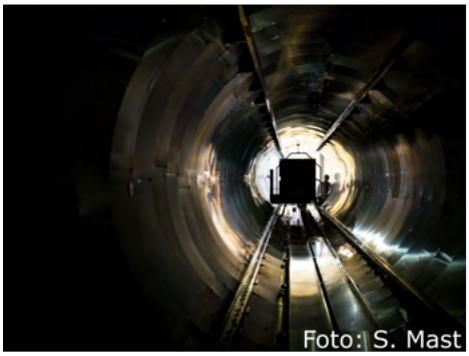


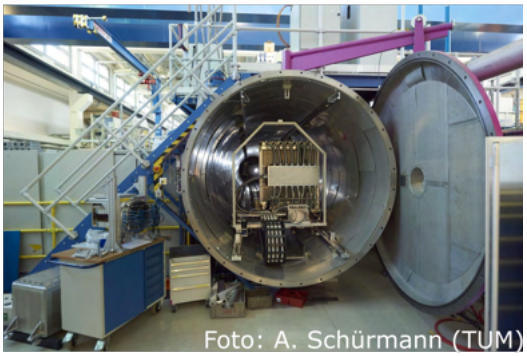


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# Abstract

Small-angle neutron scattering (SANS) can be used to investigate mesoscopic length scales and correlations from $30$ Å to $3000$ Å in bulk samples. The typical applications are very broad, ranging from studies of morphology and precipitate growth in metallic materials and alloys, biological structures and molecules, to magnetism on the nanoscale and fundamental questions in solid state physics. A compact summary of the applications of small-angle magnetic scattering is given in [1].

Magnetic nanoparticles are often iron, iron oxide, ferrite or cobalt based bulk particles in the range of a few nanometers to a few tens of nanometers. A suspension of these magnetic nanoparticles in a liquid medium is called a ferrofluid. The magnetic properties of ferrofluids are strongly dependent on the size and shape of the particles, ranging from superparamagnetic behaviour with small particles to ferromagnetism with increasing size. At high concentrations of nanoparticles in a ferrofluid, correlation effects also become important. The applications of magnetic nanoparticles are manifold, from magnetic hyperthermia in cancer therapy to magnetic dampers and actuators to fundamental questions in solid state physics.

The investigation of the magnetic properties of magnetic nanoparticles and ferrofluids demonstrates very well the strength of small-angle scattering with neutrons. Due to their magnetic moment, neutrons are sensitive to both the nuclear structure of the nanoparticles and their magnetic properties. A measurement using neutrons allows the shape, size and size distribution as well as the magnetization of the particles to be recorded microscopically using statistically relevant methods. In recent years, the modelling of the magnetic properties of samples at mesoscale lengths using micromagnetic theory has also made great progress.

The aim of this lab course is to work out the basics of small-angle neutron scattering and then to investigate some selected samples of magnetic nanoparticles and ferrofluids. For this purpose, a digital version (“digital twin”) of the neutron small angle system SANS-1 will be used. The scattering experiments are simulated with numerical Monte-Carlo methods. The magnetic response and the expected SANS signal of simple nanoparticles are calculated using micromagnetic simulations.

# Contents

# 1. Introduction and Theory

This manual aims at guiding you through the experimental lab course at the small-angle scattering instrument SANS-1 at the Heinz Maier-Leibnitz Zentrum (MLZ)[1] in Garching. At the beginning of the visit, you will be given a lecture on the basics of neutron scattering, which will be followed by an in-depth explanation of the SANS-1 instrument and its working principle by the tutor during the lab course. However, we think it will be highly beneficial to include this introductory section, both to prepare beforehand, as well as an assisting manual for the course and the report writing. A more thorough discussion on neutron scattering in general can be found in literature [2, 3, 4]. Additionally, a deeper explanation of SANS specifically can be found in [1]. Here, we will introduce only the very basics of these concepts.

## 1.1. Neutron Scattering Basics

In general, a scattering experiment involves an initial beam scattered on a sample and an outgoing beam being observed on a detector. Contrary to microscopy, in scattering experiments, the detector shows the reciprocal space image, rather than the direct space. Multiple scattering techniques exist, tailored for specific sample types and the information which one wants to obtain. These techniques differ in the probe (beam) which they use, e.g. visible light, X-rays, electrons, neutrons; in the samples measured, from thin films, through solutions, up to bulk crystals, as well a plethora of additional equipment, changing the sample environment, e.g. magnets, manipulating the beam, etc. We will, of course, focus on neutron scattering.

The advantages of using neutrons as the probe stem from four main characteristics. Firstly, typically in a scattering experiment, the wavelength of a the probe needs to match the length-scales of the sample which we want to measure. In neutron scattering experiments, the wavelength is in the range of $1\,$Å to $25\,$Å making it perfectly suited to atomic and nanoscale phenomena. Secondly, coincidentally, the energy of neutrons with these wavelengths is in the same order as many excitations in solid-state research and can, therefore, interact, e.g. with phonons. Thirdly and fourthly, neutrons interact with the sample in two ways (see Figure 1. They are uncharged and, therefore, interact via the strong nuclear force with the nucleus of the atom. This gives them an incredible penetration depth into the material, allowing for measurements of bulk samples. Neutrons carry a magnetic moment, leading to dipole-dipole interactions with the unpaired orbital electrons. This way, neutron scattering also allows studying the magnetism of the sample. [4, 2]

When a neutron scatters on an atom, a transfer of momentum and energy occurs, which due

[1] `https://mlz-garching.de/sans-1`

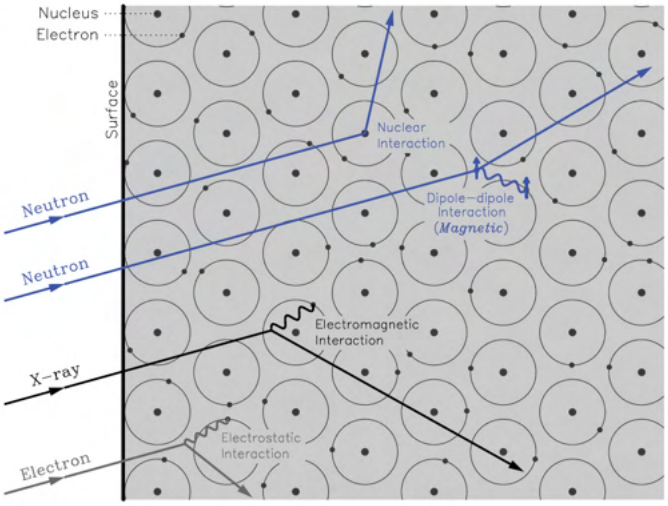


**Figure 1** Principle scattering interactions of neutrons, X-rays and electors with condensed matter samples. Taken from [2]

to momentum and energy conservation, gives:

$$\hbar\vec{Q} = \hbar\left(\vec{k} - \vec{k}'\right) , \tag{1.1}$$

$$\hbar\omega = \frac{\hbar^2}{2m}\left(k^2 - k'^2\right) , \tag{1.2}$$

where $\vec{k}$ and $\vec{k}'$ are the initial and final neutron momentum, $\vec{Q}$ is the scattering vector, $\hbar\omega$ the energy transfer and $m$ the neutron mass. When momentum changes direction but without energy transfer, we refer to it as elastic scattering. In contrast, inelastic scattering involves nonzero energy transfer. Inelastic scattering can be used, e.g. to determine the dispersion relation—typically of phonons or magnons. [5]

In a real experiment, however, the neutron beam, which we can approximate as an incoming plane wave, scatters on many atoms (for the nuclear scattering case) at once. What we see in the end as intensity on a detector (neutron count) is the result of the interference of these waves scattered from many atoms. This intensity is directly related to the probability of scattering a neutron with wavevector $\vec{k}$ into the state with wavevector $\vec{k}'$. The relation between this probability and the neutron count is described by the neutron scattering cross-section, or the double differential cross-section (DDXS), derived from the Fermi's Golden Rule. The DDXS gives the number of neutrons scattered into a solid angle $\mathrm{d}\Omega$ within energy range of $(\hbar\omega, \hbar(\omega + \mathrm{d}\omega))$, per second, divided by incoming neutron flux:

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\omega} = \left(\frac{m}{2\pi\hbar^2}\right)^2 \frac{k'}{k} \sum_{\lambda',\sigma'} \sum_{\lambda,\sigma} p_\lambda p_\sigma \left|\left\langle \vec{k}', \vec{\sigma}', \lambda' \right| \hat{U} \left| \vec{k}, \vec{\sigma}, \lambda \right\rangle\right|^2 \times \delta\left(\hbar\omega + E_\lambda - E_{\lambda'}\right) , \tag{1.3}$$

where $|\lambda\rangle$, $E_\lambda$, $p_\lambda$ are the initial state, energy and population factor of the scatterer, while $k$, $\vec{\sigma}$ and $p_\sigma$ denote the wavevector, spin state and polarisation probability of the (incoming) neutron respectively. Primes denote final state and scattered neutrons. Energy transfer $\hbar\omega$

from equation 1.2 is used in the delta function to fulfil the law of energy conservation. [5]

This formula is also known as the master formula. From an experiment perspective, the most important part is the $\hat{U}$, determining the interaction between the neutron and the scatterer. Every other part of the formula can be set, calculated, or is directly known. Depending on the nature of the scattering and the effects involved, different operators can be chosen to approximate $\hat{U}$. For pure nuclear scattering, this is usually a Fermi pseudopotential describing scattering on a set of points with positions $\vec{R}_j$, weighted with their scattering lengths $b_j$:

$$\hat{U}(\vec{r}) = \frac{2\pi\hbar^2}{m} \sum_j b_j \delta\left(\vec{r} - \hat{\vec{R}}_j\right) . \tag{1.4}$$

The scattering length $b$ is often explained as the "strength" with which a certain atom scatters the incoming neutron. The $b$ values are tabularised. They are isotope specific, spin specific (for nuclei with non-zero spin) and very importantly, do not follow any monotonic pattern with rising atomic number. This means, that the scattering length of two isotopes of the same element can be drastically different, as is the case, e.g. with hydrogen and deuterium. [2] Moreover, even a perfect crystal will never have an entirely uniform and equal $b$ value distribution due to inevitable isotope impurities in the structure. This leads to an inherent type of "background" in neutron scattering measurements called incoherent scattering. The exact derivation can be found, e.g. in [4]; here, we will only take the end results. If we simplify equation 1.3 using the assumption that the scattering is purely nuclear and inelastic, as well as adding the variation in $b$ values among atoms, we arrive at:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \propto \langle b \rangle^2 \sum_{i,j} e^{-i\vec{Q}\left(\vec{R}_j - \vec{R}_j\right)} + \left(\langle b^2 \rangle - \langle b \rangle^2\right) N \,, \tag{1.5}$$

where the angled brackets symbolise an averaging over the measured sample. The left part of the equation is called the "coherent scattering", giving us information about the structure, while the right one is the "incoherent scattering". As mentioned above, it stems from the fluctuations in the scattering length. It is $Q$-independent and, therefore, constitutes a flat noise in most measurements.

## 1.2. Small-Angle Neutron Scattering

We will now make the jump to small-angle neutron scattering. We have already mentioned that scattering experiments probe systems in the reciprocal space. Therefore, if we wants to go towards larger structures than, say, crystal unit cells, we need to focus on smaller $Q$-values. Through the Bragg's Law:

$$Q = \frac{4\pi \sin\theta}{\lambda} \,, \tag{1.6}$$

we know that this can be achieved by increasing the wavelength and decreasing the measurement angle. For this reason, SANS typically uses cold neutrons, which have longer

wavelengths and, as the name implies, small angles.

Once we increase the probed correlation distance to multiple nanometers, it is no longer viable to consider scattering length densities of singular atoms. It is, therefore, useful to introduce the concept of scattering length density (SLD) $\rho$, i.e. the scattering length density $b$ averaged over the constituent volume.

$$\rho = \frac{\sum ib_i}{\bar{V}} \tag{1.7}$$

For example, for a general two phase system, composed of phases $V_1$ and $V_2$, we get:

$$\rho(r) = \begin{cases} \rho_1, & \text{in} V_1 \\ \rho_2, & \text{in} V_2 \end{cases} \tag{1.8}$$

With the introduction of the SLD, we can write a general differencial cross-section for SANS:

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(q) = \frac{N_p}{V}\left(\rho_1 - \rho_2\right)^2 V_p^2 P(q) S(q)\,, \tag{1.9}$$

where $N_p$ and $V_p$ is the number and volume of the particles, $V$ is the illuminated sample volume, $\rho$ the scattering length density, $P(q)$ the form factor and $S(q)$ the structure factor. From an experimental point of view, the most interesting constituents of this formula are the form and structure factors. The form factor describes the shape, surface and density distribution of measured objects, while the structure factor determines the arrangement or superstructure of the objects. An example of a form factor of diluted cylinders is shown in Figure 2. Typically, one performs measurements in such a way that either $P(q)$, or $S(q)$ can be ignored at one time. For example, nanoparticle solutions are often measured at very low concentrations to avoid nanoparticle interactions and thus minimise the structure factor contribution to the scattering picture. Otherwise, it can be very challenging to discriminate between the influence of the $P(q)$ and $S(q)$ on the resulting signal, which is a convolution of both parts (see Figure 3)

Further, more detailed explanation of SANS will follow during the lab course, as well as in the introductory lecture.

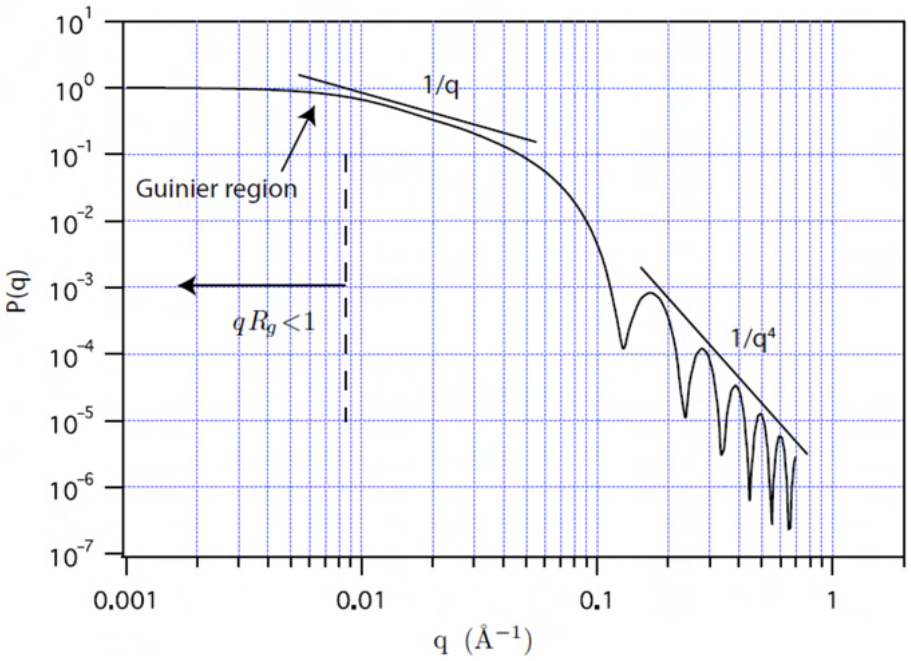


**Figure 2** Form factor $P(q)$ example, with marked Guinier and Porod regimes.

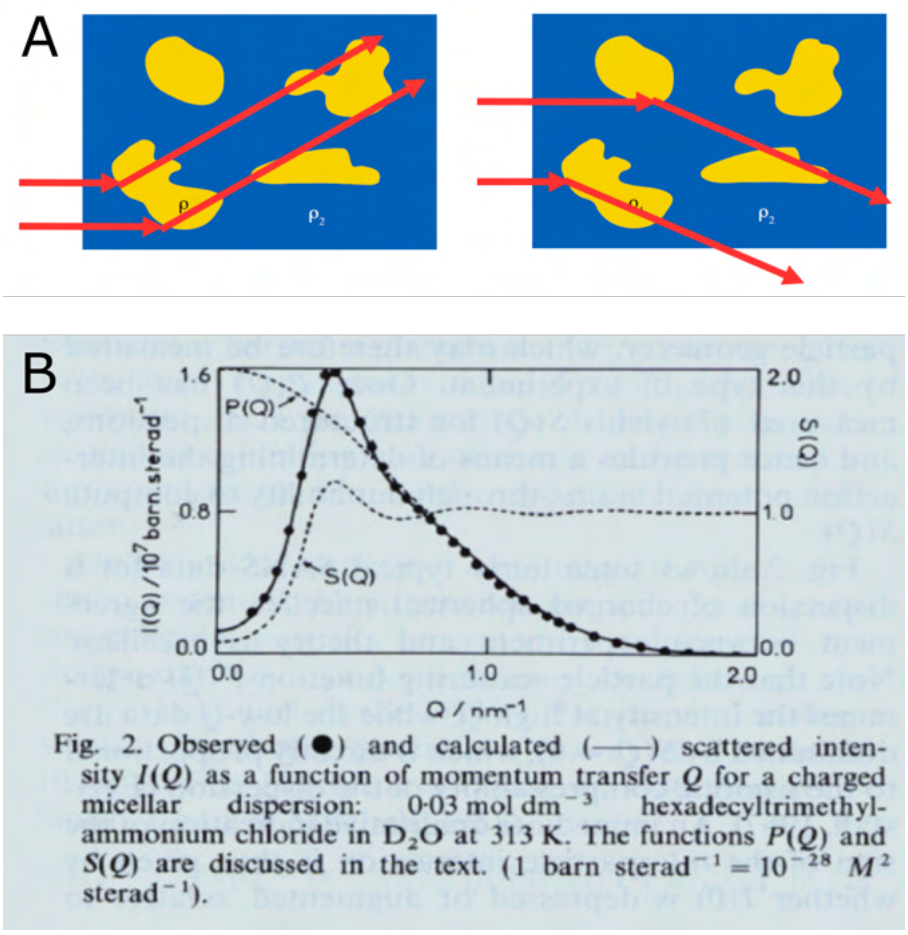


**Figure 3** A - Schematic picture of the structure factor origin with highly concentrated solutions, where constructive interference can be observed not only from within single particles, but also from their neighbours. B - Influence of the structure factor on the measured signal.

# 2. Preparatory Exercises

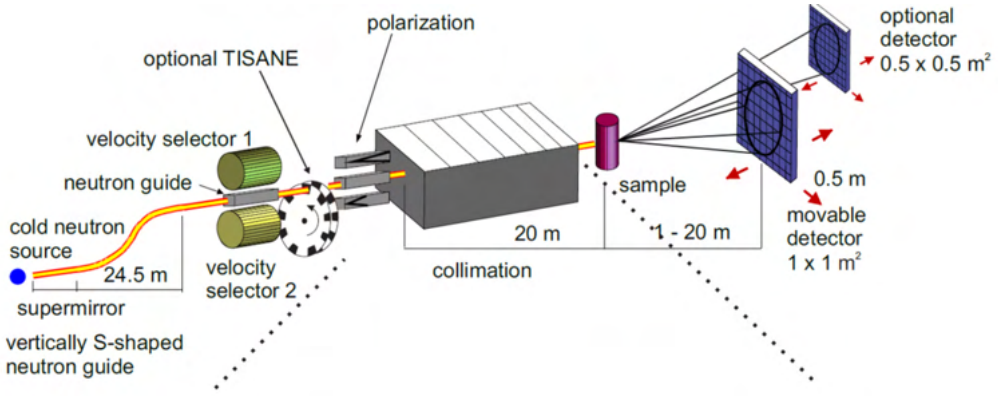


**Figure 4** Schematic view of the SANS-1 Instrument

1. We will start the experiment with a discussion about the instrument itself. However, it would be highly beneficial if you could briefly explain what is the purpose of the following instrument parts from Figure 4 and how do they work:
   a. cold source
   b. neutron guide
   c. velocity selector
   d. chopper
   e. polarizer
   f. collimator
   g. detector
2. Additionally, the following questions should help you get used to the values which we will be using.
   a. Calculate the energy, velocity and wavelength of neutrons coming out of the: i-cold source, ii-hot source, iii-thermal neutrons.
   b. Calculate the reciprocal lattice spacing of an $Fe_2O_3$ crystal at room temperature. Now calculate the reciprocal spacing of closely packed $Fe_2O_3$ nanoparticles (assume hcp structure and $30\,\mathrm{nm}$ diameter).
   c. Determine the scattering length (coherent and incoherent) of: Al, Cd, Quarz.
   d. Calculate the scattering length density of: $Fe_2O_3$, $H_2O$, $D_2O$.

# 3. Experiment Procedure

1. The individual components of the beamline SANS-1 at the FRM II are presented and explained in detail with their function.

2. The technique of small-angle neutron scattering is explained using the digital twin of the SANS-1: For this purpose, the concepts of mean scattering length density, convolution of form and structure factor are introduced and the method of contrast variation is explained. The results are validated and fitted with simple Monte Carlo simulations using the program McStas [6, 7, 8, 9, 10, 11].

3. The concept of small-angle magnetic neutron scattering is introduced by the different contributions to the magnetic contrast, e.g. by variation of the magnetization direction (spin misalignment scattering) or variation of the saturation magnetization. The basics and setup of small angle neutron scattering with polarized neutrons (SANSPOL and POLARIS) are briefly explained.

4. Simple examples of micromagnetic simulations of magnetic nanoparticles are performed.

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