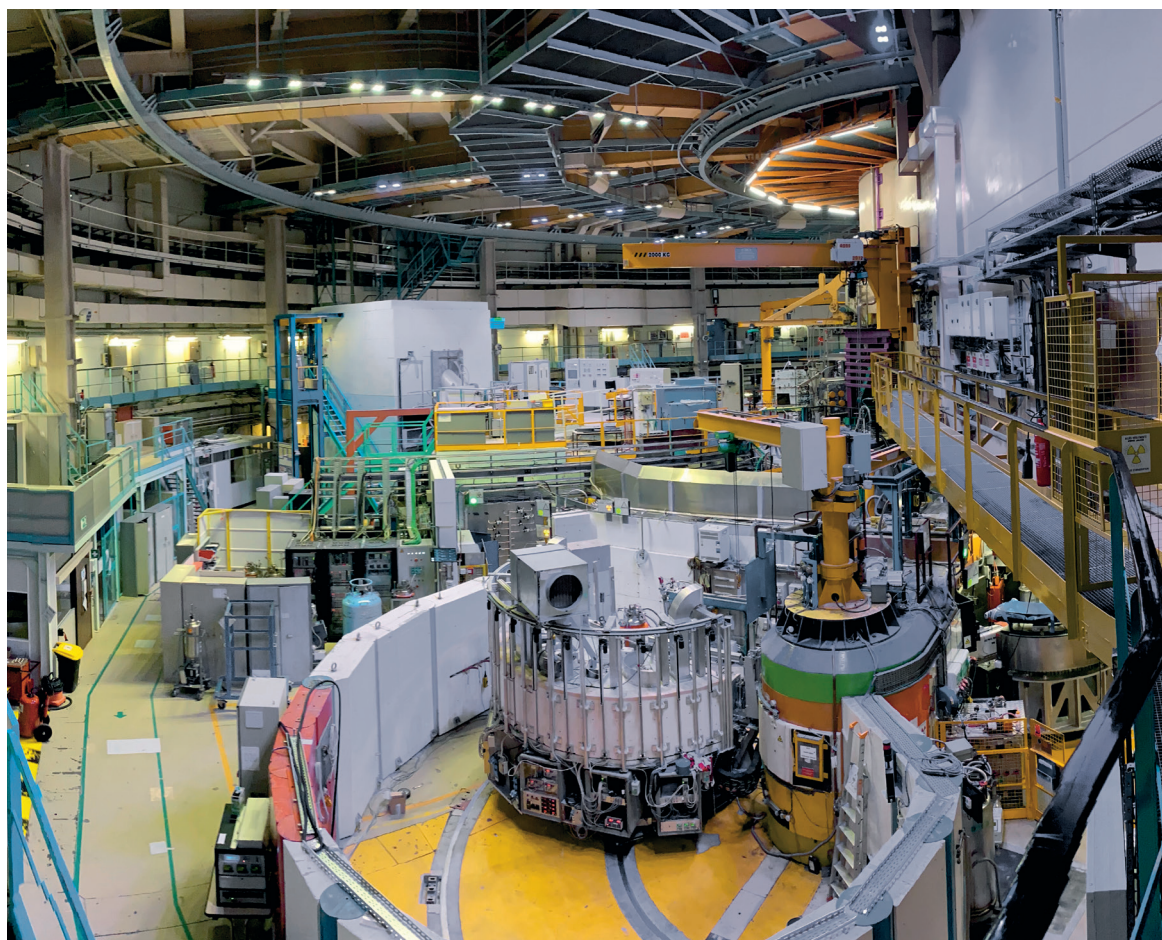




Laboratory Course

Neutron Scattering

Lectures

Irina Apanasenko, Stephan Förster, Karen Frieze, Emmanuel Kentzinger,
Margarita Kruteva, Mirijam Zobel, Reiner Zorn (Editors)

Schlüsseltechnologien / Key Technologies

Band / Volume 308

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Forschungszentrum Jülich GmbH
Jülich Centre For Neutron Science (JCNS)

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1 Introduction: Neutron Scattering in Contemporary Research

S. Förster, T. Brückel

Jülich Centre for Neutron Science 1

Forschungszentrum Jülich GmbH

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1.1 Introduction: Why Scattering?

We come across scattering phenomena every day. For example, we notice the blue sky or the red sunset, both of which originate from light scattering in the atmosphere. We see clouds thanks to light scattering at tiny water droplets. We drink milk, which appears white due to light scattering at tiny oil droplets. Understanding light scattering enables industry to produce the premium white paints.

This course will teach you that scattering methods have become one of the most powerful experimental tools in modern science. They enable us to answer a simple yet important question:

What is the structure of matter, and how does it change with time?

Not only light, but also X-rays, electrons and neutrons are scattered from matter. Scattering changes their direction, energy or phase. By carefully measuring these changes, we can reconstruct the structure and dynamics of matter. In fact, the size and structure of molecules, atoms and nuclei were first determined by scattering methods, decades before microscopy methods were developed to image them. Today, scattering methods are indispensable in fields such as condensed matter physics, chemistry, biology, materials science, nanotechnology, geology, environmental science, medicine, food science, engineering and industrial quality control. Returning to the oil droplets in milk, light scattering methods have been developed that can determine the size distribution of these and much smaller oil droplets in seconds. This method has become standard practice in many analytical laboratories.

In the following section, we will take a brief look at the use of X-ray and neutron scattering.

1.2 X-Ray Scattering in Condensed Matter Research

What requirements must radiation, such as X-rays or light, fulfil to be useful for scattering experiments? One important requirement is that the wavelength of the radiation should be of a similar size as the length scale of the structure we are interested in.

It is intuitive to understand that, if we want to measure the distance between the atoms, we need a “ruler” of comparable length. The distance between atoms is in the order of $0.1\text{ nm} = 10^{-10}\text{ m} = 0.0000000001\text{ m}$. Since the distance between atoms is such an important length scale in condensed matter science, it has been given its own unit: $0.1\text{ nm} = 1\text{ Ångström} = 1\text{ Å}$. Therefore, if we want to understand the microscopic atomic structure of matter — i.e. where the atoms are located inside our samples and how they move — we need wavelengths in Ångströms.

Figure 1.1 shows the electromagnetic spectrum and provides an overview of the different types of radiation and their wavelengths. Accordingly, X-rays with Ångström wavelengths would be very suitable for investigating atoms or molecules. In comparison, the wavelength of light is 4 000 to 7 000 times longer, making it inappropriate for measuring distances on an atomic scale.

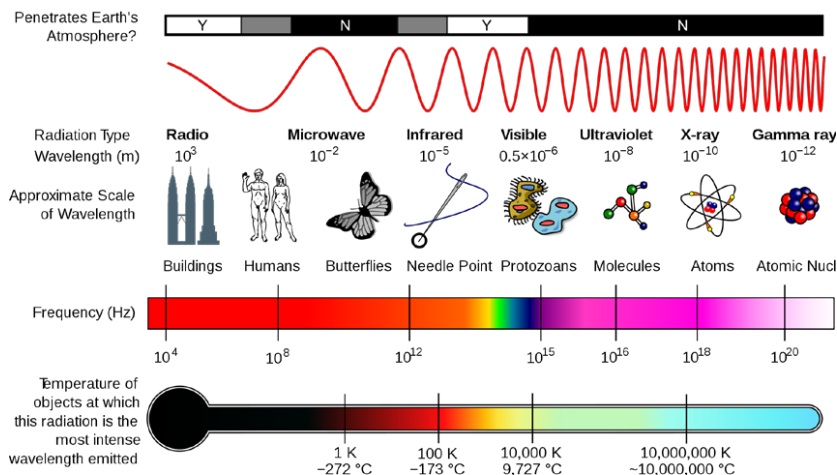


Fig. 1.1: Electromagnetic spectrum. Shown is the wavelength and frequency of electromagnetic waves, which have different names for different wavelength regions. Also given are examples for objects with sizes comparable to the wavelength. (from WIKIPEDIA)

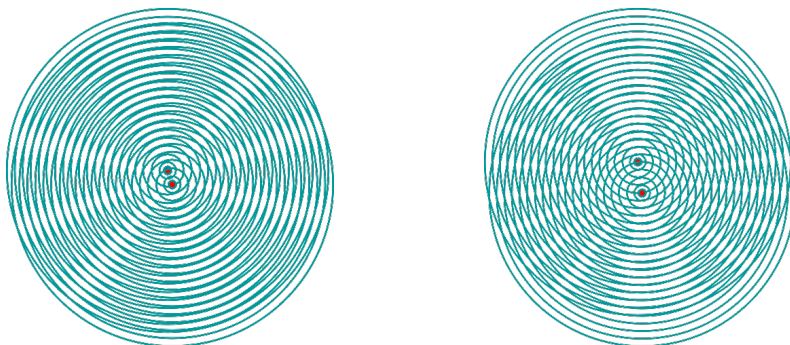


Fig. 1.2: Moiré pattern for concentric circles with equal distances representing a planar cut through spherical waves emitted from two scattering centers. The circles represent surfaces of constant phase relationship. Linear superposition of the waves gives enhancement or cancellation of the wave amplitudes along certain directions. This interference effect is mimicked by the depicted Moiré pattern. If the distance between the scattering centers is increased, the distance in the interference maxima decreases and vice versa: distances in the image created by scattering are inverse proportional – or reciprocal - to distances in the original objects which motivates the introduction of a reciprocal space to describe scattering events compared to the real space of the object under investigation.

In classical physics, electromagnetic radiation is described as the propagation of electromagnetic waves. In a scattering experiment, we select plane waves, which are waves of a certain wavelength and propagation direction, where all points on a plane in space have the same phase. When such a wave impinges on two point-like scattering centers (in a solid, these could be atoms), spherical waves are emitted from these centers. This is simply the Huygens principle for wave propagation. The emitted waves can superimpose, leading to either enhancement or cancellation of the signal in certain directions, as depicted in Figure 1.2.

As Figure 1.2 shows, scattering can be described as an interference phenomenon involving radiation waves. Since the work of de Broglie and Einstein, we know that quantum objects have a dual nature: the particle-wave duality. In the case of electromagnetic waves, the quanta that carry energy are called photons. In the detector that registers the scattering pattern, we count individual X-ray photons. This is characteristic of the quantum mechanical description: a wave picture is appropriate during the propagation of radiation, while a particle description is more appropriate for the interaction with matter. The wave and particle pictures are connected by the fact that the square of the wave magnitude at a certain position in space gives the probability density of finding the quantum particle at the corresponding position. Given this particle-wave duality, it is therefore natural to use elementary particles as probes for scattering investigations of condensed matter systems. This was first realized by Rutherford in 1909 in his famous experiment, in which he directed a beam of α -particles onto a gold foil and registered the transmitted and scattered particles. He found that many particles were backscattered, and from the ratio of transmitted to backscattered α -particles, he could deduce the structure of the atom. This model, consisting of a positively charged nucleus of size about 10 femtometer = 10 fm = 10×10^{-15} m surrounded by a cloud of negatively charged electrons with an extension of about $1 \text{ \AA} = 10^{-10} \text{ m} = 100000 \text{ fm}$, is now widely accepted. See Figure 1.3 for an illustration of this model.

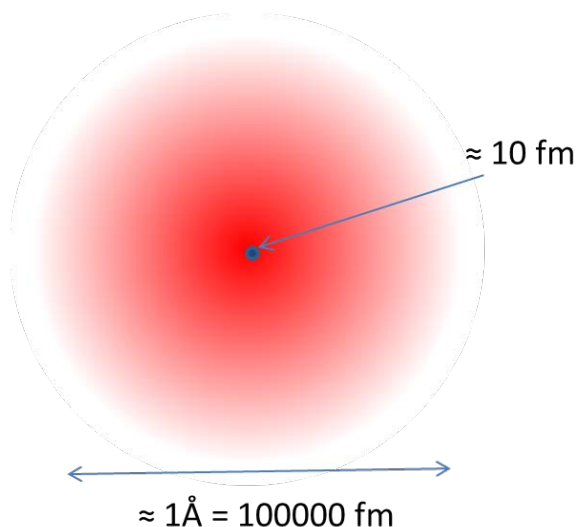


Fig. 1.3: Schematic model of an atom with the atomic nucleus consisting of neutrons and protons having a size of about 10 fm surrounded by electrons in a cloud of a size of about 1 Å.

The real breakthrough in the study of the structure of condensed matter systems came when Max von Laue used X-rays as a scattering probe. Wilhelm Conrad Röntgen discovered X-rays in 1895, and it was soon concluded that they were electromagnetic waves. Arnold Sommerfeld suggested that the wavelength of X-rays was approximately 1 Å. At the time of Max von Laue, after the experiments of Rutherford, it was accepted that matter consisted of atoms but their periodic arrangement in crystals was suggested only by the regular facets of the crystals, but could not be proven by experiment. Max von Laue was a theoretician who derived the famous Laue equation, which describes scattering from a regular, three-dimensional, periodic arrangement of scattering centers. He convinced the two experimentalists, Friedrich and Knipping, to conduct an X-ray diffraction experiment. The result is shown in Figure 1.4.

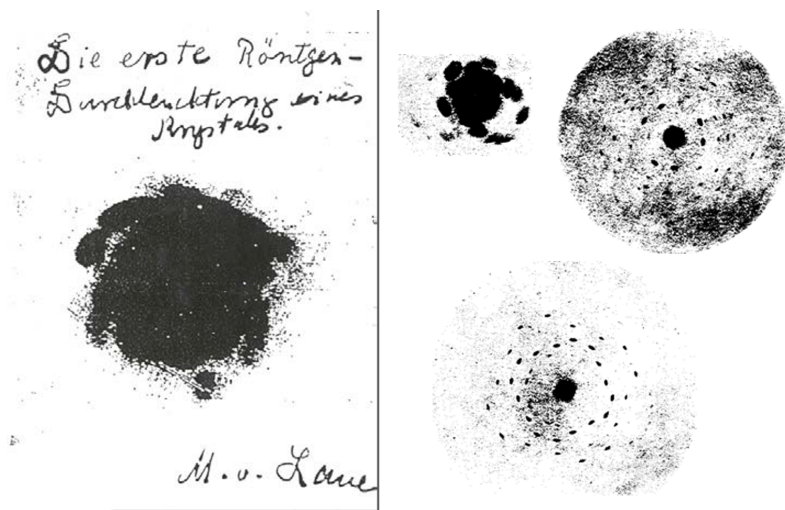


Fig. 1.4: Early x-ray diffraction diagrams recorded by a film from copper sulphite single crystals [1].

While the first Laue photograph showed little more than a blurred spot, the quality of these images was soon improved to the point where clear Laue spots could be identified. This discovery was of paramount importance: it provided definitive proof that solids consist of atoms arranged in a regular, three-dimensional, periodic array, and that X-rays are scattered as electromagnetic waves from such an atomic arrangement. Consequently, it was only natural that Max von Laue received the Nobel Prize in 1914 for this groundbreaking discovery. However, the experimentalists Friedrich and Knipping were not recognized.

Almost everything we know today about the atomic structure of matter is based on a discovery that took place 100 years ago. The techniques have, of course, been significantly refined, and nowadays X-ray diffraction is widely used to resolve the complex structures of biological macromolecules in the field of protein crystallography. Such investigations require very intense and bright X-ray beams, provided by large accelerators known as synchrotron radiation sources. Many thousands of reflections can be recorded in a matter of seconds. As electromagnetic waves, X-rays are mainly scattered by the electronic charge distribution around atoms, meaning that X-ray diffraction can be used to determine electron density in solids.

1.3 Impact of Scattering in other Fields of Science

It should be noted that scattering is a much more general scientific method, not just used by condensed matter scientists. For instance, electron scattering was employed to determine the size of the proton, which has a radius of just 0.84 femtometers. Figure 1.5 shows the electron scattering curve of a proton, as first measured by Hofstadter and McAllister in 1955. Robert Hofstadter was awarded the Nobel Prize in Physics for this work in 1961.

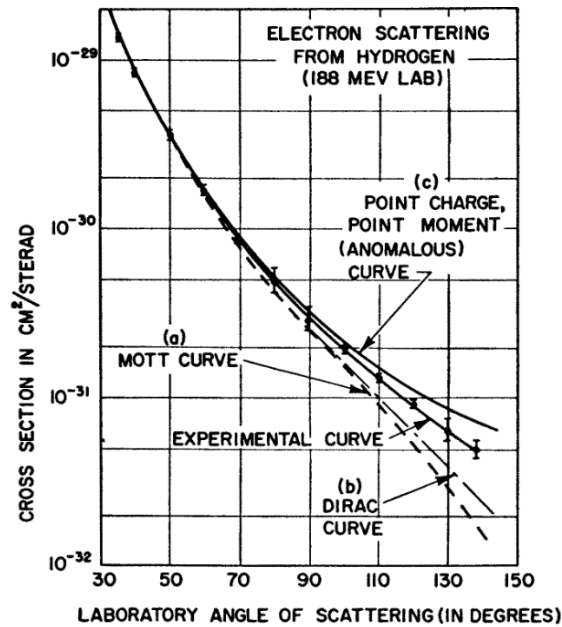


Fig. 1.5: Early electron scattering curve of protons measured by Hofstadter and McAllister in 1955 [2].

The structure of even smaller particles is determined using the world's largest accelerator, which is located close to Geneva, on the border between Switzerland and France, at the CERN research center. CERN stands for the European Organisation for Nuclear Research. The CERN site is home to many accelerators, the largest and highest energy of which is the LHC (Large Hadron Collider). The LHC lies in a 27 km tunnel, 175 m below ground level. This enormous accelerator is used for a scattering experiment in which opposing particle beams (e.g. protons at an energy of 7 TeV) collide at certain interaction points surrounded by large detectors built by major international collaborations. In inelastic scattering events, new particles can be created, among them the famous Higgs boson. It is hoped that this significant investment will help us address some of the most fundamental questions in physics and advance our understanding of the deepest laws of nature.

These large accelerators are needed to achieve high particle energies, which correspond to short wavelengths and allow one to study the fine structures within nucleons. Large detectors are required because imaging is not possible at these scales, but if all scattered particles are traced, the scattering event can be reconstructed on a computer. While new particles are created during deep inelastic scattering events at the LHC, the connection to X-ray diffraction is more evident for the former HERA accelerator, which was in operation at DESY in Hamburg until a few years ago. There, electrons were scattered from protons in head-on collisions, revealing the proton's inner structure consisting of quarks and gluons.

1.4 Why Neutrons?

Returning to the topic of condensed matter science, if X-rays are so effective in determining structures, why do we need neutrons? Neutrons have some very specific properties that make them extremely useful for studying condensed matter:

1. Neutrons are neutral particles. This means they can penetrate deeply, and can be used as non-destructive probes to study samples in severe environments such as cryomagnets or furnaces.
2. The wavelengths of neutrons are similar to atomic spacings, just as is the case for X-rays. Therefore, they can provide structural information ranging from picometers to 100 μm .
3. The energies of thermal neutrons are similar to the energies of elementary excitations in solids. Consequently, neutrons can be used to determine molecular vibrations, lattice excitations, and the dynamics of atomic motion.
4. Neutrons interact with the nucleus, unlike X-rays or electrons, which interact with the electron cloud (see Figure 1.5). Neutrons are very sensitive to light atoms, such as hydrogen. It is difficult to detect hydrogen using X-rays, since hydrogen in chemical bonds often has fewer than one surrounding electron. Neutrons can also distinguish between neighboring elements in the periodic table, such as manganese, iron and chromium. X-rays are indifferent to these elements since they have nearly the same number of electrons. One can also exploit isotopic substitution. A well-known example of this is the contrast variation in soft matter or biological macromolecules that occurs when deuterium is replaced by hydrogen in certain molecules or functional groups. Similar to staining in light microscopy, the location and movement of these functional groups can then be observed against the backdrop of the other molecules.
5. Neutrons have a magnetic moment. This dipolar moment is due to the nuclear spin. Therefore, neutrons can be used to study microscopic magnetic structures, as well as magnetic excitations in solids that have similar energies to neutrons.

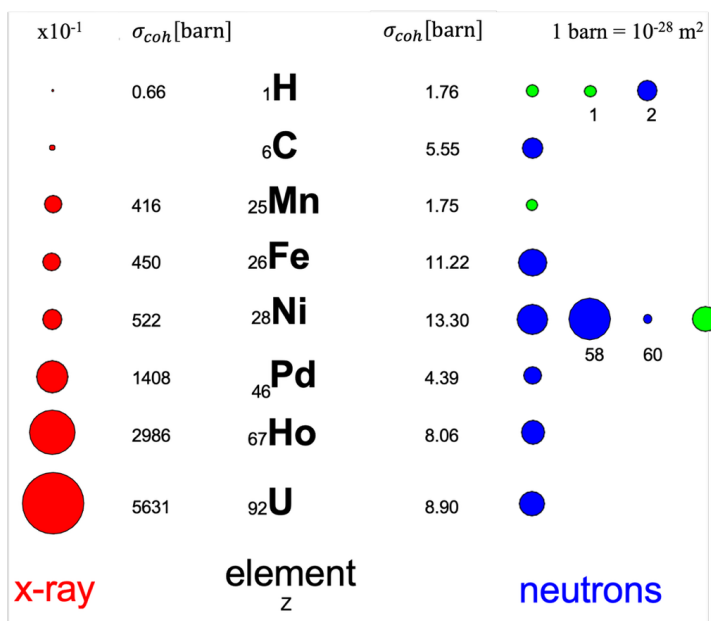


Fig. 1.6: Comparison of x-ray and neutron scattering from single atoms for a few elements of the periodic table. The filled circles represent a measure of the total cross section, i.e., of the probability for scattering. For x-rays, which are scattered from the electron cloud, this probability goes up with the number square of electrons. Therefore, hydrogen is hardly visible for x-rays in the presence of heavier atoms. The situation is quite different for neutrons, which are scattered from the atomic nucleus. Here the scattering varies not monotonically throughout the periodic table and is different for different isotopes of the same atom. Blue and green circles distinguish scattering with and without 180° phase shift, respectively.

Figure 1.7 illustrates the broad applicability of neutrons in condensed matter studies, given their unique properties. As indicated in the figure, different scattering techniques are used for different applications.

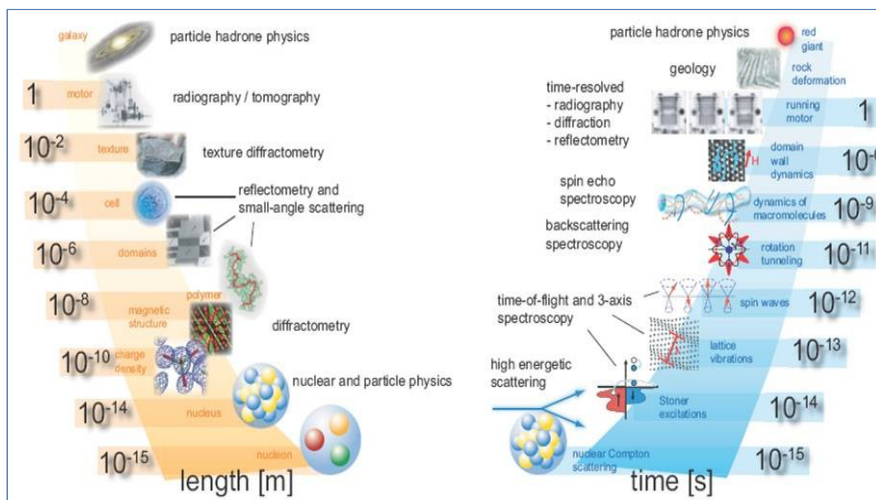


Fig. 1.7: Huge range of length (left side) and time (right side) scales covered by research with neutrons. Also indicated is the corresponding neutron technique.

Given the significant impact of neutron scattering on the study of condensed matter, it is not surprising that the Nobel Prize in Physics was awarded to two pioneers of neutron diffraction and inelastic neutron scattering: Clifford G. Shull and Bertram Brockhouse, who received the prize in 1994. Clifford Shull is also the author of the famous quote, “Neutrons tell us where atoms are and how they move”.

If you have got the impression so far that neutrons are the most ideal and universal probe for studying condensed matter on an atomic scale, you are right in principle. However, as with everything in life, there are also some drawbacks. Although neutrons are everywhere — without them, we would not exist — they are extremely difficult to produce as free particles, unbound within nuclei. Free neutrons are produced by nuclear physics reactions, which require large, high-tech installations. The two main traditional methods of producing free neutrons are:

- (1) **Fission** of the uranium 235 nuclei in a chain reaction; this process happens in research reactors.
- (2) Bombarding heavy nuclei with high energetic protons; the nuclei are “heated up” when a proton is absorbed and typically 20–30 neutrons are being evaporated. This process is called **spallation** and requires a spallation source with a proton accelerator and a heavy metal target station.

In recent years, a third method of producing free neutrons in a high-current accelerator-based neutron source (**HICANS**) has been developed, particularly at the JCNS.

- (3) Accelerating a high-current proton beam on a target where free neutrons are produced through a proton-induced nuclear reaction.

Since installations for producing free neutrons are expensive to build and operate, there are only a few sources worldwide. As shown in Figure 1.8, JCNS is present at some of the world's best sources.



Fig. 1.8: Major neutron research centres worldwide which have sources of appreciable flux and a broad instrumentation suite for condensed matter research. JCNS instruments are located at four of the leading sources worldwide: the neutron research reactor FRM II in Garching, Germany, the Institute Laue-Langevin ILL in Grenoble, France, the Spallation Neutron Source SNS in Oak Ridge, USA and the Chinese Advanced Research Reactor CARR close to Beijing, China. JCNS also has a leading involvement in the European Spallation Source project, Lund, Sweden.

The limited number of sources worldwide means that neutron scattering experiments must be organized quite differently from normal laboratory-based experiments. Users must be trained at specialist schools (our JCNS school is one example) and access to experiments must be arranged (see below).

Neutron research centers are rare, as are free neutrons. In a high-flux reactor, the neutron flux — i.e. the number of neutrons passing through a given area in a given time — is in the order of 10^{15} neutrons/cm²/s. Compared to particle fluxes in gases, the neutron density in high-flux sources corresponds to a pressure of about 10^{-6} mbar, which is considered to be high vacuum. Neutrons must be transported from the source to the experimental area. This can be achieved using simple flight tubes or so-called neutron guides. These are evacuated glass tubes (often covered with metal layers to improve performance), through which

neutrons are transported by total reflection from the side, top and bottom walls, in a manner similar to light in glass fibers. The neutron flux downstream at the scattering experiments is much lower than at the source itself, typically amounting to 10^6 – 10^8 neutrons/cm²/s. This means that long counting times must be allowed for to achieve reasonable statistics in the neutron detector. For comparison, the flux of photons from a small helium-neon laser with a power output of 1 mW (typical for a laser pointer) amounts to around 10^{15} photons per second in a beam area of less than 1 mm².

However, the low flux of neutrons is not the only limiting factor in neutron scattering experiments; the sources of neutrons are also not very bright. This means that the beams of neutrons are rather large, typically a few cm², and therefore require rather large samples in general. Typical sample sizes are also in the order of a few cm² and have masses of a few grams. Nevertheless, this does not mean that we cannot study nanosized objects with neutrons, as you will see in subsequent lectures. For neutron scattering techniques, however, we need many such objects in order to obtain ensemble averages.

1.5 The Social Practice of Neutron Scattering

The rarity of neutron sources has led to a particular social practice for neutron scattering: there are only a few major sources in Europe and worldwide. Operating each of these sources costs several million Euro per year. Therefore, efforts must be made to use the existing sources as efficiently as possible. This means: (i) continuous and reliable operation of the source for a large part of the year; (ii) a large number of high-performance instruments that can run in parallel around each source; (iii) professional operation of the instruments by highly qualified staff, with stringent risk management to minimize downtime for the instruments and auxiliary equipment; (iv) access for as many scientists as possible.

There is no commercial market for neutron scattering instruments. Therefore, research centers build these instruments, where one or a few staff scientists usually work closely with engineers and technicians to create an instrument for a specific neutron-based research application. These highly experienced scientists will later operate the instruments located at a specific neutron source. The Jülich Centre for Neutron Science (JCNS) has staff scientists located at the outstations at FRM II and ILL.

Neutron facilities are too expensive to operate for just a small number of scientists. Therefore, beamtime is offered to a large group of external users from universities, research organizations (such as the Max Planck Society or the Fraunhofer Society in Germany) and industry. To obtain access to a neutron scattering instrument, users must first find information about available instruments online, then contact the instrument scientist to discuss their planned experiments. Once they have a clear idea of the experiment and its strategy, they will write a beamtime proposal describing the scientific background, the goal of the experiment and its strategy, and any prior work. The facility issues a call for proposals at regular intervals, typically twice a year. The proposals received are distributed to members of an independent committee of international experts who perform a peer review and establish a ranking. Overload factors of between two and three on the neutron instruments typically exist, i.e. two to three times the available beam time is demanded by external users. Once the best experiments have been selected, beam time is allocated through the facility. The directors approve the committee's ranking, the beamline scientist schedules the experiments on their instrument, and the user office sends invitations to external users. Many facilities will cover the travel and accommodation costs of one or two users per experiment. It is then up to the user to prepare their experiment as well as possible. If an experiment fails due to poor preparation, it will be very difficult to obtain additional beam time for the same scientific problem. Typical experiments last between one day and two weeks. During this time, lots of data will be collected, which users then take home and spend several weeks or months processing and modelling.

A typical neutron scattering facility runs for around 200 days a year, with a few hundred visits from users all over the world. This is what makes research with neutrons so attractive to young scientists: from the outset of their careers, they will learn to work in large international collaborations and have the opportunity to work with state-of-the-art, high-tech equipment. They will also learn to organize their research as efficiently as possible. You have therefore made a good choice in attending this laboratory course!

Following this brief introduction, you can look forward to a series of fascinating lectures, during which you will gain a deeper understanding of the fundamental principles that underpin neutron experimentation. Have fun and enjoy working with this special gift of nature: the free neutron!

References

- [1] W. Friedrich, P. Knipping, M. von Laue(1912). "Interferenz-Erscheinungen bei Röntgenstrahlen". Sitzungsberichte der Mathematisch-Physikalischen Classe der Königlich-Bayerischen Akademie der Wissenschaften zu München 1912: 303.
- [2] R. Hofstadter, R. W. McAllister, Electron scattering from the proton, Phys. Rev. 98, 217 (1958).

Some useful links for research with neutrons:

- [3] German Committee for Research with Neutrons: www.neutronenforschung.de
- [4] European Neutron Portal: <http://www.neutron-eu.net/>
- [5] Neutron scattering reference material: <http://www.neutron.anl.gov/reference.html>
- [6] Neutron scattering web: <http://www.neutron.anl.gov/>
- [7] Jülich Centre for Neutron Science: <http://www.fz-juelich.de/jcms/>

Exercises

E1.1 Multiple Choice

- Electromagnetic radiation with a wavelength of 500 nm corresponds to:
 - ☐ microwaves
 - ☐ visible light
 - ☐ ultraviolet
 - ☐ X-rays

- The typical distance between atoms in a solid amounts to:
 - ☐ 10 nm
 - ☐ 1 nm
 - ☐ 0.1 nm
 - ☐ 0.01 nm

- An atomic nucleus has a typical size of:
 - ☐ 1 Å
 - ☐ 0.1 nm
 - ☐ 1 pm
 - ☐ 10 fm

- The typical wavelength of thermal neutrons is:
 - ☐ 10 nm
 - ☐ 1 nm
 - ☐ 0.1 nm
 - ☐ 0.01 nm

- Which type of radiation would you use to distinguish iron and manganese atoms in a given compound?
 - ☐ X-rays
 - ☐ neutrons
 - ☐ electrons
 - ☐ light

- Which type of radiation would you use to determine the charge density distribution in a solid?
 - ☐ X-rays
 - ☐ neutrons
 - ☐ electrons
 - ☐ light

- How many neutrons per second impact on a sample with typical lateral dimensions of 1x1 cm in a typical neutron scattering experiment?
 - ☐ 10^3
 - ☐ 10^7
 - ☐ 10^{12}
 - ☐ 10^{16}

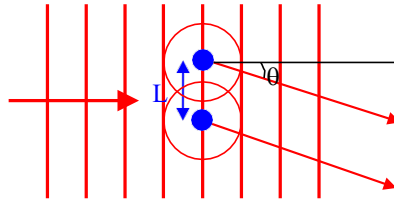
- Which type of radiation would you use to determine the magnetization density distribution in a solid?
 - ☐ X-rays
 - ☐ neutrons
 - ☐ electrons
 - ☐ light

E1.2 Comprehension

- a. What is the difference between a scattering and an imaging experiment? When would you choose one over the other?
- b. Why does one observe Laue spots when a “white” beam of X-rays is scattered from a single crystal? How about scattering from glass?
- c. Why are neutrons sensitive to the magnetic order in a crystal?
- d. Neutron scattering allows us to determine “where the atoms are and how the atoms move” in a condensed matter system. Other scattering probes include: light, x-rays, electrons, α -particles. Discuss qualitatively the strengths and weakness of these probes in comparison to neutron scattering.
- e. CO₂ has a bad reputation as green-house gas in the atmosphere. Could it, however, be useful as a scattering probe to replace neutrons? (A high flux of CO₂ molecules could e.g. be obtained by an expansion of pressurised CO₂ gas from a gas bottle through a nozzle - a flux many orders of magnitude higher than the neutron fluxes used in neutron scattering experiments!)

E1.3 Arithmetic Problem (optional): Huyens principle and coherence

A plane wave of wavelength λ is incident on a pair of identical scatterers, which are separated by a distance L perpendicular to the wave propagation, see figure:



According to the Huygens principle, spherical waves will be emitted from the two scatterers. In certain directions, these waves interfere constructively, i.e. the two scattered waves are in phase.

- Calculate the angles θ , where interference maxima occur in the far field limit.
- What happens to the interference maxima, if there is a broad distribution of wavelength in the incident wave, but the propagation direction remains well defined?
- What happens to the interference maxima, if the wavelength of the incident wave is well defined, but there are many waves of different directions impinging on our scatterers?
- How would you design an instrument to measure the distance L between the two scatterers, if light from a normal light bulb is being used as radiation? Which requirement does L have to fulfil in this case?
- According to b) and c) monochromatization and collimation are important to obtain well resolved interference pattern. The corresponding requirements for the radiation are called longitudinal (b) and transverse (c) coherence, respectively. Discuss qualitatively the relation between coherence and resolution, i.e. in our example the ability of the apparatus designed in d) to determine the distance L between the scatterers.

2 Properties of the neutron

P. Zakalek

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Forschungszentrum Jülich GmbH

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2.1 Introduction

The neutron with its unique properties as described here is used as a particularly useful probe for condensed matter investigations. The neutron is a nucleon consisting of three valence quarks, which are held together by gluons (see Fig. 2.1). It thus has an internal structure, which, however, is irrelevant for condensed matter physics, since the energy scales involved in its internal excitations are much too high. Keeping in mind the difference in length scales (diameter of an atom: about 0.1 nm = 10^{-10} m; diameter of a neutron: about 1 fm = 10^{-15} m), we can safely consider the neutron as a point-like particle without internal structure for our purposes. Due to the weak interaction, the neutron is not a stable particle. A free neutron undergoes a β -decay into proton p, electron e^- and electron-antineutrino $\bar{\nu}_e$ after an average lifetime of about 15 minutes [11]:



This leaves ample time for scattering investigations. In contrast to the massless photon, the neutron has a mass m of about one atomic mass unit $\sim 1.675 \cdot 10^{-27}$ kg. The neutron therefore has a velocity well below the speed of light and depending on its velocity can be significantly affected by gravity. The finite neutron mass is comparable to the mass of a nucleus and thus an appreciable amount of energy can be transferred during the scattering process. The neutron, with a current experimental upper limit on its electric dipole moment of about 10^{-26} e · cm, can be viewed as a neutral particle. Being neutral, the neutron experiences no strong Coulomb interaction with matter, which results in large penetration depths. Finally, the neutron has a nuclear spin of 1/2 giving rise to a magnetic dipole moment of

$$\mu_n = -1.913\mu_N \quad \text{with } \mu_N = 5.05 \cdot 10^{-27} \text{ J T}^{-1} \quad (2.2)$$

Due to this magnetic moment, the neutron can interact with the magnetic field of unpaired electrons in a sample leading to *magnetic scattering*. Thus, magnetic structures and excitations can be studied by neutron scattering.

To calculate the interference effects during the scattering process, a neutron has to be described as a matter wave with momentum

$$\mathbf{p} = m \cdot \mathbf{v} = \hbar \mathbf{k} \longrightarrow p = h/\lambda \quad (2.3)$$

and energy

$$E = \frac{1}{2} m v^2 = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2} \equiv k_B T_{\text{eq}}, \quad (2.4)$$

where v is the velocity of the neutron and T_{eq} defines the temperature equivalent of the kinetic energy of the neutron. In practical units:

$$\lambda[\text{nm}] = \frac{400}{v[\text{m/s}]} \quad (2.5)$$

$$E [\text{meV}] = \frac{0.818}{(\lambda [\text{nm}])^2} \quad (2.6)$$

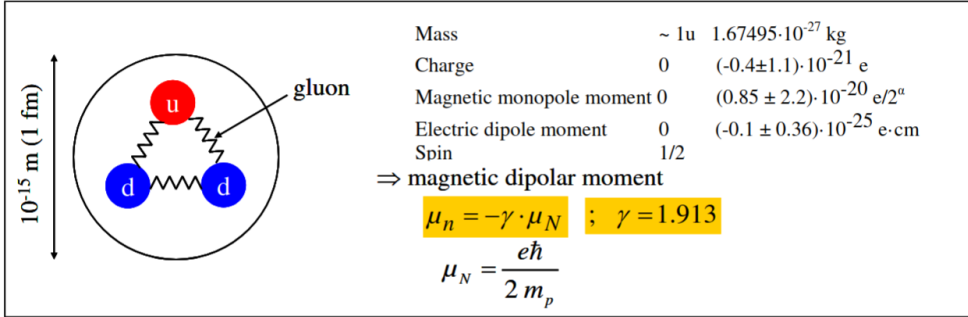


Fig. 2.1: Schematics of the neutron being composed of three quarks and gluons and the main quantities characterising the neutron as a particle.

Let us consider the example of so-called thermal neutrons from a moderator at ambient temperature corresponding to a temperature equivalent of $T_{\text{eq}} \sim 300 \text{ K}$. According to (2.4), their wavelength is 0.18 nm , closely matching the interatomic spacing. The energy of thermal neutrons is around 25 meV , which matches well the energy of elementary excitations, such as spin waves (magnons) or lattice vibrations (phonons). Together with the usually large penetration depths (charge = 0) and the magnetic interaction, these properties make neutrons so extremely useful for condensed matter investigations.

In elementary scattering theory, the relevant quantity is the interaction potential $V(\mathbf{r})$ between the probe and the system from which it is scattered. This potential enters the expression for the scattering cross section within kinematical scattering theory, as derived using either the Born approximation or Fermi's golden rule. To determine this interaction potential, we will look in more detail at the interaction of neutrons with matter. For neutrons there exist two dominant interactions: the interaction of the neutron with nuclei and its interaction with the magnetic field in the sample. The nuclear interaction results from the so-called strong interaction of particle physics, which is also responsible for the binding of neutrons and protons in the atomic nuclei. The interaction with the magnetic field is nothing but the magnetic dipole interaction of the neutron due to its dipolar moment with the magnetic field of unpaired electrons. There are other interactions, which are significantly weaker. One is the interaction of the neutron with the electric fields in the sample due to the neutron's magnetic dipole moment. This is a purely relativistic effect. Another is the magnetic dipole interaction of the neutron with the magnetic field produced by the nuclei. Since such interactions are several orders of magnitude weaker than the nuclear and magnetic interaction, they can usually be neglected and we will not discuss them further in this lecture.

2.2 Nuclear interaction: Scattering and absorption

To evaluate the cross section σ for nuclear scattering, we have to specify the interaction potential with the nucleus. Deriving this interaction potential from first principles

remains one of the fundamental challenges of nuclear physics. Instead, Fermi has proposed a phenomenological potential based on the argument that the wavelength of thermal neutrons is much larger than the nuclear radius. This means that the nuclei are point-like scatterers, which leads to isotropic, Q-independent scattering (so-called s-wave scattering, i.e. only the $\ell = 0$ partial wave contributes). We will therefore use the so-called *Fermi pseudopotential*

$$V(\mathbf{r}) = \frac{2\pi\hbar^2}{m_n} b\delta(\mathbf{r} - \mathbf{R}). \quad (2.7)$$

Although the strong interaction itself is very strong, the interaction volume is extremely small because of the small nuclear radius. Consequently, the scattering probability remains sufficiently small that the first Born approximation is applicable. The quantity b introduced in (2.7) is a phenomenological quantity describing the strength of the interaction potential and is referred to as the *scattering length*. Tabulated values of b can be found in [8] or online¹. The total cross section of a given nucleus is $\sigma = 4\pi|b|^2$, and has the same numerical value as the surface area of a sphere of radius b . Since the interaction potential obviously depends on the details of the nuclear structure, b is different for different isotopes of the given element and also for different nuclear spin states. This fact gives rise to the appearance of so-called *coherent* and *incoherent scattering*, see section 2.4. Figure 2.2 shows the variation of the scattering amplitude as a function of atomic weight throughout the periodic table. The scattering length is mostly positive but can also take negative values. Since $-1 = \exp(i\pi)$ this negative sign corresponds to a phase shift of π (or 180°) during the scattering process. The scattering length roughly follows the dashed line labelled *potential scattering* contribution, despite the fact that there are rather large excursions from this line.

In the simplest one-dimensional model shown in Figure 2.3, we can describe the nucleus as a rectangular potential well with the radius of the well equal to the nucleus radius and the depth as V_0 . The kinetic energy of the neutrons is thus adjusted with the well potential. The wave function of the neutron being scattered from such a potential well can be written as

$$\Psi(r) \sim e^{ikr} + \frac{f}{r} e^{ikr}, \quad (2.8)$$

with f as the scattering amplitude, k as the wave vector of the neutron and r as the distance to the well center. Here the first term describes the incident plane wave and the second term describes a spherical wave emitted from the nucleus. In the limit of a hard sphere, the wave function on the surface of the nucleus has to vanish since the neutron cannot penetrate inside the hard sphere. Mathematically this is described by the condition $\Psi(R) = 0$ or $-f = R$. The scattering length is defined as $b := -f = R$, so that its value is positive for most nuclei. Therefore, for pure *potential scattering*, where the nucleus is assumed to be a hard sphere, b attains the value of the nuclear radius $b = R$, which is plotted in Figure 2.2 as a dashed line: the *potential scattering* contribution. The marked deviations from this overall behaviour are due to so-called *resonance scattering*. In a simplified picture, such resonances occur, when the neutron energy is such that absorption

¹ <http://www.ncnr.nist.gov/resources/n-lengths/>

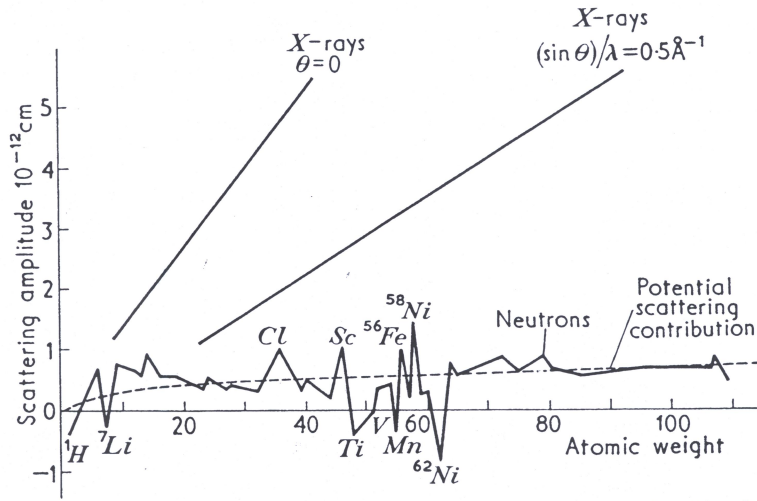


Fig. 2.2: Scattering length as a function of atomic weight throughout the periodic table (from Research, London 7 (1954), 257).

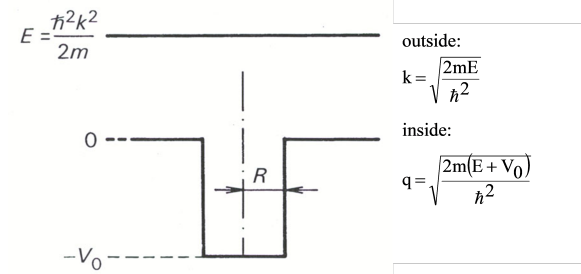


Fig. 2.3: The nucleus described as a potential well of radius R and depth $-V_0$, while the neutron has the kinetic energy $E = \frac{\hbar^2 k^2}{2m}$.

of the neutron in the nucleus produces a bound excited state. This can lead to a *resonant absorption* process, but it can also lead to *resonance scattering*, a typical second order perturbation process: in the initial state, the nucleus is in its ground state and the interaction with the neutron can be described as a virtual transition into an excited state of the compound nucleus and back with a re-emission of the neutron, where the nucleus decays back from the excited compound system into its ground state. This process $n + K \rightarrow C^* \rightarrow K + n$ has a cross section given by the famous *Breit-Wigner formula*

$$\sigma_R = 4\pi \left| R + \frac{\text{const}}{E - E_R + \frac{1}{2}i\Gamma} \right|^2. \quad (2.9)$$

Here, R denotes the nuclear radius, E the neutron energy, E_R the resonance energy, and Γ the damping parameter related to the lifetime of the excited state. As one can see, this

formula describes a very strong energy dependence with a pronounced maximum when the neutron energy equals the resonance energy. Moreover, the resonance amplitude has an imaginary part, which describes the *resonance absorption*. In the *resonant absorption* process, the neutron is captured by the nucleus, leading to a compound nucleus in an excited state, containing one more neutron than the original nucleus. In a subsequent nuclear reaction, the compound nucleus releases its excess energy. Examples for such absorption reactions will be given in the subsequent section. Finally, the Breit–Wigner formula shows that the scattering length can become negative below resonance ($E < E_R$), where the resonant term subtracts from R ; if it dominates, b flips sign.

2.3 Neutron absorption

As explained above, neutron absorption can occur during nuclear reactions. It can be divided into three regions depending on the neutron energy. Three energy regions can be distinguished: the low-energy $1/\nu$ region, the intermediate-energy resonance region, and the high-energy smooth region.

Far away from the resonance at low neutron energies, the absorption cross section is given by

$$\sigma_a \sim \lambda \sim \frac{1}{\nu}. \quad (2.10)$$

This proportionality to the wavelength λ or the inverse velocity $1/\nu$ is a result of the density of states appearing in Fermi's golden rule. This behaviour can be understood intuitively because wavelength and neutron velocity ν are inversely proportional and thus, for longer wavelength i. e. smaller velocity, the neutron remains correspondingly longer close to the nucleus increasing the probability for a reaction, which leads to a larger absorption cross section. Table 2.1 gives examples for neutron absorption processes connected with important nuclear reactions for neutron applications.

σ_a (25 meV) [barn]	Nuclear reaction
5333	$n + {}^3\text{He} \rightarrow {}^4\text{He}^* \rightarrow p + {}^3\text{T}$
940	$n + {}^6\text{Li} \rightarrow {}^7\text{Li}^* \rightarrow {}^4\text{He} + {}^3\text{T}$
3837	$n + {}^{10}\text{B} \rightarrow {}^{11}\text{B}^* \rightarrow {}^4\text{He} + {}^7\text{Li} + \gamma$
681	$n + {}^{235}\text{U} \rightarrow \text{fission}$

Table 2.1: Examples for neutron absorption processes due to nuclear reactions. The absorption cross section is given for neutrons of energy 25 meV in barn = $10^{-28} \text{ m}^2 = 100 \text{ fm}^2$.

As an example, there is a high probability that neutrons are absorbed by ${}^3\text{He}$ nuclei, because the ${}^4\text{He}$ or α -particle is very stable since it corresponds to a closed nuclear shell. However, during the absorption of the neutron, the ${}^4\text{He}$ nucleus is produced in an excited state. It gets rid of its surplus energy by decay into a proton and a triton ${}^3\text{T}$ (the triton ${}^3\text{T}$ nucleus is a hydrogen isotope with one proton and 2 neutrons). Since these two

particles have very high energies of about 0.5 MeV due to the nuclear reaction, charged particles are created during this decay, which can be used for neutron detection in a proportional counter. In a similar manner, the reaction with ${}^6\text{Li}$, ${}^{10}\text{B}$ or ${}^{235}\text{U}$ can be used to build neutron detectors. It should be mentioned, however, that the neutron absorption in ${}^3\text{He}$ is very strongly dependent on the relative orientation of the nuclear spins of both particles. While for antiparallel spin direction (singlet state), the absorption cross section is ~ 6000 barn, it reduces to 2 barn for parallel spin direction (triplet state). This effect can be used to build efficient neutron polarization filters. By optical pumping with laser light, the nuclear moment of the ${}^3\text{He}$ nuclei can be aligned along one direction (so-called hyperpolarized ${}^3\text{He}$ gas). If an unpolarized neutron beam passes a filter cell filled with hyperpolarized ${}^3\text{He}$, the neutrons with spin moment antiparallel to the nuclear moment of the ${}^3\text{He}$ have a high probability to be absorbed, while neutrons with the other spin direction have a high probability to be transmitted. For an appropriate thickness of the filter cell, a very high neutron beam polarization can be achieved in this manner.

Another class of absorption processes are so-called (n, γ) resonances at intermediate neutron energies. Examples are given in Table 2.2. In these processes, a nucleus is produced, which contains one additional neutron and this compound nucleus decays into the ground state by emission of γ -radiation. Prominent (n, γ) resonances occur for Cadmium or Gadolinium where, depending on the isotope, the absorption cross section can be very high, see Table 2.2. These metals are often used as neutron absorbers in shieldings or diaphragms, which define the size of the neutron beam. One should, however, be aware that in these reactions, γ -radiation of very high energy is being released, which requires additional lead shielding for radiation protection.

Nuclide	σ_γ [barn]	$E_{\text{resonance}}$ [meV]
${}^{113}\text{Cd}$	20600	178
${}^{151}\text{Eu}$	9200	321
${}^{155}\text{Gd}$	60900	26.8
${}^{157}\text{Gd}$	254000	31.4

Table 2.2: Examples for (n, γ) resonances with the cross section in barn and the resonance energy in meV.

As described by the Breit–Wigner formula, these resonance absorption cross sections have very strong energy dependencies. The simple proportionality to the wavelength given in equation (2.10) no longer holds close to the resonance energies.

At high neutron energies, the resonances cannot be resolved anymore and thus the absorption cross section appears to be smooth. Due to the high neutron energy, these cross sections are typically small.

As an example, we show the energy dependence of the absorption cross section for Cadmium and Gadolinium in Figure 2.4. Such data can be found in the JENDL database, accessed via JANIS (NEA) [12].

Figure 2.4 shows that for lower energies, i. e. long wavelengths, the proportionality of the absorption cross section to the wavelength holds to very good approximation. However, there is a strong resonance for a wavelength of $0.64 \text{ \AA}$ ($\approx 0.2 \text{ eV}$), where the cross section

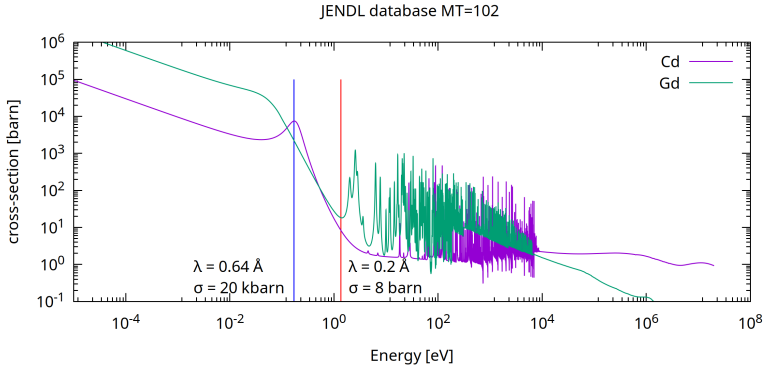


Fig. 2.4: Absorption cross section of the element Cadmium and Gadolinium as a function of energy in a double-logarithmic representation. The cross sections for Cadmium at 0.64 Å and 0.2 Å are marked with lines. Tabulated values for the absorption cross section MT = 102 were taken from the JENDL database [12].

attains a maximum of about 20 kbarn. Above this energy, i. e. for shorter wavelengths, the absorption cross section drops drastically. At a wavelength of 0.2 Å, it attains a value of only 8 barn. This shows that in the thermal energy range, Cadmium can be used as an efficient neutron absorber. However, one has to be careful and not use it for the same purpose in case of hot neutrons, where Cadmium becomes virtually transparent. There are many more resonances for higher neutron energies, which are not relevant for neutron scattering, where only hot ($T_{\text{eq}} = 2000$ K), thermal ($T_{\text{eq}} = 300$ K) and cold ($T_{\text{eq}} = 20$ K) neutrons are being used.

A similar strong energy dependence occurs for the element Gadolinium. Usually, neutron scatterers try to avoid samples containing Gadolinium since it is the most absorbing element, especially the isotope ^{157}Gd . However, the resonances lie in the thermal neutron energy range. If the scattering experiment is performed with hot neutrons, the absorption cross section of Gadolinium becomes much smaller and scattering experiments become feasible².

2.4 Coherent and incoherent scattering

As mentioned above, the nuclear interaction potential depends on the details of the nuclear structure and thus, the scattering length b is different for different isotopes of a given element and also for different nuclear spin states. In this section, we will discuss the effects of these special properties of the interaction of neutrons and nuclei for the

² Another possibility is to use isotope enriched Gadolinium. While the isotope ^{157}Gd with natural abundance 15.7% has a thermal absorption cross section of 254000 barn, the isotope ^{158}Gd , which is the most abundant with 24.8%, has an absorption cross section of only 2.2 barn.

scattering from condensed matter. Let us assume an arrangement of atoms with scattering lengths b_i on fixed positions $\mathbf{R}_i$. For this case, the scattering potential writes

$$V(\mathbf{r}) = \frac{2\pi\hbar^2}{m_n} \sum_i b_i \delta(\mathbf{r} - \mathbf{R}_i). \quad (2.11)$$

The scattering amplitude is obtained from a Fourier transform

$$A(\mathbf{Q}) = \sum_i b_i e^{i\mathbf{Q} \cdot \mathbf{R}_i}. \quad (2.12)$$

When we calculate the scattering cross section, we have to take into account that the different isotopes are distributed randomly over all sites. Also the nuclear spin orientation is random, except for very low temperatures in high external magnetic fields. Therefore, we have to average over the random distribution of the scattering length in the sample

$$\frac{d\sigma}{d\Omega}(\mathbf{Q}) \sim |A(\mathbf{Q})|^2 = \left\langle \sum_i b_i e^{i\mathbf{Q} \cdot \mathbf{R}_i} \cdot \sum_j b_j^* e^{-i\mathbf{Q} \cdot \mathbf{R}_j} \right\rangle. \quad (2.13)$$

Before evaluating this expression, we anticipate the result: the *coherent scattering* is the scattering from the average lattice, while the *incoherent scattering* comes from its deviation. The two terms in the cross section below correspond exactly to these two contributions. To see this, we evaluate the expectation value of the product of the two scattering lengths at sites i and j . According to the above assumption, the distribution of the scattering length on the different sites is completely uncorrelated. This implies that for $i \neq j$, the expectation value of the product equals to the product of the expectation values. Only for $i = j$ a correlation occurs, which gives an additional term describing the mean quadratic deviation from the average:

$$\langle b_i b_j \rangle = \begin{cases} \langle b \rangle \langle b \rangle = \langle b \rangle^2, & i \neq j \\ \langle b^2 \rangle = \langle b \rangle^2 + \langle (b - \langle b \rangle)^2 \rangle, & i = j \end{cases} \quad (2.14)$$

The line for $i = j$ results from the identity

$$\langle (b - \langle b \rangle)^2 \rangle = \langle b^2 - 2b\langle b \rangle + \langle b \rangle^2 \rangle = \langle b^2 \rangle - \langle b \rangle^2. \quad (2.15)$$

Therefore, we can write the cross section in the following form:

$$\begin{aligned} \frac{d\sigma}{d\Omega}(\mathbf{Q}) = \langle b \rangle^2 \left| \sum_i e^{i\mathbf{Q} \cdot \mathbf{R}_i} \right|^2 & \quad (\text{coherent}) \\ + N \langle (b - \langle b \rangle)^2 \rangle & \quad (\text{incoherent}) \end{aligned} \quad (2.16)$$

The scattering cross section can be written as the sum of two terms. Only the first term contains the phase factors $e^{i\mathbf{Q} \cdot \mathbf{R}_i}$, which result from the coherent superposition of the scattering from pairs of scatterers. This term takes into account interference effects and is therefore named *coherent scattering*. The scattering length averaged over the isotope- and nuclear spin-distribution enters this term. The second term in (2.16) does not contain any phase information and is proportional to the number N of atoms (and not to

N^2 as for coherent scattering in fully constructive interference!). This term is not due to the interference of scattering from different atoms. As we can see from (2.15) (line $i = j$), this term corresponds to the scattering from single atoms, which subsequently superimpose in an incoherent manner (adding intensities, not amplitudes!). This is the reason for the intensity being proportional to the number N of atoms. Therefore, the second term is called *incoherent scattering*. Coherent and incoherent scattering are illustrated in Figure 2.5.

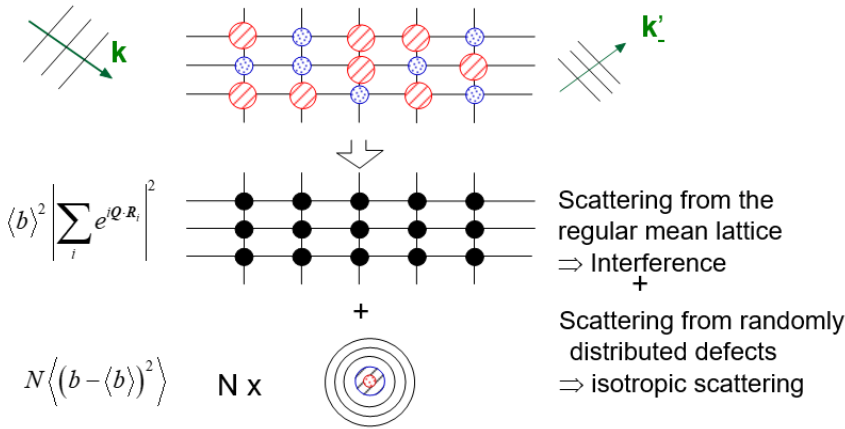


Fig. 2.5: Two-dimensional schematic illustration of the scattering process from a lattice of N atoms of a given chemical species, for which two isotopes (small dotted circles and large hatched circles) exist. The area of the circle represents the scattering cross section of the single isotope. The incident wave (top part of the figure for a special arrangement of the isotopes) is scattered coherently only from the average structure. This gives rise to Bragg peaks in certain directions. In the coherent scattering only the average scattering length is visible. Besides these interference phenomena, an isotropic background is observed, which is proportional to the number N of atoms and to the mean quadratic deviation from the average scattering length. This incoherent part of the scattering is represented by the lower part of the figure.

The most prominent example for *isotope incoherence* is elementary nickel. The scattering lengths of the nickel isotopes are listed together with their natural abundance in Table 2.3 [8]. The differences in the scattering lengths for the various nickel isotopes are enormous. Some isotopes even have negative scattering lengths. This is due to resonant bound states, as compared to the usual potential scattering.

Neglecting the less abundant isotopes ^{61}Ni and ^{64}Ni , the average scattering length is calculated as

$$\langle b \rangle \approx [0.68 \cdot 14.4 + 0.26 \cdot 2.8 + 0.04 \cdot (-8.7)] \text{ fm} \approx 10.2 \text{ fm}, \quad (2.17)$$

which gives the total coherent cross section of

$$\Rightarrow \sigma_{\text{coherent}} = 4\pi \langle b \rangle^2 \approx 13.1 \text{ barn} \quad (\text{exact: } 13.3(3) \text{ barn}). \quad (2.18)$$

Isotope	Natural Abundance	Nuclear Spin	Scattering Length [fm]
⁵⁸ Ni	68.27%	0	14.4(1)
⁶⁰ Ni	26.10%	0	2.8(1)
⁶¹ Ni	1.13%	3/2	7.60(6)
⁶² Ni	3.59%	0	-8.7(2)
⁶⁴ Ni	0.91%	0	-0.37(7)
Ni			10.3(1)

Table 2.3: The scattering lengths of the nickel isotopes and the resulting scattering length of natural Ni [8].

The incoherent scattering cross section per nickel atoms is calculated from the mean quadratic deviation:

$$\sigma_{\text{incoherent}}^{\text{Isotope}} = 4\pi [0.68 \cdot (14.4 - 10.2)^2 + 0.26 \cdot (2.8 - 10.2)^2 + 0.04 \cdot (-8.7 - 10.2)^2] \text{ fm}^2$$

$$= 5.1 \text{ barn} \quad (\text{exact: } 5.2(4) \text{ barn}) \quad (2.19)$$

Values in parentheses are the exact values taking into account the isotopes ⁶¹Ni and ⁶⁴Ni and the nuclear spin incoherent scattering (see below). From equations (2.18) and (2.19), we learn that the incoherent scattering cross section in nickel amounts to more than one third of the coherent scattering cross section.

The most prominent example for nuclear spin incoherent scattering is elementary hydrogen. The nucleus of the hydrogen atom, the proton, has the nuclear spin $I = 1/2$. The total nuclear spin of the system $\text{H} + n$ can therefore adopt two values: $J = 0$ and $J = 1$. Each state has its own scattering length: b_- for the singlet state ($J = 0$) and b_+ for the triplet state ($J = 1$) - compare Table 2.4.

Total Spin	Scattering Length	Abundance
$J = 0$ (singlet: $m_J = 0$)	$b_- = -47.5 \text{ fm}$	$\frac{1}{4}$ (one m_J state)
$J = 1$ (triplet: $m_J = -1, 0, +1$)	$b_+ = 10.85 \text{ fm}$	$\frac{3}{4}$ (three m_J state)
$\langle b \rangle = -3.739(1) \text{ fm}$		

Table 2.4: Scattering lengths for hydrogen [8].

Just as in the case of isotope incoherence, the average scattering length can be calculated

$$\langle b \rangle = \left[\frac{1}{4}(-47.5) + \frac{3}{4}(10.85) \right] \text{ fm} = -3.74 \text{ fm}. \quad (2.20)$$

This corresponds to a coherent scattering cross section of $\approx 1.76 \text{ barn}$ [8]

$$\Rightarrow \sigma_{\text{coherent}} = 4\pi \langle b \rangle^2 = 1.7568(10) \text{ barn}. \quad (2.21)$$

The nuclear spin incoherent part is again given by the mean quadratic deviation from the average

$$\sigma_{\text{incoherent}}^{\text{nuclear spin}} = 4\pi \left[\frac{1}{4}(-47.5 + 3.74)^2 + \frac{3}{4}(10.85 + 3.74)^2 \right] \text{ fm}^2 = 80.2 \text{ barn} \quad (2.22)$$

(exact : 80.26(6) barn).

Comparing (2.21) and (2.22), it is immediately clear that hydrogen scatters mainly incoherently. As a result, we observe a large background for all samples containing hydrogen. Hydrogen-containing adhesives should therefore be avoided whenever possible. Finally, we note that deuterium with nuclear spin $I = 1$ has a much more favourable ratio between coherent and incoherent scattering:

$$\sigma_{\text{coh.}}^{\text{D}} = 5.592(7) \text{ barn}; \quad \sigma_{\text{inc.}}^{\text{D}} = 2.05(3) \text{ barn} \quad (2.23)$$

The coherent scattering lengths of hydrogen (-3.74 fm) and deuterium (6.67 fm) are significantly different. This can be used for contrast variation by isotope substitution in all samples containing hydrogen, i. e. in biological samples or soft condensed matter samples, see corresponding chapters. A further important element, which shows strong nuclear incoherent scattering, is vanadium. Natural vanadium consists of 99.75 % of the isotope ^{51}V with a nuclear spin $7/2$. By chance, the ratio between the scattering lengths b_+ and b_- of this isotope is approximately equal to the reciprocal ratio of the abundances. Therefore, the coherent scattering cross section is very small and the incoherent cross section dominates [8] with

$$\sigma_{\text{coh.}}^{\text{V}} = 0.01838(12) \text{ barn}, \quad \sigma_{\text{incoh.}}^{\text{V}} = 5.08(6) \text{ barn}. \quad (2.24)$$

For this reason, Bragg scattering from vanadium is difficult to observe above the large incoherent background. However, since incoherent scattering is isotropic, the scattering from vanadium can be used to calibrate multi-detector arrangements.

Here, we will not discuss scattering lengths for further elements and refer to the values tabulated in [8].

2.5 Magnetic neutron scattering

So far, we have only discussed the scattering of neutrons by the atomic nuclei. Apart from nuclear scattering, the next important process is the scattering of neutrons by the magnetic field created within the sample from the moments of unpaired electrons. This so-called magnetic neutron scattering comes about by the magnetic dipole-dipole interaction between the magnetic dipole moment of the neutron and the magnetic field of the unpaired electrons, which has spin and orbital angular momentum contributions. This magnetic neutron scattering allows us to study the magnetic properties of a sample on an atomic level, i. e. with atomic spatial and energy resolution. The magnetic interaction strength is of the same order of magnitude as nuclear scattering, making neutrons uniquely suited for studies of magnetic structure and magnetic excitations. Here we do not discuss magnetic neutron scattering any further and refer to the corresponding chapter on "Spin Dependent and Magnetic Scattering".

2.6 Comparison of probes

In this lecture, we have so far introduced the elementary formalism to describe the scattering process and discussed the interaction of neutrons with matter. We now ask for which problems in condensed matter research neutrons are the most suitable probe compared with X-rays and electrons. To answer this question, we have to look at the ranges of energies, wavelengths or scattering vectors, which can be covered by various probes as well as the different contrast mechanisms.

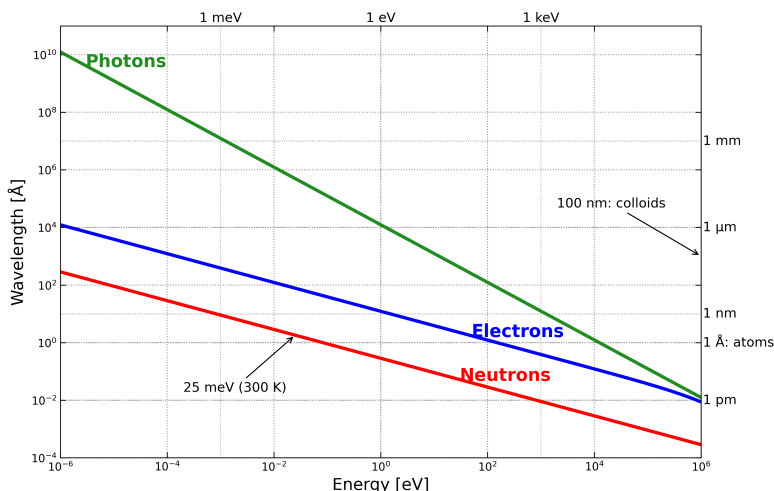


Fig. 2.6: Comparison of the three probes - neutrons, electrons and photons - in a double-logarithmic energy-wavelength diagram. Modified from Carpenter and Loong [6].

Figure 2.6 shows a double-logarithmic plot of the dispersion relation "wavelength versus energy" for the three probes neutrons, electrons and photons. The plot demonstrates how thermal neutrons of energy 25 meV are ideally suited to determine interatomic distances in the order of 0.1 nm, while the energy of X-rays or electrons for this wavelength is much higher. However, with modern techniques at a synchrotron radiation source, energy resolutions in the meV region become accessible even for photons of around 10 keV corresponding to a relative energy resolution $\Delta E/E \approx 10^{-7}$. The figure also shows that colloids with a typical size of 100 nm are well suited for the investigation with light of energy around 2 eV. These length scales can, however, also be reached with thermal neutron scattering in the small-angle region. While Figure 2.6 thus demonstrates for which energy-wavelength combination a certain probe is particularly useful, modern experimental techniques extend the range of application by several orders of magnitude.

It is therefore useful to compare the scattering cross sections as it is done in Figure 2.7 for X-rays and neutrons. Note that for the elements shown, the X-ray scattering cross sections are typically about an order of magnitude larger than the neutron scattering cross sections. This means that the signal for X-ray scattering is stronger for the same

incident flux and sample size. But care must be taken that the sample remains in the kinematical scattering regime, i.e. that single-scattering (Born) theory applies rather than dynamical theory. For X-rays, the cross section is proportional to the square of the number of electrons and thus varies in a monotonic fashion throughout the periodic table. Clearly, it will be difficult to determine hydrogen positions with X-rays in the presence of heavy elements such as metal ions. Moreover, there is a very weak contrast between neighbouring elements as can be seen from the transition metals Mn, Fe and Ni in Figure 2.7. However, this contrast can be enhanced by anomalous scattering, if the photon energy is tuned close to the absorption edge of an element. For neutrons the cross section depends on the details of the nuclear structure and thus varies in a non-systematic fashion throughout the periodic table. For example, there is a very high contrast between Mn and Fe. With neutrons, the hydrogen atom is clearly visible even in the presence of such heavy elements as uranium. Moreover, there is a strong contrast between the two hydrogen isotopes H and D. This contrast can be exploited for soft-matter investigations by selective deuteration of certain molecules or functional groups. This allows the contrast within the sample to be tailored.

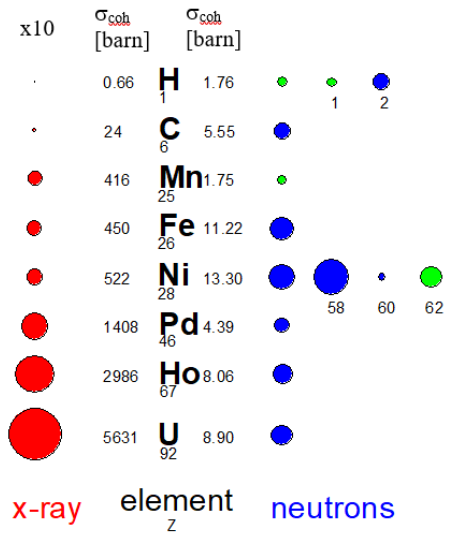


Fig. 2.7: Comparison of the coherent scattering cross sections for X-rays and neutrons for a selection of elements. The area of the colored circles represents the scattering cross section, where in the case of X-rays a scale factor 10 has to be applied. For neutrons, the blue and green circles distinguish the cases where the scattering occurs with or without a phase shift of π . For H and Ni, scattering cross sections for certain isotopes are given in addition to the averaged values for the natural element.

Finally, both neutrons and X-rays allow the investigation of magnetism on an atomic scale. Magnetic neutron scattering is comparable in strength to nuclear scattering, while non-resonant magnetic X-ray scattering is smaller than charge scattering by several or-

ders of magnitude³. Despite the small cross sections, non-resonant magnetic X-ray Bragg scattering from good quality single crystals yields good intensities with the brilliant beams at modern synchrotron radiation sources. While neutrons are scattered from the magnetic induction within the sample, X-rays are scattered differently from spin and orbital momentum and thus allow one to measure both form factors separately. Inelastic magnetic scattering such as from magnons or so-called quasielastic magnetic scattering from fluctuations in disordered magnetic systems is a clear domain of neutron scattering. Finally, resonance exchange scattering XRES of synchrotron X-rays allows one not only to get enhanced intensities, but also to study magnetism with element- and band sensitivity.

With appropriate scattering methods, employing neutrons, X-rays or light, processes in condensed matter on very different time and space scales can be investigated. Which scattering method is appropriate for which region within the scattering-vector–energy (Q–E) plane is plotted schematically in Figure 2.8. A scattering vector Q corresponds to a certain length scale, an energy to a certain frequency, so that the characteristic lengths and times scales for the various methods can be directly determined from the figure. Examples for applications and information on instrumentation will follow in subsequent lectures.

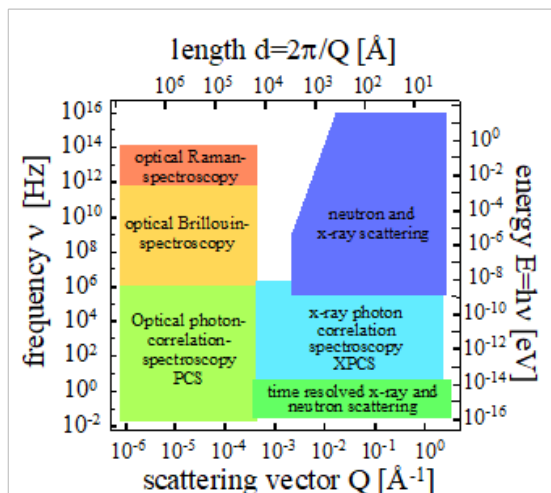


Fig. 2.8: Regions in frequency ν and scattering vector Q or energy E and length d , which can be covered by various scattering methods.

³ Typically between 6 to 9 orders of magnitude.

References

- [1] G. L. Squires, "Introduction to the Theory of Thermal Neutron Scattering" Dover (1997)
- [2] K. Sköld, D. Price (Eds.), "Methods of Experimental Physics" Neutron Scattering Part A-C, Academic Press (1987)
- [3] J. M. Cowley, "Diffraction Physics" North Holland, Amsterdam (1995)
- [4] S. W. Lovesey, "Theory of neutron scattering from condensed matter", Clarendon Press, Oxford (1987)
- [5] A. Furrer, J. Mesot, T. Strässle, "Neutron Scattering in Condensed Matter Physics", World Scientific, London (2009)
- [6] J. M. Carpenter, C.-K. Loong, "Elements of Slow-Neutron Scattering", Cambridge University Press (2015)
- [7] B. W. Batterman, H. Cole, "Dynamical Diffraction of X-Rays by Perfect Crystals", Rev. Mod. Phys. 36, 681 - 717 (1964)
- [8] A. Dianoux, G. Lander (Eds.), "Neutron Data Booklet", Institute Laue-Langevin (2002)
- [9] D. E. Garber, R. R. Kinsey, "Neutron Cross-Section II", BNL-Report (1976), also: S. Mughabghab "Atlas of Neutron Resonances" Elsevier (2006)
- [10] E. Price (Ed.), "International Tables for Crystallography, Volume C", International Union of Crystallography (2004)
- [11] R. W. Pattie, Jr. et al., Measurement of the neutron lifetime using a magneto-gravitational trap and in situ detection. Science 360, 627-632(2018)
- [12] <https://www.oecd-neutron.org/janisweb/book/neutrons>

Exercises

E2.1 Multiple choice

1. The typical diameter of an atom is closest to
 - ☐ 1 μm
 - ☐ 1 mm
 - ☐ 1 pm
 - ☐ 1 fm
2. The typical diameter of a neutron is closest to
 - ☐ 1 μm
 - ☐ 1 mm
 - ☐ 1 pm
 - ☐ 1 fm
3. Neutrons are neutral particles, neutron counting is done electronically, i.e. an electronic pulse has to be generated in a neutron detector. What would you use as counting gas in order to build a neutron detector:
 - ☐ ^3He
 - ☐ ^4He
 - ☐ H
 - ☐ D
4. You have to build a slit in order to define a beam size for neutrons of wavelength 1 Å. Which material could you use:
 - ☐ Pb
 - ☐ Gd
 - ☐ Cd
 - ☐ Al
5. For a scattering experiment on Ni, you need a sample with strong coherent scattering, but as little background as possible. Which isotope mixture would you choose?
 - ☐ 100% ^{58}Ni
 - ☐ 100% ^{61}Ni
 - ☐ 100% ^{64}Ni
 - ☐ 57% ^{62}Ni + 43% ^{61}Ni

E2.2 Neutron scattering from Ti-Zr alloys

Ti and Zr form a continuous alloy series with hexagonal crystal structure. Your task is to build a sample chamber from a $\text{Ti}_x\text{Zr}_{1-x}$ alloy for diffraction experiments with thermal neutrons. The chamber should produce as little background due to coherent Bragg reflections as possible.

- Which stoichiometry would you choose for the alloy? (It is sufficient to specify the condition, the actual calculation is optional)
- What is the disadvantage of such a sample chamber?

Nuclide	natural abundance	scattering length b [fm]	Nuclide	natural abundance	scattering length b [fm]
^{46}Ti	8.2%	4.93	^{90}Zr	51.45%	6.4
^{47}Ti	7.5%	3.63	^{91}Zr	11.32%	8.7
^{48}Ti	73.8%	-6.08	^{92}Zr	17.19%	7.4
^{49}Ti	5.4%	1.04	^{94}Zr	17.28%	8.2
^{50}Ti	5.2%	6.18	^{96}Zr	2.76%	5.5

E2.3 Neutron absorption

Aluminium has a face-centred cubic crystal structure (cubic close packed lattice) with a lattice constant of $a_0 = 4.04959 \text{ \AA}$. The absorption cross section for neutrons of velocity 2200 m/s amounts to 0.231 barn.

- Calculate the absorption cross section of Aluminium for neutrons of wavelength $\lambda = 1 \text{ \AA}$.
- Besides absorption, which other processes contribute to the total attenuation?

The following exercise parts c and d are optional!

- Due to absorption, the neutron beam is attenuated according to $dI = -\mu \cdot I \cdot dx$ or $I = I_0 e^{-\mu \cdot x}$ where μ is the linear absorption coefficient. Calculate μ for neutrons of wavelength $1 \text{ \AA}$ for Aluminium. (Hint: Calculate the absorption cross section per unit cell and compare to the unit cell dimensions).
- Determine the attenuation of a $1 \text{ \AA}$ neutron beam in an Al slab of 10 cm thickness due to absorption only in percentage of the incident flux.

E2.4 Gravity

Due to the mass of the neutron and the low velocities at lower energies, the neutron experiences gravitational forces with $g = 9.8 \text{ m s}^{-2}$. Depending on the neutron energy, these effects may not be negligible.

- a) Calculate the velocity of neutrons with energies of 0.1 meV, 1 meV, 25 meV, 10 eV and 1 MeV.
- b) Typical instrument lengths for neutron scattering range from a few meters up to 150 m. What is the vertical deviation of the flight path for instruments of 100 m length for the specified energies in a)?
- c) What impact could the deviation from the flight path have? How could this be compensated?

3 Neutron Sources

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3.1 Introduction

The neutron is a baryon without electric charge. In contrast to the charged proton, it doesn't exist as a stable free particle, but only in bound states together with protons in atomic nuclei. The free neutron has been observed first in 1930 by W. Bothe and H. Becker. They found that if energetic α particles emitted from polonium impinge on certain light elements as e.g. beryllium, boron, or lithium, an unusually penetrating radiation was produced [1].

In 1932 J. Chadwick proved that this radiation consists of neutral particles with about the same mass as the proton. This particle had earlier been proposed as a part of atomic nuclei by E. Rutherford. Since then, it was named neutron. Chadwick has been awarded the nobel prize in physics in 1935 for the discovery of the neutron [2].

In contrast to the bound neutron, the free neutron experiences a β decay

$$n \rightarrow p^+ + e^- + \bar{\nu}_e \quad (3.1)$$

into proton, electron, and electron antineutrino with a lifetime of almost 15 minutes. This lifetime is long enough to be able to use the neutron as a probe for the investigation of other objects as e.g. a solid material.

The mass m_n of the free neutron (compare: m_p of the free proton) is

$$\begin{aligned} m_n &= 1.6749 \cdot 10^{-27} \text{ kg} = 1.008665 \text{ u} \\ (m_p &= 1.6726 \cdot 10^{-27} \text{ kg} = 1.007277 \text{ u}) \end{aligned} \quad (3.2)$$

If the energy E of the neutron is taken into account, we always mean the kinetic energy.

$$E = \frac{1}{2} m_n \mathbf{v}^2 = \frac{\mathbf{p}^2}{2m_n} \quad (3.3)$$

with the velocity vector $\mathbf{v}$ and the kinetic momentum $\mathbf{p}$. A temperature equivalent T of the kinetic energy can be defined using the Boltzmann constant k_B .

$$E = k_B T \quad (3.4)$$

The neutron's wavelength λ is obtained from the de Broglie relation

$$\lambda = \frac{h}{m_n |\mathbf{v}|} = \frac{h}{|\mathbf{p}|} = \frac{h}{\sqrt{2m_n E}} \quad (3.5)$$

and the wave vector $\mathbf{k}$ describes the propagation of the neutron wave

$$\hbar \mathbf{k} = \mathbf{p} \quad \text{with} \quad k = |\mathbf{k}| = \frac{2\pi}{\lambda} . \quad (3.6)$$

A useful unit for the wavelength λ is the Ångström: $1 \text{ Å} = 0.1 \text{ nm} = 10^{-10} \text{ m}$ and for the energy E it's the electron Volt: $1 \text{ eV} = e \cdot 1 \text{ V} = 1.6022 \cdot 10^{-19} \text{ J}$ with the electron's charge e .

Some useful conversions are

$$\lambda [\text{Å}] = \frac{3956}{v [\text{m/s}]} \quad \text{and} \quad (3.7)$$

$$E [\text{meV}] = \frac{81.8}{\lambda^2 [\text{Å}]} . \quad (3.8)$$

The following table 3.1 shows the relations between energy, velocity, wavelength, and temperature of the neutron for a few examples which are commonly used. From these numbers, it immediately becomes obvious that neutrons with a temperature around room temperature have a wavelength comparable to interatomic distances, so they are useful to investigate the atomic order of condensed matter.

Energy E	Velocity v	Wavelength λ	Temperature T
1 MeV	$1.38 \cdot 10^7 \text{ m/s}$	$2.86 \cdot 10^{-4} \text{ Å}$	$1.16 \cdot 10^{10} \text{ K}$
1 eV	13800 m/s	0.286 Å	11600 K
230 meV	6600 m/s	0.6 Å	2700 K “hot neutrons”
82 meV	4000 m/s	1 Å	950 K
26 meV	2230 m/s	1.77 Å	300 K “thermal neutrons”
10 meV	1380 m/s	2.86 Å	116 K
1.7 meV	570 m/s	6.9 Å	20 K “cold neutrons”

Table 3.1: Relation between energy, velocity, wavelength, and temperature of the neutron.

3.2 Neutron Production

Stable neutrons only exist in a bound state in atomic nuclei. A nuclear reaction is always needed to release a neutron from a nucleus. In most cases, energy is needed to release a free neutron, in all cases an activation barrier has to be overcome. Today, many reaction paths are known that yield free neutrons which are presented in the following.

3.2.1 Radioactive neutron sources: (α ,n) reaction

The production of neutrons with α radiation has historically led to the discovery of the neutron [1,2]. The reaction



is still used today for small neutron sources used for detector calibration or constant activation purposes, e.g. in smoke detectors. Today's most common alpha emitter used in neutron sources is ${}^{241}\text{Am}$ (432 years half-life), artificially produced by Pu breeding in a nuclear reactor. Also ${}^{238}\text{Pu}$ or natural ${}^{226}\text{Ra}$ can be used together with Be to produce small neutron sources.



Fig. 3.1: AmBe neutron source used for detector calibration. The source's α activity is 350 MBq, yielding a neutron production of 20000 n/s. The measured dose rate emitted by this source is about 10 $\mu\text{Sv/h}$.

The neutron yield of an AmBe neutron source is about $6 \cdot 10^4$ neutrons per GBq α activity. These neutron sources are hermetically sealed, so that the material can be handled safely and the α radiation is properly shielded. The strongly penetrating neutron and γ radiations are emitted.

Figure 3.1 shows an AmBe neutron source used in our laboratory to calibrate neutron detectors for the radiation safety interlock system. The white "pig" on the picture is a neutron detector encapsulated in a polyethylene thermal moderator making it possible to measure the intensity of thermal and fast neutron fields (see sections 3.1 and 3.3.1) for radiation safety purposes.

3.2.2 Photoneutrons: (γ ,n) reactions

The absorption of highly energetic γ photons can be used to excite a lot of nuclei to release a neutron. This works as well with light nuclei as Be as with heavy nuclei as W or Pb. A combination of ^{123}Sb (activated to ^{124}Sb as γ source) and Be (as neutron source) can be activated in a the neutron field of a nuclear reactor and emits monoenergetic neutrons with an energy of 24 keV [3]. The half-life of this source is 60 days. Because of its low neutron energy it is used to keep a residual neutron field in a nuclear reactor during shutdown.

Another application of (γ ,n) reactions is a Compact Accelerator based Neutron Source (CANS) based on an electron accelerator and a thick heavy metal target. With an electron beam of some 100 MeV energy impinging on the target, a lot of highly energetic bremsstrahlung is produced whose energy is sufficient to release neutrons from the same target material. An example of this type of neutron source is the HUNS source at Hokkaido university, Japan [4]. The drawback of this kind of accelerator driven neutron source is the fact that the γ radiation produced by the electrons has an energy such high that is difficult to shield and that also in the shielding material neutrons are released by (γ ,n) processes which again have to be shielded.

3.2.3 (p,n) and (d,n) reactions

Accelerated protons or deuterons impinging on a metal target can be used to induce neutron production in a very efficient manner. Light ions can be accelerated in an electrostatic or a RF linear accelerator to energies in the range of a few MeV to a few 10 MeV. For most target materials the first neutron production channels open well below 20 MeV activation energy with additional contributions up to 100 MeV and higher. In case of deuteron beams, also the stripping of the deuteron's neutron increases the neutron production rate. Figure 3.2 shows the energy dependence of the probability of different neutron production reaction channels for deuterons impinging on Be. For the deuteron stripping, there is no energy threshold, the neutron emission from Be starts at about 2 MeV deuteron energy [5].

Due to the flexibility of the light ion accelerators, this kind of neutron source can be operated in pulsed mode at high intensities. The low energy protons or deuterons are stopped after a short penetration length in the target material. Therefore, the volume where primary neutrons are produced is small, so that the neutrons can efficiently be coupled into a thermal moderator. Based on this principle is the design of most of the Compact Accelerator based Neutron Sources (CANS), as they are being operated in many places in Asia and the United States.

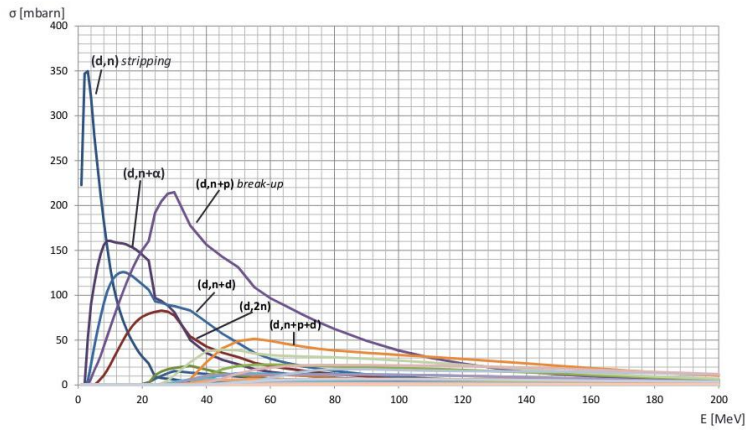


Fig. 3.2: *Calculated energy dependence of the cross sections of different neutron emitting reactions for deuterons impinging on Be based on the TENDL nuclear data library [5].*

This concept of low-energy accelerator driven neutron sources is well scalable from 100 W to 100 kW average proton beam power at the target. The smaller sources are suitable for laboratory characterization of samples along with the sample preparation or for quality control of industrial processes using dedicated instruments. The larger sources can be equipped with neutron scattering or analysis instrumentation that is competitive with the instruments installed at today's high flux research reactors.

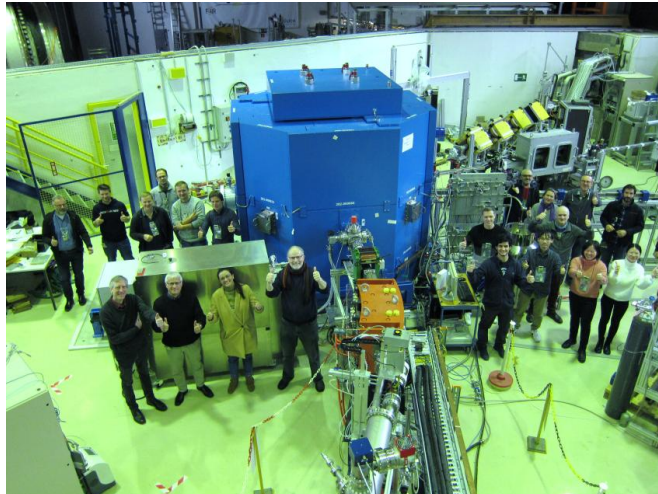


Fig. 3.3: *JULIC Neutron Platform.*

Here in Jülich and in several partner institutions in Europe, we have developed plans for High-Current Accelerator-driven Neutron Sources (HiCANS). The project of the High Brilliance neutron Source (HBS) comprises a pulsed 70 MeV proton accelerator that serves 3 target stations with different pulse schemes to provide the most suitable neutron beams for up to 36 instruments [6].

As a proof for the feasibility of the technology developed for the HBS neutron source, we built a full-scale demonstrator at the pulsed JULIC proton accelerator of the Nuclear Physics Institute (IKP). Figure 3.3 shows the JULIC Neutron Platform which had been equipped with 6 beamlines for neutron imaging, reflectometry, moderator spectroscopy, diffraction, and detector tests and was in operation from December 2022 until December 2023.

3.2.4 Nuclear fusion: d+d or d+t reactions

The neutron production by nuclear fusion of deuterium (d or ^2H) and tritium (t or ^3H) can be induced at a low ion energy (below 100 keV) that can easily be achieved with a small accelerator. The two reactions available yield monochromatic neutrons:



Technologically demanding is the fact that the target material is a gas. This is solved by using a metallic hydride as target. From time to time the target is burnt up and must be refreshed.

Figure 3.4 shows a commercial neutron generator based on the reaction (3.10). It can produce up to 10^8 n/s in continuous or pulsed operation.

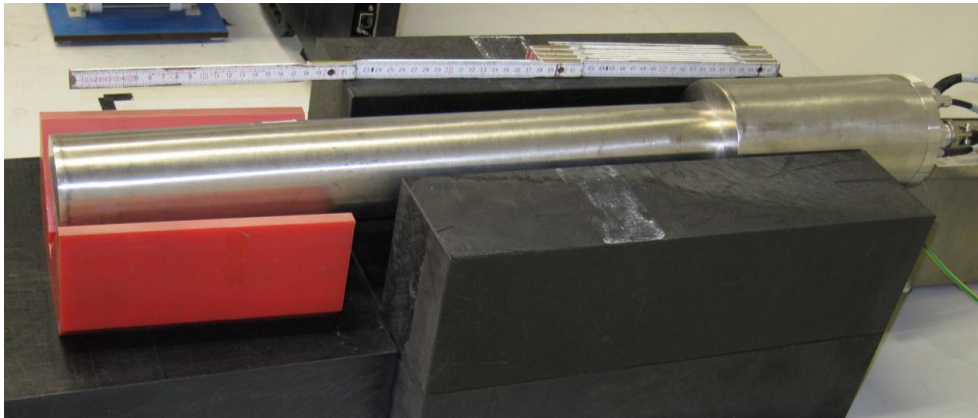


Fig. 3.4: A fusion neutron generator GENIE 16 GT commercially available from EADS Sodern. The tritium loaded metal hydride neutron production target is located 15 cm from the end of the long cylinder.

3.2.5 Nuclear fission reactors

Nuclear fission reactors are high-intensity neutron sources available since the 1940s. If ^{235}U is irradiated with thermal neutrons, the nucleus absorbs the neutron and breaks into typically two fission fragments. In this process neutrons are emitted with an average of 2.3 neutrons per fission process.

In a nuclear reactor, these fission neutrons are used to sustain a chain reaction. A sufficient amount of ^{235}U (more than the critical mass) together with a suitable thermal moderator (see section 3.3.1) that slows down the originally fast fission neutrons makes it possible that at least 1 of the 2.3 fission neutrons can again be absorbed by a ^{235}U nucleus. The remaining neutrons either escape from the core region (e.g. into a neutron beamline towards a neutron scattering experiment), or they are absorbed by the moderator or any structure material. The excess neutrons need to be absorbed by a reactor control system that can tune the chain reaction to a stable level or a slight deviation for an increase or decrease of the reaction speed, i.e. the reactor power.



Fig. 3.5: A model of the fuel element of the FRM II research reactor. The inclined plates contain the fuel, the cooling water flows in between the fuel plates. The central channel is the position of the control rod. The core of FRM-2 is the most compact ^{235}U reactor core ever built. (Copyright W. Schürmann, TU Munich)

For the reactor control it is important that a small fraction of the neutrons (0.65% in the case of ^{235}U) are not emitted immediately after the fission, but about 10 to 20 s later. If the chain reaction is leveled so that the prompt neutrons are not sufficient to sustain the chain reaction, the delayed neutrons can be used to control a slow change in reactor power. The reactor must never be operated in a state where the prompt neutrons alone sustain the chain reaction (“prompt critical reactor”) [7]. In this case, the reactor power rises exponentially in an uncontrollable manner. This happened for example at the Chernobyl accident.

In contrast to a nuclear power plant with an extended core for optimal cooling conditions, the fuel of a research reactor is arranged in a compact way to achieve high neutron fluxes that can be used for irradiation inside the moderator region or for the extraction of intensive neutron beams with relatively low thermal power. Figure 3.5 shows a model of the fuel element of the FRM II research reactor in Garching near Munich. The reactor core consists of this single fuel element loaded with highly enriched ^{235}U , a light water cooling circuit passing vertically through the fuel element and a heavy water moderator and reflector that brings back thermal neutrons to the core to sustain the chain reaction, and that feeds tangential beam tubes to extract neutrons from the reactor to use them in neutron beam lines outside the reactor vessel. The reactor power is controlled by a neutron absorber rod located in the centre of the fuel element.

Historically, and still today, nuclear reactors are the main source of high-intensity neutron beams for research applications. As most research reactors have been built in the years 1950 – 1970, they are aging and more and more of them are shut down. Their role as a supply of neutron beams for research is gradually taken over by CANS and by spallation neutron sources.

3.2.6 Spallation neutron sources

Spallation is the interaction of heavy nuclei with high-energy protons, i.e. protons with energy in the GeV range. In the collision of a nucleus with a proton at such high energy, the nucleus is completely disintegrated. At energies above 150 MeV the de Broglie wavelength of the proton is small enough that the proton interacts with the individual nucleons in the target nucleus. The nucleus is highly excited, up to 30 neutrons are evaporated from a single nucleus and several small nuclei are formed [8].

Spallation is most energy-efficient process of neutron production, but a lot of the energy is transferred onto the neutrons, so that neutrons with energies up to 500 MeV need a high effort to design a suitable shielding for the operation of such a source. Due to the large stopping length of the high energy protons, the neutron production zone is elongated to several 10 cm.

Today’s strongest pulsed neutron sources are spallation sources. The European Spallation Source ESS, which is currently being built in Lund (Sweden) will be the strongest research neutron source worldwide [9]. It is designed with a 600 m long linear proton accelerator to achieve 2000 MeV proton energy. The protons impinge on the target which is shown in figure 3.6. The wheel is 2.6 m in diameter and consists of hundreds of heavy metal Tungsten bricks encased in a disk of stainless-steel shielding. The unit weighs 11 tonnes and rotates at 23.3 rotations per minute to distribute the heat load to the entire tungsten volume, where it is removed by a He gas cooling circuit. Above and below of the target wheel are the moderators to convert the primary high-energy neutrons to a useful energy (see section 3.3.1).

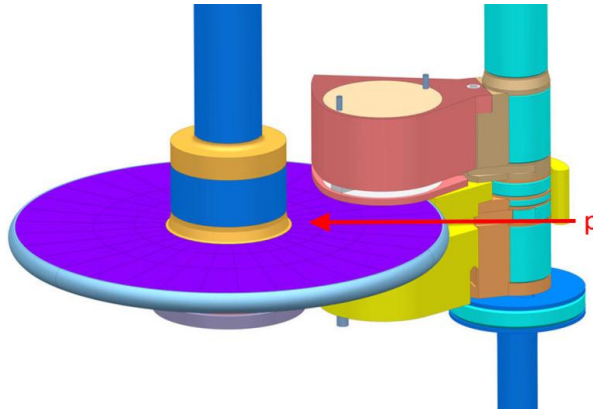


Fig. 3.6: Model of the ESS target wheel and moderator-reflector system (from [9]).

The ESS is designed as a long pulse spallation source which receives proton pulses of 2.86 ms length immediately from the linear accelerator. Other spallation sources, e.g. ISIS (UK) or SNS (USA), are constructed as short pulse spallation sources with pulse lengths down to 1 μ s. Figure 3.7 shows the schematic setup of such a source. The protons are accelerated in a linear accelerator in the form of H^- ions. The bunches coming from the linear accelerator are subsequently injected into a compressor ring for protons. At the point of injection (which is located inside a strong magnetic field) the electrons are stripped off by a carbon sieve, so that the injection of the H^- ions is performed with the opposite direction of curvature compared to the naked protons circulating in the ring.

The time of one revolution inside the ring is equal to the time distance between the bunches from the linear accelerator, so that the newly injected protons meet the already circulating protons in phase. With this technique, the length of the pulse can be reduced by ~ 1000 while the peak current is increased by the same factor.

For some instruments, the shorter neutron pulses have advantages for the energy and wavelength resolution of the measurements.

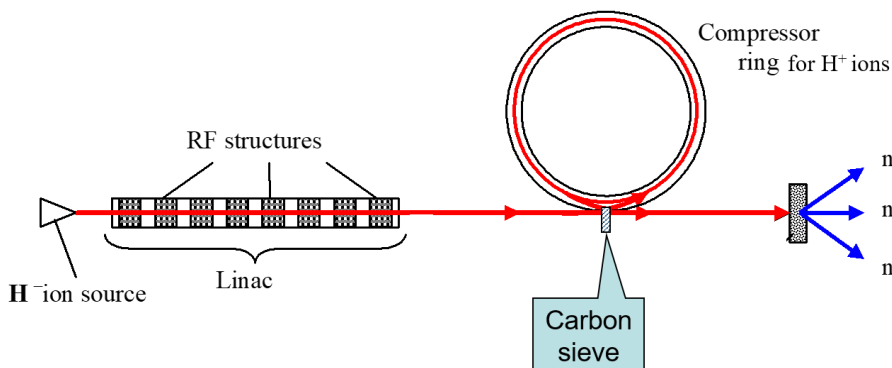


Fig. 3.7: Schematic of a short pulse spallation source with a compressor ring.

3.2.7 Efficiency of the neutron production

Table 3.2 shows the neutron yield and the heat deposition per neutron for different neutron production reaction. From this point of view, fusion is the most attractive opportunity, but the technology is not yet ready to use this for a high-flux neutron source.

Spallation is more attractive than fission, but the investments necessary for building a high energy proton accelerator are high, so that not many sources of that kind have been built yet. The (p,n) reactions seem to be not attractive, but the well confined neutron cloud emitted from the compact target compensates quite well for the reduced neutron emission probability.

Reaction	Energy/event	Yield (neutron/event)	Deposited heat (MeV/neutron)
(d,t) fusion		~1 neutron/fusion	3
²³⁵ U fission		~1 neutron/fission available outside the chain reaction	180
Pb spallation	1 GeV	~ 20 neutron/proton	23
Be (p,n)	25 MeV	0.006 neutron/proton	1200

Table 3.2: *Efficiency of different neutron production reactions.*

3.3 Manipulation of travelling neutrons

3.3.1 Moderation

Primary free neutrons that are produced in a nuclear reaction typically have an energy of a few MeV, in case of spallation it might be a lot higher. To make these neutrons useful to investigate atomic matter, this energy has to be reduced below 1 eV according to table 3.1. The useful neutron energies correspond to about room temperature, for crystallography maybe higher, for investigations of complex matter (e.g. macromolecules or layered structures) even lower. This neutron energy can be reached by bringing the neutron field into thermal equilibrium with something that has the proper temperature and that interacts strongly with the neutrons.

One important candidate to do so is hydrogen in any compound that has a high density. The hydrogen atom has approximately the same weight as the neutron, so collisions between a neutron and a hydrogen nucleus (i.e. a proton) can optimally transfer momentum from the neutron to the proton. In addition, the inelastic scattering cross section that describes the probability of an energy transfer between hydrogen nuclei and neutrons is high.

So, for neutron moderation to thermal temperatures water H₂O or heavy water D₂O are ideal. H₂O has the advantage that it is easily available and does not produce any radioactive waste, but the disadvantage of a non-negligible neutron absorption. Thermalization of a MeV neutron in H₂O needs about 7 collisions and 10 μ s of time.

D₂O has the advantage that it hardly absorbs neutrons, but if it does, radioactive tritium is produced. In addition, the interaction between neutrons and D₂O is weaker compared to H₂O, so that the moderator volume needs to be bigger and the neutron field is diluted. If the thermal load is low, also solid polyethylene is a good thermal neutron moderator, but it cannot be cooled as efficiently as liquid water. Another useful thermal moderator is Be which is solid but with a high thermal conductivity and has almost no neutron absorption. A thermal moderator efficiently delivers neutrons in the wavelength range between 0.7 and 2.5 Å.

If neutrons with longer wavelengths are desired, a "cold neutron source" is used to moderate thermal neutrons to even lower temperatures. Liquid H₂, liquid D₂, solid methane CH₄ or solid mesitylene C₉H₁₂ are the most frequently used substances in a cold neutron source. A cold neutron source efficiently delivers neutrons in the wavelength range between 2 and 8 Å. Depending on the realization, sometimes neutrons with wavelengths up to 20 Å can be used for special applications.

In some research reactors specialized beamlines for crystallography and high-energy spectroscopy are fed by a hot neutron source. A hot neutron source is a graphite moderator heated (by the γ radiation close to the fuel element) to temperatures between 2500 and 3000 K. This moderator efficiently delivers neutrons with wavelengths down to 0.2 Å corresponding to an energy up to 2 eV.

Figure 3.8 shows the neutron spectra available at the FRM II reactor. This reactor has a large D₂O tank as thermal moderator where a cold source with liquid D₂ and a hot source with a graphite moderator are inserted.

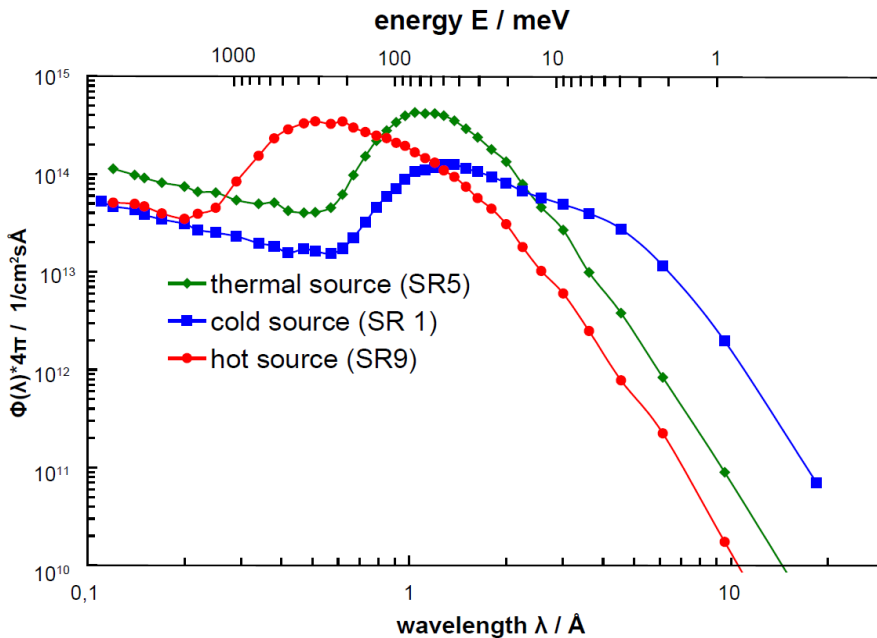


Fig. 3.8: Neutron spectra available at the beam tubes of FRM II.

3.3.2 Monochromatization

In a neutron scattering experiment it is in most cases necessary to know the neutron's wavelength or energy when it interacts with the sample. There are three methods of monochromatization commonly used:

Time-Of-Flight (TOF)

The TOF method uses the energy dependent velocity of the neutrons (eq. (3.5) and (3.7)). The neutron beam is structured in time by a rotating chopper that is transparent only for a short fraction or it is emitted from a pulsed source. When the neutron beam travels the distance between source / chopper to the detection system, the neutrons with shorter wavelength arrive earlier at the detector. With the control of the timing between source / chopper and the detector system, the wavelength of every neutron can be reconstructed from the arrival time. Figure 3.9 shows a schematic diagram of the definition of an instrument's band width and resolution in time-of-flight by several choppers. This instrument is located at a continuous source (i.e. at a research reactor).

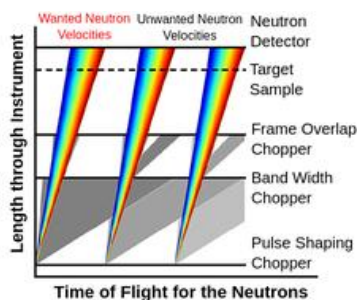


Fig. 3.9: Time-of-flight diagram for an instrument with three choppers.

It can be seen that the neutrons are only used during the opening time of the first chopper, all the remaining time the neutrons are discarded. In the case of an accelerator driven source this can be optimized so that neutrons are only produced when they can be accepted by the instruments. A duty cycle of some 2% of the source are sufficient to provide useful measurement data at the detector for some 95% of the time by just using one wavelength after the other.

Velocity selector

A velocity selector is a rotating turbine wheel with neutron absorbing channel walls, as can be seen in figure 3.10. The neutron beam impinges in a direction parallel to the turbine axis. If the speed of the neutrons matches the rotational motion of the channel, the neutrons of this speed can pass the velocity selector. This technique is used for instruments that need a monochromatic beam with moderate wavelength resolution (10-20%).



Fig. 3.10: Turbine wheel of the velocity selector used at KWS-3. The selector blades consist of a MgLi alloy with neutron absorbing ^6Li .

Monochromator crystals

Bragg reflections on a single crystal happen only, if wavelength and angle of incidence on a suitable lattice plane match. Therefore, a neutron beam with well-defined direction can be monochromatized by Bragg reflection from a monochromator crystal. Depending on the quality of the crystal, a wavelength resolution between 0.05% and 1.5% can be achieved. Sometimes "too good" crystals are treated mechanically to disturb the perfection of the lattice to be able to reflect a wider wavelength band.

Fig. 3.11 shows a double focusing Cu monochromator. It is equipped with 105 single crystals that have been hammered to increase the reflectivity. This monochromator can be focused vertically to be able to illuminate small samples more strongly and it can be focused horizontally to be able to transport a larger wavelength band (due to different Bragg angles of the individual columns of the monochromator) to the sample on the expense of a higher beam divergence.

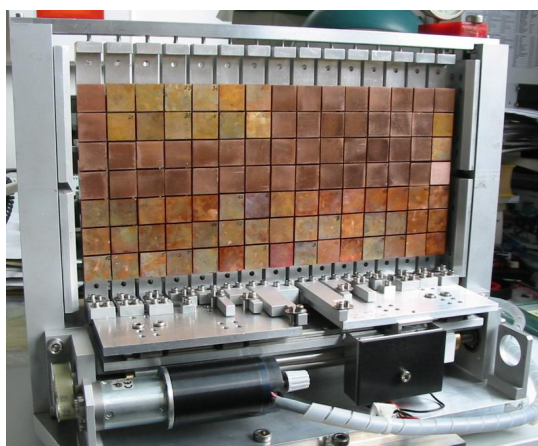


Fig. 3.11: Double focussing monochromator equipped with 105 Cu single crystals.

3.4 Neutron Transport

Originally, thermal or cold neutrons are emitted isotropically from the moderator. Instruments directly located at a beamtube of a nuclear reactor can use the entire solid angle that is illuminated through the opening of the reactor shielding. But, as space around the shielding is very limited, a way to bring neutrons efficiently to instruments at a larger distance is necessary.

Neutron guides based on the principle of total reflection (see lecture 9) are used to transport neutron beams with a limited divergence but with low losses over distances of up to 200 m. The walls of neutron guides are polished glass plates with a metal coating. A simple Ni coating offers total reflection up to the critical angle

$$\theta_c = \frac{0.1^\circ}{\text{\AA}} \cdot \lambda \quad (3.12)$$

for neutrons with the wavelength λ . These neutrons are transported without losses. Today's supermirror technology has achieved to increase the reflection angles up to $m=6$ times θ_c with reflectivities between 95% (for $m=2$) down to 60% (for the highest angles with $m=6$). From eq. (3.12) it is obvious that neutron guides are more efficient for cold neutrons with long wavelengths than for thermal neutrons. Therefore, most cold neutron instruments are located at increased distance from the reactor surface while only thermal instruments are located directly at the beamtubes.

Fig. 3.12 shows the neutron guides serving all cold neutron instruments of the neutron guide hall at the former research reactor in Jülich. Straight and slightly curved guides allow to supply neutrons to instruments that have sufficient space to be operated independently.

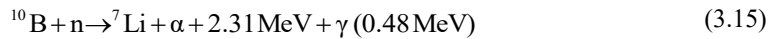


Fig. 3.12: Neutron guides serving the cold neutron instruments at the former FRJ-2 research reactor in Jülich.

3.5 Neutron detectors

Neutrons cannot be detected electronically because they carry no charge. Again, a nuclear reaction is necessary to produce charges that can be treated with electronic devices. The capture of the neutron in a suitable converter material releases charged secondary particles with high energy which are able to ionize detector material [10].

The most important nuclear capture reactions for neutron detection are



Gas detectors use the ionization of gas by particle radiation within an electrical field. The ions and electrons are moving to the electrodes and induce a charge signal that can be detected by electronics. Typical detector gases for the detection of thermal or slow neutrons are ${}^3\text{He}$ and ${}^{10}\text{BF}_3$.

In Scintillation detectors, the neutron converter is embedded in a transparent solid matrix and the energy of the secondary particles is converted into excited states of the matrix that decay with the emission of photons. These photons in a second step can be converted into electronic signals in a photomultiplier. A typical neutron scintillator material is glass with embedded ${}^6\text{LiF}$.

Both detector techniques can be used to build a position sensitive detector, where the charges are detected in a spatially resolved way. 1D or 2D spatial resolution can be achieved down to 50 μm .

References

- [1] <https://en.wikipedia.org/wiki/Neutron>
- [2] <https://www.nobelprize.org/prizes/physics/1935/chadwick/facts/>
- [3] <https://www.nrc.gov/docs/ML1122/ML11229A704.pdf>
- [4] <https://www.jcans.net>
- [5] U. Rücker et al., The Jülich high-brilliance neutron source project, *Eur. Phys. J. Plus* **131**, 19 (2016)
- [6] T. Brückel, T. Gutberlet (Eds.), Conceptual Design Report Jülich High Brilliance Neutron Source (HBS), ISBN 978-3-95806-501-7 (2020)
Free download at: go.fzj.de/hbs-tdr
- [7] M. Borlein, Kerntechnik, Vogel Buchverlag, Erlangen (2009), chapter 5
- [8] D. Filges, F. Goldenbaum, Handbook of Spallation Research, Wiley-VCH, Weinheim (2009), chapter 1.3
- [9] <https://europeanspallationsource.se/>
- [10] G. Kemmerling, lecture C5 in: 43rd IFF Spring School: Scattering Methods for Condensed Matter research, Forschungszentrum Jülich, Series Key Technologies, Vol. **33** (2012)

Exercises

E3.1 Basic relations *

Calculate the velocity (in m / s), the kinetic energy (in meV), and the temperature (in K) for

- hot neutrons ($\lambda = 0.5 \text{ \AA}$),
- thermal neutrons ($\lambda = 1.8 \text{ \AA}$),
- cold neutrons ($\lambda = 6 \text{ \AA}$).

$$m_n = 1.675 \cdot 10^{-27} \text{ kg}$$

$$h = 6.626 \cdot 10^{-34} \text{ Js}$$

$$e = 1.602 \cdot 10^{-19} \text{ As}$$

$$k_B = 1.38 \cdot 10^{-23} \text{ J / K}$$

E3.2 Neutron production in a fission reactor **

Calculate the neutron production of a 20 MW fission reactor (in 1 / s). What would be the neutron production of a hypothetical spallation source with the same thermal power?

Assuming that the reactor core is a point source and the neutrons just diffuse out of the core without absorption in the moderator: Calculate the neutron flux in 2 m, 10 m and 50 m distance from the core (in 1 / cm² s).

4 Crystallography

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4.1 Introduction

The term “crystal” derives from the Greek κρύσταλλος, which was first used as a description of ice and later - more generally - of transparent minerals with regular morphology (regular crystal faces and edges), see Fig. 4.1 as an example.



Fig. 4.1: Example: Quartz (SiO_2), mineral specimen from the Gotthard-Massif.

Matter is usually classified into three states: gaseous – liquid – solid. Crystals are representatives of the solid state. **Crystalline solids are thermodynamically stable** in contrast to glasses and are characterised by a **regular three-dimensional periodic arrangement of atoms** (ions, molecules) in space. More than 90 % of matter are (partially) crystalline. In this chapter we discuss basic concepts which are used to describe the structure of crystals. The field of “Crystallography”, though, is not only limited to the concept of crystal symmetry, but further encompasses the techniques which allow us to characterize the structure and dynamics of matter, with X-ray and neutron scattering being the key techniques. The importance of this field is mirrored in a range of Nobel Prizes in relation to crystallography and structure characterization, see Fig. 4.2.

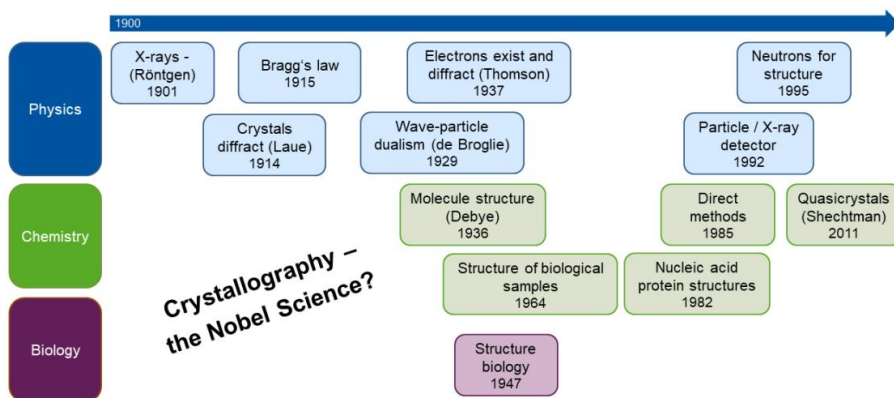


Fig. 4.2: Nobel Prizes in relation to Crystallography

4.2 Crystal lattices

The three-dimensional periodicity of crystals can be represented by the so-called crystal lattice. The repeat unit in form of a parallelepiped - known as the **unit cell** - is defined by three non-collinear basis vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$, whose directions form the reference axes X , Y , and Z of the corresponding right-handed crystallographic coordination system. The six lattice parameters are given as the lengths of the basis vectors $a = |\mathbf{a}|$, $b = |\mathbf{b}|$, $c = |\mathbf{c}|$ and the angles between the basis vectors: $\text{angle}(\mathbf{a}, \mathbf{b}) = \gamma$, $\text{angle}(\mathbf{b}, \mathbf{c}) = \alpha$, $\text{angle}(\mathbf{c}, \mathbf{a}) = \beta$. The faces of the unit cell are named as $\text{face}(\mathbf{a}, \mathbf{b}) = C$, $\text{face}(\mathbf{b}, \mathbf{c}) = A$, $\text{face}(\mathbf{c}, \mathbf{a}) = B$.

If the vertices of all repeat units (unit cells) are replaced by points, the result is the crystal lattice in the form of a **point lattice**. Each lattice point is given by a vector $\boldsymbol{\tau} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$, with u , v , w being integers. $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ act as the symmetry operation of parallel displacement also known as a **translation** and maps the atomic arrangement of the crystal (crystal structure) onto itself.

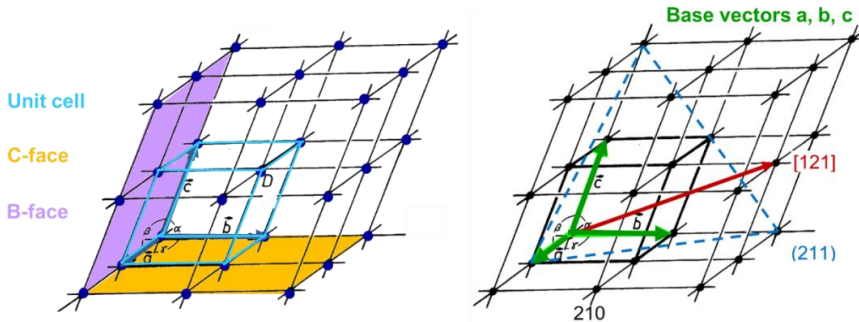


Fig. 4.3: Point lattice with unit cell, basis vectors, B- and C-face, and notation for: lattice point 210, lattice direction [121] and lattice plane (211)

A **lattice point** is named “ uvw ”, according to the coefficients (integers) of the translation vector $\boldsymbol{\tau} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$ from the origin to the lattice point. A **lattice direction** - given by the symbol $[uvw]$ - is defined by the direction of the corresponding translation vector. Nota: Watch out for the different brackets employed in crystallographic nomenclature.

A plane passing through three lattice points is known as a **lattice plane**. Since all lattice points are equivalent (by translation symmetry) there will be infinitely many parallel planes passing through all the other points of the lattice. Such a set of equally spaced planes is known as a **set of lattice planes**. If the first plane from the origin of a set of lattice planes makes intercepts a/h , b/k , c/l on the X , Y , Z axes, respectively, where h , k , l are integers, then the **Miller indices** of this set of lattice planes are (hkl) , the three factors h , k , l being enclosed in parentheses.

The equation of lattice planes can be written in intercept form as

$$\left(\frac{hx}{a}\right) + \left(\frac{ky}{b}\right) + \left(\frac{lz}{c}\right) = n, \quad (4.1)$$

where n is an integer. If $n = 0$ the lattice plane passes through the origin; if $n = 1$, the plane makes intercepts at a/h , b/k , c/l on the X , Y , Z axis respectively; if $n = 2$, the intercepts are $2a/h$, $2b/k$, $2c/l$; and so on.

The line of intersection of any two non-parallel lattice planes is a row of lattice points common to both planes. This lattice point row defines a lattice direction $[uvw]$ which is known as **zone**

axis. All lattice planes intersecting in a common lattice-point row are said to lie in the same **zone**. The condition for lattice planes to be parallel to a lattice vector $\tau = ua + vb + wc$ is the **zone equation**

$$uh + vk + wl = 0 \quad (4.2)$$

The zone axis symbol $[uvw]$ for the zone containing the two planes $(h_1k_1l_1)$ and $(h_2k_2l_2)$ is obtained by solving the simultaneous equations $uh_1 + vk_1 + wl_1 = 0$ and $uh_2 + vk_2 + wl_2 = 0$,

$$[uvw] = [k_1l_2 - k_2l_1, l_1h_2 - l_2h_1, h_1k_2 - h_2k_1] \quad (4.3)$$

4.3 Crystallographic coordinate systems

The first step in the description of a crystal structure is to choose the basis vectors of a unit cell as the smallest repeat unit of the crystal. While in physics and chemistry, Cartesian coordinate systems are commonly used, crystallography uses symmetry adapted coordinate systems. In this way a **crystal-specific coordinate system** is defined which is then used to localize all the atoms in the unit cell. Crystal symmetry requires, in three dimensions, **7 different crystal systems** and hence 7 crystallographic coordinate systems to be defined:

name of system	minimum symmetry	conventional unit cell
triclinic	1 or $\bar{1}$	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$
monoclinic	<u>one</u> diad, i.e. 2 or m (1Y)	$a \neq b \neq c$; $\alpha = \gamma = 90^\circ, \beta > 90^\circ$
orthorhombic	<u>three</u> mutually perpendicular diads, i.e. 2 or m (1X, Y and Z)	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90^\circ$
tetragonal	<u>one</u> tetrad, i.e. 4 or $\bar{4}$ (1Z)	$a = b \neq c$; $\alpha = \beta = \gamma = 90^\circ$
trigonal (hexagonal cell)	<u>one</u> triad, i.e. 3 or $\bar{3}$ (1Z)	$a = b \neq c$; $\alpha = \beta = 90^\circ, \gamma = 120^\circ$
hexagonal	<u>one</u> hexad, i.e. 6 or $\bar{6}$ (1Z)	$a = b \neq c$; $\alpha = \beta = 90^\circ, \gamma = 120^\circ$
cubic	<u>four</u> triads, i.e. 3 or $\bar{3}$ (1 space diagonals of cube)	$a = b = c$; $\alpha = \beta = \gamma = 90^\circ$

The choice of the origin of the coordinate system is arbitrary, but for convenience it is usually chosen at a centre of symmetry (inversion centre), if present, otherwise at a point of high symmetry.

In order to complete the symmetry conventions of the coordinate systems, it is necessary to add to the **seven** so-called **primitive unit cells** of the crystal systems (primitive lattice types with only one lattice point per unit cell) **seven centred unit cells** with two, three or four lattice points per unit cell (centred lattice types). These centred unit cells are consequently two, three or four

times larger than the smallest repeat units of the crystal. The resulting **14 Bravais lattice types** with their centring are compiled in figure 4.4.

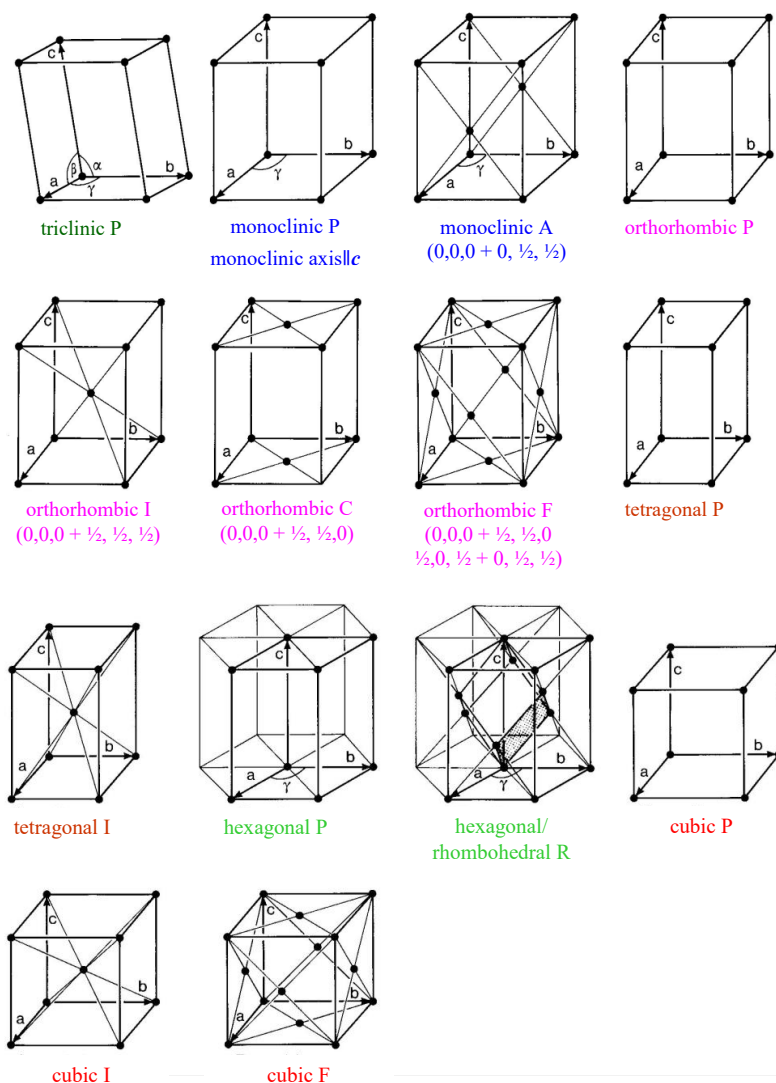


Fig. 4.4: The 14 Bravais lattices consisting of the 7 primitive lattices P for the 7 crystal systems with only one lattice point per unit cell and the 7 centred (non-primitive) lattices A, B, C, I, R and F with 2, 3 and 4 lattice points per unit cell.

A set of lattice planes (hkl) is separated by a characteristic interplanar spacing $d(hkl)$. According to the different crystallographic coordinate systems these $d(hkl)$ values are calculated in a specific manner:

For the cubic lattice ($a = b = c$, $\alpha = \beta = \gamma = 90^\circ$)

$$d(hkl) = a \cdot (h^2 + k^2 + l^2)^{-\frac{1}{2}} \quad (4.4)$$

For the hexagonal lattice ($a = b$, c , $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$)

$$d(hkl) = \left(\frac{4}{3} \frac{h^2 + k^2 + hk}{a^2} + \frac{l^2}{c^2} \right)^{-\frac{1}{2}} \quad (4.5)$$

For the tetragonal lattice ($a = b$, c , $\alpha = \beta = \gamma = 90^\circ$)

$$d(hkl) = \left(\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right)^{-\frac{1}{2}} \quad (4.6)$$

For the orthorhombic lattice (a , b , c , $\alpha = \beta = \gamma = 90^\circ$)

$$d(hkl) = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-\frac{1}{2}} \quad (4.7)$$

For the monoclinic lattice (a , b , c , $\alpha = \gamma = 90^\circ$, $\beta > 90^\circ$)

$$d(hkl) = \left(\frac{h^2}{a^2 \sin^2 \beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 \sin^2 \beta} - \frac{2hl \cos \beta}{ac \sin^2 \beta} \right)^{-\frac{1}{2}} \quad (4.8)$$

For the triclinic lattice (a , b , c , α , β , γ), the most general case,

$$d(hkl) = \left(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cdot \cos \beta \cdot \cos \gamma \right)^{\frac{1}{2}} \left(\frac{h^2}{a^2} \sin^2 \alpha + \frac{k^2}{b^2} \sin^2 \beta + \frac{l^2}{c^2} \sin^2 \gamma + \frac{2kl}{bc} (c \cdot \cos^2 \beta - \cos \alpha) + \frac{2lh}{ca} (c \cdot \cos^2 \gamma - \cos \beta) + \frac{2hk}{ab} (c \cdot \cos^2 \alpha - \cos \gamma) \right)^{-\frac{1}{2}} \quad (4.9)$$

4.4 Crystallographic symmetry operations and symmetry elements

The **symmetry operations** of a crystal are isometric transformations or motions, i.e. mappings in space which preserve distances and, hence, also angles and volumes. An object and its transformed object superpose in a perfect manner, they are indistinguishable.

The simplest crystallographic symmetry operation is the **translation**, which is a parallel displacement of the crystal by a translation vector τ (see section 4.2). There is no fixed point, the entire lattice is shifted and, hence, the crystal lattice is considered to be infinite.

Crystallographic **rotations** n around an axis by an angle $\varphi = 360^\circ/n$ (n -fold rotations) and **rotoinversions** (combination of rotations and inversions) $\bar{n}$ are called point symmetry operations because they leave at least one point in space invariant (at least one fixed point), see Fig. 4.5. An important fact of crystallographic symmetry is the restriction of the rotation angles to $\varphi = 60, 90, 120, 180$ and 360° , resulting in the rotation axes 1, 2, 3, 4 and 6. This derives from the assumption of three-dimensional translational symmetry. Only for such crystallographic rotations the space can be covered completely without gaps and overlaps. The rotoinversion $\bar{n} = \bar{1}$ is an **inversion** at a point, $\bar{n} = \bar{2} \equiv m$ (mirror plane) describes a **reflection** through a plane.

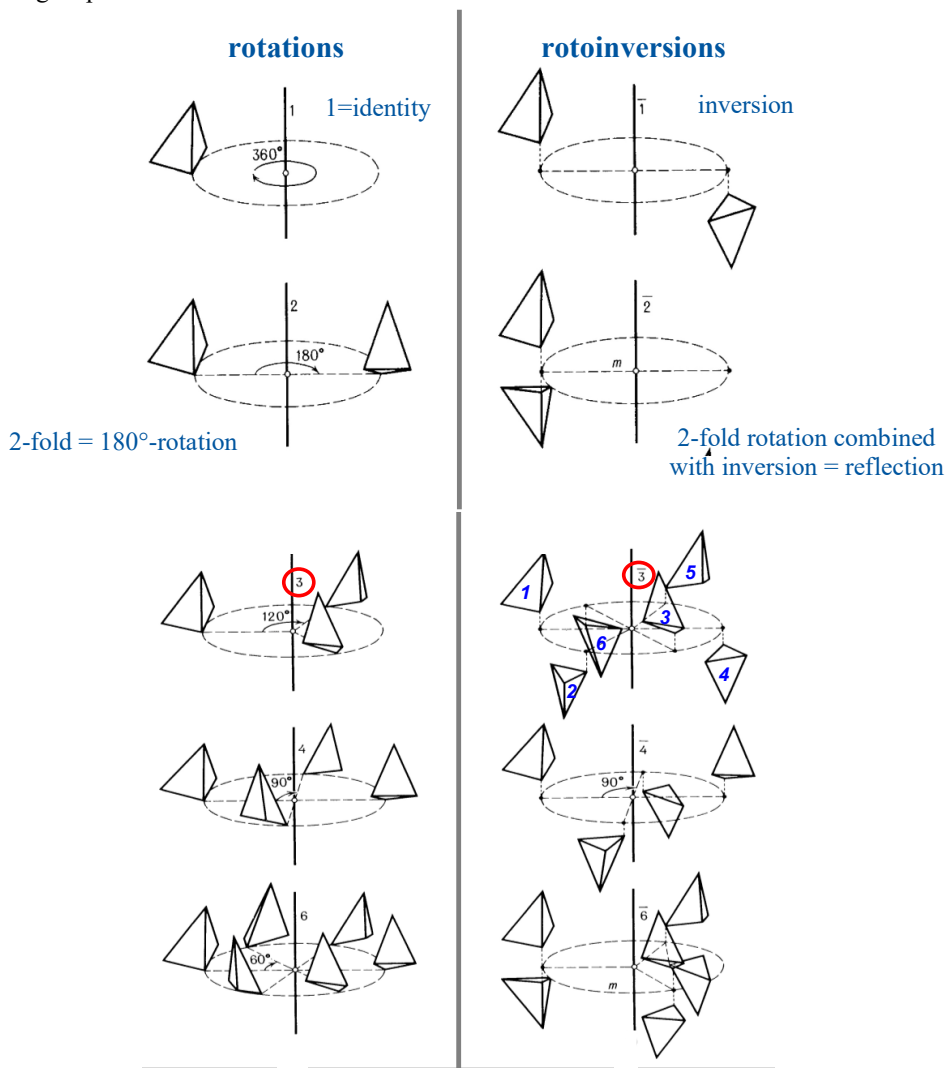


Fig. 4.5: Rotations: $n=1$ (identity), $n=2$ (angle 180°), $n=3$ (120°), $n=4$ (90°), $n=6$ (60°). Rotoinversions: $\bar{1}$ (inversion), $\bar{2} \equiv m$ (reflection), $\bar{3} = 3 + \bar{1}$, $\bar{4}$, $\bar{6} = 3/m$.

The combination of n -fold rotations with $(m/n)\cdot a$ translation components ($m < n$) parallel ($\parallel$) to the rotation axis leads to the so-called **screw rotations** n_m , e.g. $2_1, 3_2, 4_2, 6_5$. These symmetry operations have no fixed points, see Fig. 4.6.

The combination of a reflection through a plane (glide plane) with translation components (glide vectors) of $a/2, b/2, c/2, (a+b)/2, \dots \parallel$ to this plane are known as **glide reflections** $a, b, c, n, \dots, d$, see Fig. 4.7. Again, no fixed points exist for these symmetry operations.

The objects which actually relate to the symmetry operations are the **symmetry elements**. They form the geometrical locus, oriented in space, of the symmetry operation (a line for a rotation, a plane for a reflection, and a point for an inversion) together with a description of this operation. Symmetry elements are mirror planes, glide planes, rotation axes, screw axes, rotoinversion axes and inversion centres. The geometrical descriptions of selected crystallographic symmetry operations are illustrated in Figs. 4.4 - 4.6.

A **symmetry operation** transforms a point X with coordinates x, y, z (corresponding to a position vector $X = xa_1 + ya_2 + za_3$) into a symmetrically equivalent point X' with coordinates x', y', z' mathematically by the system of linear equations

$$\begin{aligned} x' &= W_{11}x + W_{12}y + W_{13}z + w_1 \\ y' &= W_{21}x + W_{22}y + W_{23}z + w_2 \\ z' &= W_{31}x + W_{32}y + W_{33}z + w_3 \end{aligned} \quad (4.10)$$

Symmetry operation in matrix notation:

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} W_{11} & W_{12} & W_{13} \\ W_{21} & W_{22} & W_{23} \\ W_{31} & W_{32} & W_{33} \end{pmatrix} \circ \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} w_1 \\ w_2 \\ w_3 \end{pmatrix}; \quad X' = W \circ X + w = (W, w) \circ X \quad (4.11)$$

The (3×3) matrix W is the rotation part and the (3×1) column matrix w the translation part of the symmetry operation. The two parts W and w can be assembled into an augmented (4×4) matrix W according to

$$\begin{pmatrix} x' \\ y' \\ z' \\ 1 \end{pmatrix} = \begin{pmatrix} W_{11} & W_{12} & W_{13} & w_1 \\ W_{21} & W_{22} & W_{23} & w_2 \\ W_{31} & W_{32} & W_{33} & w_3 \\ 0 & 0 & 0 & 1 \end{pmatrix} \circ \begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix} = W \circ X \quad (4.12)$$

Since every symmetry transformation is a “rigid-body” motion, the determinant of all matrices W and W is $\det W = \det W = \pm 1$ (+ 1: preservation of handedness; - 1: change of handedness of the object).

The sequence of two symmetry operations (successive application) is given by the product of their matrices W_1 and W_2 according to eq. 4.13, where W_3 is again a symmetry operation.

$$W_3 = W_1 \circ W_2 \quad (4.13)$$

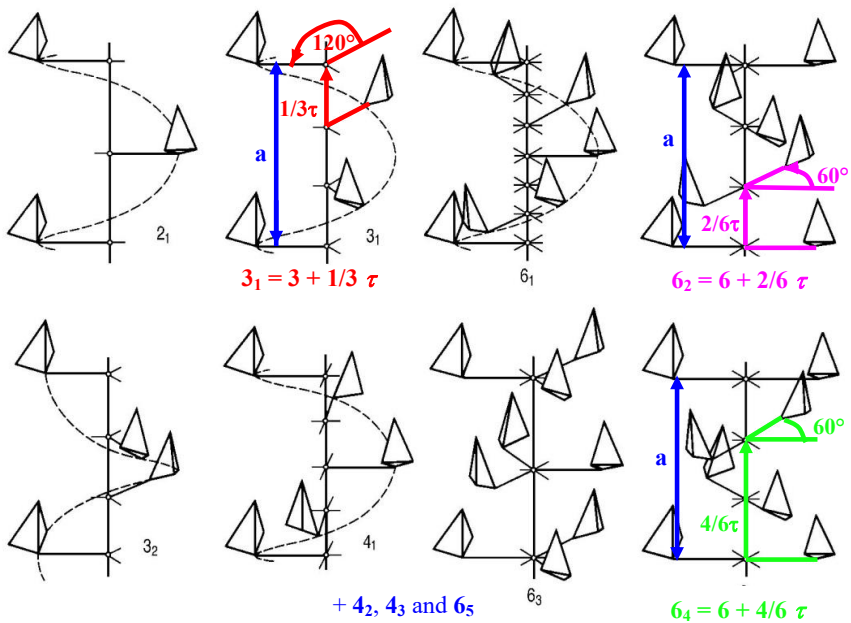


Fig. 4.6: Screw rotations n_m : combination of rotations n and translation components $(m/n) \cdot a \parallel$ to the rotation axis.

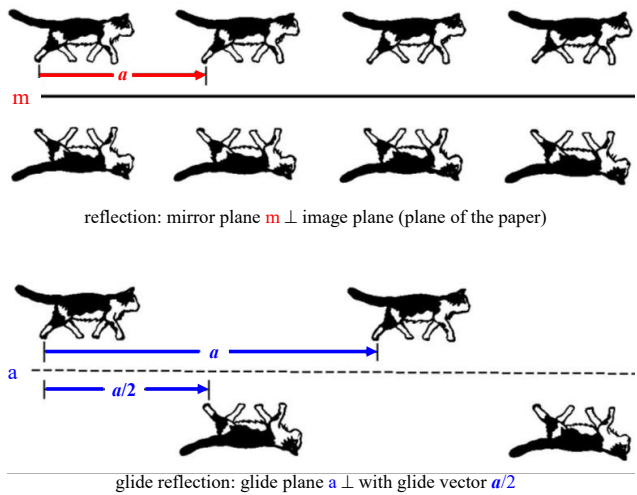


Fig. 4.7: Examples of reflections and glide reflections.

4.5 Crystallographic point groups and space groups

The symmetry of a macroscopic crystal and of its crystal structure relates to the different possibilities to fill 3D space and available point symmetry operations. All possible combinations of the crystallographic point symmetry operations in three-dimensional space lead to exactly **32 crystallographic point groups** (also called **crystal classes**).

Nota: The symmetry of the crystal structure can be described by mathematical group theory.

The symmetry operations are the group elements of a crystallographic group G , and the combination of group elements is the successive execution of symmetry operations. The 32 point groups are each of finite order, with the order being the number of elements of the group (maximum order: 48 for the cubic crystal class).

If we now combine the 32 point groups with the 14 Bravais lattice types as well as the translation-containing symmetry operations of the screw axes and glide reflections and translational symmetry, we result in **230 space groups**. Fig. 4.8 represents this schematically.

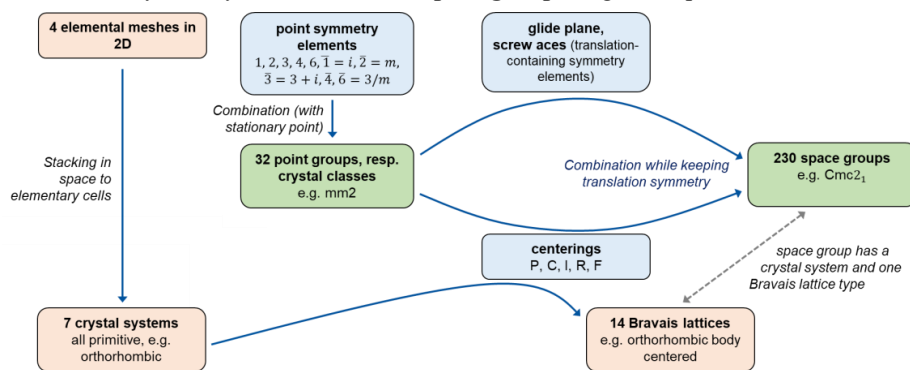


Fig. 4.8: Going from elemental meshes to space groups by combining the concept of unit cells (with and without centering), point symmetry, translation-containing symmetry elements.

In Fig. 4.8, an exemplary space group is given as “ $Cmc2_1$ ”. This is the **Hermann-Mauguin symbol**, which is internationally employed in the field of crystallography to display in a compact form the symmetry information of the crystal. Three independent main **symmetry directions** (“Blickrichtungen”) describe the entire symmetry of a crystal. These Blickrichtungen are specifically defined for the seven crystal systems, and they define the sequence, in which the symmetries are listed in the Hermann-Mauguin symbols. As an example, the Blickrichtungen of the cubic system are shown in Fig. 4.9.

Besides the Hermann-Mauguin symbol, the Schoenflies symbol is used alternatively to describe symmetry. Yet, the Schoenflies symbol only describes point group symmetry without containing information on translational symmetry. It is frequently used in chemistry to describe the symmetry of molecules, for instance in the fields of infrared and nuclear magnetic resonance spectroscopy.

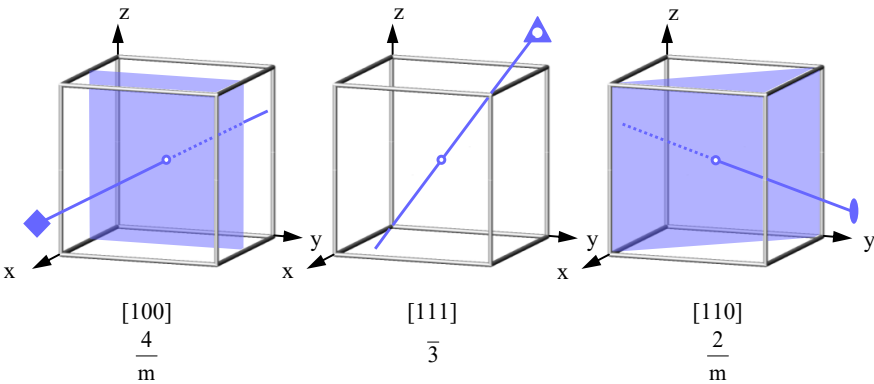


Fig. 4.9: Symmetry directions (“Blickrichtungen”) of the cubic lattice ($a = b = c$, $\alpha = \beta = \gamma = 90^\circ$): $[100]$ with symmetry $4/m$, $[111]$ with $\bar{3}$, and $[110]$ with $2/m$.

The **point group symmetries** determine the anisotropic (macroscopic) **physical properties** of crystals, i.e. mechanical, electrical, optical and thermal properties. The crystal class can be deduced from a **diffraction experiment**. However, diffraction introduces an (additional) centre of symmetry, so that only the **11 centrosymmetric Laue classes** can be distinguished:

Crystal system	Laue class
triclinic	$\bar{1}$
Monoclinic	$1\ 2/m\ 1 = 2/m$
Orthorhombic	$2/m\ 2/m\ 2/m = m\ m\ m$
Tetragonal	$4/m$ $4/m\ 2/m\ 2/m = 4/m\ m\ m$
Trigonal	$\bar{3}$ $\bar{3}\ 2/m = \bar{3}\ m$
Hexagonal	$6/m$ $6/m\ 2/m\ 2/m = 6/m\ m\ m$
Cubic	$2/m\ \bar{3} = m\ \bar{3}$ $4/m\ \bar{3}\ 2/m = m\ \bar{3}\ m$

In three dimensions all possible combinations of the point symmetries of the **32 crystallographic point groups** with the lattice translations of the **14 Bravais lattices** lead to exactly **230 space groups**, all of infinite order. As already mentioned, the combination of point symmetry operations with translations results in new symmetry operations: screw rotations and glide reflections. The conventional graphical symbols for the three-dimensional space group symmetry elements according to the International Tables for Crystallography Vol. A (ITA, 2002 [1]) are shown in figure 4.10.

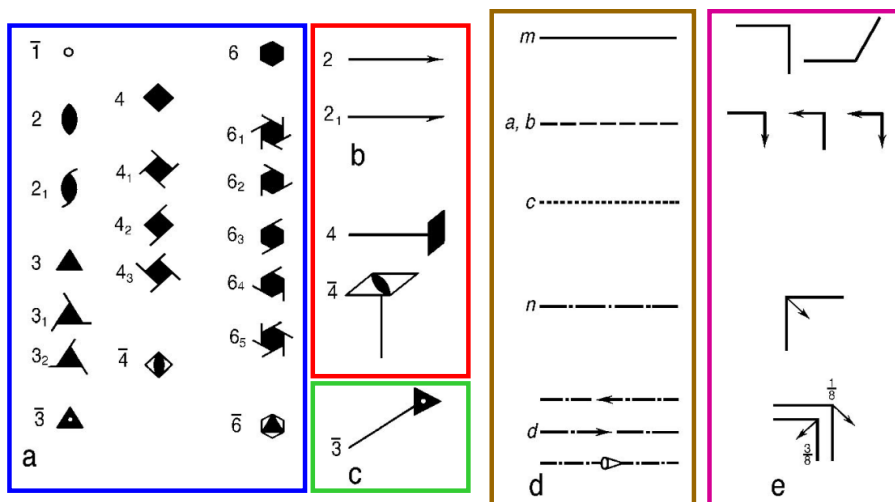


Fig. 4.10: Conventional graphical symbols for symmetry elements: Left: axes (a) perpendicular, (b) parallel, and (c) inclined to the image plane; Right: planes: (d) perpendicular and (e) parallel to the image plane.

In the *International Tables for Crystallography Vol. A* [1] all space groups are described in detail with their Hermann-Mauguin symbols and corresponding crystal classes, the relative locations and orientations of the symmetry elements with respect to a chosen origin and the crystal-specific basis vectors, a listing of the general and all special positions (with their symmetrically equivalent points) and the related reflection conditions.

Side-note: It was the first institute director of the Institute of Crystallography, RWTH Aachen University, Prof. Theo Hahn, who served the International Union of Crystallography for 40 years as Chair of the Commission on *International Tables*, as editor of the *International Tables A* (five editions). The editions of the new *International Tables Volume A*, form a major part of his lifetime achievements.

4.6 Example: crystal structure description of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

Crystal structure determination with atomic resolution is achieved by diffraction experiments with X-rays, electron or neutron radiation. As an example, the results of a structure analysis by neutron diffraction on a single crystal of the ceramic high- T_C superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with $T_C = 92$ K are presented. The atomic arrangement of the orthorhombic structure, space group Pmmm, and the temperature-dependent electrical resistivity is shown in figures 4.11.

Information from ITA on the relative locations and orientations of the symmetry elements (symmetry operations $1, 2_z, 2_y, 2_x, \bar{1}, m_z, m_y, m_x$) of the orthorhombic space group Pmmm, together with the choice of the origin (in an inversion centre), is shown in figure 4.12. The general position (site symmetry 1) of multiplicity 8 (symmetry produces 7 additional copies of

this atom in the unit cell) and all special positions with their site symmetries are listed in figure 4.13. There are no special reflection conditions for this space group.

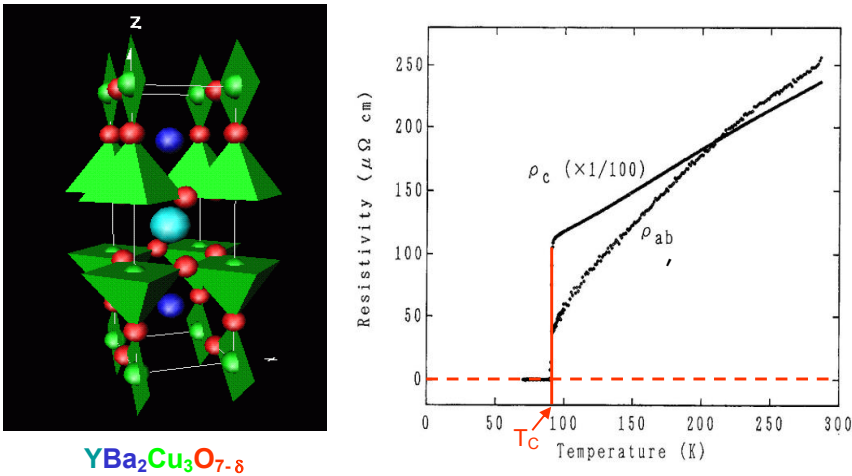


Fig. 4.11: Unit cell of YBa₂Cu₃O_{7-δ} with CuO_x-polyhedra (left) and the electrical resistivity as a function of temperature || and ⊥ to the [001] direction (right).

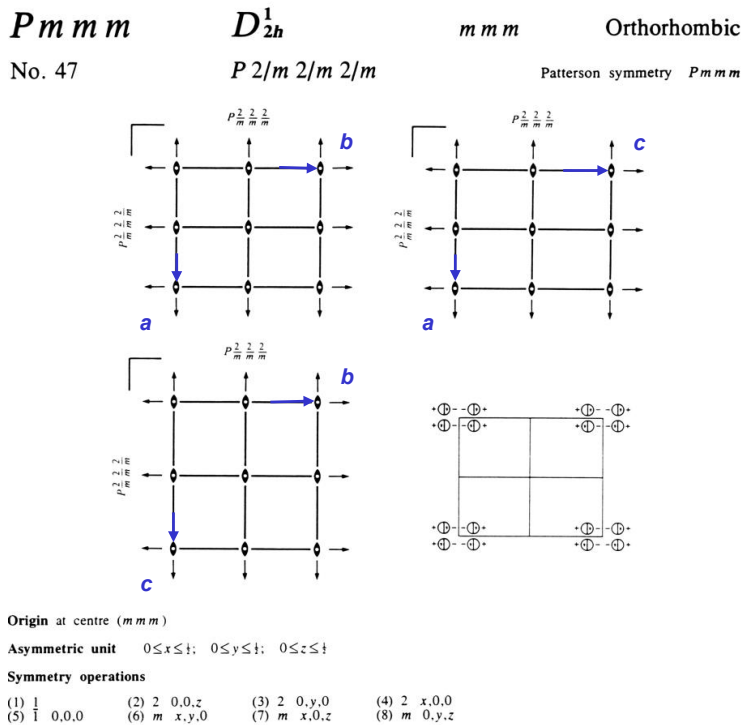


Fig. 4.12: Description of the orthorhombic space group Pmmm in [1].

CONTINUED



No. 47

 Pmm Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5)

Positions

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

Reflection conditions

General:

no conditions

Special: no extra conditions

8 α 1 (1) x, y, z (2) $\bar{x}, \bar{y}, z$ (3) $\bar{x}, y, \bar{z}$ (4) $x, \bar{y}, \bar{z}$
 (5) $\bar{x}, \bar{y}, \bar{z}$ (6) $x, y, \bar{z}$ (7) $x, \bar{y}, z$ (8) $\bar{x}, y, z$

4 z $.m$ $x, y, \frac{1}{2}$ $\bar{x}, \bar{y}, \frac{1}{2}$ $\bar{x}, y, \frac{1}{2}$ $x, \bar{y}, \frac{1}{2}$

4 y $.m$ $x, y, 0$ $\bar{x}, \bar{y}, 0$ $\bar{x}, y, 0$ $x, \bar{y}, 0$

4 x $.m$ $x, \frac{1}{2}, z$ $\bar{x}, \frac{1}{2}, z$ $\bar{x}, \frac{1}{2}, \bar{z}$ $x, \frac{1}{2}, \bar{z}$

4 w $.m$ $x, 0, z$ $\bar{x}, 0, z$ $\bar{x}, 0, \bar{z}$ $x, 0, \bar{z}$

4 v m $\frac{1}{2}, y, z$ $\frac{1}{2}, \bar{y}, z$ $\frac{1}{2}, y, \bar{z}$ $\frac{1}{2}, \bar{y}, \bar{z}$

4 u m $0, y, z$ $0, \bar{y}, z$ $0, y, \bar{z}$ $0, \bar{y}, \bar{z}$

2 t $mm2$ $\frac{1}{2}, \frac{1}{2}, z$ $\frac{1}{2}, \frac{1}{2}, \bar{z}$

2 s $mm2$ $\frac{1}{2}, 0, z$ $\frac{1}{2}, 0, \bar{z}$

2 r $mm2$ $0, \frac{1}{2}, z$ $0, \frac{1}{2}, \bar{z}$

2 q $mm2$ $0, 0, z$ $0, 0, \bar{z}$

2 p $m2m$ $\frac{1}{2}, y, \frac{1}{2}$ $\frac{1}{2}, \bar{y}, \frac{1}{2}$

2 o $m2m$ $\frac{1}{2}, y, 0$ $\frac{1}{2}, \bar{y}, 0$

2 n $m2m$ $0, y, \frac{1}{2}$ $0, \bar{y}, \frac{1}{2}$

2 m $m2m$ $0, y, 0$ $0, \bar{y}, 0$

2 l $2mm$ $x, \frac{1}{2}, \frac{1}{2}$ $\bar{x}, \frac{1}{2}, \frac{1}{2}$

2 k $2mm$ $x, \frac{1}{2}, 0$ $\bar{x}, \frac{1}{2}, 0$

2 j $2mm$ $x, 0, \frac{1}{2}$ $\bar{x}, 0, \frac{1}{2}$

2 i $2mm$ $x, 0, 0$ $\bar{x}, 0, 0$

1 h mmm $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

1 g mmm $0, \frac{1}{2}, \frac{1}{2}$

1 f mmm $\frac{1}{2}, \frac{1}{2}, 0$

1 e mmm $0, \frac{1}{2}, 0$

1 d mmm $\frac{1}{2}, 0, \frac{1}{2}$

1 c mmm $0, 0, \frac{1}{2}$

1 b mmm $\frac{1}{2}, 0, 0$

1 a mmm $0, 0, 0$

Fig. 4.13: General and special positions (coordinates of all symmetrically equivalent positions) of space group $Pmmm$ with their site symmetries and multiplicities as well as reflection conditions [1]. The special positions occupied in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -structure are indicated by frames.

The atomic parameters for $\text{YBa}_2\text{Cu}_3\text{O}_{6.96}$ obtained from the structure refinement of single crystal neutron diffraction data taken at room temperature [2] are given in the following Table:

Atomic positions of $\text{YBa}_2\text{Cu}_3\text{O}_{6.96}$ orthorhombic, space group type P $2/m\ 2/m\ 2/m$ $a = 3.858\ \text{\AA}$, $b = 3.846\ \text{\AA}$, $c = 11.680\ \text{\AA}$ (at room temperature)					
atom/ion	multiplicity	site symmetry	x	y	z
Cu1/Cu ²⁺	1	$2/m\ 2/m\ 2/m$	0	0	0
Cu2/Cu ²⁺	2	$m\ m\ 2$	0	0	0.35513(4)
Y/Y ³⁺	1	$2/m\ 2/m\ 2/m$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
Ba/Ba ²⁺	2	$m\ m\ 2$	$\frac{1}{2}$	$\frac{1}{2}$	0.18420(6)
O1/O ²⁻	2	$m\ m\ 2$	0	0	0.15863(5)
O2/O ²⁻	2	$m\ m\ 2$	0	$\frac{1}{2}$	0.37831(2)
O3/O ²⁻	2	$m\ m\ 2$	$\frac{1}{2}$	0	0.37631(2)
O4/O ²⁻	1	$2/m\ 2/m\ 2/m$	0	$\frac{1}{2}$	0

References

- 1) *International Tables for Crystallography Vol. A, Space-group Symmetry*, edited by Th. Hahn, Dordrecht: Kluwer Academic Publishers (5. Edition, 2002)
- 2) *Crystallography: An Introduction*, Walter Borchardt-Ott, Springer Berlin Heidelberg (2011)
- 3) P. Schweiss, W. Reichardt, M. Braden, G. Collin, G. Heger, H. Claus, A. Erb, *Phys. Rev. B* **49**, 1387 – 1396 (1994)
- 4) G. Redhammer et al. *Phys. Chem. Min.* **37**, 311-332, (2010)
- 5) Interactive Structure factor and Ewald sphere tutorials:
<http://www.ysbl.york.ac.uk/~cowtan/>

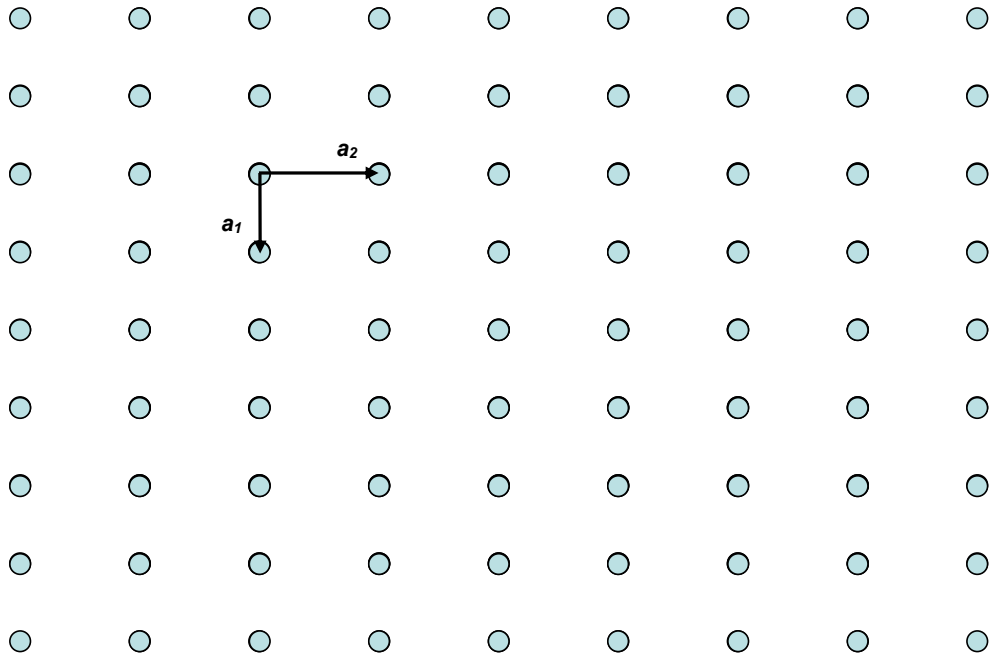
Exercises Crystallography

E4.1 Lattice points, lattice directions and lattice planes

A projection of an orthorhombic lattice on the lattice plane (001) is given in the following figure (this means a projection parallel to the c -axis). The dots represent the lattice points (not atoms) according to the translational symmetry of a crystal with the general translation vector $\tau = ua + vb + wc$ (a , b , and c are the basis vectors of the unit cell and u , v , w being integers)

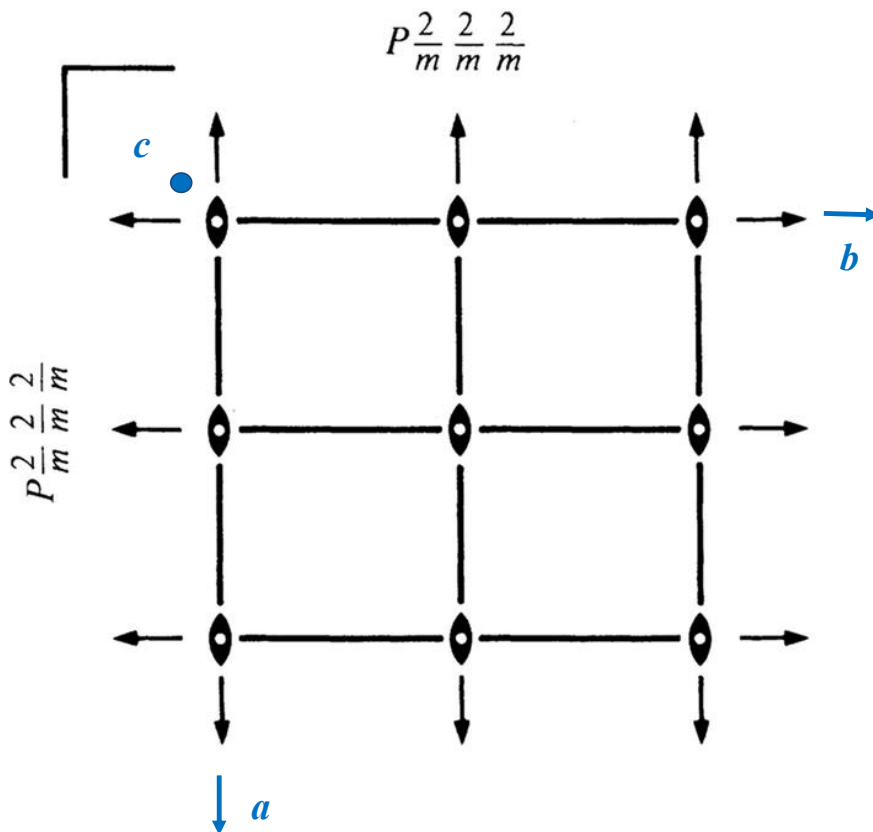
Please indicate in the figure

- The lattice points $uvw = 030$, $\bar{1}20$, $1\bar{2}0$, and 450 ,
- The lattice directions $[uvw] = [100]$, $[210]$, $[\bar{2}\bar{1}0]$ and $[\bar{2}50]$,
- The traces of the lattice planes $(hkl) = (100)$, (210) , (-210) , and (140) .



E4.2 Crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

The following figure reproduces the arrangement of the symmetry elements in the unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (see the upper left projection of fig. 4.12, taken from the international tables).



Make sure you understand the meaning of the symbols for the symmetry elements.
(see fig. 4.10)

a) Draw the positions of all atoms (Y, Ba, Cu, O) into the above given projection.
(Take the coordinates from the table of the atomic positions given in the lecture book; mark the heights (z -coordinates) of the atoms along the projection direction by attaching the corresponding coordinates to the atoms.)

b) Given the space group $P2/m2/m2/m$: What is the crystal system (*refer to the conditions for the lattice parameters on page 4.15*) and the Bravais lattice type (*see the space group symbol*) of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$?

c) How many formula units are in one unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$? (*refer to fig. 4.11*)

d) Give the coordination numbers and describe the polyhedra of oxygen around atoms Cu1 and Cu2 (*refer, for simplicity, to fig. 4.11*).

e) For all atoms: Check if the atom sits on an inversion centre (*either from the above plot or from fig. 4.11 or from the table on page 4.15.*)

Cu1: ☒ Cu2: Y: Ba: O1: O2: O3: O4:

f) Calculate the interplanar spacings $d(hkl)$ (*choose the appropriate formula on page 4.6*) for the lattice planes (100), (200), (020), (002), (00-2).

g) List all symmetry equivalent lattice planes with identical d-spacing (*including all different orientation possibilities*) for the following types of lattice planes of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$:

$(h00)$, $(00l)$, $(0kl)$, and (hkl)

Example for $(h0l)$ in the orthorhombic crystal system: $d(h0l) = d(\bar{h}0l) = d(\bar{h}0\bar{l}) = d(h0\bar{l})$.

h) How many symmetry-equivalent lattice planes result in each case? (*This is the multiplicity factor M of reflections needed as a correction factor in powder diffraction.*)

5 Diffraction/ Elastic Scattering and Structural Analysis

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5.1 Introduction

After the very qualitative introduction given in chapter 1, we now have to move to a more quantitative description of neutron scattering, giving the basic formulas for the simplest cases.

This lecture is organized as follows: First we give a very basic general introduction into elementary scattering theory for elastic scattering. Then a more rigorous derivation in the framework of the Born series follows. This section can be skipped by beginners but is provided for completeness.

We will introduce the concepts of coherence and pair correlation functions. Then we will discuss, which probes are most relevant for condensed matter investigations and present in some detail the interaction of neutrons with matter leading to the absorption and scattering cross-sections. More details can be found in [1–7]. Finally, we will discuss details of neutron diffraction experiments, in particular, how to calculate diffraction intensities and practical realizations of single and powder diffraction experiments.

We will frequently make use of the particle-wave dualism of quantum mechanics, which tells us that the radiation used in the scattering process can be described in a wave picture, whenever we are interested in interference phenomena, and in a particle picture, when the interaction with matter is relevant, e. g. for the detection process.

5.2 Elementary scattering theory: Elastic scattering

Throughout this lecture we assume that the atoms within our sample are rigidly fixed on equilibrium positions in space. Therefore we only look at those processes, in which the recoil is being transferred to the sample as a whole so that the energy change for the radiation is negligible and the scattering process appears to be elastic. In subsequent lectures, this restriction will be dropped and so-called inelastic scattering processes will be discussed. These are due to excitations or internal fluctuations in the sample, which give rise to an energy change of the radiation during the scattering process. A sketch of the scattering experiment is shown in Figure 5.1.

Here we assume the so-called *Fraunhofer approximation*, where the size of the sample is much smaller than the distance between sample and source and the distance between sample and detector. This assumption holds in all cases discussed in this lecture. In addition, we assume that the source emits radiation of one given energy, i. e. so-called *monochromatic radiation*. Then the wave field incident on the sample can be considered as a plane wave, which is completely described by a wave vector $\mathbf{k}$. The direction of $\mathbf{k}$ indicates the propagation direction of the wave. The same holds for the wave incident on the detector, which can be described by a vector $\mathbf{k}'$. In the case of elastic scattering (diffraction) we have (-with λ as wavelength):

$$k = |\mathbf{k}| = |\mathbf{k}'| = k' = \frac{2\pi}{\lambda} \quad (5.1)$$

Let us define the so-called *scattering vector* by

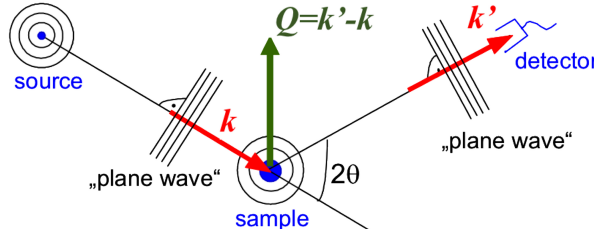


Fig. 5.1: A sketch of the scattering process for monochromatic radiation in the Fraunhofer approximation. It is assumed that plane waves are incident on sample and detector due to the fact that the distances source-sample and sample-detector, respectively, are significantly larger than the size of the sample.

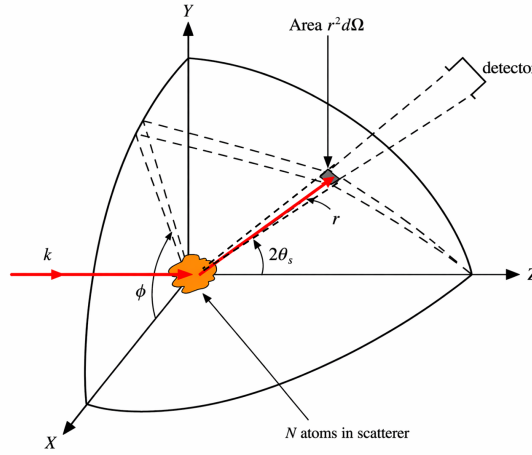


Fig. 5.2: Geometry used for the definition of the scattering cross section.

$$\mathbf{Q} = \mathbf{k}' - \mathbf{k} \quad (5.2)$$

$\hbar\mathbf{Q}$ represents the momentum transfer during scattering, since according to de Broglie, the momentum of the particle corresponding to the wave with wave vector $\mathbf{k}$ is given by $\mathbf{p} = \hbar\mathbf{k}$. The magnitude of the scattering vector can be calculated from wavelength λ and scattering angle 2θ as follows

$$Q = |\mathbf{Q}| = \sqrt{k^2 + k'^2 - 2kk' \cos 2\theta} \Rightarrow Q = \frac{4\pi}{\lambda} \sin \theta \quad (5.3)$$

A scattering experiment comprises the measurement of the intensity distribution $I(\mathbf{Q})$ as a function of the scattering vector $\mathbf{Q}$. The scattered intensity is proportional to the so-called *cross section*, where the proportionality factors arise from the detailed geometry of the experiment. For a definition of the scattering cross section, we refer to Figure 5.2.

If n' particles are scattered per second into the solid angle $d\Omega$ seen by the detector under the

scattering angle 2θ and into the energy interval between E' and $E' + dE'$, then we can define the so-called *double differential cross section* by:

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{n'}{j d\Omega dE'} \quad (5.4)$$

Here j refers to the incident beam flux in terms of particles per area and time. If we are not interested in the change of the energy of the radiation during the scattering process, or if our detector is not able to resolve this energy change, then we will describe the angular dependence by the so-called *differential cross section*:

$$\frac{d\sigma}{d\Omega}(\theta) = \int_0^\infty \left. \frac{d^2\sigma}{d\Omega dE'} \right|_\theta dE' \quad (5.5)$$

Note that the integral has to be taken for the constant scattering angle of the detector. Finally, the so-called *total scattering cross section* gives us a measure for the total scattering probability independent of changes in energy and scattering angle:

$$\sigma = \int_0^{4\pi} \frac{d\sigma}{d\Omega} d\Omega \quad (5.6)$$

For elastic scattering our task is to determine the arrangement of the atoms in the sample from the knowledge of the scattering cross section $d\sigma/d\Omega$. The relationship between scattered intensity and the structure of the sample is particularly simple in the so-called *Born approximation*, which is often also referred to as *kinematic scattering theory*. In this case, refraction of the beam entering and leaving the sample, multiple scattering events and the attenuation of the primary beam due to scattering within the sample are neglected. For simplicity, we assume that the incident beam is ideally collimated (i.e. has no angular spread) and monochromatized (i.e. has no wavelength spread) and describe it as a plane wave.

Following Figure 5.3, the phase difference between a wave scattered at the origin of the coordinate system (A) and at position $\mathbf{r}$ (D) is given by

$$\Delta\Phi = 2\pi \cdot \frac{(\overline{AB} - \overline{CD})}{\lambda} = \mathbf{k}' \cdot \mathbf{r} - \mathbf{k} \cdot \mathbf{r} = \mathbf{Q} \cdot \mathbf{r} \quad (5.7)$$

Here we see the other meaning of the scattering vector $\mathbf{Q}$: besides the momentum transfer $\hbar\mathbf{Q}$ (“particle picture”), it determines the phase shift $\mathbf{Q} \cdot \mathbf{r}$ during scattering (“wave picture”).

The amplitude of the scattered beam at position $\mathbf{r}$ depends on the type of radiation used and the interaction of this radiation with the sample. In fact, the probability for a scattering event to occur is directly proportional to the interaction potential V , as will be shown in paragraph 5.3. The total scattering amplitude is given by a coherent superposition (i.e. taking the phase $\Delta\Phi$ into account) of the scattering from all points within the sample, i. e. by the integral

$$A(\mathbf{Q}) \sim A_0 \cdot \int_{V_s} V(\mathbf{r}) \cdot e^{i\mathbf{Q} \cdot \mathbf{r}} d^3r \quad (5.8)$$

Here A_0 denotes the amplitude of the incident wave field. Eqn. 5.8 demonstrates that the scattered amplitude is connected with the interaction potential $V(\mathbf{r})$ by a simple Fourier

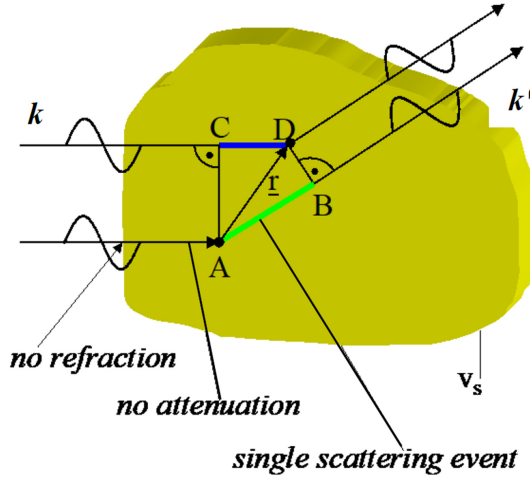


Fig. 5.3: A sketch illustrating the phase difference between a ray scattered at the origin of the coordinate system and a ray scattered at the position $\mathbf{r}$.

transform. Knowledge of the scattering amplitude A for all scattering vectors $\mathbf{Q}$ allows us to determine via a Fourier transform the potential $V(\mathbf{r})$ uniquely. This is the complete information on the sample, which can be obtained by an elastic scattering experiment. Unfortunately, nature is not so simple. On one hand, there is the more technical problem that one is unable to determine the scattering cross section for **all** values of momentum transfer $\hbar\mathbf{Q}$. The more fundamental problem, however, is that normally the amplitude of the scattered wave is not measurable. Instead only the scattered intensity

$$I(\mathbf{Q}) \sim |A(\mathbf{Q})|^2 \quad (5.9)$$

can be determined. Therefore, the phase information is lost and the simple reconstruction of the scattering potential via a Fourier transform is no longer possible. This is the so-called *phase problem* of scattering. There are ways to overcome the phase problem, e. g. by use of reference waves (e. g. holography). Then the scattering potential becomes directly accessible. The question, which information we can obtain from a conventional scattering experiment despite the phase problem will be addressed below.

Which wavelength do we have to choose to obtain the required real space resolution? For information on a length scale L , a phase difference of about $Q \cdot L \approx 2\pi$ has to be achieved. Otherwise according to Eqn. 5.7, $\mathbf{k}'$ and $\mathbf{k}$ will not differ significantly. According to Eqn. 5.3, $Q \approx 2\pi/\lambda$ for typical scattering angles ($2\theta \sim 60^\circ$). Combining these two estimates, we end up with the requirement that the wavelength λ has to be in the order of the real space length scale L under investigation. To give an example: with the wavelength in the order of $1\text{\AA} = 0.1\text{ nm}$, atomic resolution can be achieved in a scattering experiment.

5.3 Fundamental scattering theory: The Born series

In this chapter, we will give a simple formulation of scattering theory. Our purpose is to derive 5.8 from fundamental principles. The conditions under which 5.8 holds and the limitations of kinematical scattering theory will thus become clearer. The derivation will be done for particle beams - in particular neutrons - for which the Schrödinger equation holds. This is bonus-material: Beginners can skip this section.

In quantum mechanics, neutrons are described as particle wave through the Schrödinger equation:

$$\hat{H}\Psi = \left(-\frac{\hbar^2}{2m}\Delta + V \right) \Psi = i\hbar \frac{\partial}{\partial t} \Psi \quad (5.10)$$

ψ is the probability density amplitude, V the interaction potential. In case of purely elastic scattering $E = E'$, the time dependence can be described by the factor $\exp(-i\frac{E}{\hbar}t)$. Assuming this time dependence, a wave equation for the spatial part of the probability density amplitude ψ can be derived from 5.10:

$$\Delta\Psi + k^2(\mathbf{r})\Psi = 0 \quad (5.11)$$

In Eq. 5.11, we have introduced a spatially varying wave vector with the magnitude square:

$$k^2(\mathbf{r}) = \frac{2m}{\hbar^2}(E - V(\mathbf{r})) \quad (5.12)$$

Solutions of 5.10, in empty space (i. e. $V \equiv 0$) can be guessed immediately. They are given by plane waves $\Psi = \Psi_0 \exp[i(\mathbf{k} \cdot \mathbf{r} - \frac{E}{\hbar}t)]$ with $k^2 = \frac{2m}{\hbar^2}E$. The relations between magnitude of the wave vector k , wave length λ , and energy of the neutron E can be written in practical units:

$$k [\text{\AA}^{-1}] \approx 0.695 \sqrt{E[\text{meV}]} \quad (5.13)$$

$$\lambda[\text{\AA}] \approx 9.045 / \sqrt{E[\text{meV}]} \quad (5.14)$$

$$E[\text{meV}] \approx 81.8 / \lambda^2[\text{\AA}] \quad (5.15)$$

To give an example, neutrons of wavelength $\lambda = 2.4 \text{\AA} = 0.24 \text{ nm}$ have an energy of $E = 14.2 \text{ meV}$ with a magnitude of the neutron wave vector of $k = 2.6 \text{\AA}^{-1}$.

To obtain solutions of the wave equation 5.11 in matter, we reformulate the differential equation by explicitly separating the interaction term:

$$(\Delta + k^2)\Psi = \frac{2m}{\hbar^2}V \cdot \Psi =: \chi \quad (5.16)$$

Here $\mathbf{k}$ denotes the wave vector for propagation in empty space. The advantage of this formulation is that the solutions of the left-hand side are already known. They are the plane

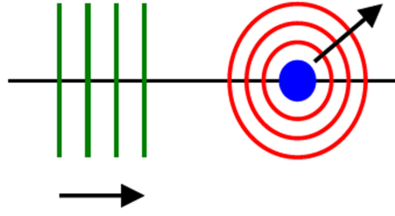


Fig. 5.4: The scattering from a point-like scatterer (δ -potential) gives an emitted spherical wave

waves in empty space. Equation 5.16 is a linear partial differential equation, i.e. the superposition principle holds: the general solution can be obtained as a linear combination of a complete set of solution functions. The coefficients in the series are determined by the boundary conditions. To solve 5.16 one can apply a method developed for inhomogeneous linear differential equations. For the moment, we assume that the right-hand side is fixed (given as χ). We define a *Green's-function* by:

$$(\Delta + k^2) G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (5.17)$$

A solution of 5.17 is given by:

$$G(\mathbf{r}, \mathbf{r}') = \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{4\pi |\mathbf{r} - \mathbf{r}'|} \quad (5.18)$$

The physical meaning of 5.18 is immediately clear: the scattering from a point-like scatterer (δ -potential) gives an emitted spherical wave. In a schematic graphical representation: Using the Green's-function $G(\mathbf{r}, \mathbf{r}')$, we can write down a formal solution of the wave equation 5.16:

$$\Psi = \Psi^o + \int G(\mathbf{r}, \mathbf{r}') \chi(\mathbf{r}') d^3 r' \quad (5.19)$$

Here, we have taken the initial conditions of an incident plane wave Ψ^o into account. Eqn. 5.19 is indeed a solution of Eqn. 5.16 as can be easily verified by substituting 5.19 into 5.16. If we finally substitute the definition of χ , one obtains the so-called *Lippmann-Schwinger* equation:

$$\Psi(\mathbf{r}) = \Psi^o(\mathbf{r}) + \frac{2m}{\hbar^2} \int_{V_s} G(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \Psi(\mathbf{r}') d^3 r' \quad (5.20)$$

Eqn. 5.20 has a simple interpretation: the incident plane wave $\Psi^o(\mathbf{r})$ is superimposed by spherical waves emitted from scattering at positions $\mathbf{r}'$. The amplitude of these spherical waves is proportional to the interaction potential $V(\mathbf{r}')$ and the amplitude of the wave field at the position $\mathbf{r}'$. To obtain the total scattering amplitude, we have to integrate over the

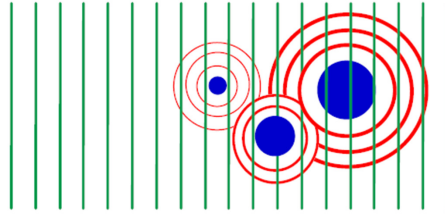


Fig. 5.5: Physical interpretation of eqn. 5.20.

entire sample volume V_s . However, we still have not solved 5.16: our solution Ψ appears again in the integral in 5.20. In other words, we have transformed differential equation 5.16 into an integral equation. The advantage is that for such an integral equation, a solution can be found by iteration. In the zeroth approximation, we neglect the interaction V completely.

This gives $\Psi = \Psi^o$. The next higher order approximation for a weak interaction potential is obtained by substituting this solution in the right-hand side of 5.20. The first non-trivial approximation can thus be obtained:

$$\Psi^1(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} + \frac{2m}{\hbar^2} \int \frac{\exp(i\mathbf{k} |\mathbf{r} - \mathbf{r}'|)}{4\pi |\mathbf{r} - \mathbf{r}'|} V(\mathbf{r}') e^{i\mathbf{k} \cdot \mathbf{r}'} d^3 r' \quad (5.21)$$

5.21 is nothing else but a mathematical formulation of the well-known *Huygens principle* for wave propagation.

The approximation 5.21 assumes that the incident plane wave is only scattered once from the potential $V(\mathbf{r}')$. For a stronger potential and larger sample, multiple scattering processes will occur. Again, this can be deduced from the integral equation 5.20 by further iteration. For simplification we introduce a new version of equation 5.20 by writing the integral over the "Green's function" as operator $\hat{G}$:

$$\Psi = \Psi^o + \hat{G}V\Psi \quad (5.22)$$

The so-called first *Born approximation*, which gives the *kinematical scattering theory* is obtained by substituting the wave function Ψ on the right hand side by Ψ^o :

$$\Psi^1 = \Psi^o + \hat{G}V\Psi^o \quad (5.23)$$

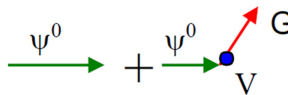


Fig. 5.6: This first approximation in Graphical representation.

This first approximation can be represented by a simple diagram as a sum of an incident plane wave and a wave scattered once from the potential V :

The second approximation is obtained by substituting the solution of the first approximation 5.23 on the right-hand side of equation 5.22:

$$\Psi^2 = \Psi^o + \hat{G}V\Psi^1 = \Psi^o + \hat{G}V\Psi^o + \hat{G}V\hat{G}V\Psi^o \quad (5.24)$$

Or in a diagrammatic form:

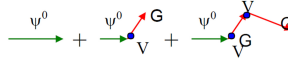


Fig. 5.7: This second approximation in Graphical representation.

I.e. in the second approximation, processes are being taken into account, in which the neutron is scattered twice by the interaction potential V . In a similar manner, all higher order approximations can be calculated. This gives the so-called *Born series*.¹ For weak potential and small samples, this series converges rather fast. Often, the first approximation, the *kinematic scattering theory*, holds very well. This is especially the case for neutron scattering, where the scattering potential is rather weak, as compared to x-ray or electron- scattering. Due to the strong Coulomb interaction potential, the probability for multiple scattering processes of electrons in solids is extremely high, making the interpretation of electron diffraction experiments difficult. But even for neutrons, the kinematic scattering theory can break down, for example in the case of Bragg scattering from large ideally perfect single crystals, where the Born series does not converge. The wave equation has to be solved exactly under the boundary conditions given by the crystal geometry. For simple geometries, analytical solutions can be obtained. This is then called the *dynamical scattering theory*. Since for neutrons, the kinematical theory holds in most cases, or multiple scattering events can often be corrected for, we will no longer discuss dynamical theory in what follows and refer to [3, 7].

Let us return to the first Born approximation 5.21. In a further approximation, the Fraunhofer approximation, we assume that the size of the sample is significantly smaller than the distance sample-detector. The geometry to calculate the far field limit of 5.21 is given in Figure 5.8 . Under the assumption $|\underline{R}| \gg |\underline{r}'|$, we can deduce from Figure 2.4 the following approximation for the emitted spherical wave:

$$\frac{\exp(ik|\underline{r} - \underline{r}'|)}{|\underline{r} - \underline{r}'|} \approx \frac{\exp\left(ik\left(R - \underline{r}' \cdot \hat{\underline{R}}\right)\right)}{R} \approx \frac{\exp(ikR)}{R} \cdot e^{-ik'\cdot\underline{r}'} \quad (5.25)$$

The probability density amplitude for the scattered wave field in the limit of large distances from the sample is thus given by:

$$\Rightarrow \Psi^1(\underline{R}) = e^{ik\cdot\underline{R}} + \frac{2m}{\hbar^2} \frac{e^{ikR}}{4\pi R} \int V(\underline{r}') e^{i\underline{Q}\cdot\underline{r}'} d^3r' \quad (5.26)$$

¹ Note that Born approximation or the Born series violates energy conservation: scattered waves are created without weakening of the incident plane wave. Born series can therefore only be applied in the limit of very weak scattering potentials.

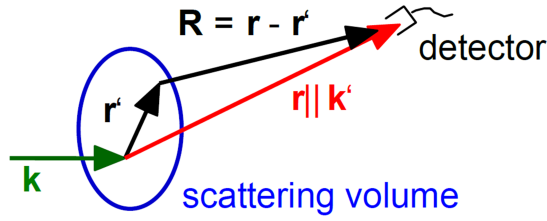


Fig. 5.8: Scattering geometry for the calculation of the far field limit at the detector. In the Fraunhofer approximation, we assume that $|\mathbf{R}| \gg |\mathbf{r}'|$.

This is just the sum of an incident plane wave and a spherical wave emitted from the sample as a whole. The amplitude of the scattered wave is given according to 5.26:

$$A(\mathbf{Q}) = \frac{m}{2\pi\hbar^2} \int V(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}} d^3r \sim F[V(\mathbf{r})] \quad (5.27)$$

The integral in the above equation is nothing but the transition matrix element of the interaction potential V between the initial and final plane wave states, therefore:

$$\frac{d\sigma}{d\Omega} = \left(\frac{m}{2\pi\hbar^2} \right)^2 |\langle \mathbf{k}' | V | \mathbf{k} \rangle|^2 \quad (5.28)$$

This formula corresponds to *Fermi's Golden Rule* from time-dependent perturbation theory, where the transition probability per time interval from state $\mathbf{k}$ to states $\mathbf{k}'$ is given by:

$$W_{k'k} = \frac{2\pi}{\hbar} |\langle \mathbf{k}' | V | \mathbf{k} \rangle|^2 \cdot \rho(E_{k'}) \quad (5.29)$$

Here, $\rho(E_{k'})$ denotes the density of states for the final states $\mathbf{k}'$.

With this exact derivation of the scattering cross section, we can now confirm by comparison with 5.8 that the scattering probability in the simple derivation of section 5.2 is given by $\frac{m}{2\pi\hbar^2} V(\mathbf{r})$ for particle beams governed by the Schrödinger equation.

We now allow for inelastic processes, where the sample undergoes a change of its state from α to α' (α denotes a set of quantum numbers characterizing an eigenstate of the sample). In this case, due to the different length of the wavevectors for incoming and outgoing waves, we have to introduce factors k' and k , which arise from the density of states factor in 5.29. Since the scattering event must fulfill energy and momentum conservation, we arrive at the double differential cross section (without detailed derivation):

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k'}{k} \left(\frac{m}{2\pi\hbar^2} \right)^2 \sum_{\alpha} p_{\alpha} \sum_{\alpha'} |\langle \mathbf{k}', \alpha' | V | \mathbf{k}, \alpha \rangle|^2 \cdot \delta(\hbar\omega + E_{\alpha} - E_{\alpha'}) \quad (5.30)$$

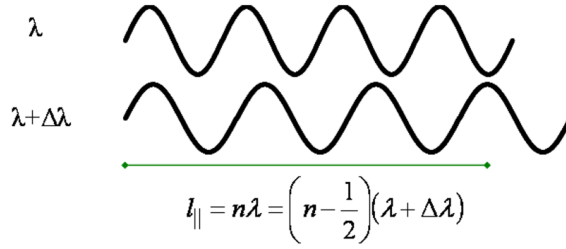


Fig. 5.9: A sketch illustrating the longitudinal coherence due to a wavelength spread.

The first summation is carried out over all possible initial states α of the system, weighted with their thermodynamic occupation probability p_α . The sum over α' is the sum over all final states allowed by energy conservation, which is guaranteed through the δ -function. $\hbar\omega$ denotes the energy transfer of the neutron to the system. This double differential cross section will be discussed in the following lectures on inelastic scattering.

5.3.1 Coherence

In the above derivation, we assumed plane waves as initial and final states. For a real scattering experiment, this is an unphysical assumption. In the incident beam, a wave packet is produced by collimation (defining the direction of the beam) and monochromatization (defining the wavelength of the incident beam). Neither the direction $\mathbf{k}$, nor the wavelength λ have sharp values but rather have a distribution of finite width about their respective mean values. This wave packet can be described as a superposition of plane waves. As a consequence, the diffraction pattern will be a superposition of patterns for different incident wavevector $\mathbf{k}$ and the question arises, which information is lost due to these non-ideal conditions. This *instrumental resolution* is intimately connected with the *coherence* of the beam. Coherence is needed, so that the interference pattern is not significantly destroyed. Coherence requires a phase relationship between the different components of the beam. Two types of coherence can be distinguished.

- *Temporal or longitudinal coherence due to a wavelength spread.*

A measure for the longitudinal coherence is given by the length, on which two components of the beam with largest wavelength difference (λ and $\lambda + \Delta\lambda$) become fully out of phase.

According to the Figure 5.9, this is the case for $l_{||} = n \cdot \lambda = \left(n - \frac{1}{2}\right) (\lambda + \Delta\lambda)$. From this, solving for n and assuming $\Delta\lambda \ll \lambda$, we obtain the *longitudinal coherence length* $l_{||}$ as:

$$l_{||} = \frac{\lambda^2}{2\Delta\lambda} \quad (5.31)$$

- *Transversal coherence due to source extension*

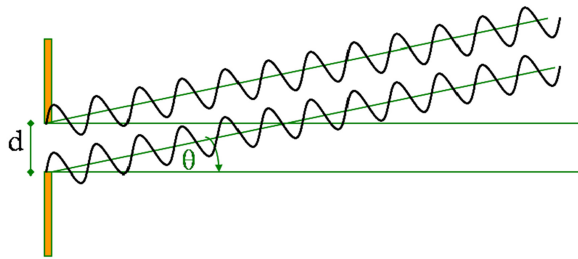


Fig. 5.10: A sketch illustrating the transverse coherence due to source extension.

Due to the extension of the source (transverse beam size), the phase relation is destroyed for large source size or large divergence. According to the Figure 5.10, a first minimum occurs for $\frac{\lambda}{2} = d \cdot \sin \theta \approx d \cdot \theta$.

From this, we obtain the *transversal coherence length* $l_{\perp}$ as

$$l_{\perp} = \frac{\lambda}{2\Delta\theta} \quad (5.32)$$

Here $\Delta\theta$ is the divergence of the beam. Note that $l_{\perp}$ can be different along different spatial directions: in many instruments, the vertical and horizontal collimations are different.

Together, the longitudinal and the two transversal coherence lengths (in two directions perpendicular to the beam propagation) define a *coherence volume*. This is a measure for a volume, in which the amplitudes of all scattered waves superimpose within the sample to produce an interference pattern. Normally, the coherence volume is significantly smaller than the sample size, typically a few 100 Å for neutron scattering, up to μm for synchrotron radiation. Scattering between different coherence volumes within the sample is no longer coherent, i.e. instead of the amplitudes the intensities of the contributions to the scattering pattern have to be added. This limits the real space resolution of a scattering experiment to the extension of the coherence volume.

5.3.2 Pair correlation functions

After having clarified the conditions under which we can expect a coherent scattering process, let us now come back to the question, which information is accessible from the intensity distribution of a scattering experiment. From 5.9 we see that the phase information is lost during the measurement of the intensity. For this reason the Fourier transform of the scattering potential is not directly accessible in most scattering experiments (note however that phase information can be obtained in certain cases).

Substituting 5.8 into 5.9 and applying the variable substitution $\mathbf{R} = \mathbf{r}' - \mathbf{r}$, we obtain for the magnitude square of the scattering amplitude, a quantity directly accessible in a scattering

experiment:

$$I \sim |A(\mathbf{Q})|^2 \sim \int d^3r' V(\mathbf{r}') e^{i\mathbf{Q}\cdot\mathbf{r}'} \int d^3r V^*(\mathbf{r}) e^{-i\mathbf{Q}\cdot\mathbf{r}} = \iint d^3r' d^3r V(\mathbf{r}') V^*(\mathbf{r}) e^{i\mathbf{Q}\cdot(\mathbf{r}'-\mathbf{r})} \quad (5.33)$$

$$= \iint d^3R d^3r V(\mathbf{R} + \mathbf{r}) V^*(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{R}} \quad (5.34)$$

This shows that the scattered intensity is proportional to the Fourier transform of a function $P(\mathbf{R})$:

$$I(\mathbf{Q}) \sim \int d^3R P(\mathbf{R}) e^{i\mathbf{Q}\cdot\mathbf{R}} \quad (5.35)$$

This function denotes the so-called *Patterson function* in crystallography or more general the *static pair correlation function*:

$$P(\mathbf{R}) = \int d^3r V^*(\mathbf{r}) V(\mathbf{r} + \mathbf{R}) \quad (5.36)$$

$P(\mathbf{R})$ correlates the value of the scattering potential at position $\mathbf{r}$ with the value at the position $\mathbf{r} + \mathbf{R}$, integrated over the entire sample volume. The Patterson function $P(\mathbf{R})$ vanishes, if no correlation exists between the values of the potential at position $\mathbf{r}$ and $\mathbf{r} + \mathbf{R}$, when averaged over the sample. If, however, a periodic arrangement of a pair of atoms exists in the sample with a difference vector $\mathbf{R}$ between the positions, then the Patterson function will have an extremum for this vector $\mathbf{R}$. Thus, the Patterson function reproduces all the vectors connecting one atom with another atom in a periodic arrangement. Quite generally, in a scattering experiment, pair correlation functions are being determined. In a coherent inelastic scattering experiment, we measure the *scattering law* $S(\mathbf{Q}, \omega)$, which is the Fourier transform with respect to space and time of the spatial and temporal pair correlation function:

$$\frac{d^2\sigma}{d\omega d\Omega} \sim S(\mathbf{Q}, \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \int d^3r e^{i\mathbf{Q}\cdot\mathbf{r}} G(\mathbf{r}, t) \quad (5.37)$$

While the proportionality factor between the double differential cross section and the scattering law depends on the type of radiation and its specific interaction potential with the system studied, the spatial and temporal pair correlation function is only a property of the system studied and independent of the probe used:

$$G(\mathbf{r}, t) = \frac{1}{N} \sum_{ij} \int d^3r' \langle \delta(\mathbf{r}' - \mathbf{r}_j(0)) \cdot \delta(\mathbf{r}' + \mathbf{r} - \mathbf{r}_i(t)) \rangle = \frac{1}{N} \int d^3r' \langle \rho(\mathbf{r}', 0) \rho(\mathbf{r}' + \mathbf{r}, t) \rangle \quad (5.38)$$

Here, the pair correlation function is once expressed as a correlation between the position of N point-like particles (expressed by the delta functions) and once by the correlation between the densities at different positions in the sample for different times. In a magnetic system, we scatter from the atomic magnetic moments, which are vector quantities. Therefore, the scattering law becomes a tensor - the Fourier transform of the spin pair correlations:

$$\mathbf{S}^{\alpha\beta}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \sum_l \int dt e^{i[\mathbf{Q}(\mathbf{R}_l - \mathbf{R}_0) - \omega t]} \langle S_0^\alpha(0) S_l^\beta(t) \rangle \quad (5.39)$$

α, β denote the Cartesian coordinates x, y, z ; $\mathbf{R}_0$ and $\mathbf{R}_l$ are the spatial coordinates of a reference spin 0 and a spin l in the system.

5.3.3 Form-factor

So far we have not specified the nature of our sample. Now we assume an assembly of N scatterers of finite size, see Figure 5.11. These could be atoms in a solid, or colloidal particles in a homogeneous solution. In what follows, we will separate the interference effects from scattering within one such a particle from the interference effects arising from scattering between different particles. With the decomposition of the vector $\mathbf{r}$ into the centre-of-gravity-vector $\mathbf{r}_j$ of particle number j and a vector $\mathbf{r}'$ within the particle, the scattering amplitude can be written as (all particles are assumed to be identical):

$$A \propto \int_{V_s} d^3r V(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} = \sum_{j=1}^N \int_{V_j} d^3r V(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} \quad (5.40)$$

$$= \sum_{j=1}^N e^{i\mathbf{Q} \cdot \mathbf{r}_j} \int_{V_j^0} d^3r' V(\mathbf{r}') e^{i\mathbf{Q} \cdot \mathbf{r}'} =: \sum_{j=1}^N e^{i\mathbf{Q} \cdot \mathbf{r}_j} V_j^{\text{tot}} f_j(\mathbf{Q}) \quad (5.41)$$

With 5.41, we have separated the scattering from within the single particles from the interference between different particles. V_j^{tot} denotes the total scattering power of the particle. The *form-factor* $f(\mathbf{Q})$ is defined as the normalized amplitude of scattering from within one particle ² (it describes the "form" of the particle):

$$f(\mathbf{Q}) \equiv \frac{\int_{V_j^0} d^3r' V(\mathbf{r}') e^{i\mathbf{Q} \cdot \mathbf{r}'}}{\int_{V_j^0} d^3r' V(\mathbf{r}')} \quad (5.42)$$

For a homogeneous sphere

$$V(\mathbf{r}) = \begin{cases} 0 & |\mathbf{r}| > R \\ C & |\mathbf{r}| \leq R \end{cases} \quad (5.43)$$

the form-factor can be calculated by using spherical co-ordinates:

$$\Rightarrow f(Q) = 3 \cdot \frac{\sin QR - QR \cdot \cos QR}{(QR)^3} \quad (5.44)$$

The function in Eqn. 5.44 is plotted in Figure 5.12. In forward direction, there is no phase difference between waves scattered from different volume elements within the sample (note:

² For simplicity we now drop the index j

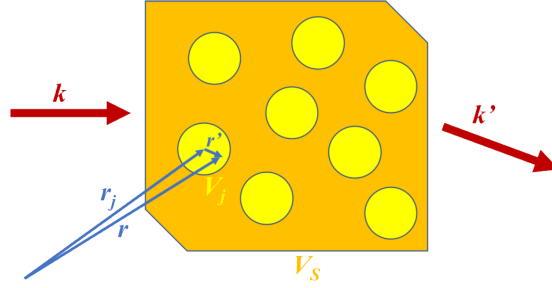


Fig. 5.11: Sketch showing the assembly of N scatterers of finite size and defining the quantities needed for the definition of the form factor.

we assume the Fraunhofer approximation and work in a far field limit): the form factor takes its maximum value of one. For finite scattering angles 2θ , the form-factor drops due to destructive interference from waves scattered from various parts within one particle and finally for large values of the momentum transfer shows damped oscillations around 0 as a function of QR .

5.4 Scattering from a periodic lattice in three dimensions

As an example for the application of 5.8 and 5.9, we will now discuss the scattering from a three dimensional lattice of point-like scatterers. As we will see later, this situation corresponds to the scattering of thermal neutrons from a single crystal. More precisely, we will restrict ourselves to the case of a Bravais lattice with one atom at the origin of the unit cell. To each atom we attribute a "scattering power"³ β . The single crystal is finite with N, M and P periods along the basis vectors $\mathbf{a}, \mathbf{b}$ and $\mathbf{c}$. The scattering potential, which we have to use in 5.8 is a sum over δ -functions for all scattering centers:

$$V(\mathbf{r}) = \sum_{n=0}^{N-1} \sum_{m=0}^{M-1} \sum_{p=0}^{P-1} \beta \cdot \delta(\mathbf{r} - (n \cdot \mathbf{a} + m \cdot \mathbf{b} + p \cdot \mathbf{c})) \quad (5.45)$$

The scattering amplitude is calculated as a Fourier transform:

$$A(\mathbf{Q}) \sim \beta \sum_{n=0}^{N-1} e^{in\mathbf{Q} \cdot \mathbf{a}} \sum_{m=0}^{M-1} e^{im\mathbf{Q} \cdot \mathbf{b}} \sum_{p=0}^{P-1} e^{ip\mathbf{Q} \cdot \mathbf{c}} \quad (5.46)$$

Summing up the geometrical series, we obtain for the scattered intensity:

$$I(\mathbf{Q}) \sim |A(\mathbf{Q})|^2 = |\beta|^2 \cdot \frac{\sin^2 \frac{1}{2} N \mathbf{Q} \cdot \mathbf{a}}{\sin^2 \frac{1}{2} \mathbf{Q} \cdot \mathbf{a}} \cdot \frac{\sin^2 \frac{1}{2} M \mathbf{Q} \cdot \mathbf{b}}{\sin^2 \frac{1}{2} \mathbf{Q} \cdot \mathbf{b}} \cdot \frac{\sin^2 \frac{1}{2} P \mathbf{Q} \cdot \mathbf{c}}{\sin^2 \frac{1}{2} \mathbf{Q} \cdot \mathbf{c}} \quad (5.47)$$

³ We will later see that this "scattering power" is connected to the so-called scattering length of the atom.

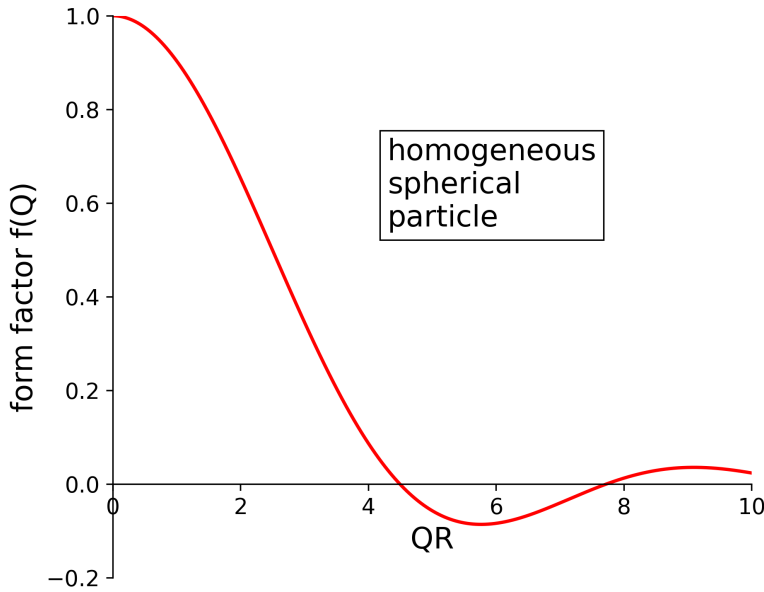


Fig. 5.12: Form-factor for a homogeneous sphere according to 5.44

The dependence on the scattering vector $\mathbf{Q}$ is given by the so-called *Laue function*, which factorizes along to the three directions in space. One factor along one lattice direction $\mathbf{a}$ is plotted in Figure 5.13. The main maxima occur at the positions $Q = n \cdot 2\pi/a$. $Q = n \cdot 2\pi/a = h\mathbf{a}^*$, where $\mathbf{a}^*$ is the reciprocal lattice vector (please see definition of reciprocal lattice at section 5.6.2, here, h , and n are integers.). The maximum intensity scales with the square of the number of periods N^2 , the half width is given approximately by $\Delta Q = 2\pi/(N \cdot a)$. The more periods contribute to coherent scattering, the sharper and higher are the main peaks. Between the main peaks, there are $N - 2$ side maxima. With increasing number of periods N , their intensity becomes rapidly negligible compared to the intensity of the main peaks. The main peaks are of course the well-known *Bragg reflections*, which we obtain for scattering from a crystal lattice. From the position of these Bragg peaks in momentum space, the metric of the unit cell can be deduced (lattice constants a, b, c and unit cell angles α, β, γ). The width of the Bragg peaks is determined by the coherently scattering volume (parameters N, M , and P) - and some other factors for real experiments (resolution, mosaic distribution, internal strains, ...). For large N , the factors in 5.47, approaches a δ function, and the scattering intensity can be written as:

$$I(\mathbf{Q}) \sim |A(\mathbf{Q})|^2 = N|\beta|^2 V_{BZ} \sum_h \delta(\mathbf{Q} - \mathbf{G}_h) \quad (5.48)$$

where V_{BZ} is the Brillouin zone volume. The physical meaning of the 5.48 is that the Bragg reflections occurs when momentum transfer ($\mathbf{Q}$) is equal to the reciprocal lattice vector ($\mathbf{G}$), which is precisely the Laue condition that will be discussed later.

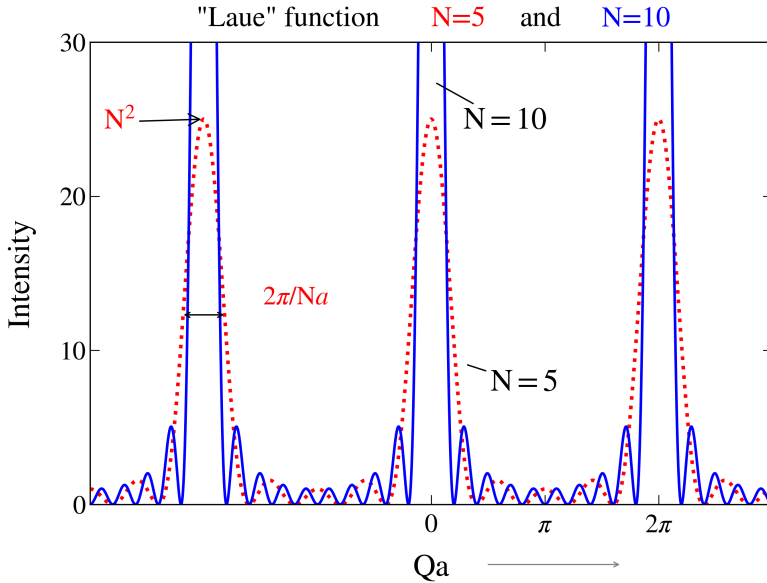


Fig. 5.13: Laue function along the lattice direction $\mathbf{a}$ for a lattice with five and ten periods, respectively.

5.5 Probes for scattering experiments in condensed matter science

In this section, we will discuss which type of radiation is suitable for condensed matter investigations. For neutron beams, we will then discuss the relevant interaction processes with matter in detail.

A list of requirements for the type of radiation used in condensed matter investigations looks as follows:

1. The achievable spatial resolution should be in the order of the inter-particle distances, which implies (see section 5.2) that the wavelength λ is in the order of the inter-particle distance L .
2. If we want to study volume effects, the scattering has to originate from the bulk of the sample, which implies that the radiation should be at most weakly absorbed within matter.
3. For a simple interpretation of the scattering data within the Born approximation (see section 5.2), multiple scattering effects should be negligible, i. e. the interaction of the radiation with matter should be weak.
4. For the sake of simplicity, the probe should have no inner degrees of freedom, which could be excited during the scattering process (i. e. avoid beams of molecules, which have internal vibrational or rotational degrees of freedom).

5. To study magnetic systems, we need a probe which interacts with the atomic magnetic moments in the sample.
6. If, in addition to structural studies, we want to investigate elementary excitations, we would like the energy of the probe to be in the order of the excitation energies, so that the energy change during the scattering process is easily measurable.

This list of requirements leads us to some standard probes in condensed matter research. First of all, electromagnetic radiation governed by the Maxwell equations can be used. Depending on the resolution requirements, we will use x-rays with wavelength λ of about 0.1 nm to achieve atomic resolution or visible light ($\lambda \sim 350 - 700$ nm) to investigate e. g. colloidal particles in solution. Besides electromagnetic radiation, particle waves can be used. It turns out that thermal neutrons with a wavelength ~ 0.1 nm are particularly well adapted to the above list of requirements. The neutron beams are governed by the Schrödinger equation of quantum mechanics. An alternative is to use electrons, which for energies of around 100 keV have wavelengths in the order of 0.005 nm. As relativistic particles, they are governed by the Dirac equation of quantum mechanics. The big drawback of electrons as a condensed matter probe is the strong Coulomb interaction with the electrons in the sample. Therefore, neither absorption, nor multiple scattering effects can be neglected. However, the abundance of free electrons and the relative ease to produce optical elements makes them very suitable for imaging purposes (electron microscopy). Electrons, but also atomic beams, are very powerful tools for surface science: due to their strong interaction with matter, both types of radiation are very surface sensitive. Low Energy Electron Diffraction LEED and Reflection High Energy Electron Diffraction RHEED are both used for in-situ studies of the crystalline structure during thin film growth, e.g. with Molecular Beam Epitaxy MBE. In what follows we will concentrate on neutron scattering as one of the probes, which is best suited for bulk studies on an atomic scale. We will introduce the properties of the neutron, discuss the absorption of neutrons in matter and derive the scattering cross sections for the main interaction processes with matter.

5.6 Introduction to neutron diffraction

As mentioned earlier, any scattering experiment—whether involving massive particles such as neutrons and electrons, or electromagnetic radiation such as X-rays or visible light—can be characterized by four fundamental attributes. These attributes determine both the nature of the scattering process and the type of information that can be obtained:

- **Elastic scattering**, in which the energy of the particle (or quantum) is conserved during the scattering process;
- **Inelastic scattering**, in which the particle gains or loses energy during the interaction;
- **Coherent scattering**, which involves interference effects between waves. According to the wave-particle duality first proposed by de Broglie (1924), each particle can be described by a wave that can interfere with other particle waves;
- **Incoherent scattering**, which occurs without interference effects.

In the following, we will focus exclusively on **neutron diffraction**, which corresponds to **elastic, coherent scattering of neutrons**. It is assumed that most readers are familiar with X-ray diffraction from crystals. First demonstrated by Laue in 1912, X-ray diffraction has since become one of the most powerful techniques for determining the structure of crystalline materials. Diffraction differs fundamentally from imaging techniques such as optical or electron microscopy. In imaging, the spatial resolution is limited to approximately half the wavelength of the radiation used (the Abbe diffraction limit). In contrast, diffraction techniques can provide structural information—such as interatomic distances—on length scales two to three orders of magnitude smaller than the wavelength of the radiation. However, unlike imaging, diffraction requires **three-dimensional periodicity** in the sample.

In the following sections, we will discuss the basic principles and specific features of neutron diffraction from both single crystals and polycrystalline materials. We begin with the geometry of diffraction from crystals, followed by a discussion of diffraction intensities, and conclude with an overview of experimental aspects related to neutron scattering instruments used in practical work. Applications of these methods will be presented at the end of this chapter in the section entitled *Structural Analysis*. The topic of **magnetic neutron diffraction** will also be addressed.

5.6.1 Diffraction geometry

For purely elastic scattering, the scattering function $S(\mathbf{Q}, \omega)$ reduces to the special case of zero energy transfer, i.e.,

$$E_0 = E_1, \quad \hbar\omega = E_0 - E_1 = 0,$$

and equal magnitudes of the incident and scattered wave vectors,

$$|\mathbf{k}| = |\mathbf{k}'|.$$

In this case, the scattering function simplifies to $S(\mathbf{Q}, \omega = 0)$, and the scattering intensity depends only on the scattering vector

$$\mathbf{Q} = \mathbf{k}' - \mathbf{k}.$$

Coherent elastic neutron scattering (i.e., neutron diffraction) provides information on the spatial distribution of atomic nuclei and the arrangement of localized magnetic moments in crystalline solids. It can also be used to determine the pair correlation function in liquids and glasses, as well as the conformation of polymer chains.

Figure 5.14 shows a schematic of a general diffraction experiment. More specifically, it represents a typical setup for a constant-wavelength, angular-dispersive diffraction experiment. Other experimental techniques—such as time-of-flight (TOF), Laue, and energy-dispersive diffraction—also exist, but these are beyond the scope of this introductory lecture. In constant-wavelength diffraction, both the energy (or wavelength) and the direction (collimation) of the incident neutron beam must be well defined. To achieve this, the diffractometer is equipped with a crystal monochromator, which selects a narrow wavelength band ($\lambda \pm \Delta\lambda/\lambda$) from the incident “white” beam. Collimators are used to control the beam direction and divergence, in a manner similar to X-ray diffraction experiments. For crystalline

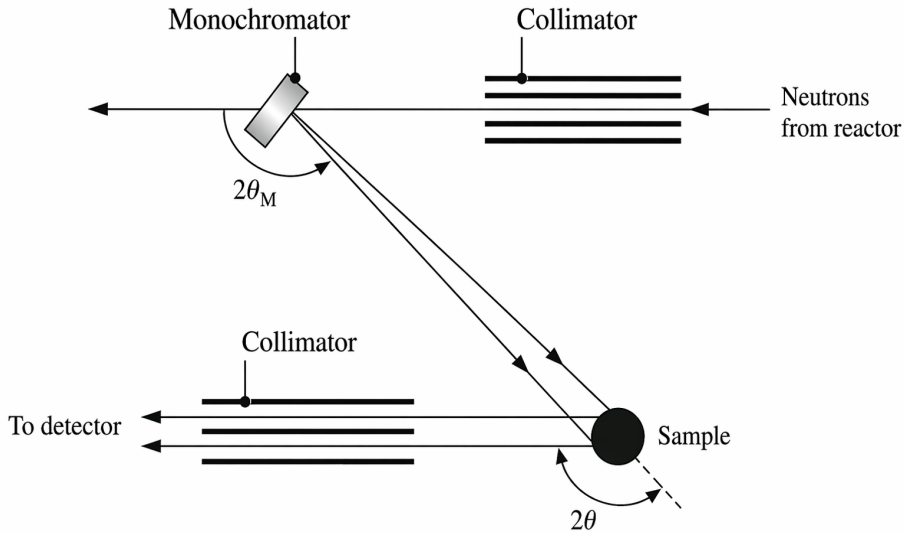


Fig. 5.14: Schematic representation of a constant wavelength powder diffractometer. Adapted from Ref. [23]

samples, the diffraction geometry is most conveniently described using the concepts of the reciprocal lattice and the Ewald construction. These concepts are well known from X-ray diffraction and will be briefly introduced in the following.

5.6.2 Reciprocal lattice

A defining characteristic of the crystalline state (see Chapter 4) is its periodic order, which can be described by a translation lattice. In three dimensions, let $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ denote the primitive lattice vectors of the direct lattice. Each lattice point can then be expressed by a general lattice vector

$$\mathbf{R} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}, \quad (5.49)$$

where n_1 , n_2 , and n_3 are integers (positive, negative, or zero).

The position of atom j within the unit cell is given by

$$\mathbf{r}_j = x_j\mathbf{a} + y_j\mathbf{b} + z_j\mathbf{c}, \quad (5.50)$$

where x_j , y_j , and z_j are fractional atomic coordinates satisfying

$$0 \leq x_j, y_j, z_j < 1.$$

Given a direct lattice defined by vectors $\mathbf{R}$, a vector $\mathbf{G}$ belongs to the reciprocal lattice if and only if

$$e^{i\mathbf{G}\cdot\mathbf{R}} = 1 \quad \text{for all } \mathbf{R}. \quad (5.51)$$

We now make two key statements:

1. The reciprocal lattice defined by this condition is itself a lattice in reciprocal space.
2. The primitive lattice vectors of the reciprocal lattice, denoted by $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$, satisfy

$$\mathbf{a}_i \cdot \mathbf{a}_j^* = 2\pi\delta_{ij}, \quad (5.52)$$

where δ_{ij} is the Kronecker delta.

These reciprocal lattice vectors can be constructed as:

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}, \quad (5.53)$$

$$\mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}, \quad (5.54)$$

$$\mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}. \quad (5.55)$$

It is straightforward to verify that these definitions satisfy the orthogonality condition. For example:

$$\mathbf{a} \cdot \mathbf{a}^* = 2\pi, \quad (5.56)$$

$$\mathbf{b} \cdot \mathbf{a}^* = 0. \quad (5.57)$$

Now, given vectors $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ satisfying Eq. 5.52, we have claimed that these are in fact primitive lattice vectors for the reciprocal lattice. Let us write an arbitrary point in reciprocal space as

$$\mathbf{G} = m_1\mathbf{a}^* + m_2\mathbf{b}^* + m_3\mathbf{c}^* \quad (5.58)$$

In order to fulfill condition $e^{i\mathbf{G}\cdot\mathbf{R}} = 1$, m_1, m_2, m_3 need to be integers. Thus, points in reciprocal lattice are precisely given by equation 5.58. A plane with Miller indices h, k, l , is normal to the reciprocal lattice vector $\mathbf{G} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$

Performing a diffraction experiment on a single crystal can be understood as taking the Fourier transform of a three-dimensionally periodic crystal structure and then evaluating the square of the resulting (complex) amplitude. The Fourier transform of the (infinite) crystal lattice is essentially the reciprocal lattice derived above and yields directly the positions of the reflections in space (directions of the diffracted beams). The Fourier transform of the unit cell contents (kind and positions of all atoms) determines the reflection intensities. These reflection intensities may be envisaged as a weight attached to the nodes of the reciprocal lattice. Doing a (single crystal) diffraction experiment therefore corresponds to measuring the positions and weights of the reciprocal lattice points.

5.6.3 Ewald construction

The concept of the reciprocal lattice provides a convenient geometrical framework for expressing the condition for Bragg diffraction through the so-called Ewald construction. This approach allows a clear visualization of the geometrical aspects of different diffraction methods.

We consider the reciprocal lattice of a crystal and place its origin at $(0, 0, 0)$, i.e. O' . As shown in Fig. 5.15, the wave vector of the incident beam, $\mathbf{k}_0$ (with $|\mathbf{k}_0| = 2\pi/\lambda$), is drawn such that its endpoint lies at the origin and its starting point is at O . A sphere of radius $|\mathbf{k}_0| = 2\pi/\lambda$ is then constructed around O , passing through the origin. This sphere is known as the *Ewald sphere*.

If a reciprocal lattice point (hkl) lies on the surface of the Ewald sphere, the diffraction condition for the corresponding set of lattice planes is fulfilled. The diffracted wave vector $\mathbf{k}$ originates at O and has the same magnitude as the incident wave vector, i.e., $|\mathbf{k}'| = |\mathbf{k}|$. The vector relation is given by

$$\mathbf{k}' = \mathbf{k} + \mathbf{G}, \quad \mathbf{Q} = \mathbf{k}' - \mathbf{k} = \mathbf{G}, \quad (5.59)$$

where $\mathbf{G}$ is a reciprocal lattice vector.

Introducing the scattering angle 2θ (and the Bragg angle θ), one obtains from the geometry

$$2|\mathbf{k}| \sin \theta = |\mathbf{G}|, \quad (5.60)$$

which directly leads to Bragg's law:

$$2d_{hkl} \sin \theta = \lambda, \quad (5.61)$$

using the relation $d_{hkl} = 2\pi/|\mathbf{G}|$.

In single-crystal diffraction, the crystal and therefore its reciprocal lattice is rotated to bring reciprocal lattice points on to the Ewald sphere, thereby satisfying the diffraction condition for measuring intensities $I(\mathbf{G})$.

A geometrical limit arises from the condition $|\mathbf{G}| \leq 4\pi/\lambda$ (diameter of the Ewald sphere), which corresponds to $d_{hkl} \geq \lambda/2$. This defines the so-called *limiting sphere*, centered at the origin of reciprocal space with radius $2\pi/\lambda$. Only reciprocal lattice points within this sphere can be brought into the diffraction condition. Conversely, if $\lambda > 2d_{\max}$ (where $d_{\max}$ is the largest interplanar spacing in the crystal), no reciprocal lattice point can intersect the Ewald sphere. This explains why diffraction of visible light (with $\lambda \sim 5000 \text{ \AA}$) cannot be observed for atomic crystals. The minimum wavelength $\lambda_{\min}$ determines the amount of structural information accessible in a diffraction experiment. Ideally, it should be sufficiently small to allow measurement of all relevant reciprocal lattice points.

In real crystals, diffraction peaks are not infinitely sharp but broadened. This broadening may arise from:

- **Mosaic spread**, i.e., local variations in crystal orientation, leading to angular broadening of $\mathbf{G}$;

- **Strain or compositional inhomogeneity**, resulting in a spread in interplanar spacings $\Delta d/d$ and thus a variation in $|\mathbf{G}|$.

Furthermore, the ideal diffraction geometry is modified by instrumental effects: the incident beam has a finite divergence and wavelength spread, and the detector has a finite acceptance. Increasing beam divergence or wavelength bandwidth enhances intensity but reduces resolution, limiting the ability to separate closely spaced Bragg reflections.

These effects can also be visualized using the Ewald construction. For example, the influence of horizontal beam divergence in single-crystal diffraction is illustrated in Fig. 5.16, assuming strictly monochromatic radiation ($\Delta\lambda/\lambda = 0$). To collect the full intensity of a broadened reflection, an ω -scan is performed, in which the crystal is rotated about an axis perpendicular to the diffraction plane. Integration over the reflection profile yields the integrated intensity.

The Ewald construction is also useful for understanding powder diffraction. An ideal polycrystalline sample consists of a large number of randomly oriented crystallites. As a result, each reciprocal lattice point is distributed over a sphere of radius $|\mathbf{G}| = 2\pi/d_{hkl}$ centered at the origin. The three-dimensional information contained in $\mathbf{G}$ is thereby reduced to one-dimensional information in $|\mathbf{G}|$.

As shown in Fig. 5.17, the intersection of this reciprocal lattice sphere with the Ewald sphere forms a circle, which corresponds to a diffraction cone in real space. These cones (Fig. 5.18) are recorded using point or position-sensitive detectors. The measured data are typically presented as intensity versus scattering angle or momentum transfer Q . All reflections with identical interplanar spacing d_{hkl} overlap completely and cannot be separated experimentally.

5.7 Diffraction intensities

Without knowledge of the phases, an approximate structural model must be assumed, together with a formalism for calculating diffraction intensities. Within the kinematical scattering approximation, this is provided by the structure factor (see below). The model is subsequently refined iteratively to minimize the difference between observed and calculated intensities, a procedure referred to as **structure refinement**.

5.7.1 Structure factor and Bragg intensities

In the kinematical approximation, the amplitude of the incident wave is assumed to be uniform throughout the specimen. This implies a small sample size, weak interaction between radiation and matter, negligible absorption, and the absence of multiple scattering. Furthermore, the diffracted beams are assumed to be much weaker than the incident beam. Under

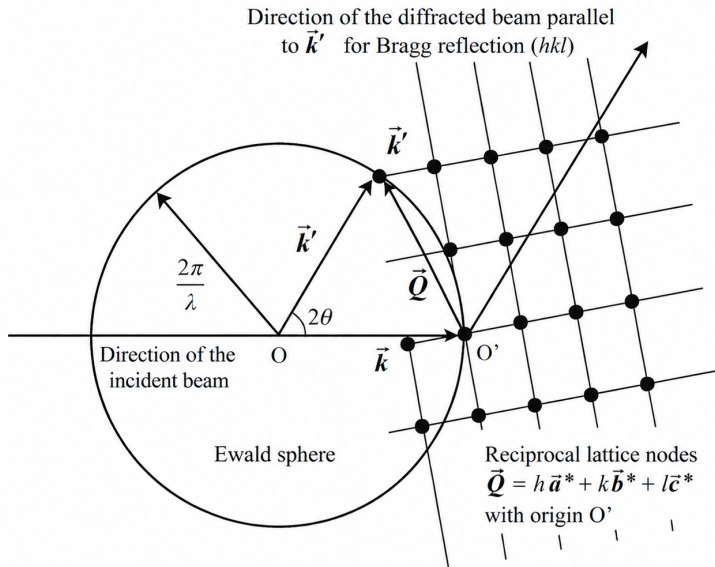


Fig. 5.15: Ewald construction in reciprocal space, showing the diffraction condition for reflection (hkl) , adapted from <https://www.epfl.ch/schools/sb/research/iphs/wp-content/>

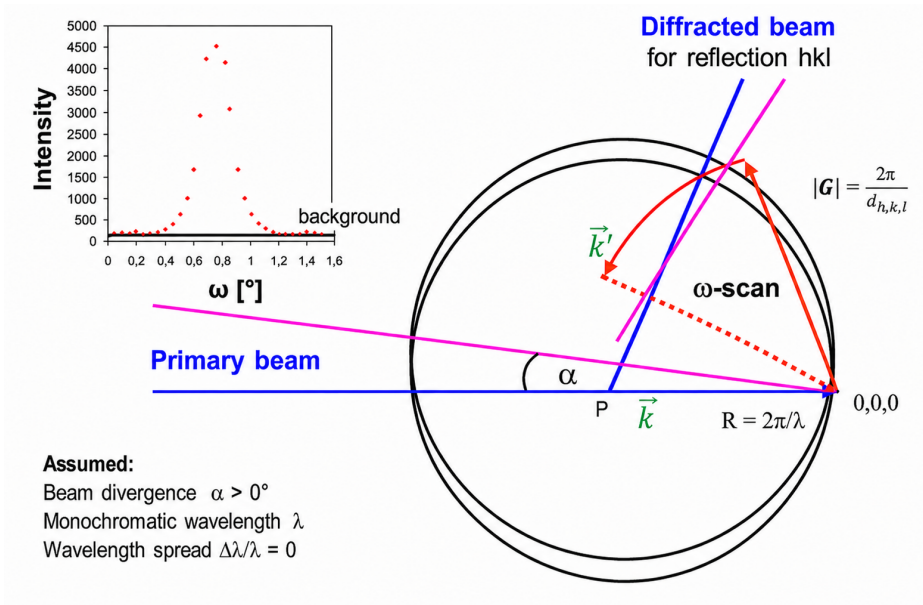


Fig. 5.16: Ewald-construction: Influence of the horizontal beam divergence on the experimental conditions for the measurement of Bragg-intensities. Inset: A typical ω -scan of a reflection.

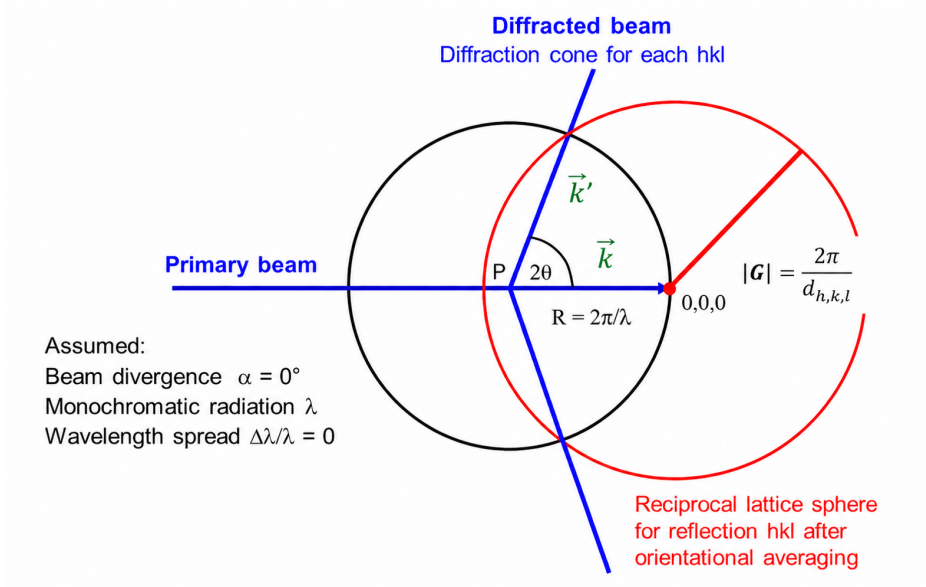


Fig. 5.17: Ewald construction for a powder diffraction experiment.

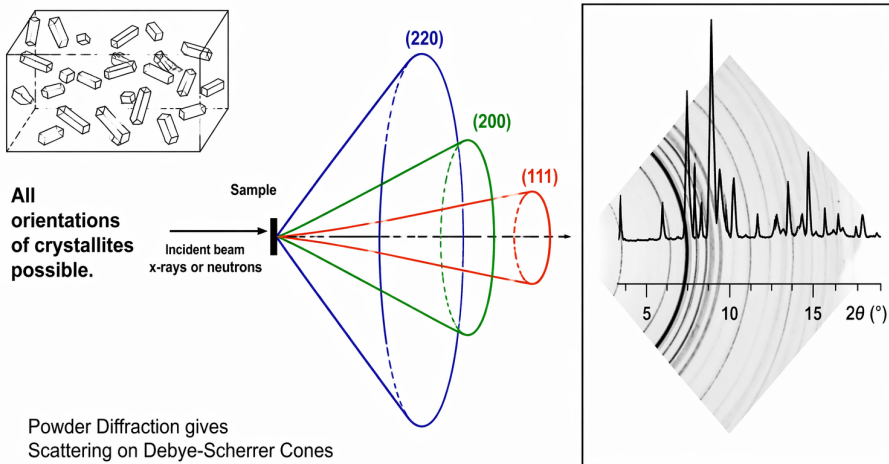


Fig. 5.18: Sketch of a powder diffraction experiment, diffraction cones are recorded on a 2D- or 1D-detector (reproduced from [9]).

these conditions, the diffracted intensity for each reflection is proportional to the square of the amplitude of the scattered wave and may be interpreted as a weight assigned to the reciprocal lattice points:

$$I(\mathbf{G}) \propto |F(\mathbf{G})|^2. \quad (5.62)$$

The structure factor $F(\mathbf{G})$ is the Fourier transform of the scattering density within the unit cell. For a three-dimensional periodic arrangement of discrete atoms, the general Fourier integral reduces to a sum over all atoms j in the unit cell. The structure factor contains complete structural information, including atomic positions $\mathbf{r}_j = x_j\mathbf{a} + y_j\mathbf{b} + z_j\mathbf{c}$, site occupancies, and thermal vibrations:

$$F(\mathbf{G}) = \sum_j b_j \exp [i(\mathbf{G} \cdot \mathbf{r}_j)] T_j. \quad (5.63)$$

In the case of nuclear neutron scattering, the structure factor has the dimension of length, as does the scattering length b_j , which is characteristic of nucleus j . The factor T_j is the Debye–Waller factor, which accounts for thermal and static displacements of atoms:

$$T_j = \exp \left(-B_j \frac{\sin^2 \theta}{\lambda^2} \right), \quad (5.64)$$

where

$$B_j = 8\pi^2 \langle u_j^2 \rangle \quad (5.65)$$

is the isotropic displacement parameter, and $\langle u_j^2 \rangle$ denotes the mean-square displacement of atom j from its equilibrium position. Using fractional coordinates, the phase factor can be written as:

$$\mathbf{G} \cdot \mathbf{r}_j = 2\pi(hx_j + ky_j + lz_j). \quad (5.66)$$

In diffraction experiments, typically only relative intensities are measured. A scale factor (SCALE) accounts for parameters that remain constant across the dataset. Additional corrections, which depend on the scattering angle, must also be applied. For nuclear neutron diffraction from single crystals, the integrated intensity is given by:

$$I(\mathbf{G}) = \text{SCALE} \cdot L \cdot A \cdot E \cdot |F(\mathbf{G})|^2, \quad (5.67)$$

where L is the Lorentz factor, A is the absorption correction, and E is the extinction correction.

Information about the crystal system, Bravais lattice, and lattice parameters ($a, b, c, \alpha, \beta, \gamma$) can be obtained from the reciprocal lattice. In particular, systematic absences (i.e., zero structure factors) can be used to identify non-primitive lattices or symmetry elements with translational components, such as screw axes and glide planes.

As an example, consider a body-centered cubic (bcc) lattice with atoms at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Neglecting the Debye–Waller factor, the structure factor becomes:

$$F(hkl) = b \left[\exp(2\pi i \cdot 0) + \exp \left(2\pi i \left(\frac{h}{2} + \frac{k}{2} + \frac{l}{2} \right) \right) \right]. \quad (5.68)$$

For centrosymmetric structures, the structure factor is real, and the exponential reduces to a cosine:

$$F(hkl) = b [1 + \cos(\pi(h + k + l))]. \quad (5.69)$$

Thus:

- If $h + k + l$ is even, $F = 2b$ (reflection present),
- If $h + k + l$ is odd, $F = 0$ (systematic absence).

These selection rules apply equally to X-ray and neutron diffraction, for both powder and single-crystal data.

For powder samples, orientational averaging reduces the diffraction information from three dimensions to one dimension. The intensity is measured as a function of 2θ , $\sin\theta/\lambda$, or the magnitude of the scattering vector $|\mathbf{G}| = 2\pi/d_{hkl}$. In this case, the intensity expression becomes:

$$I(|\mathbf{G}|) = \text{SCALE} \cdot L \cdot A \cdot E \cdot M \cdot P \cdot |F(\mathbf{G})|^2, \quad (5.70)$$

where M is the multiplicity factor, accounting for the number of symmetry-equivalent reflections, and P is the preferred orientation correction, which accounts for deviations from a random distribution of crystallite orientations.

5.7.2 Nuclear and Magnetic Structure Factors in Neutron Diffraction

Neutrons possess a magnetic moment of $\mu_n = -1.913 \mu_N$ (where μ_N is the nuclear magneton), which enables them to interact not only with atomic nuclei but also with the magnetic moments of electrons. As a result, neutron scattering from a crystal contains two distinct contributions: nuclear scattering and magnetic scattering. The elastic scattering of thermal neutrons by a crystal can therefore be expressed as the sum of these two components:

$$I = I_{\text{nuc}} + I_{\text{mag}}, \quad (5.71)$$

where I_{nuc} and I_{mag} represent the nuclear and magnetic scattering intensities, respectively. Since the scattered intensity is proportional to the square of the structure factor, one can write:

$$|F|^2 = |F_{\text{nuc}}|^2 + q^2 |F_{\text{mag}}|^2, \quad (5.72)$$

where q is the magnetic interaction vector.

The cross-section for the magnetic neutron scattering at the magnetic scattering vector $\mathbf{G}_m$ can be written as [33]:

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{el}}^M = (\gamma r_0)^2 N_M \frac{(2\pi)^3}{v_{0m}} |F_m(\mathbf{G}_m)|^2 \quad (5.73)$$

where

$$\mathbf{F}_m(\mathbf{G}_m) = \mathbf{M}_\perp(\mathbf{G}_m) \sum_j \sigma_j \exp(i\mathbf{G}_m \cdot \mathbf{r}_j) \exp(-w_j)$$

Here, $\gamma r_0 = 5.36 \times 10^{-15}$ m, N_M = Number of magnetic unit cell in the crystal, v_{0m} is the volume of the magnetic unit cell, $\mathbf{G}_m$ is the vector in magnetic reciprocal lattice vector, w_j is the Debye-Waller Factor (DWF).

$$\mathbf{M}_\perp(\mathbf{G}_m) = \hat{\mathbf{G}}_m \times (\mathbf{M}(\mathbf{G}_m) \times \hat{\mathbf{G}}_m)$$

To a good approximation, known as dipole approximation,

$$\mathbf{M}(\mathbf{G}_m) = -g_j \mu_B \mathbf{J} \mathbf{f}(\mathbf{G}_m) = \mathbf{m}(\mathbf{Q}=0) f(\mathbf{G}_m)$$

$$f(Q) = \langle j_0(Q) \rangle + \left(\frac{2 - g_J}{g_J} \right) \langle j_2(Q) \rangle \quad (5.74)$$

$$\langle j_n(Q) \rangle = \int_0^\infty j_n(Qr) r^2 R^2(r) dr, \quad (5.75)$$

where $j_n(Qr)$ is a spherical Bessel function.

$$\text{When } Q = 0, \quad \langle j_0 \rangle = 1, \quad \langle j_2 \rangle = 0, \quad \text{and } M(Q=0) \simeq m. \quad (5.76)$$

g_j is the Landé g-factor. $\sigma_j = \pm 1$ in this case (depending on the relative orientation of the magnetic moment for the collinear magnetic structure) and j denotes magnetic atoms in the magnetic unit cell.

The vector part of the magnetic structure factor can be factored out so that

$$\mathbf{m} = \hat{\mathbf{m}} m, \quad (5.77)$$

where m is now a scalar. The cross-section can be written as:

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega} \right)_{el}^M &= (\gamma r_0)^2 N_M \frac{(2\pi)^3}{v_{0m}} |F_m(\mathbf{G}_m)|^2 \\ &= (\gamma r_0)^2 N_M \frac{(2\pi)^3}{v_{0m}} m^2 f^2(G_m) \left| \hat{\mathbf{G}}_m \times (\hat{\mathbf{m}} \times \hat{\mathbf{G}}_m) \right|^2 \left| \sum \sigma_j \exp(i\mathbf{G}_m \cdot \mathbf{r}_j) \exp(-w_j) \right|^2 \end{aligned}$$

For collinear structures, all the atomic moments are either parallel or antiparallel to $\hat{\mathbf{m}}$, which in this case is independent of $\mathbf{Q}$. The intensity of a magnetic Bragg reflection is proportional to $|M_\perp|^2$, and

$$|\hat{M}_\perp|^2 = 1 - (\hat{\mathbf{m}} \cdot \hat{\mathbf{G}}_m) \quad (5.78)$$

$$= \sin^2 \alpha \quad (5.79)$$

$$= q^2, \quad (5.80)$$

where α is the angle between the moment direction $\hat{\mathbf{m}}$ and the scattering vector $\mathbf{G}_m$ (see Fig. 5.19). The factor $1 - (\hat{\mathbf{m}} \cdot \hat{\mathbf{G}}_m)^2$, often referred to as q^2 , is the means by which the moment direction in a magnetic structure can be determined from intensity measurements.

$$F_{\text{mag}} = \sum_j \sigma_j e^{2\pi i(hx_j + ky_j + lz_j)}, \quad (5.81)$$

Depending on the positions of the magnetic atoms F_{mag} can be easily calculated (ignoring the DW factor). If the intensities are obtained from measurements on polycrystalline samples, then the average of q^2 over all the different $\mathbf{G}_m$ contributing to the powder line must be taken

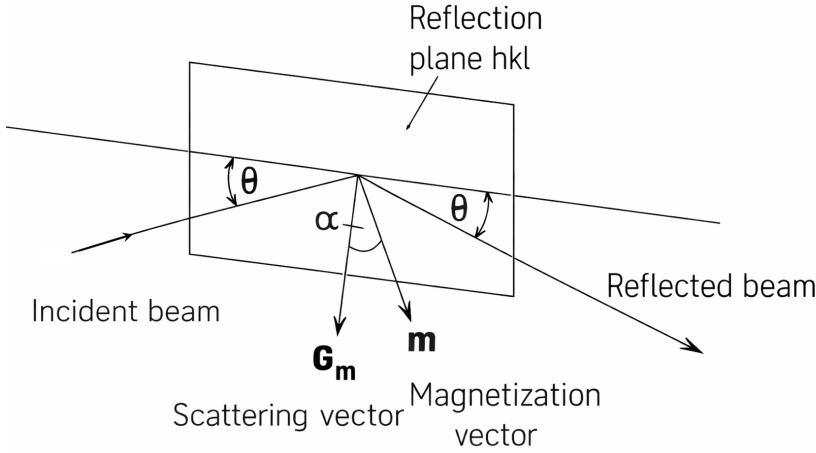


Fig. 5.19: Vector relation between the incident neutron beam, the diffracted beam, the orientation of the reflecting plane, and the magnetization direction. The scattering intensity is proportional to $\sin^2 \alpha$, i.e., the intensity is maximum when the magnetic moments lie in the reflecting (hkl) plane. (reproduced from [31]). In a neutron diffraction experiment, one is sensitive to the moment component perpendicular to the scattering vector $\mathbf{G}_m$

into account. Similarly, the coherent elastic nuclear scattering cross-section can be written as:

$$\left(\frac{d\sigma}{d\Omega}\right)_{elastic}^N = N_N \frac{(2\pi)^3}{v_0} |F_N(\mathbf{G}_N)|^2 \quad (5.82)$$

$$F_N(\mathbf{G}_N) = \sum_j b_j \exp(i\mathbf{G}_N \cdot \mathbf{r}_j) \exp(-w_j)$$

where symbols have usual meaning similar to magnetic scattering and b_j is the nuclear scattering length for the j^{th} ion. Ignoring the DW-factor, the nuclear structure factor has the following simple form:

$$F_N = \sum_j b_j e^{2\pi i(hx_j + ky_j + lz_j)}, \quad (5.83)$$

where b_j is the nuclear scattering length of atom j , and (x_j, y_j, z_j) are the fractional coordinates of the atom in the unit cell. An important feature of neutron nuclear scattering is that the scattering lengths b_j are independent of the scattering angle, in contrast to X-ray scattering.

Form Factor

A quick note on the atomic form factor^a: Neutrons interact with matter through the magnetic dipole moment of unpaired electrons. If the orbital angular momentum is not completely quenched, the magnetic form factor has contributions from both the electron's spin and its orbital motion. In magnetic neutron scattering, only the outermost unpaired electrons—those responsible for magnetism—contribute to the scattering. This is in contrast to X-ray scattering, where all electrons in the atom contribute. As a result, the magnetic neutron form factor decreases more rapidly with increasing momentum transfer than the X-ray form factor. For nuclear scattering, the situation is different. The neutron wavelength is typically several orders of magnitude larger than the nuclear radius, so the nucleus can be treated as a point scatterer. Consequently, there is essentially no form factor decay for nuclear scattering. The form-factor fall off is depicted in the following figure.

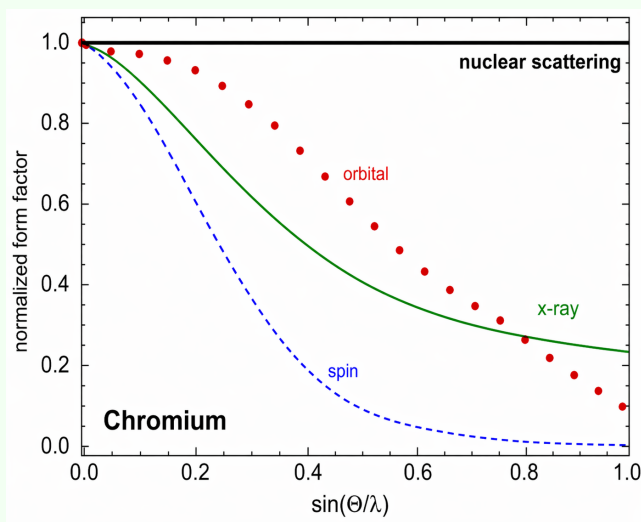


Fig. 5.20: This figure shows the normalized form factors for chromium as a function of scattering variable $\sin(\Theta/\lambda)$, comparing different scattering mechanisms. [11]

^a The atomic form factor in X-ray/ neutron scattering describes the scattering from the electron/ magnetic density around an atom, whereas in SAXS and SANS the form factor describes the scattering arising from the overall size, shape, and internal scattering-length-density distribution of larger objects such as nanoparticles, polymers, or pores.

5.7.3 Comparison with X-ray Structure Factor

For comparison, the structure factor in X-ray diffraction is given by:

$$F_{\text{X-ray}} = \sum_j f_j^X e^{2\pi i(hx_j + ky_j + lz_j)}, \quad (5.84)$$

where f_j^X are the atomic form factors describing the electron density distribution and is shown in the form factor figure above.

5.7.4 Physical Significance

The key distinction between neutron and X-ray diffraction lies in their sensitivity:

- Neutron diffraction probes nuclear positions and magnetic moments.
- X-ray diffraction probes the electron density distribution (except magnetic x-ray scattering, the reader is encouraged to read Ref. [37] for details of magnetic x-ray scattering).

Magnetic neutron diffraction is particularly powerful because it allows direct determination of:

- The arrangement and orientation of magnetic moments,
- The magnetic unit cell and propagation vector,
- The magnitude of ordered magnetic moments,
- The spatial distribution of unpaired electrons.

Thus, neutron diffraction provides a unique and indispensable tool for studying magnetic structures in crystalline materials.

5.7.5 Intensity Corrections in Diffraction Experiments

Absorption Correction

Absorption refers to the attenuation of the incident and diffracted neutron beam as it passes through the sample. The extent of absorption depends on the linear absorption coefficient (μ), the sample geometry, and the path length of neutrons within the material. Since neutrons traverse different distances depending on the scattering angle and crystal shape, the measured intensity can vary accordingly. The transmission factor is given by:

$$A = \frac{I}{I_0} = \frac{1}{V} \int_V \exp(-\mu l) dv \quad (5.85)$$

where I_0 and I are the incident and transmitted intensities, l is the neutron path length, and V is the sample volume. Absorption corrections become necessary when the factor $e^{-\mu l}$ deviates significantly from unity.

In neutron diffraction, absorption is often weak ($\mu R < 1$) and may be neglected. However, for strongly absorbing materials (e.g., containing Eu, Gd, Sm, Dy), absorption effects are significant and must be corrected. The magnitude of absorption also depends strongly on sample shape, and optimized geometries such as annular cylindrical holders can substantially improve transmission and reduce intensity loss.

Extinction Correction

Extinction is a reduction in the observed intensity of Bragg reflections caused by multiple scattering within the crystal. Due to the relatively low absorption of neutrons, they penetrate deeply into the sample, increasing the likelihood of repeated scattering events. When a diffracted beam undergoes further reflections from the same set of lattice planes, it can interfere with the primary (incident) beam, leading to a reduction in intensity. This results in an effective screening of deeper crystal regions. Two types of extinction are distinguished:

- **Primary extinction:** occurs within a single, nearly perfect crystal domain (mosaic block) due to coherent multiple scattering.
- **Secondary extinction:** arises from interactions between beams scattered by different mosaic blocks, reducing the intensity reaching deeper regions.

Extinction primarily affects strong reflections, leading to systematic underestimation of their intensities. It is minimized in small or imperfect crystals and is largely absent in powder diffraction, where crystallites are sufficiently small.

Lorentz Factor

The Lorentz factor is a geometrical correction that accounts for how diffraction intensities are measured and integrated in reciprocal space. It arises because Bragg reflections have a finite width, and the observed intensity corresponds to an integration over the angular range during which the diffraction condition is satisfied. The exact form of the Lorentz factor depends on the experimental geometry and measurement method.

Lorentz Factor in Single-Crystal Diffraction

In single-crystal, constant wave-length diffraction, a Bragg reflection is observed by rotating (rocking) the crystal so that the reciprocal lattice point passes through the Ewald sphere. Because the diffraction condition is satisfied only over a finite angular range, the measured intensity depends on how long the reflection remains in the diffracting condition. This leads to the Lorentz factor:

$$L_{\text{single}} \propto \frac{1}{\sin 2\theta} \quad (5.86)$$

This correction ensures that reflections measured at different scattering angles are properly normalized, removing geometrical biases from the measured intensities.

Lorentz Factor in Powder Diffraction

In powder diffraction, additional geometrical factors arise due to the random orientation of crystallites. For a given (hkl) reflection, only a fraction of grains satisfies the Bragg condition, and this fraction is proportional to the circumference of the Debye–Scherrer cone, which scales as $\cos \theta$. Furthermore:

- The detector captures only a fraction of the diffracted intensity, introducing a factor proportional to $1/\sin 2\theta$.
- Integration over the finite width of the Bragg peak contributes an additional factor of $1/\sin 2\theta$.
- Equivalent planes contribute via the multiplicity factor m_{hkl} .

Combining these contributions, the Lorentz factor for powder diffraction is given by [34]:

$$L_{\text{powder}} \propto \frac{m_{hkl} \cos \theta}{\sin^2 2\theta} = \frac{m_{hkl}}{2 \sin \theta \sin 2\theta} \quad (5.87)$$

This correction ensures that measured intensities are properly normalized to reflect the intrinsic structure factor, independent of crystallite orientation and experimental geometry. For the time of flight neutron powder diffraction experiment the Lorentz factor is different and the reader is encouraged to read Refs. [23, 35].

5.8 Diffractometers

Monochromator and collimator

In constant-wavelength diffraction, both the energy (wavelength) and the direction (collimation) of the incident neutron beam must be well defined. For this purpose, the diffractometer is equipped with a crystal monochromator, which selects a narrow wavelength band ($\lambda \pm \Delta\lambda/\lambda$) from the incident “white” beam according to Bragg’s law for the monochromator reflection (hkl):

$$2d_{hkl} \sin \theta_{hkl} = \lambda, \quad (5.88)$$

where d_{hkl} is the interplanar spacing and $2\theta_{hkl} = 2\theta_M$ is the monochromator scattering angle.

The relative wavelength spread $\Delta\lambda/\lambda$, which determines the resolution in momentum transfer Q , depends on several factors: the beam divergences before and after the monochromator (defined by the collimations α_1 and α_2), the mosaic spread of the monochromator crystal, and the monochromator angle $2\theta_M$.

To increase the intensity of the monochromatic beam at the sample position, the monochromator crystal is often bent in the vertical direction, i.e., perpendicular to the diffraction plane. This increases the vertical beam divergence and thereby enhances the neutron flux, but at the expense of reduced resolution in reciprocal space.

The diffracted intensity from the sample is measured as a function of the scattering angle 2θ and, in the case of single crystals, the sample orientation. The scattering angle is defined by the collimation system placed in front of the detector.

Since no energy analysis of the scattered beam is performed in a two-axis diffractometer, the energy resolution $\Delta E/E$ is not well defined and is typically of the order of a few percent. Consequently, in addition to the dominant elastic scattering, quasi-elastic and some inelastic scattering contributions are also detected.

Neutron filters and the problem of $\lambda/2$ contamination

Unfortunately, monochromator crystals do not only select the desired wavelength λ via diffraction from a given set of lattice planes (hkl), but also reflect higher-order wavelengths such as $\lambda/2$, $\lambda/3$, etc., originating from the planes $(2h, 2k, 2l)$, $(3h, 3k, 3l)$, and so on, at the same diffraction angle. This follows directly from Bragg's law:

$$\sin \theta = \frac{\lambda}{2d_{hkl}} = \frac{\lambda/2}{2d_{2h,2k,2l}} = \frac{\lambda/3}{2d_{3h,3k,3l}}. \quad (5.89)$$

The only requirement for such higher-order reflections is that the corresponding structure factors are sufficiently large. As a consequence, higher-order wavelength contamination can lead to significant intensities at otherwise forbidden reflection positions. In addition, it can alter the measured intensities at allowed reflections. This effect may seriously compromise the correct determination of the unit cell parameters and the space group symmetry, particularly when relying on systematic absences.

To mitigate this problem, higher-order contamination (especially $\lambda/2$) must be reduced. This is typically achieved using wavelength filters that suppress shorter wavelengths more effectively than the desired wavelength. One approach employs resonance absorption filters, analogous to the suppression of the K_β line in X-ray diffraction.

Another commonly used method exploits the scattering properties of materials such as beryllium or graphite. These filters rely on the fact that no Bragg diffraction occurs when

$$\lambda > 2d_{\max}, \quad (5.90)$$

where $d_{\max}$ is the largest interplanar spacing of the filter material. In this regime, the Ewald sphere is too small to intersect any reciprocal lattice point, and therefore no diffraction occurs. For shorter wavelengths ($\lambda < 2d_{\max}$), the neutron beam is attenuated due to Bragg scattering within the filter material. This property is used to effectively suppress higher-order wavelength components. Commonly used filter materials include polycrystalline beryllium and graphite. Due to their lattice parameters, they are particularly suitable for experiments with cold neutrons, as they efficiently suppress wavelengths shorter than approximately 3.5 Å and 6 Å, respectively.

Resolution function:

An important characteristic of any diffractometer is its angular resolution. Fig. 5.21 shows the resolution function (reflection half width as a function of scattering angle) for the four circle single crystal neutron diffractometer HEiDi at FRM II. The resolution depends on a number of factors, among them the collimation, the monochromator type and quality, the 2θ and (hkl) of the reflection used for monochromatization etc.

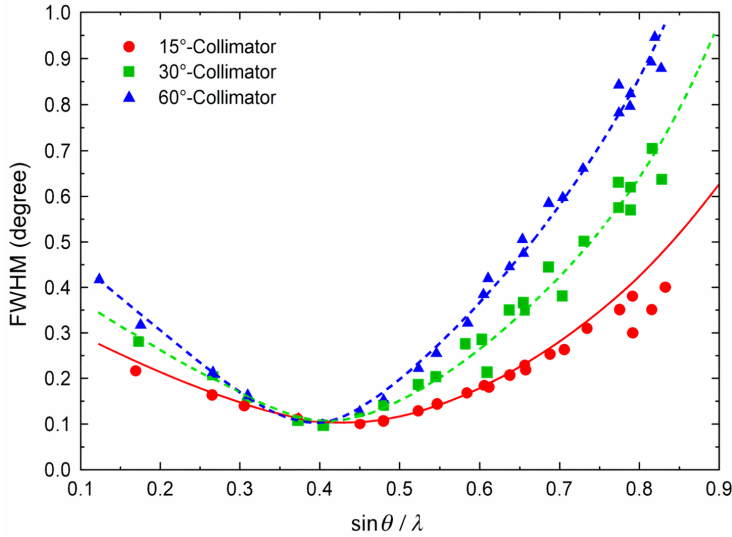


Fig. 5.21: Resolution function of HEiDi for different collimations, monochromator: Cu (220), $2\text{Mono} = 40^\circ \rightarrow \lambda = 0.873 \text{ \AA}$ [11]

5.9 Introduction to Structural and Magnetic Analysis by Diffraction

The analysis of crystal structures and magnetic ordering is primarily based on diffraction phenomena arising from the interaction of matter with radiation such as X-rays, neutrons, or electrons. Although modern electron microscopy techniques, such as high-resolution transmission electron microscopy (HRTEM), can achieve atomic resolution, a detailed and quantitative determination of three-dimensional (3D) atomic arrangements, magnetic structures, and spin density distributions is most effectively obtained using diffraction methods.

In general terms, diffraction corresponds to coherent and elastic scattering of radiation. The fundamental theoretical framework used for structural analysis, namely the kinematical theory of diffraction, is broadly applicable to all types of radiation. However, due to the different physical properties of X-rays, neutrons, and electrons, and their distinct interactions with matter, these techniques provide complementary information.

For X-rays and thermal neutrons, the wavelengths are comparable, typically in the range $0.5 \text{ \AA} < \lambda < 2.4 \text{ \AA}$. Despite this similarity, their scattering mechanisms differ significantly. X-rays, being electromagnetic radiation, interact with the electron cloud of atoms and thus probe the electron density distribution within a crystal. In contrast, neutrons interact with atomic nuclei, providing sensitivity to the nuclear structure, and additionally couple to magnetic moments, making them uniquely suited for probing magnetic structures and magnetization densities associated with unpaired electrons.

X-ray diffraction, using either laboratory sources or synchrotron radiation, is the most widely employed technique for crystal structure determination. However, neutron diffraction is indis-

pensable in many cases, particularly when studying light elements, distinguishing isotopes, or investigating magnetic ordering.

5.10 Basic Principles of Structural Analysis: Example of Iron-Based Superconductors

The discovery of iron-based superconductors in 2008 opened a new and exciting field in condensed matter physics. Unlike conventional superconductors, where electron pairing is mediated by phonons, iron-based superconductors exhibit a strong interplay between magnetism, electronic correlations, and structural degrees of freedom. Among the various families, the so-called “122” compounds, with chemical formula $A\text{Fe}_2\text{As}_2$ ($A = \text{Ba}, \text{Sr}, \text{Ca}$), have been extensively studied due to the availability of high-quality single crystals and their rich phase diagrams.

BaFe_2As_2 is a prototypical parent compound of this family. At high temperatures, it crystallizes in a tetragonal structure (space group $I4/mmm$). Upon cooling, it undergoes a structural phase transition to an orthorhombic phase, accompanied or closely followed by the onset of antiferromagnetic order. The magnetic structure is characterized by a stripe-like arrangement of Fe moments. Superconductivity can be induced by chemical doping (e.g., Co, Ni, K, or P substitution) or by applying external pressure, which suppresses the magnetic and structural transitions and leads to superconductivity with transition temperatures up to ~ 38 K.

In this section, we highlight the basic principles of structural analysis using iron-based superconductors as a representative example. These materials can be synthesized both as single crystals and as polycrystalline (powder) samples, and their structural characterization forms the basis for understanding their physical properties.

A fundamental aspect of materials characterization is the assessment of sample quality. Key questions include:

- **Phase purity:** Are there any impurity phases present?
- **Crystal structure:** What is the symmetry and atomic arrangement?
- **Degree of crystallinity:** How well ordered is the sample?

The most straightforward and widely used technique to address these questions for polycrystalline samples is powder X-ray diffraction (PXRD), which can be performed rapidly using laboratory-based X-ray sources. The resulting diffraction pattern serves as a fingerprint of the material and allows identification of crystalline phases through comparison with reference data.

For high-quality single crystals, single-crystal X-ray diffraction provides detailed information about the atomic structure, including precise lattice parameters and atomic positions. This approach was crucial in the early studies of BaFe_2As_2 , where accurate structural determination laid the foundation for understanding its electronic and magnetic properties. Diffraction

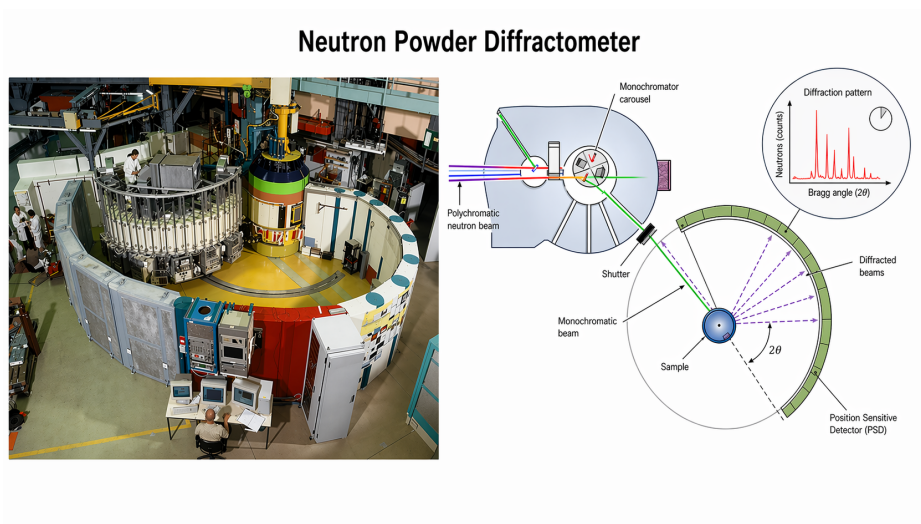


Fig. 5.22: Neutron powder diffractometer D20 at ILL, Grenoble. Left: Comparison between a real neutron diffractometer and its schematic representation (right), illustrating beam conditioning, sample environment, and detection geometry with position sensitive detector (PSD). Adapted from <https://www.ill.eu>.

techniques, both for powders and single crystals, provide the essential starting point for investigating novel materials. They establish the structural framework upon which further studies, such as magnetic neutron diffraction and transport measurements, can be built, enabling a comprehensive understanding of the interplay between structure, magnetism, and superconductivity in iron-based compounds.

5.10.1 Crystal structure analysis using powder x-ray and neutron diffraction (Example of BaFe_2As_2)

Powder X-ray Diffraction of BaFe_2As_2

Powder X-ray diffraction (PXRD) is a fundamental technique used to determine the crystal structure and assess the phase purity of polycrystalline materials. In the case of BaFe_2As_2 , a parent compound of iron-based superconductors, PXRD provides essential information about structural symmetry, lattice parameters, and sample quality. At room temperature, BaFe_2As_2 crystallizes in the tetragonal ThCr_2Si_2 -type structure with space group $I4/mmm$. In this structure (as shown in the inset of Fig. 5.23), Ba atoms occupy the corners of the unit cell, Fe atoms form a square planar lattice, and As atoms are located above and below the Fe plane, forming FeAs_4 tetrahedra. The layered arrangement of FeAs slabs separated by Ba layers

Table 5.1: Crystal structure and refinement parameters of BaFe_2As_2 at 297 K ($I4/mmm$, $Z = 2$). $a = b = 3.9625(1)$ Å, $c = 13.0168(3)$ Å, $V = 204.38(1)$ Å³. Data points: 8700; reflections: 50; atomic parameters: 4; profile parameters: 4; d -range: 0.979–6.508 Å. Reliability factors: $R_p = 0.0273$, $wR_p = 0.035$, $R(F^2) = 0.0522$, $\chi^2 = 1.431$. The table is adapted from Ref. [25].

Atom (Site)	x	y	z	U_{iso} (Å ²)
Ba ($2a$)	0	0	0	0.0095(5)
Fe ($4d$)	$\frac{1}{2}$	0	$\frac{1}{4}$	0.0057(6)
As ($4e$)	0	0	0.3545(1)	0.0099(5)

plays a crucial role in determining the electronic and magnetic properties of the material. In a PXRD experiment, a finely ground sample is irradiated with monochromatic X-rays, and the diffracted intensity is recorded as a function of the scattering angle (2θ). The resulting diffraction pattern consists of Bragg peaks corresponding to different crystallographic planes. Using Bragg's law,

$$n\lambda = 2d \sin \theta, \quad (5.91)$$

the interplanar spacings (d -values) can be determined and indexed.

Phase purity for the BaFe_2As_2 was examined by high-resolution PXRD measurements using a Huber G670 Guinier imaging plate diffractometer, employing Cu-K_I radiation and a Ge(111) monochromator [25]. The instrument was equipped with a closed-cycle helium cryostat to allow temperature-dependent measurements. The diffraction data were analyzed by Rietveld refinement using the GSAS software package, where the peak profiles were modeled using Thompson–Cox–Hastings pseudo-Voigt functions with asymmetry corrections.

The measured diffraction pattern, as shown in Fig. 5.23, of BaFe_2As_2 could be completely fitted using a single-phase structural model, as demonstrated by the excellent agreement between observed and calculated intensities. No additional reflections attributable to secondary phases were detected within the resolution limits of the measurement. Any possible impurity contributions were estimated to be below approximately 1%, indicating high phase purity of the sample. The structural parameters from the refinement is shown in Table 5.1.

Rietveld analysis

Rietveld analysis provides a quantitative way to extract structural information from powder diffraction data, even when individual reflections cannot be resolved. The conversion from 3D- to 1D-intensity data caused by the averaging over all crystallite orientations in a powder sample severely restricts the informative value of powder neutron (or x-ray) diffraction experiments and makes the resolution function of the instrument even more important than in the single crystal case. Even with optimized resolution, the severe overlap of reflections on the 2θ -axis often prohibits the extraction of reliable integrated intensities from the experiment. Instead, the Rietveld method, also referred to as full pattern refinement, is used to refine a given structural model against powder diffraction data. The method, which is widely used in powder x-ray diffraction, has actually been invented by Hugo Rietveld in 1969 [10] for the structural analysis from

powder neutron data. Full pattern refinement means that along with the structural parameters (atomic coordinates, thermal displacements, site occupations) which are also optimized in a single crystal structure refinement, additional parameters like the shape and width of the reflection profiles and their 2θ -dependence, background parameters, lattice parameters etc. need to be refined.

In the Rietveld method, the refined parameters include not only the structural parameters, such as atomic positions, lattice constants, site occupancies, and thermal displacement parameters, but also profile-related parameters such as peak shape, peak width, background, scale factor, and instrumental resolution parameters. The refinement is performed by minimizing the weighted least-squares function

$$S = \sum_i w_i [y_i^{\text{obs}} - y_i^{\text{calc}}]^2, \quad (5.92)$$

where y_i^{obs} is the observed intensity at the i th data point, y_i^{calc} is the calculated intensity, and w_i is the statistical weight assigned to that point. For counting-statistics-limited data, the weight is often approximated as

$$w_i = \frac{1}{y_i^{\text{obs}}}. \quad (5.93)$$

The calculated intensity at each point in the diffraction pattern is obtained by summing the contributions from all Bragg reflections k and the background:

$$y_i^{\text{calc}} = s \sum_{hkl} [m_k L_k |F_k|^2 f(2\theta_i^k) + y_i^{\text{bkg}}], \quad (5.94)$$

where s is a scale factor, m_k is the multiplicity of the reflection, L_k is the Lorentz factor, F_k is the structure factor, $f(2\theta_i^k)$ is the peak-shape function, and y_i^{bkg} is the background intensity. $2\theta_i$ is the scattering angle for the i th step and $2\theta_k$ is twice the Bragg angle for the k th reflection. For a constant-wavelength neutron diffractometer, the peak shape may often be approximated by a Gaussian function:

$$f(2\theta_i^k) = \frac{2}{H_k} \sqrt{\frac{\ln 2}{\pi}} \exp \left[-\frac{4 \ln 2 (2\theta_i - 2\theta_k)^2}{H_k^2} \right], \quad (5.95)$$

where H_k is the full width at half maximum (FWHM) of the k th reflection. The angular dependence of the peak width is commonly described by the Caglioti's relation:

$$H_k^2 = U \tan^2 \theta + V \tan \theta + W, \quad (5.96)$$

where U , V , and W are refinable parameters that describe instrumental and sample-related peak broadening. The quality of a Rietveld refinement is commonly assessed using reliability factors. One of the most important is the weighted profile factor,

$$R_{wp} = \left[\frac{\sum_i w_i (y_i^{\text{obs}} - y_i^{\text{calc}})^2}{\sum_i w_i (y_i^{\text{obs}})^2} \right]^{1/2}. \quad (5.97)$$

Another useful quantity is the goodness of fit,

$$\chi^2 = \frac{\sum_i w_i (y_i^{\text{obs}} - y_i^{\text{calc}})^2}{N - P}, \quad (5.98)$$

where N is the number of data points and P is the number of refined parameters. A satisfactory refinement should yield a small value of R_{wp} and a goodness of fit close to unity, provided that the errors are properly estimated. The expected profile factor is given by

$$R_{\text{exp}} = \left[\frac{N - P}{\sum_i w_i (y_i^{\text{obs}})^2} \right]^{1/2}. \quad (5.99)$$

The ratio

$$\chi^2 = \left(\frac{R_{wp}}{R_{\text{exp}}} \right)^2 \quad (5.100)$$

is also commonly used as a measure of refinement quality and should approach the value of unity. R_{wp} should be close to the statistically expected R value i.e. for a good Rietveld refinement [23].

Important Points

The Rietveld method is powerful because it uses the full diffraction pattern rather than individual integrated intensities. This makes it especially useful for powder diffraction data, where overlapping Bragg reflections are common. In a typical Rietveld refinement, one refines: scale factor, background parameters, lattice parameters, atomic positions, site occupancies, thermal displacement parameters, peak-shape parameters, peak-width parameters, preferred orientation parameters, if required.

Neutron Powder Diffraction of BaFe₂As₂

Neutron powder diffraction (NPD) provides complementary information to PXRD, particularly due to its sensitivity to atomic nuclei and magnetic moments. Neutron diffraction measurements on BaFe₂As₂ were carried out using neutrons with a wavelength of $\lambda = 2.079$ Å on the high-resolution powder diffractometer BT1 at the NIST Center for Neutron Research (NCNR) [30]. A typical neutron powder diffraction setup, along with its corresponding schematic diagram, is shown in Fig. 5.22. The sample temperature was controlled using a closed-cycle refrigerator.

At high temperature (e.g., 175 K), the diffraction pattern as shown in Fig. 5.24 is well described by the tetragonal $I4/mmm$ structure, consistent with PXRD results. The structural refinement requires only a small number of parameters, including the z position of the As atoms and isotropic thermal displacement parameters. The agreement between neutron and X-ray diffraction results as shown in Table 5.1 and Table 5.2 is excellent, confirming the robustness of the structural model. It should be noted that thermal displacement parameters

Table 5.2: Structural and magnetic parameters of BaFe₂As₂ according to Ref. [30].**(a) 175 K, tetragonal phase (*I*4/*mmm*, No. 139)**

$a = b = 3.95702(4)$ Å, $c = 12.9685(2)$ Å; $R_p = 4.71\%$, $wR_p = 6.06\%$, $\chi^2 = 1.109$.

Atom	Site	x	y	z	B (Å ²)
Ba	$2a$	0	0	0	0.53(5)
Fe	$4d$	$\frac{1}{2}$	0	$\frac{1}{4}$	0.72(2)
As	$4e$	0	0	0.35405(8)	0.80(3)

(b) 5 K, orthorhombic phase (*Fmmm*, No. 69)

$a = 5.61587(5)$ Å, $b = 5.57125(5)$ Å, $c = 12.9428(1)$ Å; $R_p = 3.61\%$, $wR_p = 4.58\%$, $\chi^2 = 1.825$.

Atom	Site	x	y	z	B (Å ²)	M_x (μ_B)
Ba	$4a$	0	0	0	0.20(4)	
Fe	$8f$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0.35(2)	0.87(3)
As	$8i$	0	0	0.35406(7)	0.47(3)	

are sometimes expressed in different notations, related by:

$$B = 8\pi^2 U_{\text{iso}}. \quad (5.101)$$

A key difference between neutron and X-ray diffraction lies in the scattering mechanism. While X-rays probe the electron density, neutrons scatter from atomic nuclei and magnetic moments. As a result, neutron diffraction intensities do not decrease as rapidly at high scattering angles as in X-ray diffraction, where the atomic form factor leads to a significant intensity fall-off. This difference is clearly observed when comparing PXRD and NPD patterns of BaFe₂As₂: neutron diffraction retains significant intensity at high angles, whereas X-ray diffraction intensities are strongly suppressed due to the electron form factor.

Crystal structure analysis using single crystal x-ray and neutron diffraction

In principle, the crystal structure can be analyzed using single crystal x-rays and neutron diffraction methods. In both the techniques a large number of Bragg peak intensities are collected at a specified temperature and further analyzed using the crystal structure model.

Single-Crystal x-ray diffraction on BaFe₂As₂

Single-crystal X-ray diffraction (SCXRD), which is one of the most widely used and accessible techniques for structural characterization. Unlike neutron diffraction, SCXRD can

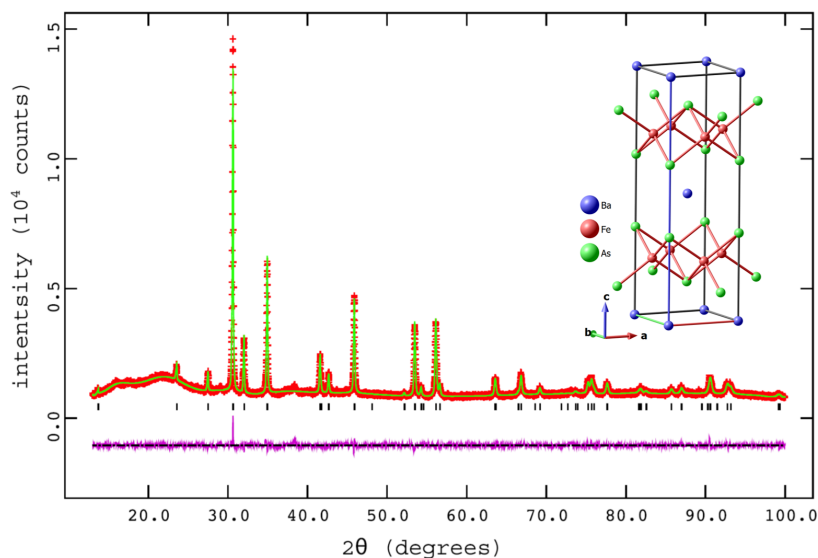


Fig. 5.23: X-ray powder diffraction pattern (+) and Rietveld refinement fit of BaFe_2As_2 at 297 K (space group $I4/mmm$). Reprinted from Ref. [25]. Copyright by the American Physical Society. Inset: BaFe_2As_2 crystal structure with space group $I4/mmm$.

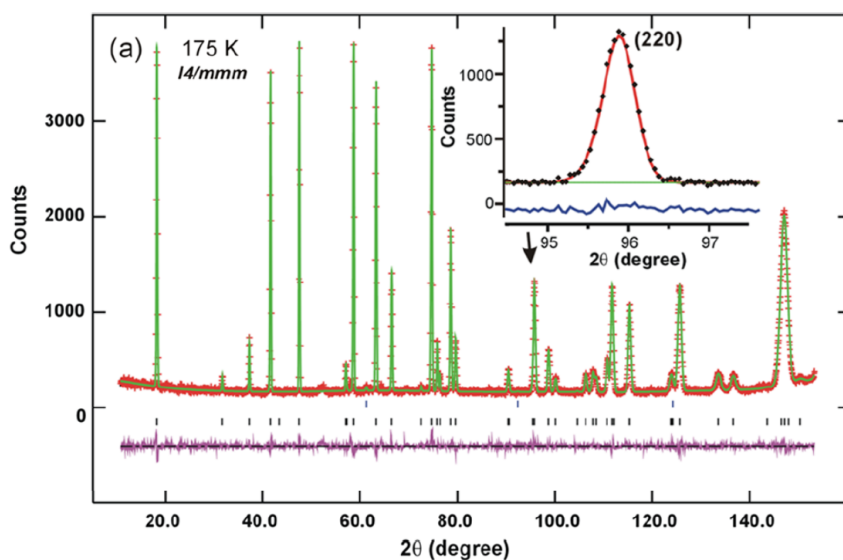


Fig. 5.24: Neutron powder diffraction spectra at 175 K and is shown. The high-temperature data are refined using the tetragonal $I4/mmm$ structure. Reprinted from Ref. [30]. Copyright by the American Physical Society.

be routinely performed in laboratory environments using commercial diffractometers such as those from Rigaku or Oxford Diffraction. Moreover, SCXRD requires only a very small crystal volume, making it particularly suitable for newly synthesized materials. Single-crystal X-ray diffraction is a powerful method for determining the crystal structure, atomic positions, and symmetry of crystalline materials. For example, the SuperNova system is equipped with a micro-focus X-ray source (typically Mo $K\alpha$, Cu $K\alpha$, or Ag radiation), providing high brilliance and stability. The X-ray beam is focused and monochromated using multilayer mirror optics, resulting in a well-defined and intense beam suitable for weakly diffracting samples. During the experiment, a single crystal of BaFe_2As_2 is mounted on a multi-axis goniometer and precisely aligned in the incident X-ray beam. As the crystal is rotated, diffraction spots corresponding to different lattice planes are recorded, satisfying Bragg's law:

$$n\lambda = 2d \sin \theta. \quad (5.102)$$

The diffracted intensities are collected using a CCD or hybrid pixel area detector, allowing rapid acquisition of diffraction data over a wide range of reciprocal space. Dedicated software, such as CRYBALISPRO, is used for indexing, integration, and scaling of the diffraction data. Following data collection, the measured intensities are corrected for absorption, Lorentz, and polarization effects and converted into structure factors. The crystal structure is then solved using methods such as direct methods or Patterson techniques and refined using least-squares procedures (e.g., SHELX or OLEX2) to obtain precise atomic coordinates, thermal displacement parameters, and reliability factors.

Figure 5.25 shows representative diffraction images of single crystalline BaFe_2As_2 collected at different temperatures using a CCD detector. The diffraction images clearly demonstrate the high crystalline quality of the sample through sharp and well-defined Bragg peaks. At low temperature, the splitting of peaks is observed, indicating the structural phase transition from tetragonal to orthorhombic symmetry. Such measurements provide direct insight into structural distortions and symmetry breaking, which are closely linked to the magnetic and electronic properties of iron-based superconductors. Furthermore, single crystal data can be analyzed using different crystal structure models as it has been done by Rotter *et al.* [36] for crystal growth of BaFe_2As_2 from a Sn flux. It was found that a few percentage of Sn was incorporated into the crystal structure and occupy As 4e Site.

Single-Crystal Neutron Diffraction on BaFe_2As_2 (D9, ILL)

For the single crystal neutron diffraction measurements, a high-quality single crystal of BaFe_2As_2 was grown using the self-flux method. The crystal quality was confirmed by preliminary characterization, ensuring suitability for neutron diffraction measurements. Single-crystal neutron diffraction experiments were performed on the four-circle diffractometer D9 at the Institut Laue-Langevin (ILL), Grenoble [32]. A schematic diagram of a four-circle diffractometer, along with a photograph of the instrument, is shown in Fig. 5.26. The instrument operates on a hot neutron source at the high-flux reactor, providing high-intensity monochromatic neutron beams suitable for precise structural refinements. The sample was mounted in a closed-cycle refrigerator, allowing measurements at controlled temperatures,

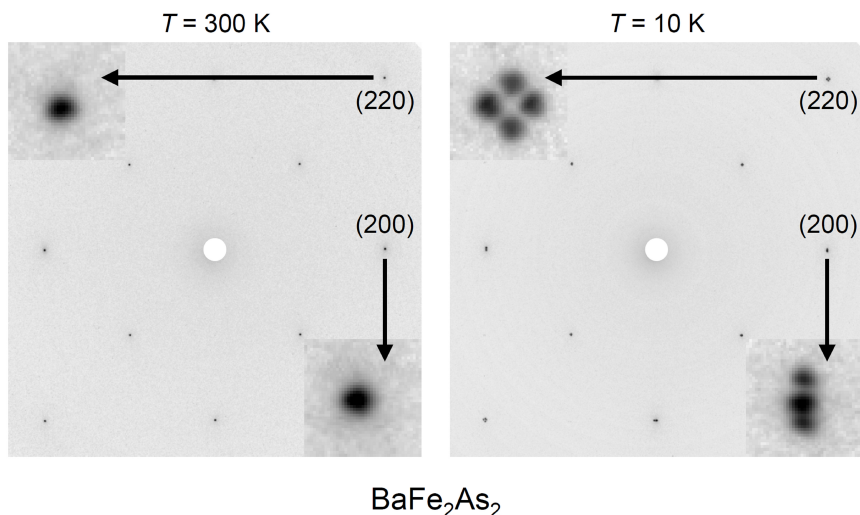


Fig. 5.25: Representative diffraction images of BaFe_2As_2 showing Bragg peaks at $T = 300$ K (left) and $T = 10$ K (right) in the $[100]$ – $[001]$ plane. The splitting of peaks at low temperature reflects the structural transition from tetragonal to orthorhombic symmetry. Picture Courtesy: Andreas Kreyssig, Ames Lab, USA.

including $T = 200$ K. Integrated intensities of Bragg reflections were collected using two different neutron wavelengths. A set of 70 independent reflections with $\sin \theta / \lambda \leq 0.85 \text{ \AA}^{-1}$ was measured using $\lambda = 0.84 \text{ \AA}$, and an additional set of 90 reflections with $\sin \theta / \lambda \leq 1.0 \text{ \AA}^{-1}$ was obtained using $\lambda = 0.52 \text{ \AA}$. The intensities were corrected and averaged over symmetry-equivalent reflections to obtain reliable experimental structure factors.

The crystal structure was refined using a least-squares procedure based on the measured integrated intensities. The refined parameters included:

- the z coordinate of the As atom,
- isotropic thermal displacement parameters (B) for Ba, Fe, and As,
- a single extinction parameter g describing the mosaic spread of the crystal.

The refinement results confirm that BaFe_2As_2 crystallizes in the tetragonal $I4/mmm$ structure at 200 K. The refined structural parameters are summarized in Table 5.3. The extinction parameter was found to be very small ($g = 1.4(1.6) \text{ rad}^{-1}$), indicating negligible extinction effects and confirming the high quality of the crystal. The reliability factors obtained from the refinement further demonstrate the excellent agreement between observed and calculated intensities. Overall, the single-crystal neutron diffraction measurements on D9 provide precise structural parameters and validate the crystallographic model of BaFe_2As_2 , complementing results obtained from X-ray and powder neutron diffraction techniques.

Table 5.3: Parameters obtained in least-squares refinements of integrated intensities measured at $T = 200$ K on D9.

Atom	Position in $I4/mmm$			z	B ($\text{\AA}^2$)
	Site	x	y	z	
Ba	$2a$	0	0	0	0.62(4)
Fe	$4d$	$\frac{1}{2}$	0	$\frac{1}{4}$	0.43(3)
As	$4e$	0	0	z	0.3543(1)
Extinction		g (rad^{-1})		1.4(1.6)	
R_{cryst}		$\lambda = 0.84$ $\text{\AA}$		3.8	$\lambda = 0.51$ $\text{\AA}$
					2.7

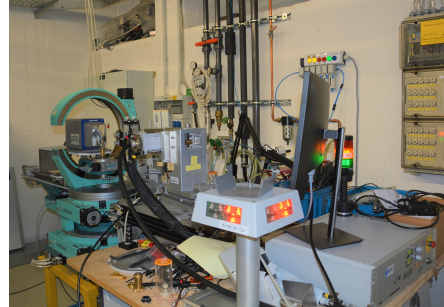
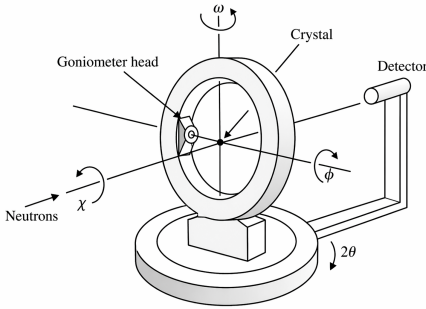


Fig. 5.26: Principle components of a constant wavelength single crystal diffractometer. Adapted from Ref. [23]. A picture of the 4-circle diffractometer at the JCNS 2.

5.10.2 Magnetic structure analysis using powder neutron diffraction

After successful synthesis and structural characterization of BaFe_2As_2 , various physical properties such as electrical resistivity, heat capacity, and magnetization are measured to understand its electronic and magnetic behavior. For both single-crystal and polycrystalline samples, these measurements reveal a clear phase transition in the temperature range $T \approx 140$ – 180 K (see Fig. 5.27). Electrical resistivity measurements, performed using a standard four-probe technique, show a sharp drop at the structural transition temperature $T_S \approx 142$ K, indicating a first-order phase transition. Temperature-dependent X-ray diffraction measurements further confirm that this transition corresponds to a structural change from the high-temperature tetragonal phase to a low-temperature orthorhombic phase as shown in Fig. 5.28. Magnetization measurements suggest that a magnetic transition also occurs near the same temperature. However, bulk measurements alone cannot determine the nature of magnetic ordering. Therefore, neutron diffraction is required, as it provides a direct probe of magnetic structures through the interaction of neutrons with magnetic moments.

Neutron Powder Diffraction Experiment

Neutron powder diffraction measurements were performed using neutrons with wavelength $\lambda = 2.079 \text{ \AA}$ on the high-resolution powder diffractometer BT1 at the NIST Center for Neutron Research (NCNR) [30]. Below T_S , additional Bragg peaks appear in the diffraction pattern that cannot be indexed within the nuclear unit cell. These extra reflections originate from magnetic scattering and indicate the onset of long-range magnetic order. The magnetic propagation vector is determined to be:

$$\mathbf{q} = (101)_O, \quad (5.103)$$

where the subscript O denotes the orthorhombic setting.

Magnetic Structure Determination

Once the propagation vector is known (typically obtained using the K-SEARCH program in FULLPROF software suite using the positions of the observed magnetic reflections), the next step is to determine the complete magnetic structure. This involves identifying:

- the direction of the ordered magnetic moments,
- the arrangement of magnetic moments within the magnetic unit cell,
- the magnitude of the ordered magnetic moment.

Given the crystal structure and propagation vector, symmetry analysis is performed to determine all possible magnetic structures consistent with the crystallographic symmetry. This is achieved using representational analysis tools such as SARAh, FULLPROF, MAG2POL, or ISODISTORT and the possible magnetic structures are shown in Fig. 5.29 for BaFe_2As_2 .

Representation Analysis

Representational analysis decomposes the magnetic representation into irreducible representations (irreps), each associated with basis vectors describing symmetry-allowed spin configurations. For BaFe_2As_2 , several candidate magnetic structures are obtained, corresponding to different moment directions and arrangements as shown in Fig. 5.29. Each of these candidate structures is used to simulate neutron diffraction patterns, which are then compared with experimental data using Rietveld refinement.

Selection of the Magnetic Structure

The correct magnetic structure is identified as the one that provides the best agreement between calculated and observed diffraction intensities. For BaFe_2As_2 , refinement of neutron diffraction data at low temperature (e.g., $T = 5 \text{ K}$, shown in Fig. 5.30) shows that the Fe moments are aligned along the orthorhombic a axis. The resulting magnetic structure is a stripe-type antiferromagnetic order characterized by:

- antiferromagnetic coupling along the a direction,
- ferromagnetic alignment along the b direction,
- antiferromagnetic coupling along the c direction.

Alternative models, such as moments aligned along the b or c axes, result in significantly poorer agreement and can be excluded. The refined magnetic and structural parameters obtained from combined nuclear and magnetic refinement are summarized in Table 5.2 (b), and the corresponding magnetic structure is illustrated in Fig. 5.29.

Physical Interpretation and Conclusion

The combination of propagation vector analysis, symmetry-based representational analysis, and Rietveld refinement provides a robust and systematic approach to determining magnetic structures. The stripe-type antiferromagnetic ordering observed in BaFe_2As_2 is a characteristic feature of iron-based superconductors and is closely related to their electronic anisotropy and magnetic interactions within the FeAs layers. Thus, powder neutron diffraction serves as an essential tool for uncovering the magnetic ground state and understanding the interplay between crystal structure, magnetism, and superconductivity in these materials.

5.10.3 Magnetic structure analysis using single crystal neutron diffraction

While powder neutron diffraction is often sufficient to determine magnetic structures, it may fail to uniquely resolve the direction of magnetic moments in more complex systems due to the averaging over crystallographic orientations. In such cases, single-crystal neutron diffraction, using either polarized or unpolarized neutrons, becomes essential for accurately determining the moment direction and spin arrangement. Although the magnetic structure of BaFe_2As_2 could be reliably established using powder diffraction, complementary single-crystal neutron diffraction studies were carried out by Su *et al.* [24] on BaFe_2As_2 and by Goldman *et al.* [26] on the isostructural compound CaFe_2As_2 , respectively.

In particular, for CaFe_2As_2 , single-crystal neutron diffraction experiments were performed on the D10 four-circle diffractometer at the Institut Laue-Langevin, using a wavelength of $\lambda = 2.36 \text{ \AA}$. A two-dimensional area detector mounted on the scattering arm was used for data collection. A pyrolytic graphite filter was employed to suppress higher-order contamination to less than 10^{-4} of the primary beam intensity. The sample was mounted on the cold finger of a helium flow cryostat, providing temperature stability better than 0.1 K during

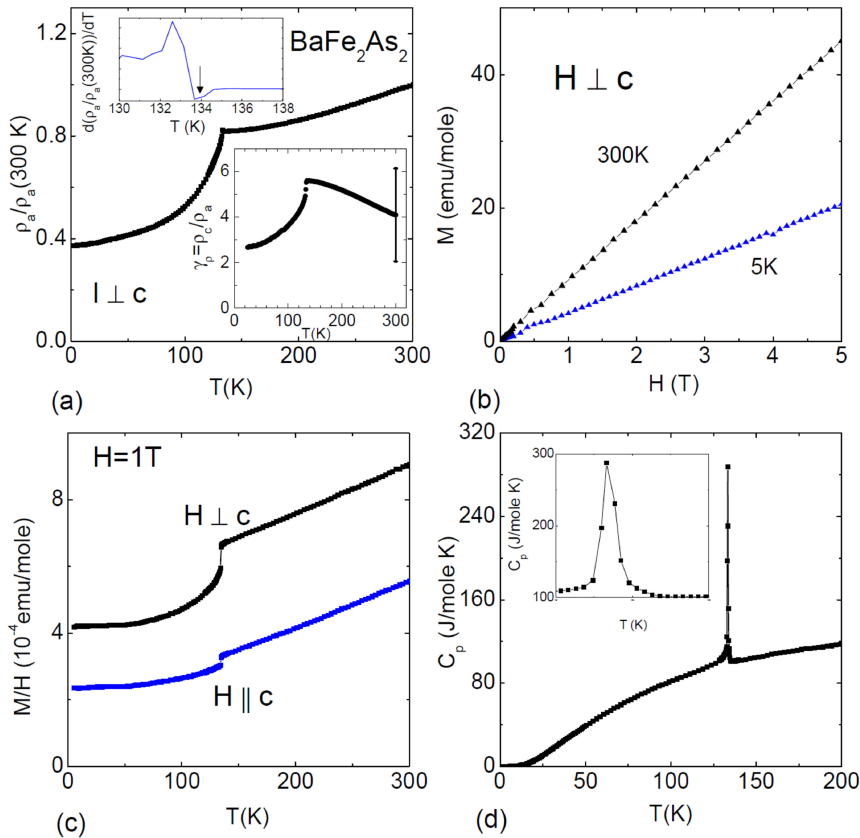


Fig. 5.27: Single-crystalline BaFe_2As_2 grown from FeAs flux: (a) Normalized in-plane resistivity $\rho_a(T)/\rho_a(300\text{ K})$ as a function of temperature. Inset: derivative $d[\rho_a(T)/\rho_a(300\text{ K})]/dT$ near the phase transition (upper left), and anisotropy parameter $\gamma = \rho_c/\rho_a$ (lower right). (b) Magnetization M vs. magnetic field H at 5 K and 300 K with $H \perp c$. (c) Magnetic susceptibility M/H vs. temperature at 1 T with $H \parallel c$ and $H \perp c$. (d) Specific heat C_p vs. temperature. Inset: enlarged view of C_p near the phase transition. Reprinted from Ref. [27].

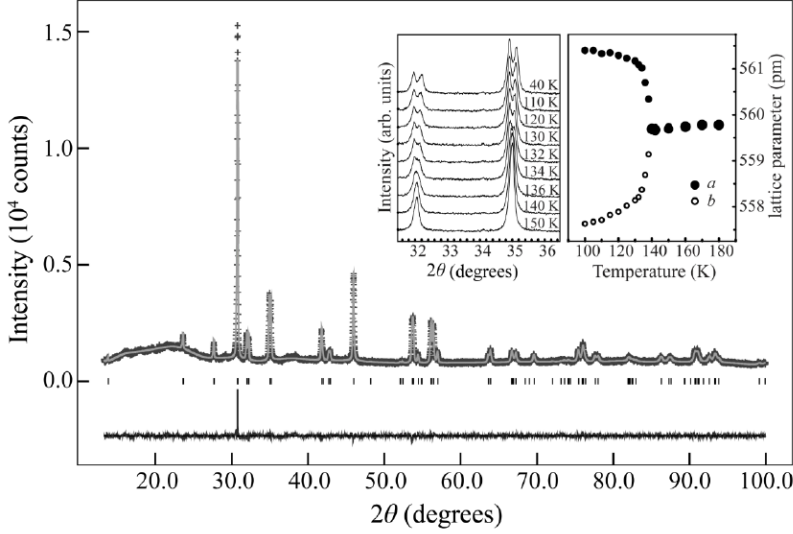


Fig. 5.28: X-ray powder pattern (+) and Rietveld fit (–) of BaFe_2As_2 at 20 K (space group $Fmmm$). The splitting of the (110) and (112) reflections and the temperature dependence of lattice parameters are also shown. For comparison, lattice parameters in the tetragonal phase above 140 K are multiplied by $\sqrt{2}$. Reprinted from Ref. [36].

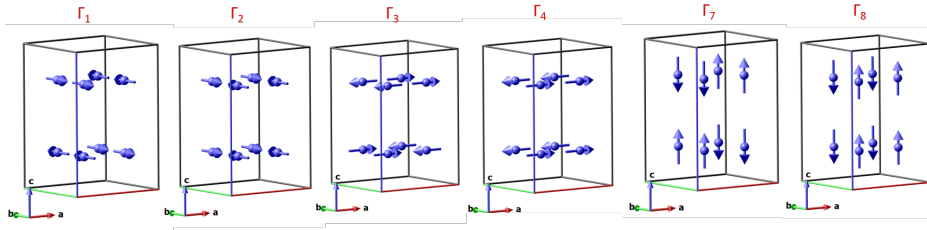


Fig. 5.29: The decomposition of the magnetic representation for the Fe site $(.25, .25, .25)$ is $\Gamma_{Mag} = 1\Gamma_1^1 + 1\Gamma_2^1 + 1\Gamma_3^1 + 1\Gamma_4^1 + 0\Gamma_5^1 + 0\Gamma_6^1 + 1\Gamma_7^1 + 1\Gamma_8^1$. The atoms of the nonprimitive basis are defined according to 1: $(.25, .25, .25)$, 2: $(.75, .75, .75)$.

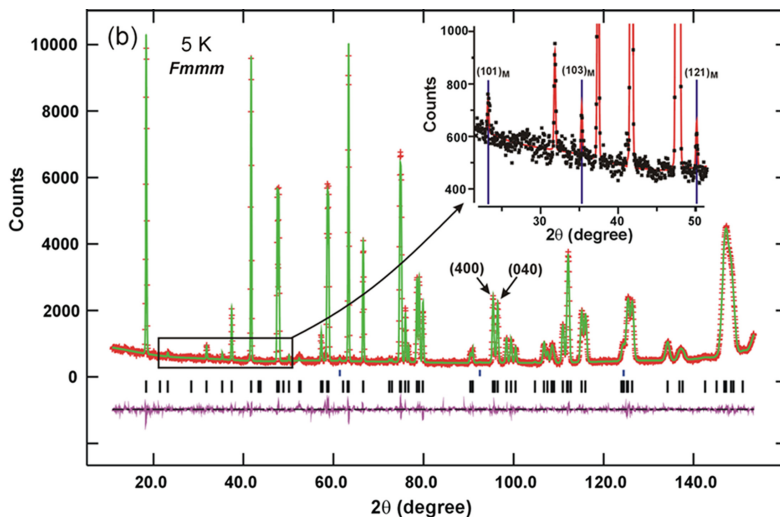


Fig. 5.30: Neutron powder diffraction spectra at 5 K. The low-temperature data are fitted with the orthorhombic $Fmmm$ structure, including the magnetic ordering. The (220) Bragg reflection splits into the (400) and (040) reflections due to the orthorhombic distortion. Magnetic reflections at 5 K are highlighted in the inset. Reprinted from Ref. [30]. Copyright by the American Physical Society.

measurements. Single crystals of CaFe_2As_2 were grown from a Sn flux using conventional high-temperature solution growth techniques. A single crystal of mass ~ 7 mg with dimensions of approximately $3 \times 2 \times 0.2$ mm³ was selected for neutron diffraction measurements. X-ray and neutron Laue diffraction confirmed the high quality of the sample, with a mosaic spread of approximately 0.5° (full width at half maximum), and verified that the tetragonal c axis is perpendicular to the flat plate surface of the crystal.

Magnetic Structure Refinement

At low temperature ($T = 10$ K), a set of nuclear reflections and magnetic Bragg peaks was collected for the refinement of the chemical and magnetic structures using the FULLPROF suite, taking proper account of orthorhombic twinning [26]. Below the structural transition temperature T_S , the crystal structure is well described by the orthorhombic space group $Fmmm$. The refined atomic position for arsenic is $z_{\text{As}} = 0.3664(5)$ at the $4e$ site. Magnetic structure refinement using a propagation vector $\mathbf{q} = (1\ 0\ 1)$ yields an ordered Fe moment of $0.80(5) \mu_B/\text{Fe}$ aligned along the longer orthorhombic a axis. The magnitude and direction of the Fe moment were determined from a least-squares fit to 35 magnetic reflections, resulting in a satisfactory agreement factor of $R = 8.8\%$. A refinement assuming the Fe moments aligned along the shorter b axis resulted in a significantly poorer fit ($R = 84\%$), thereby ruling out this configuration. The magnetic unit cell coincides with the chemical unit cell, with Fe moments coupled ferromagnetically along the b direction and antiferromagnetically

along the a and c directions. The refinement quality indicators are:

$$\begin{aligned} R_{F^2} &= 8.84\%, \\ R_{F^2_w} &= 13.2\%, \\ R_F &= 23.3\%, \\ \chi^2 &= 9.50. \end{aligned}$$

The refined Fe magnetic moment is:

$$M_{\text{Fe}} = 0.807(9) \mu_B. \quad (5.104)$$

Comparison of Calculated and Observed Structure Factors

The reliability of the magnetic structure refinement was further evaluated by comparing the calculated and observed structure factors. Figure 5.31 shows the relationship between F_{calc}^2 and F_{obs}^2 for the measured magnetic reflections. A good agreement is observed for strong reflections, which lie close to the ideal $F_{\text{calc}}^2 = F_{\text{obs}}^2$ line, confirming the validity of the proposed magnetic structure. Larger deviations are observed for weak reflections, which is expected due to lower counting statistics and background contributions.

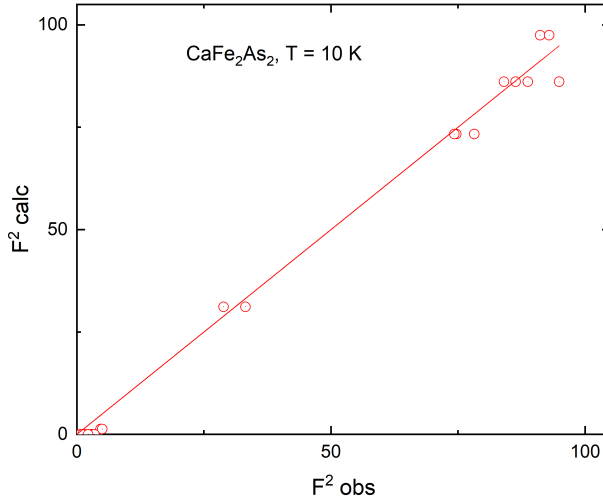


Fig. 5.31: F_{calc}^2 versus F_{obs}^2 for CaFe_2As_2 magnetic reflections [26]. The solid line represents perfect agreement.

5.10.4 Magnetization density using neutron diffraction

As a final example for the application of neutron diffraction in structural analysis, we briefly sketch how a 3-dimensional map of the magnetization density, that is: the density of magnetic

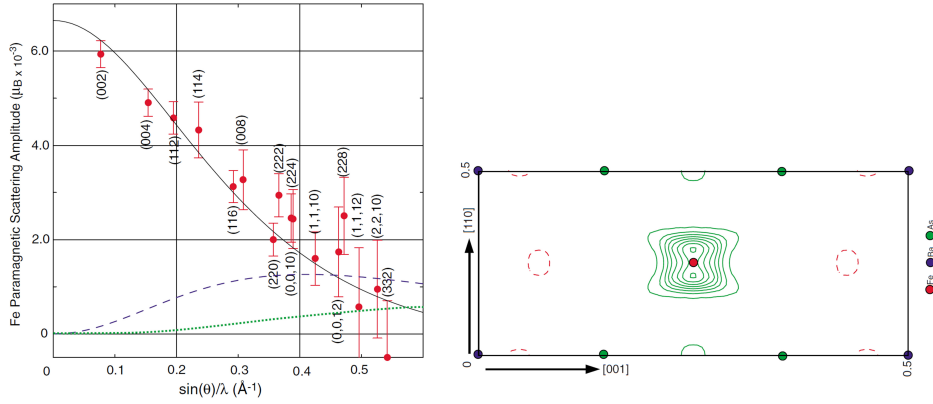


Fig. 5.32: Paramagnetic scattering amplitudes measured for Fe in BaFe_2As_2 at 200 K. The solid curve represents the $\langle j_0 \rangle$ form factor for neutral Fe [29], scaled to the paramagnetic magnetization of $6.65 \times 10^{-3} \mu_B/\text{Fe}$. The dashed (blue) and dotted (green) curves correspond to the $\langle j_2 \rangle$ and $\langle j_4 \rangle$ form factors, respectively, which contribute to the anisotropic components of the magnetic scattering. Maximum-entropy reconstruction of the magnetization density in tetragonal BaFe_2As_2 at 200 K, projected along the $[1\bar{1}0]$ direction. Contours are drawn at intervals of $10^{-2} \mu_B \text{\AA}^{-2}$. Reprinted from Ref. [32]. Copyright by the American Physical Society.

moments (spin- as well as orbital-moments) within the unit cell can be determined. These maps are sometimes lucidly called ‘spin density maps’, but in systems with non-vanishing orbital moments, the term magnetization density is really the correct one.

Polarized neutron diffraction is a powerful technique used to determine the spatial distribution of magnetization in crystalline materials. In such experiments, the neutron spin is aligned either parallel or antiparallel to an applied magnetic field, allowing separation of nuclear and magnetic scattering contributions. The key observable is the flipping ratio,

$$R = \frac{I^+}{I^-}, \quad (5.105)$$

where I^+ and I^- are the scattered intensities for neutron spins parallel and antiparallel to the applied magnetic field, respectively. In the limit of small induced magnetic moments, the flipping ratio can be approximated as [38]:

$$R \approx 1 - \frac{2\gamma r_0}{\mu_B} \frac{F_M(\mathbf{Q})}{F_N(\mathbf{Q})}, \quad (5.106)$$

where $\gamma r_0 = 5.36 \times 10^{-15} \text{ m}$ is a constant, μ_B is the Bohr magneton, and $F_M(\mathbf{Q})$ and $F_N(\mathbf{Q})$ are the magnetic and nuclear structure factors at reciprocal lattice vector $\mathbf{Q}$, respectively. Since the nuclear structure factor $F_N(\mathbf{Q})$ is known from unpolarized neutron diffraction, and the flipping ratio R is measured experimentally, the magnetic structure factor $F_M(\mathbf{Q})$ can be determined as is shown in Fig 5.32 as a function of $\frac{\sin \theta}{\lambda}$. Using the $F_M(\mathbf{Q})$, the magnetization induced by an external magnetic field can be reconstructed in real space using

Maximum-entropy reconstruction. For example, in BaFe_2As_2 , polarized neutron diffraction measurements under a magnetic field of 9 T in the tetragonal phase reveal that the magnetization density is localized primarily around the Fe atoms, with negligible contributions from As and Ba atoms (See Fig. 5.32). A maximum-entropy reconstruction of the magnetization projected onto the (110) plane shows that the magnetization distribution is highly anisotropic and non-spherical, extending along the $\langle 111 \rangle$ directions. This anisotropy indicates that the electrons contributing to the paramagnetic susceptibility are predominantly localized in Fe $3d$ orbitals, with a significant contribution ($\sim 60\%$) from orbitals of d_{xy} symmetry. These results demonstrate that polarized neutron diffraction provides direct insight into the orbital character and spatial distribution of magnetic electrons in correlated electron systems.

Why Polarized Neutrons?

The advantage of polarized neutrons becomes evident when detecting weak magnetic signals. Consider a case where:

$$F_M = 0.1 F_N. \quad (5.107)$$

For unpolarized neutrons, the measured intensity is:

$$I = F_N^2 + F_M^2 = 1.01 F_N^2, \quad (5.108)$$

so the magnetic contribution represents only about 1% of the total signal. For polarized neutrons, the interference between nuclear and magnetic scattering yields:

$$I^+ = F_N^2 + F_M^2 + 2F_N F_M = 1.21 F_N^2, \quad (5.109)$$

$$I^- = F_N^2 + F_M^2 - 2F_N F_M = 0.81 F_N^2. \quad (5.110)$$

The difference between the two intensities corresponds to a $\sim 20\%$ effect, demonstrating that the magnetic signal is significantly enhanced through interference. This makes polarized neutron diffraction highly sensitive to weak magnetic amplitudes.

References

- [1] K. Sköld, D. Price (Eds.), *Methods of Experimental Physics Neutron Scattering Part A-C*, Academic Press (1987).
- [2] G. L. Squires, *Introduction to the Theory of Thermal Neutron Scattering*, Cambridge University Press, Revised Edition (March 29, 2012).
- [3] J. M. Cowley, *Diffraction Physics*, North Holland, Amsterdam (1995).
- [4] S. W. Lovesey, *Theory of neutron scattering from condensed matter*, Clarendon Press, Oxford (1987).
- [5] A. Furrer, J. Mesot, T. Strässle, *Neutron Scattering in Condensed Matter Physics*, World Scientific, London (2009).
- [6] J. M. Carpenter, C.-K. Loong, *Elements of Slow-Neutron Scattering*, Cambridge University Press (2015).
- [7] B. W. Batterman, H. Cole, *Dynamical Diffraction of X-Rays by Perfect Crystals*, Rev. Mod. Phys. **36**, 681(1964).
- [8] G. Redhammer *et al.*, Phys. Chem. Min. **37**, 311(2010).
- [9] Reproduced from: Braggs world, talk by Th. Proffen <http://ebookbrowse.com/proffen-talk-bragg-pdf-d59740269> retrieved: 2015-05-05
- [10] H. M. Rietveld, J. Appl. Cryst. **2**, 65(1969).
- [11] The lecture note is adapted from Prof. G. Roth, RWTH Aachen and Prof. Th. Brueckel, JCNS lab course (Band/ Volume 255)
- [12] E. F. Bertaut, J. Appl. Phys. **33**, 1138 (1962); E. F. Bertaut, Acta. Cryst. **A24**, 217 (1968); E. F. Bertaut, J. de Physique Colloque, **C1**, 462 (1971); E. F. Bertaut, J. Magn. Magn. Mat. **24**, 267 (1981).
- [13] Yu. A. Izyumov, V. E. Naish, and R. P. Ozerov, *Neutron Diffraction of Magnetic Materials*, Consultants Bureau, New York (1991).
- [14] C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids*, Clarendon Press, Oxford (1972).
- [15] A. P. Cracknell, *Magnetism in Crystalline Materials*, Pergamon Press, Oxford (1975).
- [16] A. S. Wills, J. de Physique, *in press* (2001).
- [17] A. S. Wills, Phys. Rev. B **63**, 064430 (2001).
- [18] A. S. Wills, Physica B **276**, 680 (2000), program available from www.ccp14.ac.uk
- [19] O. V. Kovalev, *Representations of the Crystallographic Space Groups*, Gordon and Breach Science Publishers, Switzerland (1993).

- [20] J. Rossat-Mignod, in *Methods of Experimental Physics*, Vol. 23, edited by K. Sköld and D. L. Price, Academic Press, New York (1987).
- [21] J. Rossat-Mignod, in *Systematics and the Properties of the Lanthanides*, edited by S. P. Sinha, D. Reidel Publishing Company, Dordrecht (1983).
- [22] While the *Jones faithful representations* conventionally correspond to the vector formed from the operation of the rotation part of the element, R , on the site coordinates (x, y, z) , here we use it to demonstrate the effect of the complete symmetry operator, g .
- [23] B. T. M. Willis and C. J. Carlile, *Experimental Neutron Scattering*, Oxford University Press, Oxford (2009).
- [24] Y. Su, P. Link, A. Schneidewind, Th. Wolf, P. Adelmann, M. Xiao, R. Mittal, M. Rotter, D. Johrendt, Th. Brückel, and E. Bourges, *Phys. Rev. B* **79**, 064504 (2009).
- [25] M. Rotter, M. Tegel, and D. Johrendt, *Phys. Rev. Lett.* **101**, 107006 (2008).
- [26] A. I. Goldman, D. N. Argyriou, B. Ouladdiaf, T. Chatterji, A. Kreyssig, S. Nandi, N. Ni, S. L. Bud'ko, P. C. Canfield, and R. J. McQueeney, *Phys. Rev. B* **78**, 100506(R) (2008).
- [27] N. Ni, Magnetic and Structural Phase Transitions in BaFe_2As_2 -Based Compounds, Ph.D. Thesis, Iowa State University (2009).
- [28] P. J. Brown, K. R. A. Ziebeck, J. M. Mignot, D. Givord, and J. Schweizer, *J. Phys.: Condens. Matter* **13**, 10017 (2001).
- [29] P. J. Brown, in *International Tables for Crystallography*, Vol. C, edited by E. Prince, Kluwer Academic, Dordrecht (2004).
- [30] Q. Huang, Y. Qiu, W. Bao, M. A. Green, J. W. Lynn, Y. C. Gasparovic, T. Wu, G. Wu, and X. H. Chen, *Phys. Rev. Lett.* **101**, 257003 (2008).
- [31] G. Will, *Angew. Chem.* **82**, 307 (1970); *Angew. Chem. Int. Ed.* **8**, 356 (1969).
- [32] P. J. Brown, T. Chatterji, A. Stunault, Y. Su, Y. Xiao, R. Mittal, Th. Brückel, Th. Wolf, and P. Adelmann, *Phys. Rev. B* **82**, 024421 (2010).
- [33] G. L. Squires, *Introduction to the Theory of Thermal Neutron Scattering*, Cambridge University Press, Cambridge (1978).
- [34] D. F. McMorrow, *Elements of Modern X-ray Physics*, Wiley, Chichester (2011).
- [35] Y. Zhang, J. Liu, and M. G. Tucker, *J. Appl. Crystallogr.*, **54**, 1235 (2021).
- [36] M. Rotter, High-Temperature Superconductivity in Doped BaFe_2As_2 , Ph.D. Thesis, Ludwig-Maximilians-Universität München (2009).
- [37] S. Nandi, *Magnetic X-ray Scattering*, in *Characterization of Materials*, Wiley (2012).
- [38] S. Nandi *et al.*, *Phys. Rev. B* **88**, 184413 (2013).

Exercises

E5.1 Multiple choice

Kinematic scattering theory takes into account

- ☐ refraction
- ☐ attenuation
- ☐ multiple scattering
- ☐ none of the above

E5.2 Multiple choice

You have measured the scattered intensity $I(\mathbf{Q})$ as a function of the scattering vector $\mathbf{Q}$. Which of the following statements are correct for kinematic scattering:

- ☐ The Fourier transform of $I(\mathbf{Q})$ is proportional to the scattering density.
- ☐ $I(\mathbf{Q})$ is always described by the Laue function.
- ☐ $I(\mathbf{Q})$ is the Patterson- or static pair correlation function.
- ☐ The phase problem does not allow one to determine the atomic position directly by a simple mathematical procedure.

E5.3 Bragg scattering

Bragg had the idea to describe scattering from a three-dimensional periodic arrangement of scatterers (e.g. atoms in a crystal) by the interference of waves reflected from parallel atomic planes, see

1. After scattering, the waves reflected from the two planes show a path length difference. Which relation does this path length difference have to fulfill in order to achieve coherent superposition and thus an intensity maximum (See Figure 5.33) ?
2. Derive the condition for the occurrence of such a Bragg peak in terms of wavelength λ , scattering angle 2θ and distance between the planes d , the so-called Bragg equation.
3. How does the Bragg equation relate to the Laue conditions?

E5.4 Reciprocal lattice

A two-dimensional rectangular crystal has a unit cell with sides $a_1 = 0.468$ nm and $a_2 = 0.342$ nm.

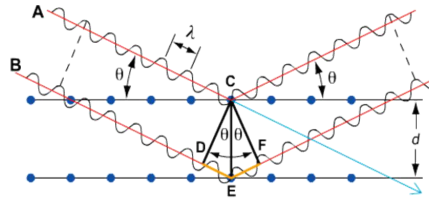


Fig. 5.33: Bragg scattering: For constructive interference, sharp intensity maxima appear as a function of scattering angle. These peaks are called “Bragg reflections”.

- Find out the reciprocal lattice vectors and Draw to scale a diagram of the reciprocal lattice.
- Label the reciprocal lattice points for indices in the range $0 \leq h \leq 3$ and $0 \leq k \leq 3$.

E5.5 Types of Scattering Experiments

- Discuss/define the following terms: A. Elastic scattering, B. Inelastic scattering, C. Coherent scattering, D. Incoherent scattering
- What does the term “diffraction” correspond to in this context?

E5.6 Filtering

- What is the purpose of a beryllium (or graphite) filter for neutron diffraction?
- To discuss how it works: Use the Ewald construction for a given reciprocal lattice and a very short / very long wavelength.

E5.7 Structure factor equation

The structure factor equation is the central formula that allows us to calculate diffracted intensities from structural parameters. It corresponds to a Fourier-transform of the unit cell contents.

- Write down the structure factor equation
- Identify and discuss all parameters in the formula.
- Under which conditions does this formula hold (kinematical diffraction conditions)?
- Explain the difference in diffraction pattern (x-ray powder) although both have fcc NaCl type crystal structure (Figure 5.34 in the next page).

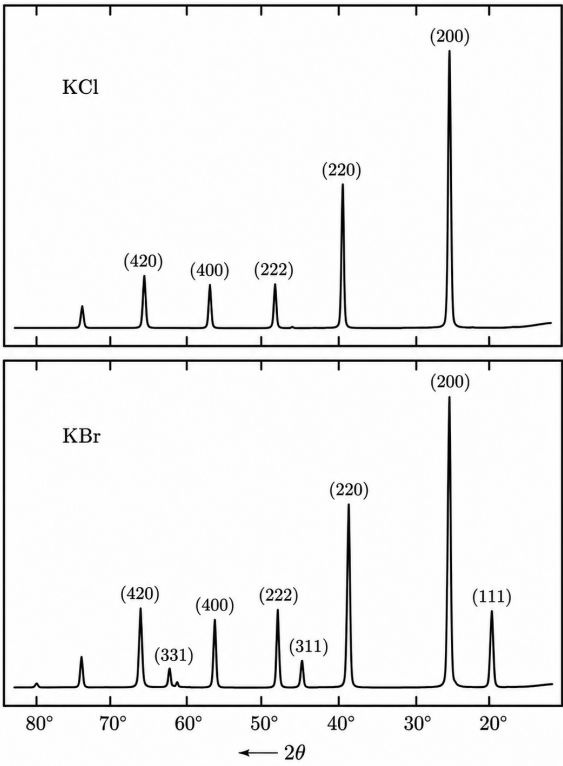


Fig. 5.34: X-ray powder diffraction of KCl and KBr.

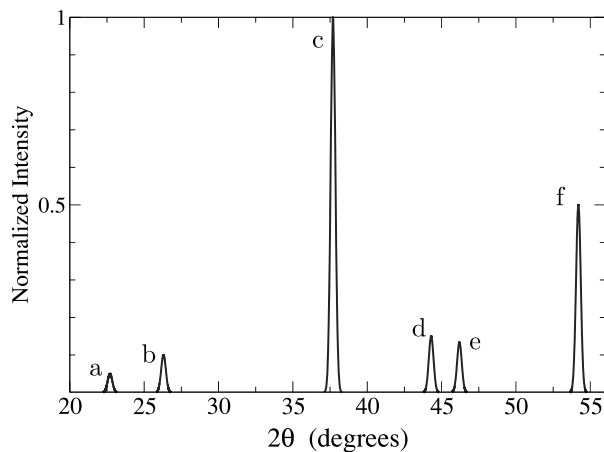


Fig. 5.35: Powder diffraction of neutrons from PrO_2 . The wavelength of the neutron beam is $\lambda = 0.123$ nm. (One should assume that Lorentz corrections have been removed from the displayed intensities.). The approximate peak positions are: a: 22.7° , b: 26.3° , c: 37.7° , d: 44.3° , e: 46.2° , f: 54.2°

E5.8 Neutron diffractometers

- What is the purpose of a monochromator?
- How does it work?
- What does the term “collimation” mean?
- What is the resolution function of a diffractometer? (sketch)
- Why is it important?
- What is the purpose of a hot neutron source?
- How does it work?

E5.9 Calculation of lattice constant

Consider the powder diffraction data from PrO_2 shown in the above Figure (Fig. 5.35).

- Find out the lattice type (assume some sort of Cubic structure).
- Find out the lattice constant.

E5.10 Magnetic Structure Factor

Consider the possible magnetic structures shown in Fig. 5.29. Use the structural parameters given in Table 5.2. For simplicity, neglect the Debye–Waller factor.

1. Identify the correct magnetic structure among the possible models shown in Fig. 5.29.
2. Calculate the magnetic structure factor for the correct magnetic structure in the $(h, 0, l)$ reciprocal-lattice plane.
3. Which magnetic reflections would you measure in order to distinguish between the magnetic structures corresponding to Γ_1 and Γ_3 ? Explain how the selection of reflections depends on the magnetic moment direction and the magnetic structure factor.

6 Small-Angle Neutron Scattering – SANS

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6.1 Introduction

Small-Angle Scattering (SAS) investigates structures in samples that generally range from approximately 0.5 nm to a few 100 nm. This can both be done for isotropic samples such as blends and liquids, as well as anisotropic samples such as quasi-crystals. In order to obtain data about that size regime scattered intensity, mostly of x-rays or neutrons, is investigated at angles from close to zero, still in the region of the primary beam up to 10° , depending on the wavelength of the incoming radiation.

The two primary sources for SAS experiments are x-ray (small-angle x-ray scattering, SAXS) sources and neutron (small-angle neutron scattering, SANS) sources, which shall be the two cases discussed here. Also scattering with electrons or other particle waves is possible, but not the main use case for the purpose of this manuscript.

For most small-angle scattering instruments, both SAXS and SANS, the science case covers the investigation of self-assembled polymeric and biological systems, multi-scale systems with large size distribution of the contained particles, solutions of (nano-)particles and soft-matter systems, protein solutions, and material science investigations. In the case of SANS this is augmented by the possibility to also investigate the spin state of the sample and hence perform investigations of the magnetic structure of the sample.

In the following sections the general setup of both SAXS and SANS instruments shall be discussed, as well as data acquisition and evaluation and preparation of the sample and the experiment in general. The information contained herein should provide sufficient information for planning and performing a SAS experiment and evaluate the gathered data.

6.1.1 General concept

All SAS experiments, irrespective of the setup used in any specific case, rely on the concept of pinhole cameras to work. Fig. 6.1 illustrates the geometric concept of the interplay between pinhole cameras and SAS.

In the case of direct image projection, as done in pinhole cameras, every point of the sample (object) is mapped to a discrete point on the screen (film or detector) (see Fig. 6.1a)). The smaller the hole, the better the point-to-point mapping works, since in the ideal case only a single path between object and image is available. However, this of course comes with a penalty in intensity, since the smaller hole lets less light pass through. Due to the geometry, an image taken with a pinhole camera is always upside down. While the mathematical implications shall be discussed later on in this manuscript at this point we only want to grasp the underlying concept. The information about the object is at the beginning stored in real space. Colors (wavelength) and locations are given as points on the surface of the object. When all beams have converged to the single point that is ideally the pinhole, the information is then encoded in direction of the path (or light-beam) and the wavelength of the light. This is the change between direct and indirect space, locations and directions. When the light falls onto the screen the information is reversed again, to location and color of a spot on the screen, into direct space.

This concept is exploited by SAS (see Fig. 6.1b)). In this case only angular resolution

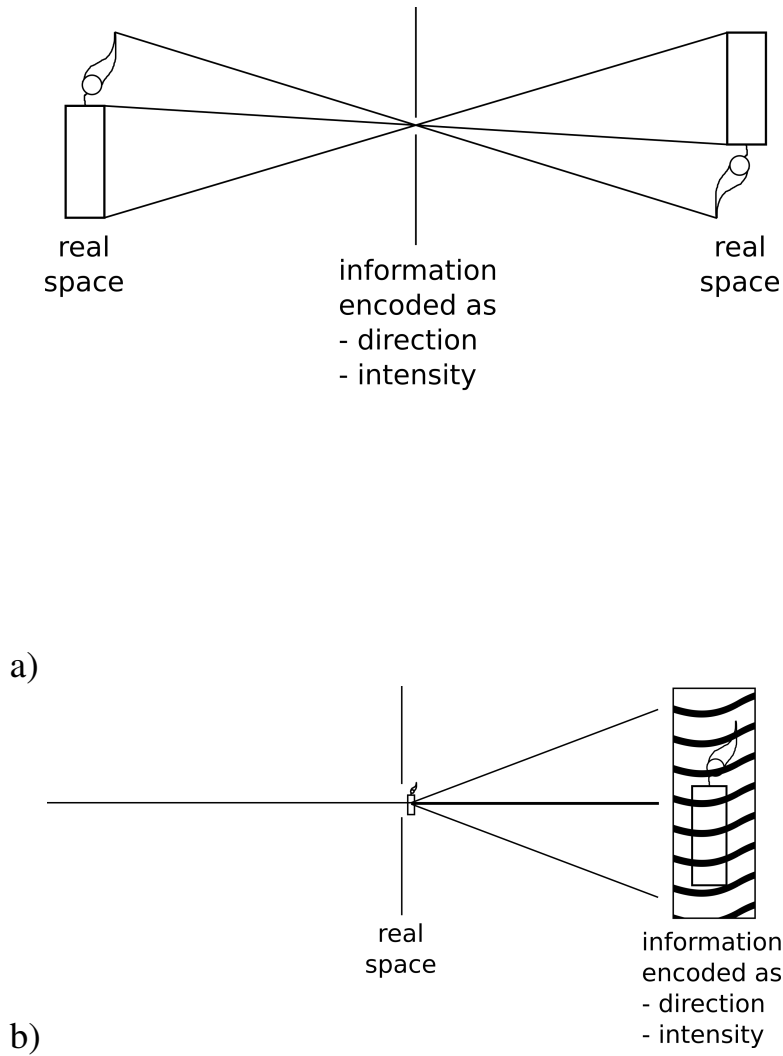


Fig. 6.1: a) Sketch of a pinhole camera and b) a simplified SAS instrument. The encoding of the real space information is in one case done inside the pinhole, in the other case the direction (and wavelength) encoded information is directly displayed on the screen (shaded area with waves). Positioning of the screen farther away improves the angular resolution and therefore the encoded information.

matters, which is easy to increase simply by increasing the distance between pinhole and screen. Here, instead of using the information that has been transferred to real space again, this time the object in real space is put close to the window. This way, the information about the location of atoms and molecules in the sample is encoded into direction or indirect space. Since there should be no information about the light before the pinhole, the light needs to be collimated down to a small, point-like source with no angular divergence.

Pinhole cameras such as in Fig. 6.1a) were in use before lenses became wide spread in optical photography. One can easily imagine that a smaller aperture leads to a higher resolution at the cost of intensity. Even with optical lenses cameras operate roughly the same way. You try to offset the smaller aperture and sharper image by using a lens that focuses more light through the aperture.

For SAS, you essentially delete all information from the incoming radiation by collimating the beam (every particle/ray is going the same direction) and separating the incoming wavelength (so everything has the same energy, or in the case of visible light, color). Then the information is picked up at the sample and transferred to a screen.

6.2 SAXS instruments

In general there are two classes of SAXS instruments. One is the laboratory type setup that can be set-up in a single laboratory with a conventional x-ray tube, or more general any metal anode setup, while the other one is a large-scale facility setup at a synchrotron that can provide higher intensities. Since the setup of both instruments differs, and also the use case is not fully identical, we shall discuss both setups separately. One thing that should be kept in mind is that the fundamental principle is identical, i.e. any experiment that can be performed at a synchrotron can also in principle be performed at a laboratory SAXS setup and is only limited in intensity. This is important for the preparation of beamtimes at a synchrotron, which in general should be thoroughly prepared in order to fully exploit all capabilities offered there.

6.2.1 Laboratory SAXS setup

Over the years a wide range of specialized SAXS instruments has become commercially available. The oldest concepts date back to the early 20th century, right after the discovery of x-rays. [1] Most of them offer specific advantages in certain use cases, such as the measurement of isotropic samples in a Kratky Camera [2], or highly adaptable sample environments. Here we shall only concentrate on the basic principle of operation. A general sketch of a SAXS instrument is shown in Fig.6.2. The x-rays are produced in an x-ray tube and then collimated by a set of slits. Here the collimation as such is already sufficient to obtain a coherent beam, since most of the intensity of standard x-ray tubes (and essentially all metal target x-ray sources) is concentrated into the characteristic spectral lines of the target material (see Fig.6.3). Common materials for the target anode are copper and molybdenum, delivering wavelengths of the most intensive K- α lines of 1.54 Å and 0.71 Å respectively. Under the assumption of a usual characteristic spectrum for the anode material the x-ray

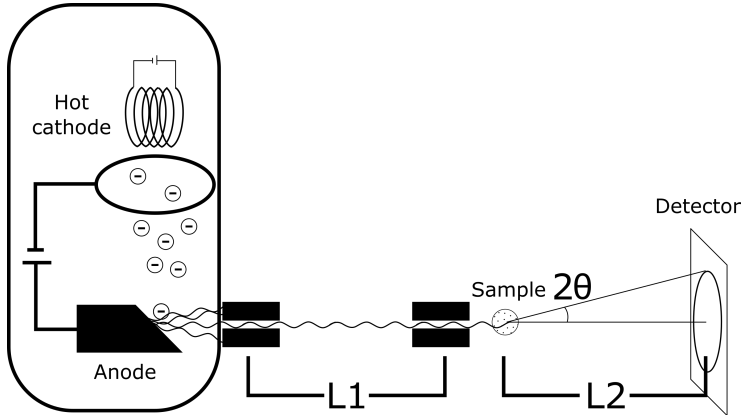


Fig. 6.2: Laboratory SAXS setup. The left box is a sketch of a x-ray tube, all the components are in vacuum. The flight path is also usually evacuated. L1 and L2 are the collimation and sample detector distance (SDD) respectively. In the case of laboratory setup those range usually from about 20 cm up to 1-2 m in modern setups. The collimation blocks for L1 and L2 are usually set up in both x and y direction to constrict the flight path, widely used openings are around 1 mm×1 mm or below. In some setups, also a slit collimation instead of a point collimation is realized to increase the intensity.

tubes can be considered monochromatic sources.

In order to achieve spatial as well as wavelength coherence most x-ray tubes work with a focused beam that is as small as technically feasible. This allows very narrow collimation slits, since it is not improving the coherence, and therefore the signal-to-noise ratio, to narrow the slit further than the initial beam spot or the pixel size of the detector, whichever be smaller. This however leads to a very high energy density, why some x-ray tube designs forgo a solid anode all together and either opt for a rotating anode, where the energy of the beam spot is distributed over a larger surface or a metal-jet anode, where the material is refluxed and can therefore not heat up beyond the point of deformation and therefore also defocussing of the beam.

Some performance figures of current laboratory SAXS setups are given in Tab.6.1. It is worth noting that with the last generation of metal-jet anode setups even laboratory setups can achieve intensities comparable to what was achievable one or two decades ago at a world-class synchrotron. While this of course allows for faster measurements and smaller beam, it also means that beam damage to the sample has to be taken into account.

6.2.2 Synchrotron SAXS setups

While the setup in general is similar to that of a laboratory setup there are some key differences between a synchrotron and a laboratory SAXS setup. Most of the differences are based on radio protection needs and are therefore immaterial to this description in terms

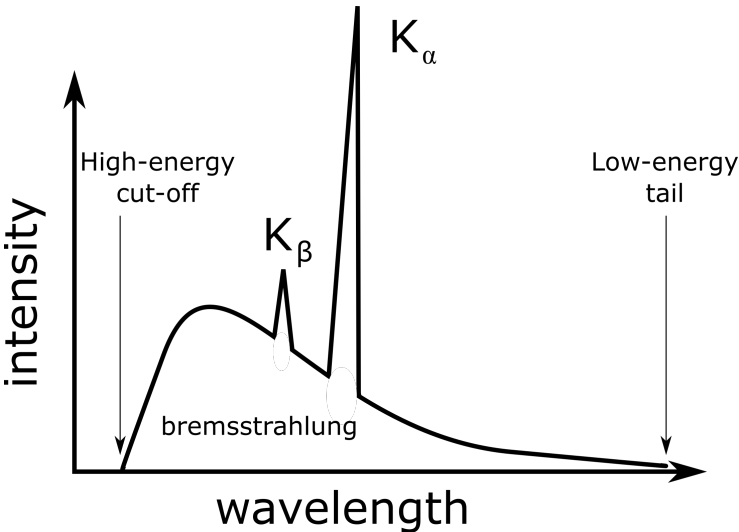


Fig. 6.3: Characteristic x-ray spectrum from a metal anode x-ray tube. The high-energy cut-off wavelength is given for the case that a single electron, fully accelerated by the voltage in the x-ray tube, deposits all its kinetic energy in a single photon. In an optimal setup this distribution is very narrow. Then the K_{α} line fully dominates the spectrum and gives a clean wavelength to perform a SAXS instrument.

Parameter	value
SDD	0.8-4 m
Pixel resolution	$172 \times 172 \mu\text{m}$
Flux	$10^7 \text{ photons s}^{-1}$
wavelength λ	$1.35 \text{ \AA}$
Q-range	$4 \cdot 10^{-3} - 8 \cdot 10^{-1} \text{ \AA}^{-1}$

Table 6.1: Performance parameters for state of the art laboratory SAXS setups, in this case with a liquid metal jet anode at the GALAXI instrument. [3]

Parameter	value
SDD	0.8-4 m
Pixel resolution	$172 \times 172 \mu\text{m}$
Flux	$10^{18} \text{ photons s}^{-1}$
wavelength λ	0.54 - 1.38 Å

Table 6.2: Performance parameters for a state of the art synchrotron SAXS beamline, here P03 at DESY. [5]

of the SAXS measurement itself. The other main difference is in the production of the x-rays itself. Current setups at synchrotrons use undulators in order to periodically accelerate charged particles (usually electrons/positrons) perpendicular to the direction of propagation of the particle beam. This creates a very brilliant, nearly perfectly monochromatic x-ray beam along the direction of the electron beam. The monochromaticity can further be improved by a monochromator crystal. Fig.6.4 shows an example of an synchrotron SAXS setup. After that, the collimation is very similar to that of a laboratory SAXS setup, only the materials are chosen to be thicker in most cases to improve the absorption characteristics. Due to the monochromaticity the brilliance, coherence and signal-to-noise ratio are significantly better than that of a laboratory SAXS setup, since there is no bremsstrahlung spectrum to contribute to the background. In terms of achievable wavelength there is no limitation to use a specific K- α line of any specific material. Often common wavelengths are chosen to better correspond to laboratory measurements on identical samples. One option that is also available in some synchrotrons is the tunability of the wavelength in order to measure resonance effects in the atomic structure of the sample (anomalous SAXS, ASAXS) [4] or better chose the accessible Q space. Tab.6.2 summarizes some of the performance figures of current synchrotron SAXS setups. For most synchrotron SAXS beamlines beam damage, especially for organic samples, is an issue and has to be taken into account when planning an experiment.

6.3 SANS setups

In contrast to x-rays, sufficient numbers of free neutrons can only be obtained by nuclear processes, such as fission, fusion and spallation. As large-scale facilities are needed to create the processes at a suitable rate to perform scattering experiments with them, the only facilities where neutron scattering today can be performed is at fission reactor sources and spallation sources. This of course also leads to larger efforts in terms of biological shielding.

It is an inherent feature of those reactions that the reaction products show a wide distribution of energies, with peak energies ranging up to 3 MeV kinetic energy per neutron. This leads to deBroglie wavelengths in the femtometer region, which is unsuitable for SANS scattering experiments. Thus, in order to obtain a coherent beam it is not only necessary to collimate the neutrons but also to moderate and monochromatize them. Both processes result in losses in usable flux, since the phase space of neutrons cannot be compressed by lenses, as is the case for photons.

The moderation process is performed by collision processes in a moderator medium. The

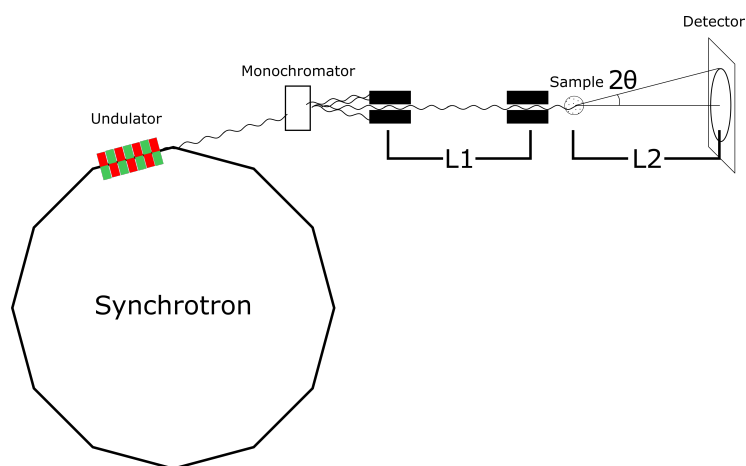


Fig. 6.4: Synchrotron SAXS setup. Here the radiation is produced in the storage ring of a synchrotron. In earlier designs, the x-rays were produced at the bending magnets in the ring (kinks in the ring here). This however lead to a wide spread of the produced wavelength and a high angular distribution of the radiation. An undulator from a magnet array as depicted here produces a narrow distribution of wavelength and angular divergence. The rest of the setup is comparable to the laboratory setup, albeit the intensity of the radiation is orders of magnitude higher, which allows for finer collimation slits and longer collimation distances and SDDs.

moderator is a material at temperatures around 25 K or below and the resulting neutron spectrum is a Maxwell-Boltzmann spectrum of the corresponding temperature. This results in peak wavelengths around 4 Å for the neutron beam. Neutron scattering instruments can be run both in time-of-flight mode or monochromatic mode.

A schematic of a SANS instrument is shown in Fig.6.5. Both cases with a monochromator and a chopper setup for time-of-flight are presented. In a continuous source the neutron flux has to be interrupted for the timing of time-of-flight mode while for pulsed sources there is an inherent interruption of the neutron flux.

This moderation and collimation process in consequence means that neutrons always show an, albeit small, distribution of wavelengths and therefore a lower signal to noise level than x-ray sources. Spin and isotopic incoherence add to that. Beam damage however is high on impossible with the weakly interacting neutrons.

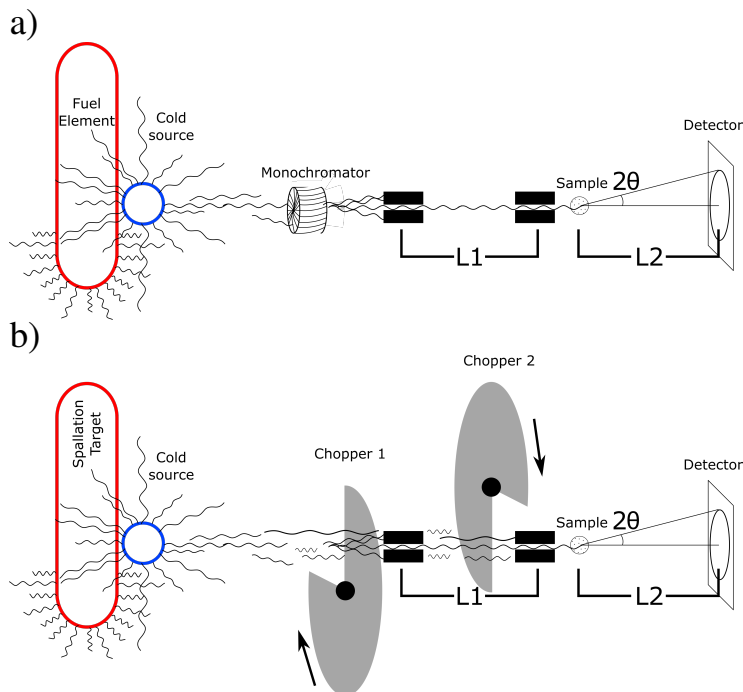


Fig. 6.5: a) Continuous source SANS setup and b) pulsed source SANS Setup. In both cases the neutron source (red) creates hot neutrons of a short wavelength. A cold source (blue) vessel (usually filled with cold ^2H or ^2D) is moderating the neutrons down to slower speeds, i.e. longer wavelengths. In both cases the collimation distance and SDD is widely adjustable for most instruments, with lengths between 1 m up to 30 m. In a SANS instrument at a continuous source a monochromator (a turbine with slightly inclined channels) selects a certain wavelength (usually between 3 and 15 Å) and afterwards the setup is very much like the one shown for SAXS setups, except that the whole instrument is larger. In case of a pulsed source, choppers (rotating discs with transparent openings for neutrons) define a start and an end time for each pulse. Since neutrons, different from x-rays, are particle waves, their wavelength determines their speed. Thus, the wavelength is determined by measuring the time of arrival at the detector for each neutron. For an optimized neutron transport all components are usually evacuated.

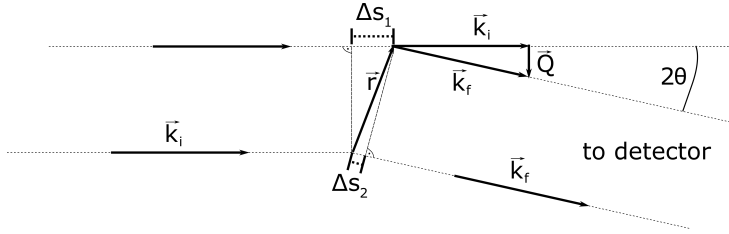


Fig. 6.6: Construction of $\mathbf{Q}$. The incoming and final wavevectors $\mathbf{k}_i$ and $\mathbf{k}_f$ define both the scattering vector $\mathbf{Q}$ as well as the path length difference $\delta = \Delta s_1 - \Delta s_2$. Here it is important to note that the selection of the center of origin is arbitrary and thus can be chosen to be at the center of the construction. The calculation of the length of $\mathbf{Q}$ is then given by Eq.6.2.

6.4 Indirect space and Small-Angle Scattering

The need for the resolution of small angles can be directly derived from Bragg's equation

$$n\lambda = 2d \cdot \sin \theta \quad (6.1)$$

with n being the order of the diffraction, d being the distance between two scatterers, 2θ as the scattering angle and λ the wavelength of the incoming beam. In order to get interference the incoming beam has to have a wavelength that corresponds to the investigated size regime, which in both cases is on the order of a few Angstroms. Using Bragg's equation with $n = 1$, $d = 50\text{\AA}$ and $\lambda = 1\text{\AA}$ we arrive at $0.01 = \sin \theta \approx \theta$. Thus, the largest structures to be resolved are determined by the smallest achievable angle.

In order to allow for a setup and wavelength independent data evaluation the data is recorded in terms of Q or indirect space. The construction of that Q space from two scattering points is shown in Fig.6.6. From that the magnitude of $\mathbf{Q}$, which here for simplicity is $|\mathbf{Q}| = Q$, can be derived as

$$Q = \frac{4\pi}{\lambda} \sin \theta. \quad (6.2)$$

Even though $\mathbf{Q}$ is strictly speaking a vector, for most small angle problems only the absolute value Q is of interest, hence this simplification is reasonable. This is due to the isotropic scattering picture of a majority of small-angle scattering data. Another simplification that is often used is the small-angle approximation for the sine with $\sin \theta = \theta$, which is very well valid for small angles. Combining Eqs.6.1 and 6.2 also delivers a useful expression for the approximation of inter-particle distances or correlation lengths

$$d = \frac{2\pi}{Q}. \quad (6.3)$$

6.5 Resolution limits

SAS is working based on the interference of coherent radiation. That in itself imposes some limitations on the samples and properties that can be investigated. Any loss of coherence will limit the resolution.

In terms of size, the path length difference due to the scattering at the object has to be of the same order of magnitude as the wavelength of the incoming radiation, analogous to light interference at a double slit. Concerning the analysis in indirect space, also the limited size of the detector and coherence volume of the sample has to be taken into account.

6.5.1 Coherence resolution limit

Coherence can be measured along the beam propagation, where different speeds of neutrons can mean that after a certain flight time they are not in the same wave package anymore. Essentially this longitudinal coherence is a measure of the wavelength measured in its own spread, i.e.

$$L_{coh} = \frac{\lambda^2}{\Delta\lambda} = \lambda \left(\frac{\Delta\lambda}{\lambda} \right)^{-1} \quad (6.4)$$

This essentially measures, how many multiples of the wavelength a neutron can propagate, before the error is large enough to make up a full wavelength. With neutrons often a $\Delta\lambda/\lambda = 0.1$ is achieved in instrumentation, which means that the longitudinal coherence length L_{coh} is approximately 10 times the wavelength, so on the order of 3-10 nm. This is not a hard upper resolution limit, but it limits the path length difference created by scattering events. If the path length differences are too large then this will not be visible. Using Bragg's equation 6.1 we can calculate the angle belonging to a certain path length difference. Assuming a 10 nm structure and a 20° angle we arrive at approximately 7 nm path length difference. This means, for $7\text{Å} = 0.7\text{nm}$ wavelength neutrons this will not affect them in a neutron scattering instrument. However, this is usually limited by the angular Q-resolution as shown in the next section.

This also explains why small-angle scattering is so powerful with relatively large objects. In equation 6.1 the size of the object and the sine of the angle are a product. If the object becomes large, with a smaller angle you can compensate and still fulfil the conditions for coherent interference scattering.

6.5.2 Smallest and largest structure

From Eq.6.3 it is apparent that to measure small distances in the sample structure, large Q are required and vice versa. The large Q -values in the case of SAS are limited by the size of the detector, nuclear distances are usually measured in diffractometer instruments which cover a larger solid angle.

Large detectors for a SAS instrument would cover an angle of +/- 20°. This results in

$Q = 0.7 \text{ \AA}^{-1}$ for a wavelength of $3 \text{ \AA}$ and hence a distance of approximately $9 \text{ \AA}$ for the smallest resolvable structure. In order to reach a much larger path length difference, where the coherence limit would impact the measurement larger detectors and measurements of smaller distances would be necessary, which are outside the experimental scope for SAS experiments.

More interesting is the lower angular limit, so the largest observable structure. This is for a lot of SANS instruments on the order of 0.1° or even smaller. This means, with the same wavelength as above of $3 \text{ \AA}$ this results in a maximum observable size of 300 nm at $Q \approx 3 \cdot 10^{-3} \text{ \AA}^{-1}$. If this can be reduced farther, where some instruments can reach on the order of $Q \approx 10^{-4} \text{ \AA}^{-1}$ which results in an observable size up to a micrometer in the extreme limit.

6.6 Fourier Transform and Phase Problem

Considering the spacing of only two scattering centers as in the last section needs to be extended to an arrangement of scattering centers for evaluation of macroscopic samples, where each atom/molecule can contribute to the scattered intensity. Since the incoming wave at location $\mathbf{x}$ can be considered to be an plane wave it can be described by

$$\psi(\mathbf{x}, t) = A_{\text{inc}} \exp [i(\mathbf{k} \cdot \mathbf{x} - \omega t)], \quad (6.5)$$

where ψ is the wave amplitude, A_{inc} the incoming amplitude, ω the angular frequency, and $\mathbf{k}$ the incoming wave vector [1].

In order to calculate the phase shift $\Delta\phi$ between waves scattered from two centers, as shown in Fig. 6.6, we need the difference in travelled distance δ between the two waves. This yields

$$\Delta\phi = \frac{2\pi\delta}{\lambda} = \mathbf{Q} \cdot \mathbf{r}, \quad (6.6)$$

where the scattering vector is defined as

$$\mathbf{Q} = \mathbf{k}' - \mathbf{k}. \quad (6.7)$$

This then leaves us with the wave scattered by the first scattering center

$$A_1(\mathbf{x}, t) = A_{\text{inc}} b \exp [i(\mathbf{k}' \cdot \mathbf{x} - \omega t)], \quad (6.8)$$

where b is the scattering length, and the corresponding scattered wave from the second scattering center

$$A_2(\mathbf{x}, t) = A_1(\mathbf{x}, t) \exp(i\Delta\phi). \quad (6.9)$$

Here the wave number is defined as $|\mathbf{k}| = \frac{2\pi}{\lambda}$.

Therefore

$$A_2(\mathbf{x}, t) = A_{\text{inc}} b \exp[i(\mathbf{k}' \cdot \mathbf{x} - \omega t)] \exp(i\mathbf{Q} \cdot \mathbf{r}). \quad (6.10)$$

This can then be combined into the full description of the amplitude with both contributions to

$$A(\mathbf{x}, t) = A_1(\mathbf{x}, t) + A_2(\mathbf{x}, t) \quad (6.11)$$

$$= A_{\text{inc}} b \exp[i(\mathbf{k}' \cdot \mathbf{x} - \omega t)] (1 + \exp(i\mathbf{Q} \cdot \mathbf{r})). \quad (6.12)$$

note that the scattering efficiency b for each scattering center will later be discussed for both x-rays and neutrons.

Since only intensity can be observed at the detector, we need to consider the modulus square, calculated with the complex conjugate of the expression itself

$$I(\mathbf{Q}) = \frac{1}{V_{\text{sample}}} A(\mathbf{x}, t) A^*(\mathbf{x}, t) \quad (6.13)$$

$$= \frac{A_{\text{inc}}^2 b^2}{V_{\text{sample}}} (1 + \exp(i\mathbf{Q} \cdot \mathbf{r})) (1 + \exp(-i\mathbf{Q} \cdot \mathbf{r})). \quad (6.14)$$

Here the time and absolute location dependencies in Eq.6.12 have cancelled each other out, so we can neglect them and are left with a function that solely depends on the scattering vector $\mathbf{Q}$ and the relative position of the particles $\mathbf{r}$ with respect to each other. The normalisation to the scattering volume V_{sample} is due to the fact, that the scattered intensity is directly proportional to the scattering volume. Utilising those dependencies allows us to generalize Eq. 6.12 to the case of N identical scattering centers with

$$A(\mathbf{Q}) = A_{\text{inc}} \sum_{i=1}^N b_i \exp(i\mathbf{Q} \cdot \mathbf{r}_i). \quad (6.15)$$

For identical scatterers with constant scattering length b , this simplifies to

$$A(\mathbf{Q}) = A_{\text{inc}} b \sum_{i=1}^N \exp(i\mathbf{Q} \cdot \mathbf{r}_i). \quad (6.16)$$

The $\mathbf{r}_i$ here signify the relative locations of all scattering centers in the sample, relative to either simply the first scattering center or any arbitrary center chosen. Indeed the choice of coordinate origin is arbitrary and any choice is mathematically identical. Replacing the sum by a weighed integral allows also the calculation for the case of a (quasi)continuous sample with number density $\rho(\mathbf{r})$:

$$A(\mathbf{Q}) = A_{\text{inc}} b \int_{V_{\text{sample}}} \rho(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) dV. \quad (6.17)$$

This is the Fourier transform of the number density of scattering centers with identical scattering efficiency b , it can also be applied for numerous scattering efficiencies, if a space dependent scattering power (scattering length density) $\rho_b(\mathbf{r}) = b(\mathbf{r})\rho(\mathbf{r})$ is used under the integral.

In the following, the incoming amplitude is normalized to unity, $A_{\text{inc}} = 1$, such that all intensities are given relative to the incoming beam intensity.

However, since the phase information got lost while obtaining the intensity as an absolute square of the amplitudes, there is no direct analytic way of performing an inverse Fourier transform. This is why this is called the phase problem. Also, as described above, in a wide range of cases it is enough to investigate the modulus of $\mathbf{Q}$, neglecting its vector nature.

6.7 Scattering Efficiency

Since the physical scattering event is very dissimilar for x-rays and neutrons they shall be discussed separately here. However, it should be noted, that the nature of the scattering process does not impact on the method of data evaluation in general. Only in very specific cases, such as contrast matching or polarized scattering there is any discernible difference.

6.7.1 Scattering with x-rays

X-rays, as photons, interact with the sample via electromagnetic interaction. For the purpose of this manuscript it is sufficient to note that the vast majority only interact with the electron shell around the atoms and thus effectively map the electron density within the sample. Interactions with the nucleus would only occur at very high energies, which are not usually used in elastic scattering. In a rough approximation the strength of the electromagnetic interaction scales with Z^2 , meaning that heavy elements, such as a wide range of common metals, scatter considerably stronger than light ones, like hydrocarbon compounds. For element analyses there is also the possibility of resonance scattering, where the chosen x-ray energies are close to the resonance gaps in the absorption spectrum of specific elements (ASAXS). [4]

Based on Thomson scattering the scattered intensity at angle 2θ is

$$I(2\theta) = I_0 \left(\frac{e^2}{mc^2} \right) \frac{1 + \cos^2 2\theta}{2} \quad (6.18)$$

$$\frac{I}{I_0} = \left(\frac{d\sigma}{d\Omega} \right)_2 = r_e^2 \frac{1 + \cos^2 2\theta}{2} \quad (6.19)$$

Here we also introduced the differential scattering cross section $\frac{d\sigma}{d\Omega}$ for a single electron and r_e being the radius of an electron. This means that the total probability for a scattering event to occur into a solid angle $d\Omega$ is exactly that value for a single, isolated electron. This probability is in units of an area. Thus, the scattering length for a single electron b_e is defined as the square root of that:

$$b_e = r_e \sqrt{\frac{1 + \cos^2 2\theta}{2}} \quad (6.20)$$

With those previous equations it is again important to note that small-angle scattering is mainly concerned with small angles, thus that $\cos 2\theta \approx 1$ is a very good approximation. This is also, together with backscattering, the location of the highest intensity and negligible polarization effects. The numeric values for the constants used here are $r_e = 2.818 \times 10^{-15}$ m and the scattering cross section for a single electron $\sigma_e = 6.65 \times 10^{-29} \text{ m}^2 = 0.665 \text{ barn}$ after integration over the full solid angle. As apparent with integration over the full solid angle, the relation is $\sigma = 4\pi b_e^2$.

Since usually the goal is to find the distribution of scattering centers in a volume, the density of scattering length per unit volume is of interest. This is the scattering length density (SLD)

$$\rho_b(\mathbf{r}) = \sum_i b_i N_i = \int_V b(\mathbf{r}) dV. \quad (6.21)$$

Here b_i is the scattering length of each individual scattering center. For the second equality in this equation we did a transition from discrete scattering centers to a continuous spatial distribution of scattering length in the scattering volume V .

A very common way of expressing scattering efficiency is using electron units. As can be seen in Eq.6.15 the scattering amplitude is only determined by the scattering length of a single electron apart from the Fourier transform of the local density. This means the scattering intensity in electronic units can be expressed as

$$I_{eu}(Q) = \frac{I(Q)}{I_0 b_e^2} \quad (6.22)$$

This means, with appropriate calibration, if there is an intensity of $I_{eu} = 200 b_e^2$ at a certain Q , that the size scale corresponding to that Q vector has 200 electrons per unit volume.

Since photons interact mainly with the electron shell, there is also an angle dependency accounting for the time averaged location probability of the electrons in the shell, which may or may not be spherical, depending on the electronic configuration of that specific atom. This would then lead to a SLD in terms of $b_e(Q) = b_e f(Q)$ with f being the atomic scattering factor for any specific element. This important to take note of, when there is a structure or form factor on the same size scale as a single atomic distance $Q = \frac{2\pi}{1.54 \text{ \AA}} = 4.08 \text{ \AA}^{-1}$. This is usually not in the regime of interest for small-angle scattering and will mostly vanish in the incoherent background.

Another incoherent background effect is Compton scattering, where inelastic processes change the wavelength during the scattering process. This is however again strongly suppressed at small angles. The wavelength shift occurring based on Compton scattering is following this expression

$$\Delta\lambda = \frac{h}{mc} 2 \sin^2 \theta \quad (6.23)$$

The prefactor is $\frac{h}{mc} = 0.02426 \text{ \AA}$. It is also obvious that at large angles $2\theta = 180^\circ$ the energy transfer is maximal. Since we are always investigating angles close to $\theta = 0$ the wavelength shift and hence the incoherent background is negligible compared to other experimental factors, such as slits and windows scattering.

6.7.2 Scattering with neutrons

6.7.2.1 Scattering length

While we could rely on classical electromagnetic scattering theory for x-rays, for neutrons we have to apply quantum mechanics for the calculation. While for photons we could rely on the relatively long-range electromagnetic interaction of the electron shell there is no simple corresponding expression for neutrons, since the neutron always experiences the potential of the nucleus directly. This means, the potential experienced is both directly influenced by the weight of the core, i.e. number of nuclei, which corresponds to the depth of the potential, as well as radius of the core, which corresponds to the width of the potential. Keep in mind, the same calculation could be done for an electromagnetic potential and the result would be the Thomson scattering formula 6.19. Similar approaches to the one shown here were shown by Hammouda or Tong [6, 7]. For additional details, see Appendix 6.12.

In order to calculate the scattering length density, we have to start with the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi. \quad (6.24)$$

With $k_1^2 = \frac{2m(E+V_0)}{\hbar^2}$ we can write a solution for this for weak scattering potentials V_0 at low scattering energies E , which is exactly the case for neutron scattering. The solution for the scattering length $a_s = b$ incorporates the radius of the scattering nucleus a :

$$a_s = b = a - \frac{\tan(k_1 a)}{k_1}. \quad (6.25)$$

A representation of this is given in Fig. 6.7. The strong variation due to minute changes in the numerical value make it clear, why tabulated values are used in most cases. In addition, until here we only considered spherically symmetric s-wave scattering. Since magnetic moments are not spatially uniform a lot of the approximations used above would not work in that case.

Based on that we usually rely on tabulated values for the cross sections and scattering lengths of different elements and isotopes (see Tab.6.3) and can then write the cross section and scattering length relation as

$$\frac{d\sigma}{d\Omega} = b^2 \quad (6.26)$$

One important correlation between the two, if taking a naive approach to the view of a sphere that is hit from one side, which in projection is a circle, is that the total scattering

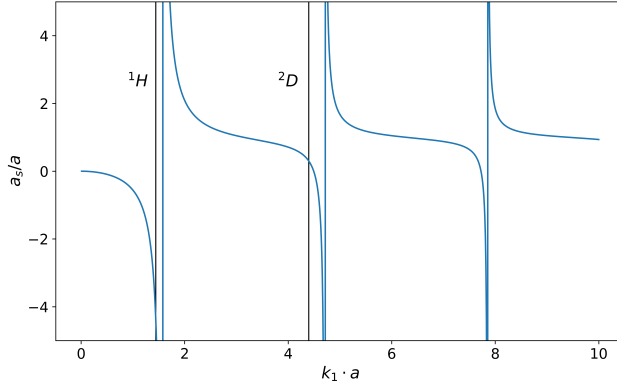


Fig. 6.7: Behavior of scattering length $b = a_s$ as a function of nuclear radius a and k_1 . Using representative values for example for hydrogen ($a = 8.5 \cdot 10^{-16}$ m) and deuterium ($a = 2.1 \cdot 10^{-15}$ m) it becomes apparent how those strong differences in scattering length happen, and also why this has an especially strong impact for light elements, where the radius strongly changes by adding or removing one nucleon. Values for hydrogen and deuterium are marked. As a side note, this can also be used to calculate the depth of the nuclear potential via neutron scattering, since the energy E of the neutron is known and the only free parameter is V_0 .

Element	scattering length $b_{coh}/10^{-14}m$
1H	-0.374
2D	0.667
C	0.665
N	0.936
O	0.580
Si	0.415
Br	0.680

Table 6.3: Coherent scattering length of several elements and isotopes.

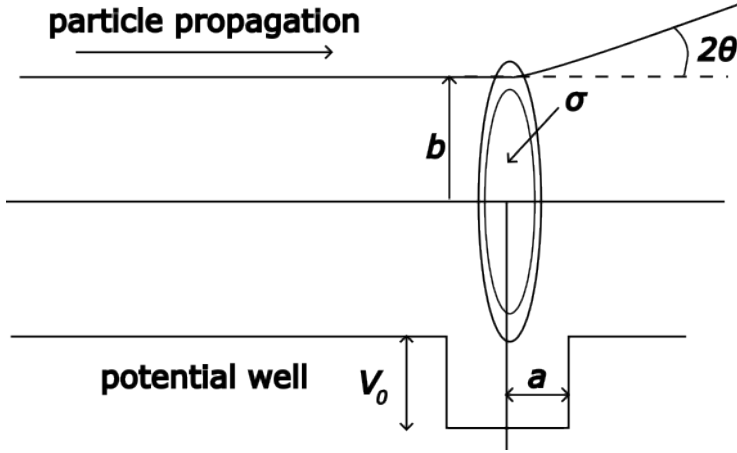


Fig. 6.8: Sketch of scattering length b , scattering cross section σ , potential depth V_0 and radius a for a particle scattering event. Please note that σ , which could be seen as a circle here is quantum mechanically rather a sphere.

cross section is given by the surface of a sphere with radius b . This counterintuitive fact can be understood as a quantum mechanical particle not only interacting with the projected surface, but with the whole surface of the potential:

$$\sigma = 4\pi b^2 \quad (6.27)$$

The general correlation between the different entities is shown in a sketch in Fig.6.8

That said, only coherent scattering can form interference patterns, i.e. no change of the nature of the radiation can take place during the scattering process. However, since the neutron can change its spin orientation through spin-spin coupling during the scattering process that may happen, depending on the spin orientation of the sample nuclei. Those are completely statistical processes.

As neutrons are fermions, which have spin $1/2$ the possible outcomes after a scattering process with a nucleus of spin i are $i + 1/2$ and $i - 1/2$, and the associated possible spin states are

$$\text{number of states } i + 1/2 : 2(i + 1/2) + 1 = 2i + 2 \quad (6.28)$$

$$\text{number of states } i - 1/2 : 2(i - 1/2) + 1 = 2i \quad (6.29)$$

$$\text{total number of states} : 4i + 2. \quad (6.30)$$

This immediately shows, that only for the case $i = 0$ there can be only two states. Since it is impossible to know the spin state of non-zero spin nuclei under ambient conditions, the differential cross section becomes a two-body problem of the form:

$$\frac{d\sigma}{d\Omega} = \sum_{i,j} \langle b_i b_j \rangle \exp -i\mathbf{Q}(\mathbf{r}_i - \mathbf{r}_j) \quad (6.31)$$

Here $\langle b_i b_j \rangle$ is the expectation value of the product of scattering lengths for each $b_i b_j$ combination possible given isotope and spin variability. For this there is only one coherent outcome, where $b_i = b_j$, which then results in

$$\langle b_i b_i \rangle = \langle b_i^2 \rangle = \langle b^2 \rangle. \quad (6.32)$$

All other cases result in $b_i \neq b_j$ and therefore

$$\langle b_i b_j \rangle_{i \neq j} = \langle b_i \rangle \langle b_j \rangle = \langle b \rangle^2. \quad (6.33)$$

This then results in

$$\frac{d\sigma}{d\Omega} = \langle b^2 \rangle \cdot \sum_{j,k} \exp(-i\mathbf{Q}(\mathbf{r}_i - \mathbf{r}_j)) + N(\langle b^2 \rangle - \langle b \rangle^2). \quad (6.34)$$

Here $\sqrt{\langle b^2 \rangle} = b_{coh}$ signifies the coherent scattering length, since it contains information about the structure of the sample via $\mathbf{r}_{ij}$ and $\sqrt{\langle b^2 \rangle - \langle b \rangle^2} = b_{inc}$ is the incoherent scattering length not allowing for coherent constructive interference. This cannot be suppressed instrumentally; therefore, isotopes with low incoherent scattering length are often chosen in neutron scattering to suppress the incoherent background. Both coherent and incoherent scattering lengths can be used separately together with Eq.6.21 to obtain the corresponding scattering length densities.

For the calculations above it is useful to recall the difference between the squared mean $\langle x \rangle^2$ and the mean squared $\langle x^2 \rangle$. Mean squared squares every value, sums it up and then divides by the number of values, which therefore is a combination of autocorrelation and fluctuations around zero, while squared mean measures the coherent average overall. They are connected by the variance $\langle x^2 \rangle - \langle x \rangle^2 = Var(x)$, which makes it immediately apparent that a strongly fluctuating sample (in this case a lot of different scattering centers) result in a high variance, low autocorrelation (with identical scatterers) and a large incoherent background. This can also be seen with the example of a simple statistical white noise signal (see Fig. 6.9).

6.7.3 Scattering Cross Section and Contrast Matching

As described above there is a Z^2 dependency of the cross section of atoms in case of x-rays and the cross section values for neutrons are taken from tabulated values. The resulting differences in cross section are illustrated in Fig.6.10. Because different isotopes have very different cross sections for neutron scattering, in some cases it is possible to replace certain isotopes in order to arrive at desired contrast conditions.

One of the most important examples for that technique, called contrast matching, is replacing hydrogen by deuterium. This leaves the chemical composition of the sample unchanged, and

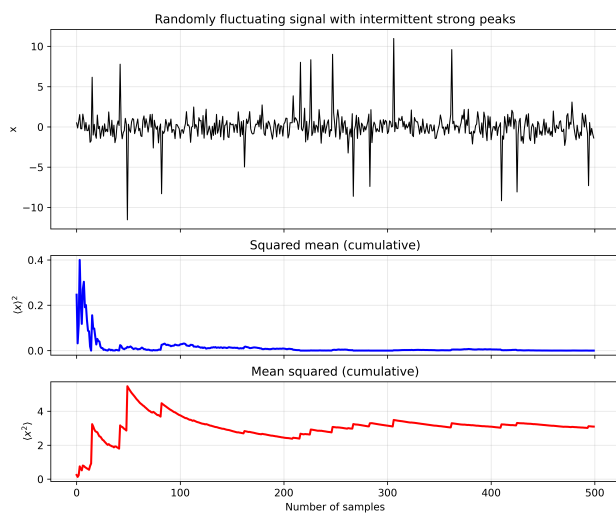


Fig. 6.9: Illustration on the difference between squared mean and mean squared to show the idea of autocorrelation for similar scattering centers in mean squared and the idea of summing over non-identical scattering centers for squared mean.

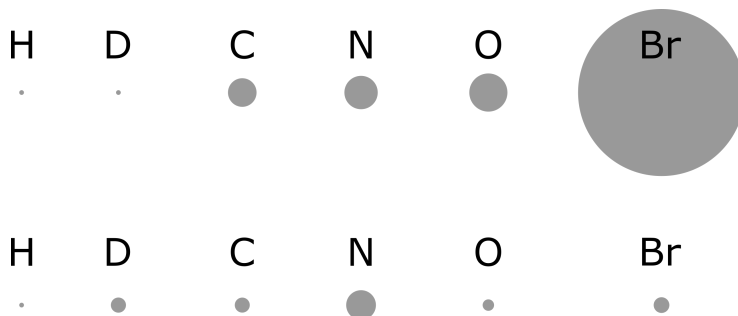


Fig. 6.10: Coherent cross-sections for selected elements for x-rays (top) and neutrons (bottom). The coherent scattering cross section scales linearly with the diameter of the circles. It is apparent, that the Z^2 dependency strongly emphasizes heavy elements in x-ray scattering, whereas for neutrons even single isotopes can be distinguished. However, for neutrons there is no simple analytic expression for the scattering cross-sections.

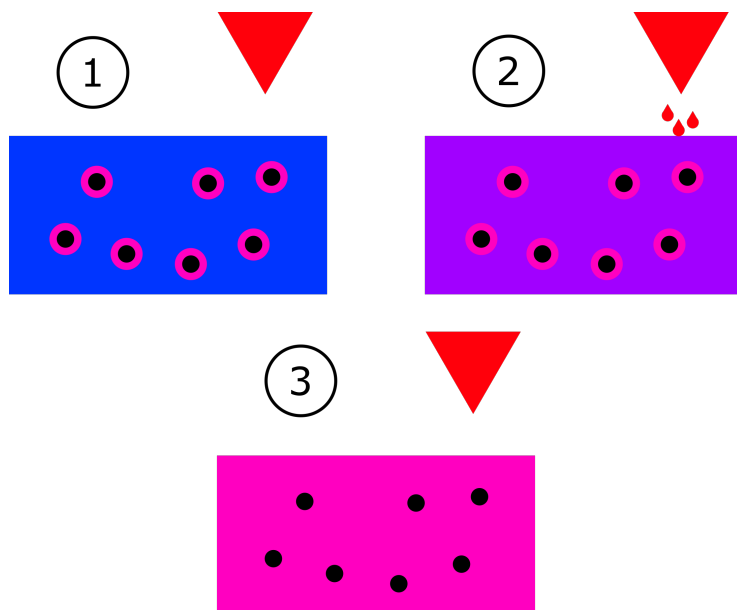


Fig. 6.11: Illustration of the concept of contrast matching. In step ① there are micelles with a corona (pink) dissolved in a solution (blue). The scattering length density of the corona is between the SLD of the solvent and its deuterated counterpart (red). In step ② the deuterated solvent is added to the solution, which changes the contrast conditions. Finally, in step ③ a sufficient amount of deuterated solvent has been added, so the contrast between the corona and the solvent has vanished. Now the micellar cores can be measured directly.

hydrogen is extremely abundant in most organic compounds. The concept can in some cases be extended to be used as the Babinet principle, in order to suppress background scattering, since it is extremely preferable to have a solvent with a low background and a solute with a higher background than vice versa. A sketch of the concept is shown in Fig.6.11.

This method allows highlighting otherwise hidden features of the sample or suppressing dominant scattering in order to better determine a structure with a lower volume fraction and therefore less scattering contribution. Examples for that application are highlighting the shell of a sphere, by matching the core or vice versa. Also for protein samples certain structures can be matched, so that only distinct features are visible.

In order to apply contrast matching, mostly the solvent is changed. In some rare cases also the polymer or other sample is synthesized with a different isotope composition. Here the finding of the correct H/D fraction of the solvent shall be shown. Fig.6.12 gives an example of how to find the correct H/D fraction in a semi-analytic way. The underlying principle is expressed by

$$\rho_{b,sample} = \rho_{b,H_2O} \times H + \rho_{b,D_2O} \times D \quad (6.35)$$

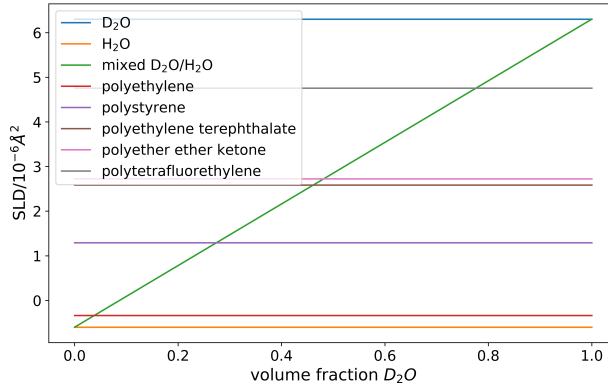


Fig. 6.12: Semi-analytic way to determine the necessary solvent deuteration for contrast matching. The concentration at the matching point, where the solvent has the same SLD as the polymer particles, is determined by the crossing of the mixed D_2O/H_2O SLD line and the SLD line of the respective polymer. For the calculation the scattering length density of water is calculated to $-0.6 \cdot 10^{-6} \text{ \AA}^2$ and the SLD of heavy water is calculated to $6.3 \cdot 10^{-6} \text{ \AA}^2$.

$$H \equiv 1 \quad (6.36)$$

$$D = \frac{\rho_{b, \text{sample}} - \rho_{b, H_2O}}{\rho_{b, D_2O}}. \quad (6.37)$$

This way the volume of heavy water for each unit volume of protonated (usual) water can be calculated. It is also apparent from that calculation that only mixtures with a scattering length density between water and heavy water can be matched, and that the equations above only cover the non-trivial cases, where pure water or heavy water is not suitable. The actual volumes can then be calculated with $V_{\text{water}} = \frac{H}{H+D}$ and $V_{\text{heavy water}} = \frac{D}{H+D}$.

A prominent example for contrast matching is the matching out of the shell or core of a micelle. The contrast behavior and the resulting scattering curves are shown in Fig. 6.13. Essentially contrast matching can improve the fitting procedure, if well known parts of the structure are matched out or emphasized by the contrast matching. This then delivers two or more different data sets that all should return comparable results. Another option is the reconstruction of embedded particles in a larger structure. Also here, the overall fitting procedure can benefit from two fits with mutually corroborating results.

One concept that shall also be mentioned here is magnetic (spin-) contrast. In this context Fig. 6.11 can be understood to be particles with a magnetic shell. As long as the spins are not aligned there is no contrast between the shell and the solvent (step ③). When an external magnetic field aligns the spins in the shell, a contrast between the shell and the solvent emerges (①). Several other possibilities with and without polarization analysis are possible, however that is beyond the scope of this manuscript.

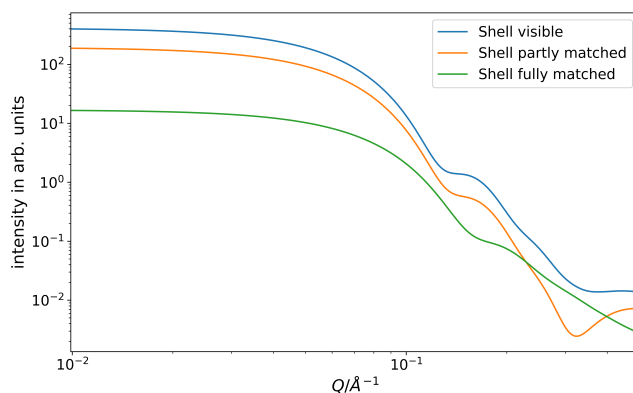


Fig. 6.13: Scattering curves for micelles with unmatched, partially matched and completely matched corona. The curves correspond to the scenarios ①, ② and ③ in Fig.6.11. Here two effects can be observed. The corona is only 50% of the radius of the core, hence it influences the scattered intensity at higher angles than the core itself, the scattering feature at $Q=0.15 \text{\AA}^{-1}$ corresponding to the micellar core is therefore quite stable, while the intensity at higher Q changes drastically. Considering the forward scattering the dependence of the scattering contrast between solvent and core is directly visible. The matched out corona shows the least contrast, and therefore the lowest forward scattering intensity, while the unmatched corona has the highest contrast and the highest intensity. This approach is also used, when an analytic approach to find the matching $\text{D}_2\text{O}/\text{H}_2\text{O}$ concentration cannot be found. Several concentrations are tested and where a minimum in the scattered intensity is found, the contrast can be assumed to be matched.

6.8 Form factors

There are different usages of the term form factor in the literature. The term applied in SAS is the squared magnitude of the Fourier transform of the scattering length density contrast of an individual particle, describing scattering from particles of a given shape and size. Note this is structurally similar, but not identical to the atomic form factor in X-ray crystallography, where the form factor is the Fourier transform of the electron density around an atom and therefore represents a scattering amplitude. The scattered intensity is obtained from the squared magnitude of this quantity.

As described above, the phase problem usually prevents an analytic reconstruction of the structure from the scattered intensity by an inverse Fourier transform. There are approaches attempting the direct reconstruction of direct space information [8] or reconstruction from bead model annealing / Monte Carlo simulation [9, 10]. All these approaches have in common that a direct analytic expression for the scattering is not foreseen, and therefore it is hard to use them as a starting point of the analysis. In the past, the model based analysis has been the most applied approach for the analysis of small-angle scattering data. Here, predetermined structures undergo a Fourier transform, whose result is then used to calculate a scattering pattern. This results in the most cases in analytic expressions that can be directly fitted to the data and are often used in a reference-based manner in order to determine the structure of the sample. As most geometric forms can be approximated either as a sphere, a disk or a rod (see Fig.6.14) these forms are discussed below. More elaborate structures are available and can in principle be calculated for any structure where the form can be described by an analytic expression. A short, and by no means complete, list of programs for the evaluation of SAS data is SasView (<https://www.sasview.org>), SasFit (<https://kur.web.psi.ch/sans1/SANSSoft/sasfit.html>) and Scatter (<http://www.esrf.eu/UsersAndScience/Experiments/CRG/BM26/SaxsWaxs/DataAnalysis/Scatter#>).

The mathematical rationalization for the use of form (and actually structure) factors comes from Eqs. 6.14 and 6.15. With those two equations we can write

$$I(\mathbf{Q}) = \frac{1}{V_{\text{sample}}} \langle A(\mathbf{Q}) A^*(\mathbf{Q}) \rangle = \frac{b^2}{V_{\text{sample}}} \left\langle \left\{ \sum_i^{N_{\text{scatterers}}} \exp(-i\mathbf{Q} \cdot \mathbf{r}_i) \right\} \left\{ \sum_j^{N_{\text{scatterers}}} \exp(i\mathbf{Q} \cdot \mathbf{r}_j) \right\} \right\rangle. \quad (6.38)$$

Here we are running the sums over all scattering centers $N_{\text{scatterers}}$ in the sample. Exploiting the properties of the sum and the exponential function we can pull this together in one term of the form

$$I(\mathbf{Q}) = \frac{b^2}{V_{\text{sample}}} \left\langle \sum_i^{N_{\text{scatterers}}} \sum_j^{N_{\text{scatterers}}} \exp[-i\mathbf{Q} \cdot (\mathbf{r}_j - \mathbf{r}_i)] \right\rangle. \quad (6.39)$$

This expression means that we sum over all scattering centers at positions $\mathbf{r}_i$ with identical scattering power b . Since the expression is independent of the choice of coordinate origin, we may separate the sum into contributions originating from scattering centers within the

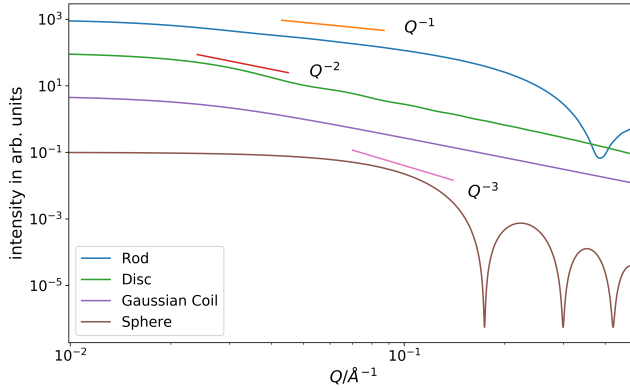


Fig. 6.14: Form factors for several scattering geometries. The slopes at the onset of the form factor after the plateau are shown, which is mostly determined by the fractal dimension of the scattering object. Here it also becomes apparent that solely relying on that slope may lead to misinterpretation between similarly scaling objects, here Gaussian coils and discs.

same particle and from scattering centers belonging to different particles.

For an assembly of N identical particles and using $\mathbf{r}_{ji} = \mathbf{r}_j - \mathbf{r}_i$, this becomes

$$I(\mathbf{Q}) = \frac{NN_{\text{scatterers}}b^2}{V_{\text{sample}}} \left\langle \frac{1}{N_{\text{scatterers}}} \left\{ \sum_{i,j \text{ in same particle}}^{N_{\text{scatterers}}} \exp(-i\mathbf{Q} \cdot \mathbf{r}_{ji}) \right\} \right. \quad (6.40)$$

$$\times \left. \left\{ 1 + \frac{1}{N} \sum_{k,l \text{ centers of different particles}}^N \exp(-i\mathbf{Q} \cdot \mathbf{r}_{kl}) \right\} \right\rangle. \quad (6.41)$$

Two things happened here: In Eq. 6.40, since all particles are identical, we only need to perform the internal sum once and multiply it by N , since this is the number of particles. Also, we need to be careful about $N_{\text{scatterers}}$. While it denoted all scattering centers in a sample before, here it only denotes the scattering centers belonging to one particle. We normalize by the number of scattering centers, so that at $Q = 0$ this whole section becomes 1. You may find in other textbooks this normalization is missing, if the scatterers are considered in a continuum (see 6.17). Then this normalization is included into the density of scattering centers in space. Note for the following sections, if only 6.40 is considered it cancels immediately out, so this is only necessary if both intra- and inter-particle relations are considered.

In Eq. 6.41 we define $\mathbf{r}_{kl} = \mathbf{r}_k - \mathbf{r}_l$ as the distance between the centers of different, but identical, scattering particles. So here the sum is running over all particles, instead of the scattering centers within the particle. We obtain the term 1 from the self-correlation contribution with $\mathbf{r}_{kl} = 0$, for which $\exp(0) = 1$. Furthermore, the second term is divided by N in order to avoid counting inter-particle distances multiple times.

Here we can include a simple mental check: In Eq. 6.38 we ran over each particle twice, once in the left sum, once in the right sum. In Eqs. 6.40 and 6.41 we also run over each particle twice, once inside the particle and again for each particle that is there. Also, looking at Eq. 6.41 we can see the Fourier transform of the location of particles. If the particles have a strong correlation the Fourier transform will return a non-zero value for some $\mathbf{Q}$ -values, imagine the Fourier transform of a sine-wave where you get two Dirac δ functions for the frequency of the sine wave either side of zero. If the particles show no correlation at all, you have a Fourier transform of an average constant distribution, which in turn is a sine of cosine wave with some amplitude. In the limit of many particles, the division by N means the second term essentially goes to zero, so you are only left with the leading 1, which gives you exactly the form factor and no additional contributions from correlation between the particles, as is expected if there is no correlation between the particles.

Until this point no approximation has been made; we merely reordered the sums according to the particle arrangement inside the scattering volume. For the sake of simplicity we assume from here on identical particles, no coupling between intra- and inter-particle correlations, and particles that are orientationally averaged as indicated by $\langle A(\mathbf{Q})A^*(\mathbf{Q}) \rangle$.

This allows us to write the scattered intensity from a collection of identical particles in the form

$$I(\mathbf{Q}) = \frac{N N_{\text{scatters}} A_0^2}{V_{\text{sample}}} F(Q) S(Q) \quad (6.42)$$

$$= \frac{N N_{\text{scatters}} \Delta \rho_b^2 V^2}{V_{\text{sample}}} F(Q) S(Q) \quad (6.43)$$

$$= \rho N_{\text{scatters}} \Delta \rho_b^2 V^2 F(Q) S(Q), \quad (6.44)$$

with

$$\rho = \frac{N}{V_{\text{sample}}}, \quad (6.45)$$

$$A_0 = A(Q=0) = \Delta \rho_b V, \quad (6.46)$$

$$f(\mathbf{Q}) = \frac{1}{\sqrt{N_{\text{scatters}}}} \sum_{i \text{ in same particle}}^{N_{\text{scatters}}} \exp(-i\mathbf{Q}\mathbf{r}_i), \quad (6.47)$$

$$F(Q) = |f(\mathbf{Q})|^2 = \frac{1}{N_{\text{scatters}}} \sum_{i,j \text{ in same particle}}^{N_{\text{scatters}}} \exp(-i\mathbf{Q}\mathbf{r}_{ji}), \quad (6.48)$$

and

$$S(\mathbf{Q}) = 1 + \frac{1}{N} \sum_{k,l \text{ centers of different particles}}^N \exp(-i\mathbf{Q} \cdot \mathbf{r}_{kl}). \quad (6.49)$$

Here, ρ is the particle number density, V the particle volume, and $\Delta \rho_b$ the scattering length density contrast. The forward scattering amplitude is given by

$$A_0 = A(Q=0) = \Delta \rho_b V. \quad (6.50)$$

Please note here that A_0 is the amplitude for a complete particle, not for individual scattering

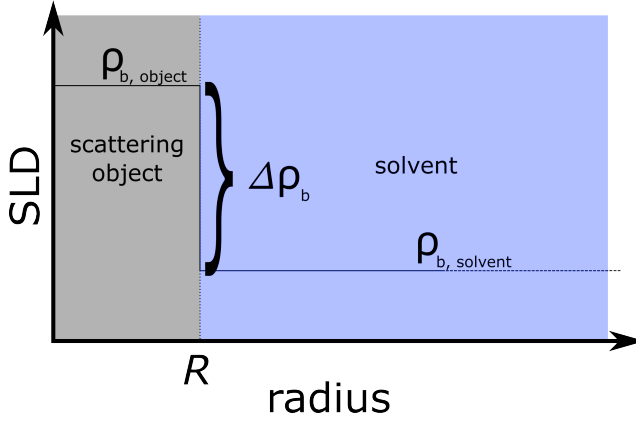


Fig. 6.15: Depiction of the SLD distribution along the radius of a sphere. ρ_0 is the SLD contrast, i.e. the SLD difference between the scattering particle and the solvent. R is the radius of the sphere.

centers.

This defines the form factor $F(\mathbf{Q})$ and structure factor $S(\mathbf{Q})$ as dimensionless descriptions of the particle shape and the inter-particle correlations, respectively. The incoming beam intensity was normalized by setting $A_{\text{inc}} = 1$ in section 6.6.

6.8.1 Sphere

The analytic expression for the scattering created by identical spheres of radius R with a number density of ρ is

$$I(Q) = \rho \left[3V \Delta \rho_b \frac{\sin(QR) - QR \cos(QR)}{(QR)^3} \right]^2 = \rho \Delta \rho_b^2 V^2 F(Q), \quad (6.51)$$

with V the volume of a single sphere, and $\Delta \rho_b = \rho_{b,\text{sphere}} - \rho_{b,\text{solvent}}$ the SLD contrast between the sphere and the solvent.

Following the convention that $f(Q)$ is the form factor amplitude and $F(Q) = |f(Q)|^2$ the corresponding form factor amplitude is

$$f(Q) = 3 \frac{\sin(QR) - QR \cos(QR)}{(QR)^3}, \quad (6.52)$$

and therefore

$$F(Q) = |f(Q)|^2. \quad (6.53)$$

This expression can be reached by using a SLD description like a step function as depicted

in Fig.6.15. As a sphere is already spherically symmetric this can be directly put into the Fourier transform

$$f(\mathbf{Q}) = \frac{1}{V \Delta \rho_b} \mathcal{F}(\rho_b(\mathbf{r})) \quad (6.54)$$

$$= \frac{1}{V \Delta \rho_b} \int_V \rho_b(\mathbf{r}) \exp(-i\mathbf{Q} \cdot \mathbf{r}) dV \quad (6.55)$$

$$= \frac{1}{V \Delta \rho_b} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^R \rho_b(\mathbf{r}) \exp(-i\mathbf{Q} \cdot \mathbf{r}) r^2 \sin \theta dr d\theta d\phi \quad (6.56)$$

$$= \frac{1}{V \Delta \rho_b} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^R \rho_b(r) \exp(-iQr \cos \theta) r^2 \sin \theta dr d\theta d\phi \quad (6.57)$$

$$= \frac{1}{V \Delta \rho_b} \int_{\phi=0}^{2\pi} \int_{u=-1}^1 \int_{r=0}^R \rho_b(r) \exp(-iQru) r^2 dr du d\phi \quad (6.58)$$

$$= \frac{4\pi}{V \Delta \rho_b} \int_{r=0}^R \rho_b(r) \left(\frac{\sin(Qr)}{Qr} \right) r^2 dr \quad (6.59)$$

$$= \frac{4\pi}{V} \int_{r=0}^R \frac{\sin(Qr)}{Qr} r^2 dr \quad (6.60)$$

$$= \frac{4\pi \sin(QR) - QR \cos(QR)}{V Q^3} \quad (6.61)$$

$$= 3 \frac{\sin(QR) - QR \cos(QR)}{R^3 Q^3} \quad (6.62)$$

$$= 3 \frac{\sin(QR) - QR \cos(QR)}{(QR)^3}. \quad (6.63)$$

Here Eq. 6.57 used the identity $\mathbf{Q} \cdot \mathbf{r} = Qr \cos \theta$ with θ being the enclosed angle and in Eq. 6.58 $\cos \theta$ was replaced by u . In addition, spherical symmetry was exploited for the integration over the solid angle.

This corresponds exactly to the squared term in Eq. 6.52, which is nothing else than the squared form factor amplitude calculated here. As this is only the scattering for a single isolated sphere, the number density needs to be included to reflect the absolute scattered intensity. In case of neutron scattering this is the case for most instruments. X-ray instruments are often not calibrated to absolute scattering intensities and therefore require an arbitrary scaling factor. Similar approaches can be used for other analytic representations of form factors.

6.8.2 Cylinder

In order to derive the same form factor for a cylinder we assume a cylinder with

- radius R
- length L

- the symmetry axis running along z for cylindrical coordinates
- uniform scattering length density $\Delta\rho_b$

and we separate the coordinate along the symmetry axis and the coordinate perpendicular to the symmetry axis with

$$q_z = q \cos \alpha \quad (6.64)$$

$$q_\perp = q \sin \alpha \quad (6.65)$$

$$\Rightarrow \quad (6.66)$$

$$\mathbf{Q} \cdot \mathbf{r} = q_\perp r \cos \phi + q_z z \quad (6.67)$$

with α being the angle between the Q -vector and the cylinder symmetry axis and ϕ being the coordinate angle. Here the scattering vector is defined as $\mathbf{Q} = \mathbf{k}' - \mathbf{k}$ [1].

With that

$$f(\mathbf{Q}) = \frac{1}{V\Delta\rho_b} \mathcal{F}(\rho_b(\mathbf{r})) \quad (6.68)$$

$$= \frac{1}{V} \int_V \exp(-i\mathbf{Q} \cdot \mathbf{r}) dV \quad (6.69)$$

$$= \frac{1}{V} \int_{-L/2}^{L/2} \int_0^{2\pi} \int_0^R \exp(-i(q_\perp r \cos \phi + q_z z)) r dr d\phi dz \quad (6.70)$$

$$= \frac{1}{V} \int_{-L/2}^{L/2} \exp(-iq_z z) dz \int_0^{2\pi} \int_0^R \exp(-iq_\perp r \cos \phi) r dr d\phi. \quad (6.71)$$

Now we consider the longitudinal part

$$\int_{-L/2}^{L/2} \exp(-iq_z z) dz = L \frac{\sin(q_z L/2)}{q_z L/2}. \quad (6.72)$$

and the radial part separately.

$$\int_0^{2\pi} \exp(-iq_\perp r \cos \phi) d\phi = 2\pi J_0(q_\perp r) \quad (6.73)$$

creates a zero-th order Bessel function from the angular integral, leaving only the radial coordinate for integration. This leads to

$$2\pi \int_0^R r J_0(q_\perp r) dr = 2\pi R^2 \frac{J_1(q_\perp R)}{q_\perp R}. \quad (6.74)$$

Note here that we used that the order of the Bessel-functions can be increased by integration.

The longitudinal and angular part can now be combined by drawing out the cylinder volume $V = \pi R^2 L$ from the constants in both results, resulting in

$$f(Q, \alpha) = 2 \frac{\sin\left(\frac{1}{2}QL \cos \alpha\right)}{\frac{1}{2}QL \cos \alpha} \frac{J_1(QR \sin \alpha)}{QR \sin \alpha}. \quad (6.75)$$

Following the convention that $F(Q) = |f(Q)|^2$, the corresponding intensity form factor is

$$F(Q, \alpha) = |f(Q, \alpha)|^2. \quad (6.76)$$

Here we assume the cylinders are very thin, i.e. $R \ll L$ and therefore $QR \ll 1$. This results in the approximation

$$2 \frac{J_1(x)}{x} \approx 1 \quad (6.77)$$

eliminating the second part of the formfactor. With that

$$F(\mathbf{Q}, \alpha) = |f(Q, \alpha)|^2 \quad (6.78)$$

$$= \left[\frac{\sin\left(\frac{1}{2}QL \cos \alpha\right)}{\frac{1}{2}QL \cos \alpha} \right]^2. \quad (6.79)$$

For randomly oriented cylinders we now perform the orientational average over α

$$F(\mathbf{Q}) = \int_0^{\pi/2} F(Q, \alpha) \sin \alpha \, d\alpha \quad (6.80)$$

$$= \int_0^{\pi/2} \left[\frac{\sin\left(\frac{1}{2}QL \cos \alpha\right)}{\frac{1}{2}QL \cos \alpha} \right]^2 \sin \alpha \, d\alpha \quad (6.81)$$

$$\text{substitute } u = \cos \alpha \quad (6.82)$$

$$= \int_0^1 \left[\frac{\sin\left(\frac{1}{2}QL u\right)}{\frac{1}{2}QL u} \right]^2 du \quad (6.83)$$

$$\text{substitute } a = \frac{QL}{2} \quad (6.84)$$

$$= \int_0^1 \left[\frac{\sin(au)}{au} \right]^2 du \quad (6.85)$$

$$\text{substitute } t = au \quad (6.86)$$

$$= \frac{1}{a} \int_0^a \left[\frac{\sin t}{t} \right]^2 dt \quad (6.87)$$

$$\text{substitute } \text{Si}(x) = \int_0^x \frac{\sin t}{t} dt \quad (6.88)$$

$$= \frac{1}{a} \left[\text{Si}(2a) - \frac{\sin^2 a}{a} \right] \quad (6.89)$$

$$\text{reinsert } a = \frac{QL}{2} \quad (6.90)$$

$$= \left[\frac{2\text{Si}(QL)}{QL} - \frac{4 \sin^2(QL/2)}{(QL)^2} \right] \quad (6.91)$$

$$\text{substitute } 4 \sin^2 \left(\frac{QL}{2} \right) = 2(1 - \cos QL) \quad (6.92)$$

$$= \left[\frac{2\text{Si}(QL)}{QL} - \frac{2(1 - \cos QL)}{(QL)^2} \right] \quad (6.93)$$

This is the form factor for a very thin cylinder of length L .

6.8.3 Circular Disc

For the calculation of the disc form factor we again apply cylindrical coordinates. Following the convention that $f(Q)$ is the form factor amplitude and $F(Q) = |f(Q)|^2$ the corresponding form factor amplitude is [1]

$$f(\mathbf{Q}) = \frac{1}{V \Delta \rho_b} \mathcal{F}(\rho_b(\mathbf{r})) \quad (6.94)$$

$$= \frac{1}{V \Delta \rho_b} \rho_{b,\text{contrast}} \int_V \exp(-i\mathbf{Q} \cdot \mathbf{r}) dV \quad (6.95)$$

$$\text{thin disc approximation } dV = r dr d\phi \cdot t \quad (6.96)$$

$$= \frac{t}{V} \int_0^{2\pi} \int_0^R \exp(-iQ_\perp r \cos \phi) r dr d\phi. \quad (6.97)$$

where $Q_\perp = Q \sin \alpha$ and α is the angle between $\mathbf{Q}$ and the disk normal, so that $\alpha = 90^\circ$ means we are looking directly at the disc face and therefore $\mathbf{Qr} = Q_\perp r \cos \phi$. This means, ϕ is the angle that would rotate the disk from a flat to a side view.

We again separate directions, now radial and angular, since the disk is considered to be very thin with thickness t . We start with the angular integration over ϕ using a Bessel function

$$\int_0^{2\pi} \exp(-ix \cos \phi) d\phi = 2\pi J_0(x) \quad (6.98)$$

$$\rightarrow \quad (6.99)$$

$$f(Q, \alpha) = \frac{2\pi t}{V} \int_0^R r J_0(Q_\perp r) dr. \quad (6.100)$$

and the radial integration with the increase of the order of the Bessel function by integration

$$\int r J_0(ar) dr = \frac{r J_1(ar)}{a} \quad (6.101)$$

$$\rightarrow \quad (6.102)$$

$$f(Q, \alpha) = \frac{2\pi t}{V} \left[\frac{r J_1(Q_\perp r)}{Q_\perp} \right]_0^R \quad (6.103)$$

$$= \frac{2\pi t}{V} \frac{R J_1(Q_\perp R)}{Q_\perp} \quad (6.104)$$

$$= 2 \frac{J_1(QR \sin \alpha)}{QR \sin \alpha}. \quad (6.105)$$

This is the scattering function of a thin circular disc with α the angle between the surface normal of the disk and $\mathbf{Q}$. This is exactly what we would expect, since the fraction in the second term goes to 1 for $\sin \alpha = 0$ and therefore it would look like a round disk.

For creating the average over all disk orientations, we create the scattered intensity from the amplitude

$$F(Q, \alpha) = |f(Q, \alpha)|^2 \quad (6.106)$$

$$= 4 \left[\frac{J_1(QR \sin \alpha)}{QR \sin \alpha} \right]^2. \quad (6.107)$$

The orientational average then becomes

$$F(Q) = \int_0^{\pi/2} F(Q, \alpha) \sin \alpha d\alpha \quad (6.108)$$

$$= 4 \int_0^{\pi/2} \left[\frac{J_1(QR \sin \alpha)}{QR \sin \alpha} \right]^2 \sin \alpha d\alpha \quad (6.109)$$

$$= \frac{2}{Q^2 R^2} \left(1 - \frac{J_1(2QR)}{QR} \right). \quad (6.110)$$

This is the orientation averaged form factor of a thin disc with radius R .

6.8.4 Non-particulate scattering from a flexible chain

Since a flexible polymer chain does not have a geometric form that could be used for the Fourier transform here the approach is to derive the intensity directly from the pair correlation of scattering centers between particles i and j along the chain:

$$\langle (\mathbf{r}_i - \mathbf{r}_j)^2 \rangle = |i - j| a_p^2 \quad (6.111)$$

with the persistence length a_p between two segments.

$$\langle \exp(-i\mathbf{Q}(\mathbf{r}_i - \mathbf{r}_j)) \rangle = \exp\left(-\frac{Q^2}{6} \langle (\mathbf{r}_i - \mathbf{r}_j)^2 \rangle\right) \quad (6.112)$$

$$\rightarrow \quad (6.113)$$

$$I(Q) = b^2 \sum_{i,j} \exp\left(-\frac{Q^2 a_p^2}{6} |i - j|\right). \quad (6.114)$$

We are turning this sum into a double integral over i and j to s and s' variables with identical scattering length b for all scattering centers

$$I(Q) = b^2 \int_0^N \int_0^N \exp(-a|s - s'|) ds ds' \quad (6.115)$$

with $a = \frac{Q^2 a_p^2}{6}$. From that we exploit the symmetry

$$I(Q) = 2b^2 \int_0^N ds \int_0^N \exp(-a|s - s'|) ds' \quad (6.116)$$

and replace the distance between the two scattering centers by a constant $u = s - s'$

$$I(Q) = 2b^2 \int_0^N ds \left[\int_0^s \exp(-au) du \right] ds. \quad (6.117)$$

Evaluation of the integral in the bracket gets

$$\int_0^s \exp(-au) du = \frac{1 - \exp(-as)}{a} \quad (6.118)$$

which leads to

$$I(Q) = \frac{2b^2}{a} \int_0^N (1 - \exp(-as)) ds \quad (6.119)$$

$$= \frac{2b^2}{a} \left(N - \frac{1 - \exp(-aN)}{a} \right) \quad (6.120)$$

$$= 2b^2 \left(\frac{N}{a} - \frac{1 - \exp(-aN)}{a^2} \right) \quad (6.121)$$

$$= 2b^2 N^2 \frac{\exp(-aN) - 1 + aN}{(aN)^2} \quad (6.122)$$

$$\text{substitute radius of gyration } R_g = \frac{Na_p^2}{6} \quad (6.123)$$

$$\text{and previous resubstitution } aN = Q^2 R_g^2 \quad (6.124)$$

$$= I(Q=0) \cdot \frac{2(\exp(-Q^2 R_g^2) - 1 + Q^2 R_g^2)}{(Q^2 R_g^2)^2} \quad (6.125)$$

which is the Debye scattering law:

$$I(Q) = I(Q = 0) \cdot \frac{2(\exp(-Q^2 R_g^2) - 1 + Q^2 R_g^2)}{(Q^2 R_g^2)^2} = \rho \Delta \rho^2 V^2 F_{\text{Debye}}(Q) \quad (6.126)$$

with $I(Q = 0) = b^2 N^2 = \Delta \rho_b^2 V^2$.

6.8.5 Polydispersity

All analytic form factors, that deliver the scattered intensity, are determining the scattered intensity for particles of one exact size. In real systems, however, there are mostly distributions of different sizes. This leads to a superposition of scattering from different particle sizes. Since most particle sizes follow a Gaussian distribution, this is also a good way to fold in the particle size distribution analytically. For extremely long, or very polydisperse, particles then Schulz-Zimm distribution is used, which looks very similar to the Gaussian distribution, however has a cut-off at zero to prevent negative sizes of the particles. For specialized problems also other distributions, such as La-Place, multi-modal or other size distribution functions can be used.

The general idea is that the scattered intensity $I(Q, r)$ is folded with the size distribution function $f(r)$

$$I_{\text{real}}(Q, r) = I_{\text{ideal}}(Q, r) * f(r). \quad (6.127)$$

Here the subscripts real and ideal identify the real measured intensity or the ideal intensity for any calculated particulate size and form.

The effects of the convolution can be seen in Fig.6.16. Most notably, the minima are smeared out, and in some cases vanish completely, so they can only be estimated. Another important effect is that the slopes of inclinations cannot be completely reproduced anymore, which is especially important to distinguish scattering from different contributions. The magnitude of the polydispersity is described by the polydispersity index $PDI = \sigma(f(r))/\mu(f(r))$ where $\sigma(f(r))$ is the standard deviation of the size distribution function and $\mu(f(r))$ is the mean of the size distribution function. Values of $PDI \geq 0.3$ are usually discarded during fitting, as then the results become unreliable in such a polydisperse sample.

In addition to this, the usual polydispersity (approximated by a Gaussian distribution) is by its very nature similar to a resolution smearing of the instrument itself. Therefore, it can easily happen to overestimate the polydispersity. If the resolution function of the instrument is known, it should be used for deconvolution before performing the fits.

6.9 Structure Factors

Structure factors in general describe the scattered intensity due to the arrangement of single particles. This can be because the solution is becoming to dense, and therefore the particles

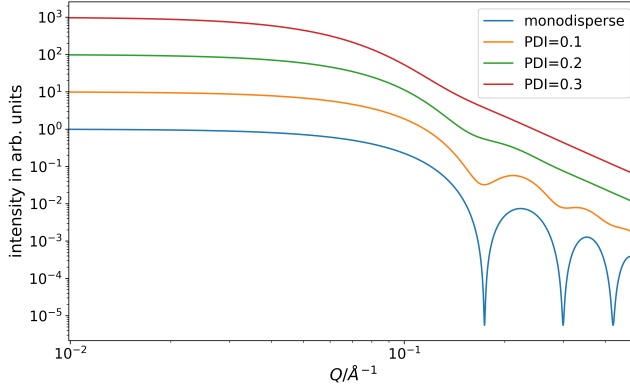


Fig. 6.16: Effect of polydispersity. While the positions of the minima can still be found at higher polydispersity, the higher order undulations of the form factor vanish.

arrange following a nearest neighbor alignment or because the particles are attractive to each other and form aggregates. Thus, more generally a structure factor $S(Q)$ is a measure of interaction between the single particles in the solution and connected with the correlation function $c(r)$ (the probability to find a particle at a certain distance) and the particle density ρ with the relation

$$S(Q) = 1 + \frac{1}{N} \sum_{i,j \text{ not in same particle}} \exp(-i\mathbf{Q} \cdot \mathbf{r}_{ji}) = \frac{1}{1 - nc(Q)}. \quad (6.128)$$

From this equation it also follows, that for a system of uncorrelated, identical particles the structure factor must be $S(Q) = 1$, or in the case of a very low particle density. Since the correlation between particles usually leads to either an aggregation or repulsion of particles over long length scales the contribution of the structure factor is most prominent at low Q values. Also, this means that for large distances the structure factor has to level out to unity, to preserve the fact that at large Q only the inner structure of the particle is visible, not its arrangement in space. A few instructive examples for the structure factor are shown in Fig.6.17.

6.9.1 Hard Sphere Structure Factor

The hard sphere structure factor assumes an infinitely high potential below a radius R and a zero potential at higher radii. This can be described by

$$V(r) = \begin{cases} \infty & \text{for } r \leq R \\ 0 & \text{for } r > R. \end{cases} \quad (6.129)$$

Using Eq.6.128 this can be rewritten as

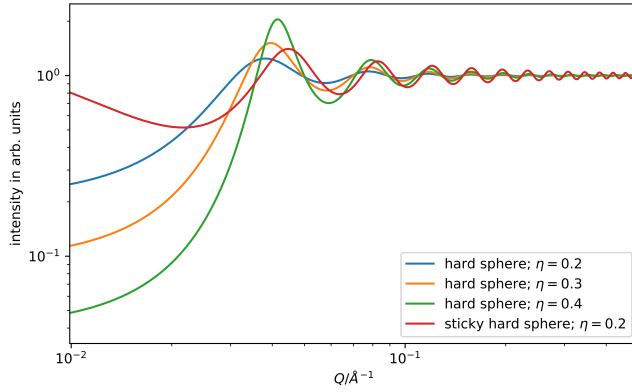


Fig. 6.17: Examples for structure factors. The intensity of the peaks roughly scales with the volume fraction η of the particles. Also the position of the peaks is slightly dependent on that volume fraction, which makes a direct calculation of $R = \frac{2\pi}{Q_{max}}$ invalid (The hard sphere radius used here was 60 Å). A distinct difference can be noted at low Q . Here, in general, attractive interaction (sticky hard spheres) leads to an increase in scattering, while repulsive interaction leads to a decrease in intensity.

$$S(Q) = \frac{1}{1 + 24\eta_{HS}G(2QR)/2QR}. \quad (6.130)$$

Here $G(x)$ is defined as

$$G(x) = \alpha \frac{(\sin(x) - x\cos(x))}{x^2} + \quad (6.131)$$

$$= \beta \frac{(2x \sin(x) + (2 - x^2) \cos(x - 2))}{x^3} + \quad (6.132)$$

$$= \gamma \frac{(-x^4 \cos(x) + 4[(3x^2 - 6) \cos(x) + (x^3 - 6x) \sin(x) + 6])}{x^5} \quad (6.133)$$

with these definitions for α, β and γ :

$$\alpha = \frac{(1 + 2\eta_{HS})^2}{(1 - \eta_{HS})^4} \quad ; \quad \beta = \frac{6\eta_{HS}(1 + \eta_{HS}/2)^2}{(1 - \eta_{HS})^4} \quad ; \quad \gamma = \frac{\eta_{HS}/2(1 + 2\eta_{HS})^2}{(1 - \eta_{HS})^4}. \quad (6.134)$$

In all equations the volume fraction that is occupied by hard spheres of radius R is designated η_{HS} .

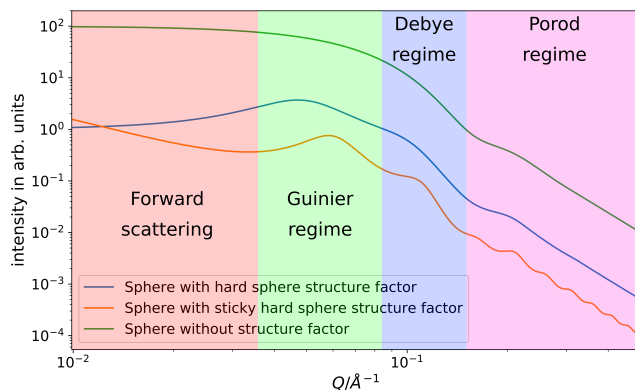


Fig. 6.18: Diverse scattering curves from identical spherical form factor and different structure factors.

6.10 Reading a curve

In an experimental environment it can be useful to determine the fundamental features in a preliminary fashion without computer aided data evaluation, also known as fitting. In addition, this helps determining good starting parameters for fits. In order to do so, we are going to look at the curves shown in Fig.6.18. There we can determine different regions of the scattered intensity (forward scattering, Guinier regime, Debye regime and Porod regime) and determine several properties of the sample from that intensity. When applying the described techniques for directly reading a curve it has to be kept in mind that most of them are either restricted in their validity to specific regions of Q space or are very general and rough descriptions of the sample.

6.10.1 Forward scattering

As pointed out in the discussion of the structure factor, large aggregates are typically characterized by an increased scattering intensity at low Q . This behaviour is also evident from Eq.6.3 into account. This means, in general, an increased scattering at low Q is indicative of large aggregates being present in the sample. This also correlates with an attractive potential between the single particles.

Another possibility is strongly suppressed scattering at low Q . This can be the case for strongly repulsive interaction potentials between the particles, close to what is described for the hard sphere factor above.

A levelling out of the intensity at low Q is indicative of an either dilute solution or a very weak potential between the particles. Then there is no influence at low Q and only the structure factor of the single particles is visible.

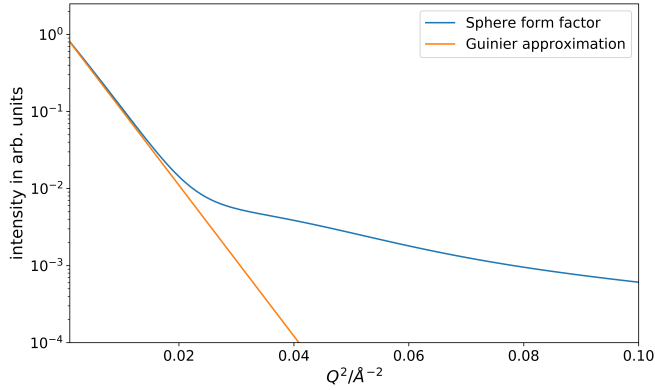


Fig. 6.19: Sphere form factor and Guinier approximation from Eq.6.135 in a Guinier plot. The radius of gyration is 25.8 Å. The estimated slope by eye was $m = -185$. With $R_g = \sqrt{-3 \cdot m} = 23.5 \text{ Å}$ the error is within 10%, which is suitable for a naked eye approximation.

6.10.2 Guinier regime

The Guinier regime is usually the crossover region, where the forward scattering is not dominant anymore and the slope of the scattering curve changes to the scattered intensity of the form factor. In this regime the overall size of the particle can be examined. This is similar to seeing something from far away: One may be able to discern the size of the particle but the distinct form remains hidden. Imagine a football and a pumpkin seen from 100 m away. They are close in size, you can properly judge it to be approximately 20 cm in diameter, but the exact form (ridges, stem of the pumpkin) remains hidden. A description that is only taking into account the scattered density of the particles as a whole, valid in that scattering regime is the Guinier Law:

$$I(Q) = \Delta\rho_b V^2 \exp\left(-\frac{Q^2 R_g^2}{3}\right) \quad (6.135)$$

For details of derivation, which include a Taylor series expansion around zero of the scattered amplitude (Eq.6.55) and an averaging over all directions, please refer to the literature. [11, 12] Another option is to develop a series expansion for the Debye Law (Eq.6.126) at low Q .

In order to evaluate the data using the Guinier Law, the data needs to be plotted as shown in Fig.6.19. The log-log representation and plotting versus Q^2 allow to directly read the inclination of the system, multiply by 3 and use the square root in order to retrieve the particle radius.

6.10.3 Debye regime

In contrast to the Guinier regime, where the data can be evaluated by the Guinier law, the Debye regime signifies the area, where the particulate form manifests in the scattering, which in general cannot be fitted by the Debye law. The Debye law is only valid for the scattering from Gaussian chains. As can be seen in the form factors section 6.8, there is a direct correlation to the dimensionality of the scattering particle (sphere, disc, rod) and the slope in log-log plot, since the scattering scales with $I(Q) \sim Q^{-D}$, where D is the dimensionality of the scattering object (sphere: $D = 3$; disc: $D = 2$; rod: $D = 1$). Also the scattering from fractal objects is possible, which then results in non-integer numbers for the slope. It should be noted that this is an approximation that is only valid for the case when $1/\text{particle radius} \ll Q \ll 1/\text{fundamental building block}$. The fundamental building block in this case can be for example atoms or single monomers of a chain.

6.10.4 Porod regime

The Porod regime, is the regime where the interface between the particle and the solvent dominates the scattered intensity. It is valid for large Q (before leveling out into the incoherent background) and therefore a good approach is extrapolating the sphere form factor to large Q . The decisive property of the scattered intensity is the scaling of $I(Q) \sim Q^{-4}$. This behavior can be derived from an extrapolation of the sphere form factor (Eq.6.52) to very large Q :

$$I(Q) \propto \left(\frac{4}{3}\pi R^3\right)^2 \frac{9(\sin QR - QR \cos QR)^2}{Q^6 R^6} \quad (6.136)$$

$$= 8\pi^2 \left(\frac{R^2(1 + \cos 2QR)}{Q^4} - \frac{2R \sin 2QR}{Q^5} + \frac{1 - \cos 2QR}{Q^6} \right) \quad (6.137)$$

The higher order terms vanish at large Q delivering the characteristic Q^{-4} behavior of the scattered intensity. Here only proportionality is claimed, which is strictly true in this case. If the scattered intensity is recorded in absolute intensities, here also information about the surface of the particles can be obtained. This then follows the form

$$\lim_{Q \rightarrow \infty} I(Q) = \frac{8\pi \Delta\rho_b S}{Q^4}. \quad (6.138)$$

$\Delta\rho_b$ is here the SLD difference between the particle and the surrounding medium and S the inter-facial area of the complete sample between particles and medium. This means, the absolute intensity of the Porod regime allows to determine the complete amount of surface in the sample.

6.10.5 Estimation of particle and feature Size

As described previously for low Q in most cases it is a good approximation to assume all particles in the sample have spherical symmetry (Section 6.10.2). The roots of the expression for the spherical form factor are in the locations $\tan(QR) = QR$, which is true for $QR \approx 4.49, 7.73, 10.90, \dots$. In many cases anyway only the first minimum of the form factor will be visible. This allows a fast approximation of the radius with $R \approx 4.5/Q_{\min}$. Here it needs to be noted, that this is the rotational average of the particle, neglecting any structure of the particle whatsoever.

Another approach of determining the size or correlation of features is using Eq.6.3:

$$d = \frac{2\pi}{Q}. \quad (6.139)$$

Although this is in general only strictly true for lamellar systems and the corresponding correlations, it is still a good approximation for a summary data examination during the experiment. With that restriction in mind it can be used for virtually any feature in the scattering curve and the size of the corresponding feature in the sample.

6.11 Further Reading

Most of the concepts shown in this manuscript are based on previous publications. The following selection of textbooks gives the reader a good overview of the principles of SAS.

6.11.1 A. Guinier: X-ray diffraction in crystals, imperfect crystals, and amorphous bodies

This early textbook concentrates on SAXS, as neutron scattering at the time of writing was still in its infancy. While some of the terminology may have changed slightly over time, in many aspects this book still gives a good fundamental overview of what can be done with small-angle scattering, and how to perform a solid data analysis. In addition, this is literally the book on the Guinier Law, and where some of the basic ideas of reading scattering curves were first collected.

6.11.2 R.J. Roe: Methods of x-ray and neutron scattering in polymer science

Here the author nicely manages to emphasize the commonalities and differences between x-ray and neutron scattering. An overview of the methods and technologies is given, as well as a helpful mathematical appendix, reiterating some of the concepts used in the book.

6.11.3 G. Strobl: The physics of polymers

For soft-matter researchers this book, even though not being focused on scattering as such, gives a good overview of applicable concepts for scattering with soft-matter samples. A wide range of helpful examples highlight in which particular area any evaluation concept of the data is applicable and useful.

6.12 Appendix: Calculation of the Scattering Length by solution of Schrödinger's equation

In order to calculate the scattering length density, we have to start with the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi. \quad (6.140)$$

Using separation of variables as shown in quantum mechanics textbooks [?] we can create a radially symmetric version of Schrödinger's equation with

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \quad (6.141)$$

where the radial part of the wave function is captured by $R(r)$. This allows us to rewrite Schrödinger's equation as

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} \right] u = Eu. \quad (6.142)$$

Here we substituted $u(r) = rR(r)$, $R = u/r$, $dR/dr = [r(du/dr) - u]/r^2$ and $(d/dr)[r^2(dR/dr)] = r d^2u/dr^2$. l is the quantum number for angular momentum, and this is called the radial Schrödinger equation. m in this instance are still masses, not quantum numbers.

For this we now only account for solutions $V(r)$, since we assume the nuclei to be radially symmetrical. For non-symmetric solutions $V(r, \theta, \phi)$ this becomes more complicated and in the case of neutrons is exclusively interesting for magnetic scattering or high energy interaction. Magnetic scattering is using another potential, which is often weak combined with the nuclear interaction. Higher energy interactions are not the focus of this course, since for neutron scattering the energies for thermal (25 meV) and cold (1 meV) neutrons always are too low to reach higher excitations the $l = 0$ and s-wave scattering. This is a sensible assumption since we will only be scattering with cold neutrons at low energies. This also implies that the potential is a lot deeper than the energy of the incoming neutron $E \ll V_0$. So let us consider a potential of the form

$$V(\mathbf{r}) = \begin{cases} -V_0 & \text{if } r \leq \text{radius } a \\ 0 & \text{if } r > \text{radius } a \end{cases} \quad (6.143)$$

All this leads to neutrons interacting with the nuclei directly, which results in the atomic form factor being always spherically symmetric (billiard balls) and them being sensitive to different isotopes and spin-spin coupling. In contrast to x-rays, there is no simple expression for scattering strength as a function of isotope or atomic number. Directly neighbouring elements and isotopes may have vastly different cross sections.

This is due to the fact that the Schrödinger equation has to be solved for each combination of incoming neutron and nucleus. The solution for the problem is illustrated by Hammouda or Tong [6, 7] in more detail.

In order to achieve a solution, we consider the continuity for the wave-function and its derivative at the boundaries. The radial Schrödinger equation for $l = 0$ for potential V_0 inside the well is

$$\frac{d^2 u}{dr^2} + \left[k_1^2 - \frac{1}{r^2} \right] u = 0 \quad (6.144)$$

With $k_1^2 = \frac{2m(E+V_0)}{\hbar^2}$. The general solution for this is

$$u_I = A j_l(k_1 r) + B n_l(k_1 r) \quad (6.145)$$

with j_l being the spherical Bessel function and n_l being the spherical Neumann function. For $r = 0$ the Neumann function goes to infinity, which is unphysical, so $B = 0$. So the general solution inside the well is

$$u_I = A j_l(k_1 r). \quad (6.146)$$

Outside the well $V = 0$ so $k^2 = \frac{2mE}{\hbar^2}$ which renders the general solution

$$u_{II} = C j_l(kr) + D n_l(kr). \quad (6.147)$$

Since $r \neq 0$ in all cases, all parameters are allowed.

We consider positions far from the origin, where the particle is free

$$j_0(kr) \sim \frac{1}{kr} \sin(kr) \quad (6.148)$$

and

$$n_0(kr) \sim \frac{1}{kr} \cos(kr) \quad (6.149)$$

which leads to

$$u_{II} \sim \sin(kr + \delta_0) \quad (6.150)$$

The phase shift encodes the effect of the potential well as different from a completely free particle with

$$\tan \delta_0 = -\frac{D}{C}. \quad (6.151)$$

With the continuity condition at $r = a$ we get

$$u_I(a) = u_{II}(a) \quad (6.152)$$

meaning

$$A j_0(k_1 a) = C j_0(ka) + D n_0(ka). \quad (6.153)$$

In addition the derivative needs to be continuous

$$A j'_0(k_1 a) = C j'_0(ka) + D n'_0(ka). \quad (6.154)$$

The $l = 0$ condition gives

$$j_0(x) = \frac{\sin x}{x} \quad (6.155)$$

and

$$n_0(x) = -\frac{\cos x}{x} \quad (6.156)$$

which results in the general solutions

Inside:

$$u_I(r) = A \sin(k_1 r) \quad (6.157)$$

and outside:

$$u_{II}(r) = C \sin(kr) + D \cos(kr). \quad (6.158)$$

We remember the small perturbation trick with the δ from the general solution and get

$$u_{II}(r) = F \sin(kr + \delta_0) = F \cos \delta_0 \sin(kr) + F \sin \delta_0 \cos(kr) \quad (6.159)$$

meaning $C = F \cos \delta_0$ and $D = F \sin \delta_0$ which is equivalent to our previous definition with $\tan \delta_0 = D/C$. The difference in sign is due to the asymptotic nature of the Neumann function, which by convention is then written negative. For the sine and cosine solution used here, the positive δ_0 as a small perturbation is the convention.

Again, applying the continuity condition for both the solution itself and its derivative at $r = a$ we get

$$A \sin(k_1 a) = F \sin(ka + \delta_0) \quad (6.160)$$

for the solution itself and

$$Ak_1 \cos(k_1 a) = Fk \cos(ka + \delta_0) \quad (6.161)$$

for its derivative.

Now we have two functions containing δ_0 we can use to solve for it. Dividing the derivative of the function by the function itself gives

$$\frac{Ak_1 \cos(k_1 a)}{A \sin(k_1 a)} = \frac{Fk \cos(ka + \delta_0)}{F \sin(ka + \delta_0)} = k_1 \cot(k_1 a) = k \cot(ka + \delta_0). \quad (6.162)$$

We solve this for the phase shift δ_0 . We remember the complete perturbation (the nuclear core, which is responsible for the actual scattering) is contained in there.

$$\cot(ka + \delta_0) = \frac{k_1}{k} \cot(k_1 a) \quad (6.163)$$

which leads to

$$\delta_0 = -ka + \tan^{-1} \left(\frac{k}{k_1} \tan(k_1 a) \right). \quad (6.164)$$

In the literature you will find this usually as the s-wave phase shift for a finite spherical square well.

In order to interpret this physically we remember the definitions of the different k 's being $k = k_1 (V_0 = 0)$. In physical terms this means that the solution inside and outside are only different in the way, that outside the well (k -solution) the potential is zero, whereas inside the well (k_1 -solution) the potential is finite negative $-V_0$.

Looking at the solution for delta, if there was no potential at all, $k_1 = k$ would be true in all cases, so would be $k_1/k = 1$. This leads to

$$\delta_0 = -ka + \tan^{-1}(\tan(ka)) = -ka + ka = 0 \quad (6.165)$$

which is exactly what we expect. For very low energies $ka \ll 1$ we can approximate $\delta_0 \approx -ka_s$, with a_s chosen as a radius for low energy, s-wave scattering:

$$\delta_0 = -ka_s = -ka + \frac{k}{k_1} \tan(k_1 a) \quad (6.166)$$

which directly leads to an expression for the scattering length $a_s = b$, which is exactly the radius of a given weak potential:

$$a_s = b = a - \frac{\tan(k_1 a)}{k_1}. \quad (6.167)$$

References

- [1] A. Guinier, P. Lorrain, D. S.-M. Lorrain, and J. Gillis, “X-ray diffraction in crystals, imperfect crystals, and amorphous bodies,” *Physics Today*, vol. 17, p. 70, 1964.
- [2] H. Stabinger and O. Kratky, “A new technique for the measurement of the absolute intensity of x-ray small angle scattering. the moving slit method,” *Die Makromolekulare Chemie*, vol. 179, no. 6, pp. 1655–1659.
- [3] E. Kentzinger, M. Krutyeva, and U. Rücker, “Galaxi: Gallium anode low-angle x-ray instrument,” *Journal of large-scale research facilities JLSRF*, vol. 2, p. 61, 2016.
- [4] H. Haubold, P. Hiller, H. Jungbluth, and T. Vad, “Characterization of electrocatalysts by in situ saxs and xas investigations,” *JAPANESE JOURNAL OF APPLIED PHYSICS-SUPPLEMENT*, vol. 38, no. 1, pp. 36–39, 1999.
- [5] S. Roth, G. Herzog, V. Körstgens, A. Buffet, M. Schwartzkopf, J. Perlich, M. A. Kashem, R. Döhrmann, R. Gehrke, A. Rothkirch, *et al.*, “In situ observation of cluster formation during nanoparticle solution casting on a colloidal film,” *Journal of Physics: Condensed Matter*, vol. 23, no. 25, p. 254208, 2011.
- [6] B. Hammouda, “A tutorial on small-angle neutron scattering from polymers,” *Gaithersburg: National Institute of Standards and Technology*, 1995.
- [7] D. Tong, “Lectures on topics in quantum mechanics: Scattering theory,” 2017.
- [8] B. Weyerich, J. Brunner-Popela, and O. Glatter, “Small-angle scattering of interacting particles. ii. generalized indirect fourier transformation under consideration of the effective structure factor for polydisperse systems,” *Journal of Applied Crystallography*, vol. 32, no. 2, pp. 197–209, 1999.
- [9] A. Koutsoubas, S. Jaksch, and J. Pérez, “Denfert version 2: extension of ab initio structural modelling of hydrated biomolecules to the case of small-angle neutron scattering data,” *Journal of applied crystallography*, vol. 49, no. 2, pp. 690–695, 2016.
- [10] T. D. Grant, “Ab initio electron density determination directly from solution scattering data,” *Nature methods*, vol. 15, no. 3, p. 191, 2018.
- [11] A. Guinier, *x-ray diffraction in crystals, imperfect crystals and amorphous bodies*.
- [12] R. Roe, *Methods of x-ray and neutron scattering in polymer science*.

Exercises

- 1.) The resolution of a SANS experiment is determined by
 - ☐ The chosen wavelength
 - ☐ The achieved coherence of the beam at sample position
 - ☐ The sample size
- 2.) Which components of a SANS instrument define the beam?
 - ☐ Monochromators/Choppers
 - ☐ Slits
 - ☐ Detectors
- 3.) Which pairs are correct, when trying to understand a SANS curve?
 - ☐ Forward scattering: Aggregation
 - ☐ Guinier Regime: Approximation of the particle shape
 - ☐ Porod Regime: Size of particles
- 4.) The difference between coherent and incoherent scattering in SANS and SAXS is
 - ☐ Core/neutron interactions do not allow for pure coherent scattering.
 - ☐ Current SANS instruments are not developed enough to suppress incoherent scattering.
 - ☐ For isotopically pure samples, there would be no difference.
- 5.) Form factors ...
 - ☐ ... are used to deal with the phase problem.
 - ☐ ... are used because experimenters are lazy and like quick answers.
 - ☐ ... do not necessarily render unique results for each particle form.
- 6.) Contrast matching experiments ...
 - ☐ ... are unique neutron scattering experiments.
 - ☐ ... are possible because different isotopes give different contrasts.
 - ☐ ... distort the results, because the sample chemistry is changed.
- 7.) The structure factor ...
 - ☐ ... can be calculated by the experimental setup of the experiment.
 - ☐ ... encodes the correlation between particles in the sample.
 - ☐ ... shows the structure of the scattering particles.
- 8.) Find the first two root of the intensity scattered by a sphere. Use this value to create a sketch that:
 - a.) Show the scattered intensity by a sphere.
 - b.) Indicate a change happening when polydispersity is increased.
 - c.) Indicate a change by an increase of aggregation in the sample.

Bonus: What would this curve look like if there was no aggregation, but the particles would push away from each other?

9.) Decide and explain which properties of the scattering curve you need to evaluate if you are interested in

- a) the particle size.
- b) the size distribution.
- c) shape of the particle.
- d) interaction between particles.

7 **Macromolecules (structure)**

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7.1 Introduction

Macromolecules are an integral part of Soft and Living Matter. In *Living Matter*, macromolecule-based functional systems are built from molecular units consisting of only a few different building blocks: amino acids are assembled into proteins, which in turn function individually, or cooperatively in nano- and micro-machines. The secret of success is the intrinsic hierarchical structuring over a large range of length scales. In *Soft Matter*, synthetic macromolecules are of much simpler structure. Nevertheless, there is a vast variety of material properties that can be realized with synthetic macromolecules. Theoretical concepts have been developed and are essential for the rational design of soft materials, that are of paramount importance in a multitude of technical applications.

Synthetic polymers have crucially changed daily life since its development in the 1930ies. Modern polymers can be divided into two major classes (i) commodity polymers for daily life use which are produced in millions of tons per year and (ii) specialty polymers for high-performance applications which are niche products but highly profitable [1]. Typical commodity polymers are polyolefines like polyethylene (PE) or polypropylene (PP) used for packaging, films etc. Examples for specialty polymers are polydimethylsiloxane (PDMS) derivatives used in dental implants.

Currently, both classes of polymers in use are based on petrochemical feedstock, thus considered not “carbon-neutral” and “environment-friendly”. Due to changing global conditions and growing concerns about the mounting disposal problems, research on sustainable commodity polymers has been intensified during the last decade, both on the level of fundamental research and applied science [2]. To find the required balance between material properties and bioavailability/-degradability is the key for establishing sustainable polymers on a large-scale industrial level and therefore a major challenge of future polymer science.

The development of new biomimetic specialty polymers is another major challenge. Biopolymers, like spider silk, are high-performance materials with material properties superior to any synthetic polymer. To transfer these properties to artificial biomimetic polymers, one must fully understand, on the molecular level, the structure-property-relationships and enzymatic synthesis processes in living organisms.

In this lecture some applications of neutron scattering methods to characterize quantitatively on a microscopic length scale structure and interactions of synthetic macromolecules and its hierarchical structuring are given. A more comprehensive overview is found e.g. in [3].

7.2 Linear Polymers

A linear polymer is a linear sequence of molecular repetition units, the monomers, continuously linked by covalent bonds. The degree of polymerisation, D_p , i.e. the number of monomers constituting the polymer, its (weight average) molecular weight, $M_w = D_p$

M_m , with M_m the molecular weight of the monomer and the radius of gyration, $R_g \sim M_w^\nu$, are the most important structural parameters of a (linear) polymer. On a coarse-grained level, structural details arising from the explicit chemical composition of the polymer like bond lengths and angles can be neglected and what remains is the so-called scaling relation given above that links molecular weight to size and which is generally valid for all polymers [4]. The numerical value of the scaling exponent ν depends on the strength of interactions. When monomer-monomer interactions are as strong as monomer-solvent interactions (θ -solvent), the polymer structure can be described by a random walk, therefore Gaussian chain statistics are valid and $\nu=1/2$, see chapter 6, section 8.4. When monomer-solvent interactions are stronger than monomer-monomer interactions (“good” solvent), so called excluded volume forces are effective, the polymer chain is “swollen” and $\nu=3/5$, the so-called Flory exponent. When monomer-solvent interactions are weaker than monomer-monomer interactions (“bad” solvent), the polymer chain collapses to a solid sphere and $\nu=1/3$, and finally phase separation occurs.

Here one must emphasize that synthetic polymers, unlike biopolymers, always have an intrinsic polydispersity, i.e. there is a distribution of molecular weights. The polydispersity is given usually in terms of M_w/M_n , with M_n the number average molecular

weight. The averages are defined as $M_n = \frac{\sum_{i=1}^{\infty} n_i M_i}{\sum_{i=1}^{\infty} n_i}$ and $M_w = \frac{\sum_{i=1}^{\infty} n_i M_i^2}{\sum_{i=1}^{\infty} n_i M_i}$ with $M_i = i M_M$ the molecular weight of an i -mer and n_i the number of i -mers.

The polydispersity depends on the polymerisation reaction by which the polymer was synthesized. For a (theoretical) monodisperse polymer $M_w/M_n=1$ holds, the most monodisperse synthetic polymers with $M_w/M_n=1.02$ can be synthesized by “living” anionic polymerisation, classical polycondensation yields $M_w/M_n=2$, radical polymerisation can even result in extremely broad distributions, $M_w/M_n > 10$.

Although in technical applications polymers are mostly used as bulk materials, polymer characterisation is usually performed in (dilute) solution. Historically, light scattering was the method of choice to characterise synthetic polymers [5], but nowadays size exclusion chromatography (SEC), also called gel permeation chromatography (GPC), is the standard technique to characterize routinely polymers [6].

Neutron scattering, due to its limited accessibility and high experimental costs, usually is found in basic academic research, but here it played a crucial role in confirming fundamental theoretical concepts of polymers [3].

For macromolecules the measured intensity $I(Q)$ in absolute units [cm^{-1}] can be expressed in first approximation as a product of polymer form factor $F(Q)$ given by the intramolecular architecture, i.e. the particle geometry, and intermolecular structure factor $S(Q)$ arising due to direct and/or indirect polymer-polymer interactions. Please note, that both $F(Q)$ and $S(Q)$ must be properly normalized, $F(Q)_{Q=0} = 1$ and $S(Q)_{QR \gg 1} = 1$, for details see chapter 6, pages 26–29:

$$I(Q) = \frac{\Delta \rho^2}{N_a} \phi V_w F(Q) S(Q) \quad (7.1)$$

Here $\frac{\Delta \rho^2}{N_a}$ is the contrast factor, with $\Delta \rho = (\rho_p - \rho_o)$ given by the difference in scattering length density of polymer ρ_p and solvent ρ_o and Avogadros number N_a . ϕ is the polymer volume fraction and $V_w = M_w/d$ is the molecular volume and d the polymer density in $[\text{g}/\text{cm}^3]$.

To characterize properly the *intramolecular* form factor $F(Q)$ one has therefore to investigate a concentration series in the dilute regime and extrapolate finally to infinite dilution. The form factor of a Gaussian chain (Debye function) is given by (for its detailed derivation see chapter 6, section 8.4).

$$F_{Debye}(x) = \frac{2}{x^2} (\exp(-x) - 1 + x) \quad (7.2)$$

With $x = Q^2 R_g^2$ and R_g the radius of gyration describing the overall dimension of the single linear polymer chain.

The Debye function describes the (ideal) polymer scattering well from length scales of the overall coil down to length scales where the polymer becomes locally rigid. The corresponding asymptotic limits are:

$$F(Q) \sim N \left(1 - \frac{1}{3} Q^2 R_g^2\right) \text{ for small } Q \quad (7.3)$$

$$\sim 2N / (Q^2 R_g^2) \text{ for large } Q \quad (7.4)$$

Equation 7.3 describes the conventional Guinier scattering of the overall polymer (compare chapter 6, equation 6.126), equation 7.4 describes a power law. At these length scales, the sub-chains of different lengths are self-similar and so they reveal a fractal behaviour. The prefactor is connected to the magnitude R_g^2/N that is the effective segment size. From this magnitude, one can calculate back to the local rigidity that is responsible for the effective segments.

Polymer theory distinguishes several concentration regimes spanning from *dilute* over *semi-dilute* to *concentrated* and finally approaching the *melt* state where no solvent molecules are present [4]. A crucial concentration separating *dilute* and *semi-dilute* regime is the so-called *overlap concentration* $\phi^* = (V_w/N_a) / (\frac{4}{3} R_g^3)$, which describes the “internal concentration” per volume of a single polymer chain. Related to the *overlap concentration* ϕ^* is the so-called *blob size* or *screening length* ξ , a further very important parameter in polymer theory. At length scales smaller than ξ excluded volume interactions are effective whereas for larger length scales these are *screened*. Therefore,

locally at $r < \xi$ swollen chain behaviour is observed with $\nu=3/5$, but for $r \gg \xi$ a scaling exponent $\nu=1/2$ is found resulting from a “Gaussian chain of blobs”.

Polymer-polymer interactions as seen in $S(Q)$ are weak in the dilute regime, but still effective, so that one can apply the virial expansion.

$$\phi/I(Q=0) = 1/V_w + 2A_2\phi + \dots \quad (7.5)$$

Equation 7.5 is formulated neglecting the contrast factor, so it holds for all types of scattering experiments, i.e. SANS, SAXS and SLS.

The value of the second virial coefficient A_2 directly reflects polymer-polymer interactions, i.e. a positive A_2 is found for repulsive interactions (“good” solvent i.e. excluded volume interactions), a negative one for attractive interactions (“bad” solvent) and finally $A_2=0$ characterizes no interactions at all (θ -solvent). Without any data fitting, this distinction can easily be made by plotting the intensity data $I(Q)$ of a concentration series normalized to the corresponding volume fractions $I(Q)/\phi$ (Since scattering arises due to an exchange of a volume element of solvent by a volume element of polymer with different scattering contrast, the natural concentration unit for any scattering experiment should be volume fraction ϕ). This is schematically shown in Figure 7.2. If no particle-particle interactions are present all data for all Q -vectors exactly fall on top of each other.

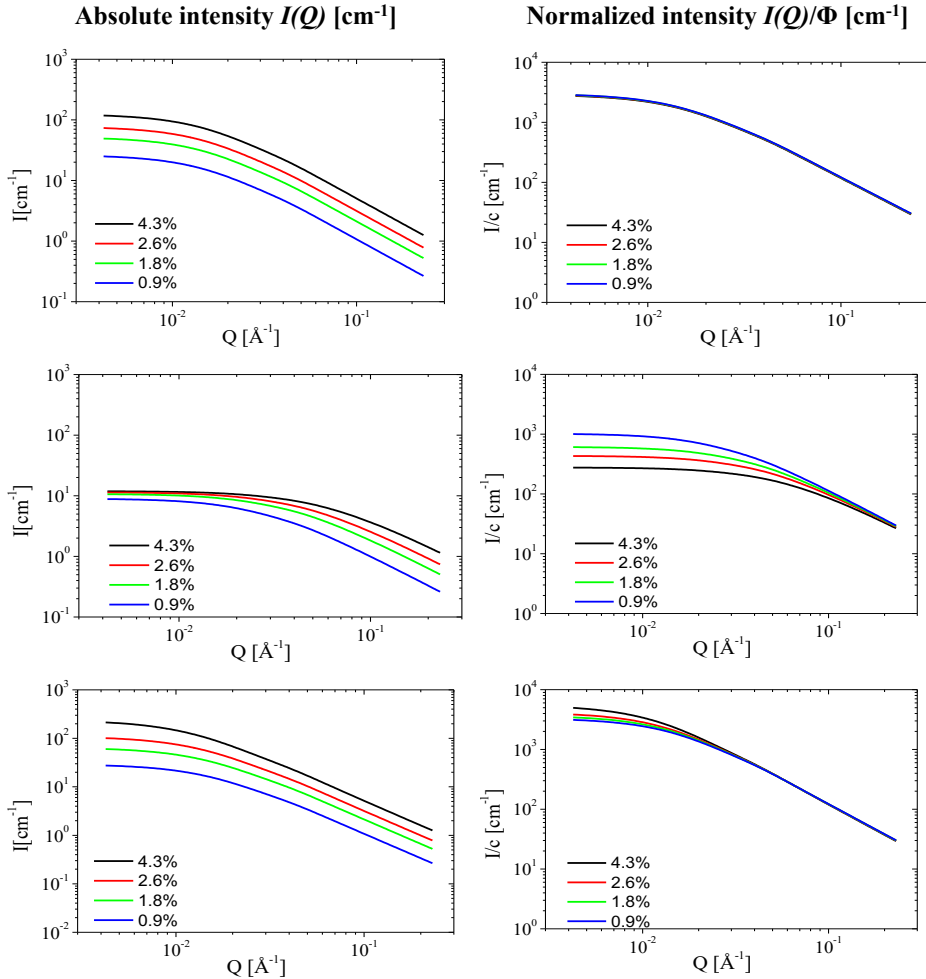


Figure 7.1: Calculated scattering intensities in absolute units $I(Q)$ (left) and normalized to polymer volume fraction $I(Q)/\phi$ (right) for solutions of a linear polymer at different volume fractions given in percent, see legends, assuming a virial ansatz for particle interactions Equation 7.6. From top to bottom: No interactions $A_2=0$ (θ -solvent, repulsive interactions $A_2>0$ “good” solvent, attractive interactions $A_2<0$ “bad” solvent).

Irrespective what kind of interactions are present this also holds for high Q -vectors, since high Q -vectors mean small length scales and the local (*intramolecular*) structure is not affected by particle-particle interaction ($S(Q)=1$). In contrary, at low Q -vectors there are crucial differences between the individual concentrations in this representation. For

repulsive interactions the forward scattering is reduced by $S(Q)$ therefore the lowest concentration shows the highest normalized intensity. For attractive interactions, on the other hand, the forward scattering is increased by $S(Q)$, therefore the lowest concentration shows the lowest normalized intensity. This sequence can be easily understood, because attractive interactions finally result in clustering of the individual particles.

In detail, all curves show in Figure 7.1 are calculated by combining Equation 7.1 and 7.5:

$$I(Q) = \frac{\Delta \rho^2}{N_a} \frac{\phi}{\left[1/(V_w F(Q)) + 2 A_2 \phi\right]} \quad (7.6)$$

following a “generalized” Zimm approach.

For more details about synthesis and characterisation of polymers/macromolecules the interested reader is referred to standard textbooks e.g. [7], [8].

7.3 Branched polymers

Branching crucially influences the mechanical properties of polymers therefore characterisation and control of branching reactions during polymerisation processes are of vital interest not only for polymer industry to tune semi-empirically material properties, but also for fundamental research to derive a proper quantitative structure property relationship.

The simplest branched polymer is a regular star polymer, where f arms, each of same molecular weight $M_{w,arm}$, are emanating from a microscopic central branch point, the star core. Experimentally, such regular star polymers are nowadays most precisely realized by using chlorosilane dendrimers as branch points. The arms forming the star corona or shell are grafted to the dendrimer core by “*living*” anionic polymerisation [9]. The precise control of the dendrimer generation is reflected in the precise functionality of the final star polymer so that functionalities as high as $f=128$ can be achieved. However, with increasing functionality there is a polydispersity in functionality since the last arms are extremely difficult to graft since they must diffuse through the already very crowded star polymer corona to react at the star core [10].

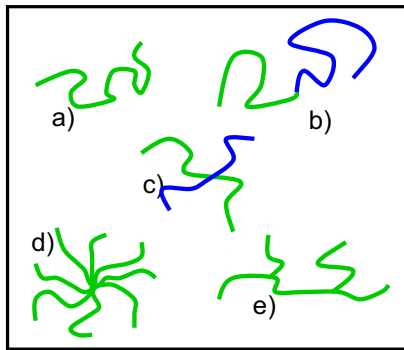


Figure 7.2: Schematic illustration of different polymer architectures: a) linear homopolymer, b) linear block copolymer, c) regular mikto-arm star polymer ($f=4$), d) regular star polymer ($f=8$), and e) comb polymer.

The form factor of a regular star polymer with Gaussian chain statistics has been derived by Benoit already in 1953 [11].

$$F_{star}(Q) = \frac{2}{fQ^4 R_{g,arm}^4} \left[Q^2 R_{g,arm}^2 - (1 - e^{-Q^2 R_{g,arm}^2}) + \frac{f-1}{2} (1 - e^{-Q^2 R_{g,arm}^2})^2 \right] \quad (7.7)$$

The overall size of the star polymer $R_{g,star}$ is related to the size of the individual arm by

$$R_{g,star} = \sqrt{\frac{(3f-2)}{f}} R_{g,arm}.$$

There is no rigorous analytical formula for a star polymer with swollen chain statistics, but experimental data for star polymers in a “good” solvent can be nicely described either by the Dozier function [12] or the approach derived by Beaucage [13]. His equation can be viewed as a “universal form factor” for an arbitrary mass fractal that can also be applied to many other polymeric systems:

$$F(Q) = G \exp(-Q^2 R_g^2/3) + B \left(\frac{1}{Q} \right)^{D_f} \quad (7.8)$$

with $Q^* = Q/[erf(QkR_g/\sqrt{6})]^3$. Here erf is the error function and G and B are amplitudes, which for mass fractals can be related to each other by $B = G \cdot P / R_g^P \cdot \Gamma(P)$ (polymeric constraint). D_f is the fractal dimension of the internal substructure, k an empirical constant found to be ≈ 1.06 and Γ is the Gamma function. The fractal dimension is related to the scaling exponent by $D_f = 1/\nu$. The Beaucage expression can be nicely extended to describe hierarchical structures over multiple levels i $F(Q) = \sum_i P F_i(Q)$ where $F_i(Q)$ are given by Equation 7.7. Figure 7.4 shows form factors obtained for polybutadiene (PB) star polymers with varying functionality f but same $R_g \approx 50$ nm in d-cis-decalin.

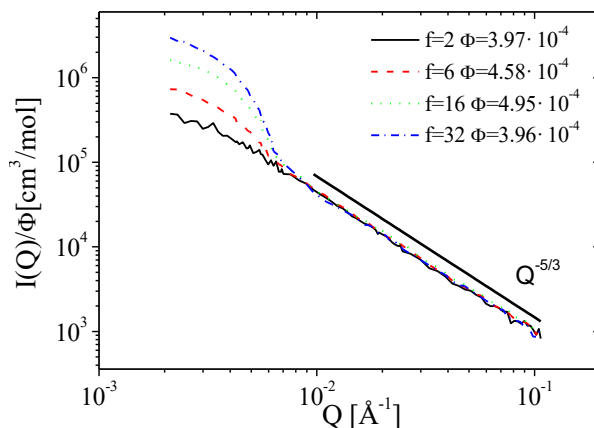


Figure 7.3: SANS intensity $I(Q)$ normalized by volume fraction ϕ for regular polybutadiene star polymers with varying functionality f but same radius of gyration $R_g \approx 50\text{nm}$. The asymptotic power law observed at high scattering vectors $I \sim Q^{-5/3}$ clearly indicates excluded volume interactions relevant in a “good” solvent, i.e. swollen chain statistics [14] (Reprinted by permission of Springer Nature: Springer, Appl. Physics A: Materials Science & Processing, partial structure factors in star polymer/colloid mixtures, J. Stellbrink et al., copyright 2007)

At low Q -vectors, $Q \leq 8 \times 10^{-3} \text{ \AA}^{-1}$, data could be modelled using the Benoit form factor, Equation 7.6 for a Gaussian star, which gives the explicit dependence on functionality f . For describing the complete data set we used the Beaucage form factor, Equation 7.7, which describes also the observed power law at high Q -vectors. One should note that this power law extends over more than one order of magnitude in Q and starts at the same Q -value of $\approx 8 \times 10^{-3} \text{ \AA}^{-1}$ for all f due to the same R_g . The observed power law slope of $I(Q) \sim Q^{-5/3}$ reflects the “good” solvent quality of cis-decalin for polybutadiene and decreases slightly with increasing f , indicating increasing arm stretching due to the increasing monomer density in the star corona.

The effect of branching becomes easily visible by using a so-called Kratky representation, $I(Q) Q^2$ vs. Q . Whereas a linear polymer with Gaussian chain statistics reaches monotonically an asymptotic plateau, any branched structure shows a maximum. For the here discussed regular star polymer the height quantitatively depends on the arm number or functionality f , see figure 7.4.

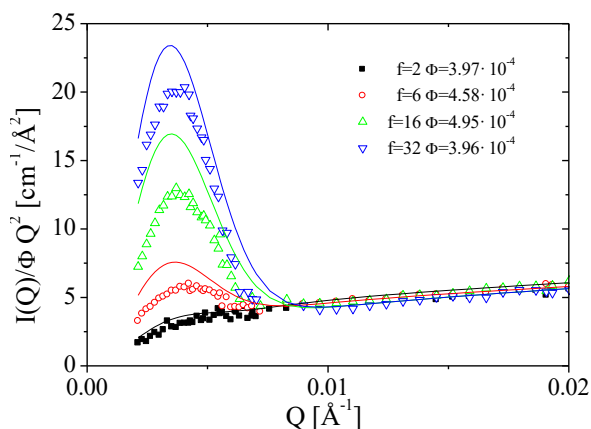


Figure 7.4: Kratky representation $I(Q) Q^2$ vs. Q for same data as in Figure 7.4. The increasing peak height with increasing functionality f due to branching becomes clearly visible as well as the discrepancy between experimental data (symbols) and Beaucage function used to model the data. The fact that no asymptotic plateau is observed results from the excluded volume interactions relevant in a “good” solvent, i.e. swollen chain statistics.

7.4 In-situ experiments during polymerisation

For understanding and controlling any chemical reaction a detailed understanding of reaction mechanism, type and role of intermediate species as well as reaction kinetics are prerequisite. How the microscopic structure of a growing polymer chain is evolving in the different steps of polymerisation reactions has to be resolved by non-invasive, real-time measurements. The ideal tool is small angle neutron scattering (SANS), since the microscopic structure of polymer-based materials can be resolved on a micrometer-to-nanometer-level by modern neutron scattering techniques. In addition, contrast variation, i.e. H/D exchange, can even “stain” certain parts of the polymers giving access to unprecedented structural information. So neutron scattering is a unique and outstanding technique to investigate polymerising systems in real-time, in particular since new, more powerful neutron sources became available worldwide (FRM-2, SNS, J-PARC). But for a complete description of the polymerisation process additional information in terms of reaction kinetics etc. are prerequisite. Thus, in-situ SANS experiments must be supported by complementary methods like NMR, SEC, UV/VIS and IR spectroscopy, favourably also in real-time mode.

Recently we investigated reaction mechanism and kinetics of different polymerisation techniques like “living” anionic polymerisation [15] or post-metallocene catalyzed olefin polymerisation [16] by such an in-situ multi technique approach. Figure 7.6 shows time resolved SANS intensities $I(Q)$ in absolute units obtained during the polymerisation of 1-octene by a pyridylamidohafnium catalyst in toluene at 20°C. Experiments have been performed using the KWS-1 instruments at the former FRJ-2 reactor in Jülich which allowed a temporal resolution of about several minutes.

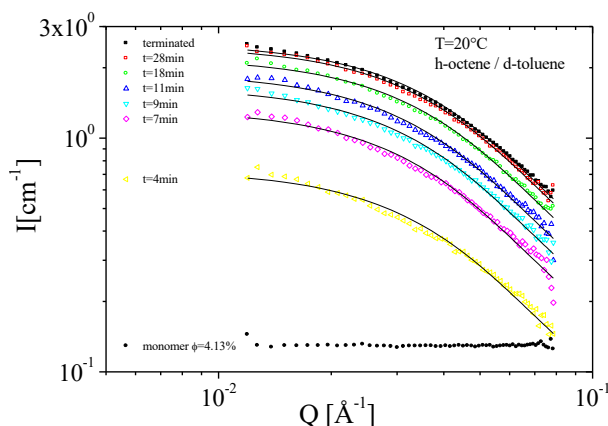


Figure 7.5: Time resolved SANS intensities $I(Q)$ in absolute units obtained during the polymerisation of 1-octene by a pyridylamidohafnium catalyst in toluene at 20°C [16] (reprinted with permission from Macromolecules, **42**, 1083, 2009. Copyright 2009, American Chemical Society)

The monomer solution shows a Q -independent intensity over the whole accessible SANS Q -range typical for small molecules, which act as “incoherent scatterers”. Note: The actual incoherent background for all components can be estimated by $\frac{d\Sigma(Q)^{inc}}{\Omega} = \frac{\Sigma \sigma_i^{inc}}{4\pi} \frac{N_A}{V_w}$. After four minutes a polymer is already formed and the Q -dependence of the intensity can be described by a Beaucage form factor, equation 7.7. With ongoing polymerisation, increasing polymerisation time t the general shape of $I(Q)$ does not change any further, only the forward scattering $I(Q=0)$ is increasing due to the increasing molecular weight and concentration of the growing polymer chain. Finally, the polymerisation is almost finished after half an hour as can be seen by comparison with the terminated polymer. A detailed quantitative analysis of $I(Q,t)$ reveals that during this type of polymerisation reaction no aggregation phenomena of the growing polymer chain are relevant. Similar experiments at high flux sources allow today temporal resolutions smaller than 1 second if experiments are repetitively performed using a stopped flow mixer.

References

- [1] C J.R. Severn and J.C. Chadwick, *Tailor-Made Polymers*, (Wiley-VCH, Weinheim, 2008)
- [2] G.W. Coates and M.A. Hillmyer, *Polymers from Renewable Resources*, *Macromolecules*, **VI2**, 7987 (2009); C.K. Williams, M.A. Hillmyer, *Polymer Rev.* **48**, 1 (2008)
- [3] J. S. Higgins and H. C. Benoit, *Polymers and Neutron Scattering*; (Clarendon Press, Oxford, U.K., 1994).
- [4] P.G. De Gennes, *Scaling Concepts in Polymer Physics*, (Cornell University Press, 1979)
- [5] W. Brown, *Light Scattering: Principles and development*, (Oxford University Press, 1996)
- [6] S. Mori and H.G. Barth, *Size Exclusion Chromatography*, (Springer, 1999)
- [7] P.J. Flory, *Principles of Polymer Chemistry*, (Cornell University Press, 1953)
- [8] H.G. Elias, *Macromolecules*, (Wiley-VCH, Weinheim, 2009)
- [9] G. S. Grest, L. J. Fetters, J. S. Huang, and D. Richter, *Adv. Chem. Phys.* **94**, 67 (1996)
- [10] J. Allgaier, K. Martin, H. J. Räder, and K. Müllen, *Macromolecules* **32**, 3190 (1999)
- [11] H.J. Benoit, *J. Polym. Sci.*, **11**, 507 (1953).
- [12] William D. Dozier, John S. Huang, Lewis J. Fetters, *Macromolecules* **24** 2810 (1991)
- [13] G. Beaucage, *J. Appl. Crystallogr.* **28**, 717(1995)
- [14] J. Stellbrink et al., *Applied Physics A* **74**, S355 (2002)
- [15] J. Stellbrink et al. *Macromolecules*, **31**, 4189 (1998)
- [16] A.Z. Niu et al., *Macromolecules* **42** 1083 (2009)

Exercises

E7.1* Contrast or no contrast?

Due to synthetic (and financial) limitations only protonated material is available for a SANS experiment, for both polymer (poly(ethylene propylene), PEP, and solvent dimethylformamide, DMF.

a) Calculate the contrast factor $\frac{\Delta\rho^2}{N_A}$ following equation 7.1.

b) What is the necessary molecular weight M_w to achieve a signal-to-background ratio of 5 at $Q=0$ for a given polymer volume fraction $\phi=0.01$? (Remember: The incoherent scattering contributes to the background too and there is an empirical “rule of thumb” that the experimental incoherent scattering is twice the theoretical value due to inelastic and multiple scattering!)

c) At which Q -value the signal vanishes in the background?

(Assuming good-solvent conditions with a prefactor 0.01 [nm] for the R_g - M_w -relation and assuming the Guinier approximation for $F(Q)$)

d) For which combination of molecular weight and volume fraction ϕ the experiment could be performed in the dilute regime, i.e. $\phi \leq 0.1\phi^*$?

Given are sum formulae and densities

h-PEP = C_5H_{10} , $d_{PEP}=0.84\text{g/cm}^3$

h-DMF = C_3H_7NO , $d_{PEO}=0.95\text{g/cm}^3$

and coherent and incoherent scattering lengths b_{coh} and b_{inc} in units [cm]:

C: $b_{coh}=6.65\text{E-}13$, $b_{inc}=0$

H: $b_{coh}=-3.74\text{E-}13$, $b_{inc}=2.53\text{E-}12$

D: $b_{coh}=6.67\text{E-}13$, $b_{inc}=4.04\text{E-}13$

O: $b_{coh}=5.80\text{E-}13$, $b_{inc}=0$

N: $b_{coh}=9.36\text{E-}13$, $b_{inc}=0$

E7.2 Interactions of Gaussian chains

Calculate $S(Q)$ for Gaussian chains at a volume fraction $\phi = \phi^*$.

8 Spin-dependent and Magnetic Scattering of Polarized Neutrons

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8.1 Introduction

Among the properties that make the neutron a unique and valuable probe for condensed matter research, its spin and magnetic moment is of particular importance in the scattering process. There are two aspects to consider, firstly, the strong nuclear interaction of the neutron with a nucleus depends on the either parallel or antiparallel alignment of the spins of neutron and nucleus, and secondly, the neutron's magnetic moment interacts with the unfilled electron shells of atoms or ions in magnetic scattering. The scattering process will also have an impact on the spin state of the neutron probe. Hence, one may expect that controlling the neutron spin in a scattering experiment will provide further valuable information, which leads us to the subject of this lecture: polarized neutron scattering and polarization analysis. Indeed, it is possible by working with polarized neutron and polarization analysis to separate scattering terms with respect to their different structural or magnetic origins, and moreover, to uncover scattering contributions that remain hidden in usual unpolarized scattering experiments.

The method of polarized neutron scattering is mature and well developed. The theoretical description of magnetic neutron scattering by Halpern and Johnson 1939 [1] was essentially completed by the general theory by Blume and Maleyev, independently, in 1963 [2,3]. The first implementation of neutron polarization analysis by Moon, Riste and Koehler [4] laid the foundation for experimental work and some of their examples will be discussed in this lecture. In 1972, Mezei [5] developed the neutron spin echo technique, ten years later Schärpf accomplished the XYZ polarization analysis on a multidetector spectrometer, the D7 at ILL [6], and from 1988 Tasset and Brown developed neutron polarimetry [7,8].

This lecture will give an introduction first to polarized neutrons, how they interact with magnetic fields and upon experimental devices. The following sections will cover the scattering interaction of polarized neutrons with matter, the nuclear and magnetic scattering, followed by applications.

The impact for magnetic scattering studies seems to be quite obvious, however, with respect to the high spin-dependent cross-section of hydrogen, polarization analysis opens up new possibilities for interesting soft-matter research. More information is available, if by experimental means we are able to define and distinguish the spin state of the neutron probe before and after the scattering process, which leads us to the subject of this lecture: neutron scattering with polarization analysis. The history of polarized neutron work started early; essentially all principles experimentally and theoretically were developed in the 50s and early 60s of the past century. With still ongoing improvements in instrument performance for using polarized neutrons and polarization analysis, a steadily increasing number of research is published utilizing neutron polarization techniques.

8.2 Neutron spins in magnetic fields

Basic properties

The neutron has a spin $S = \pm 1/2$ with angular momentum $\mathbf{L} = \hbar \mathbf{S}$. The magnetic moment of the neutron results from the spins of the individual quarks and their orbital motions, and the relation between spin and magnetic moment is given by the neutron g -factor, $g_n = -3.8260837(18)$, in units of the nuclear magneton $\mu_N = \frac{e\hbar}{2m_p} = 5.05078324(13) \cdot 10^{-27} \text{JT}^{-1}$

$$\mu_n = g_n S \mu_N \simeq \mp 1.913 \mu_N = \pm \gamma_n \mu_N,$$

where $\gamma_n = -g_n S$ is the gyromagnetic factor of the neutron (see Refs. [9]) . Because of the small ratio $\mu_n/\mu_B = m_e/m_p$, the neutron magnetic moment μ_n is small compared to the magnetic moment of the electron $\mu_e = g_e S \mu_B \approx 1 \mu_B$, with the Bohr magneton $\mu_B = \frac{e\hbar}{2m_e}$ and the Lande-factor $g_e = 2(1 + \alpha/2\pi - 0.328\alpha^2/\pi^2) \approx 2$ (see Refs. [10]), α is the fine structure constant. A peculiarity to note is that different to the electron and proton, the neutron magnetic moment is aligned opposite to its spin.

Polarization

Next we consider the many particle ensemble of neutrons in a neutron beam. Polarization of a neutron beam is defined by the normalized average over the neutron spins.

$$\mathbf{P} = 2\langle \mathbf{S} \rangle \quad (8.1)$$

Applying a magnetic field $\mathbf{H}$ defines a quantization axis and the neutrons split in spin up and down states, $n_\uparrow$ and $n_\downarrow$ respectively. Measuring the beam polarization will take the projection of the spins in up- and down state states with proper normalization.

$$-1 < P = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow} < 1. \quad (8.2)$$

8.2.1 Interaction of neutrons with magnetic fields

Zeeman splitting

The dipolar interaction potential of a neutron with the magnetic field is given by

$$V_m = -\boldsymbol{\mu}_n \cdot \mathbf{B} \quad (8.3)$$

where $\mathbf{B}$ is the magnetic induction. For neutrons passing from zero-field into a magnetic field the potential energy changes by the Zeeman term $\pm \mu_n B$ depending on the relative orientation of the magnetic moment. The according change in kinetic energy to conserve the total energy is small, $0.06 \mu\text{eV}/\text{T}$, which in experimental practice is of relevance only in rare cases.

Equation of motion and Larmor precession

The characteristic motion of the neutron magnetic moment in a magnetic field is Larmor precession, which for simplicity can be considered in a classical treatment. In fact, even the quantum mechanical treatment, which introduces Pauli spin matrices $\hat{\sigma}$ into the Schrödinger equation, is effectively a classical treatment considering the origin of these matrices. Originally [11], they result from the problem of mapping three dimensions onto two by introducing a complex component describing the classical problem of a spinning top. [12] The

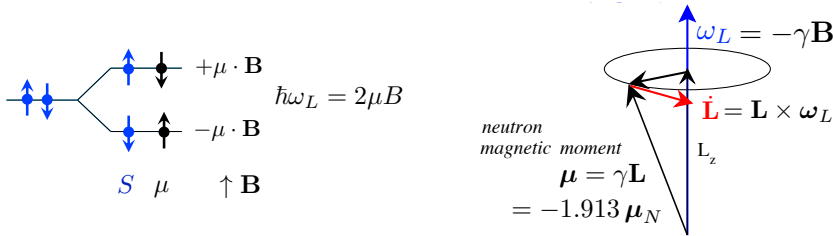


Fig. 8.1: Zeeman splitting (left) and Larmor precession (right). The motion of the neutron in a constant magnetic field conserves energy and angular momentum.

magnetic interaction tends to align the neutron moment with the magnetic induction in order to minimize the interaction energy. The magnetic moment is related to the angular momentum as

$$\mu = \gamma \mathbf{L}, \quad (8.4)$$

where γ is the gyromagnetic ratio given by $\gamma = 2\mu_n/\hbar = 2\gamma_n\mu_N/\hbar = -1.83 \cdot 10^8 \text{ s}^{-1}\text{T}^{-1}$ or, in cgs units, $\gamma/2\pi = -2916 \text{ Hz/Oe}$. There is a torque $\mu \times \mathbf{B} = \dot{\mathbf{L}}$ equal to the time derivative of the angular momentum, which leads to the Bloch equation of motion:

$$\dot{\mu} = \gamma \mu \times \mathbf{B}. \quad (8.5)$$

Because of the cross product, the time derivative of the magnetic moment is always perpendicular to the moment itself. Therefore, the resulting motion is a precession, where the angular momentum, the component L_z along the field, and the energy are constants of the motion, see Fig.8.1. The precession frequency is the *Larmor frequency* $\omega_L = -\gamma B$, and $\hbar\omega = 2\mu B$, the Zeeman splitting energy.

Motion in time dependent fields

The polarization will behave like the individual neutron spin in a constant magnetic field and will be a constant of motion. However, if we consider time-dependent fields, the finite velocity distribution in a neutron beam will result in a different time dependence. Hence de-phasing of neutrons spins and degrading of the polarization are possible experimental effects and have to be taken into account.

Thermal neutrons move with a speed of thousands of meters per second. When passing through spatially varying magnetic fields, the neutrons experience time-dependent field changes in their reference system. Replacing the constant $\mathbf{B}$ by $\mathbf{B}(t)$, the differential equation Eq. (8.5) can be used to calculate numerically the effect of all relevant field variations in an experimental set-up.

Asymptotic cases

Usually, it is possible to work within two simple limiting cases of either **(i) slow adiabatic field variation**, in which the non-precessing spin component parallel to the field smoothly follows the field direction, or of **(ii) sudden field reversal**, in which the non-precessing spin component has no time to reorient itself, when traversing abruptly from a parallel to anti-parallel field or vice versa. Slow field variation means that the field $\mathbf{B}$ changes or rotates in the coordinate system of the neutron with a frequency that is small compared to the Larmor frequency, see Fig. 8.2.

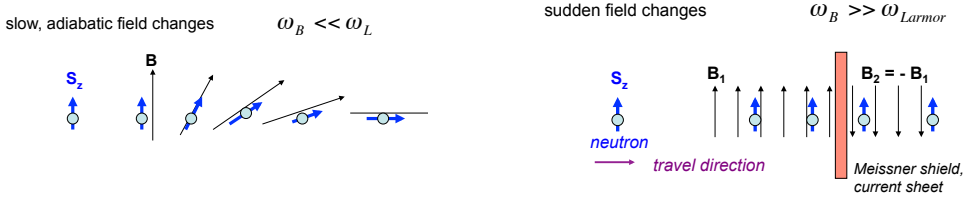


Fig. 8.2: Neutron polarization can be best preserved in the asymptotic cases of either slowly or suddenly varying fields. The second case is used in a cryoflipper to reverse the polarization with respect to the external field.

8.2.2 Experimental devices

Polarizer and polarization analyzer

The most common methods to polarize neutrons are (i) using the total reflection from magnetic multi-layers, (ii) using Bragg reflection of polarizing single crystals (typically Heusler crystals) and (iii) polarized He-3 filters, in which for anti-parallel spins the (n,³He)-compound has a large absorption cross-section while all neutrons with parallel spins may pass the filter cell. The first two methods use an interference effect of nuclear and magnetic scattering amplitudes having the same absolute value as discussed below.

(i) Polarizing total reflecting supermirrors are an easy experimental tool to obtain a broad wavelength band of cold polarized neutrons. The angle of total reflection for a single ferromagnetic (FM) layer is given by

$$\Theta_c^\pm = \lambda \sqrt{n(b \pm p)/\pi}. \quad (8.6)$$

Hence, the critical angle may vanish for one orientation of the neutron spin and there is total reflection for the other one. Here n denotes the particle density and b and p the nuclear and

magnetic scattering lengths, respectively. However, the critical angle can be further increased by artificial multi-layers (supermirrors) of alternating FM and non-magnetic layers of varying thickness [13], see Fig. 8.3. The λ dependence of the total reflectivity makes this type of polarizer less favorable for thermal neutrons of shorter wave length as it reduces the accepted divergence of the beam.

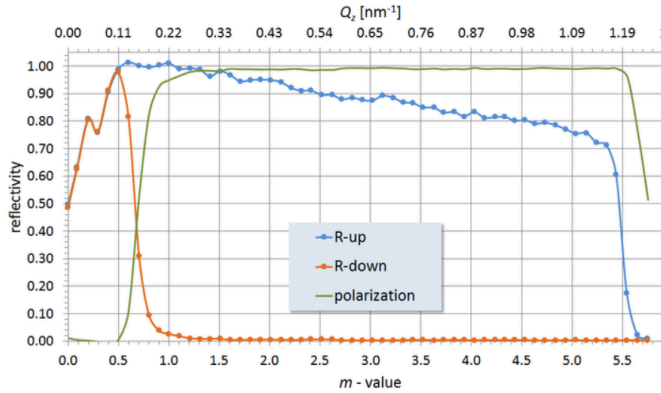


Fig. 8.3: Spin dependent reflectivity and polarisation of Fe/Si polarizing super-mirror $m = 5.5$. $m=1$ corresponds to the total reflectivity of Ni. (from SwissNeutronics.ch [14])

(ii) Bragg reflection from a crystal monochromator with similar nuclear and magnetic scattering amplitudes b and p , which yields constructive interference $b + p$ for one spin state and destructive interference $b - p$ for the other. *E.g.* the (111) Bragg reflection of the Cu_2MnAl Heusler alloy gives 95 % polarization. However, the reflectivity of such crystals is low compared to usual non-polarizing monochromators and a saturating field is required over the entire monochromator, which makes it technically more complicated to combine with focusing though this is feasible.

(iii) ^3He filter cells, see Fig. 8.4, are of growing importance for polarizing neutrons, particularly for the more challenging case of thermal neutrons, although such cells are technically rather demanding and still under development. In case of spin-exchange optical pumping (SEOP) the spin polarization of ^3He gas is achieved in several steps. The cell is filled with additional Rb, K and N_2 vapor. Rb electrons are polarized with a circular polarized laser, by collisions the spin is exchanged with K, which most efficiently exchanges spin with ^3He . Since polarization results from absorption, such a device does not interfere with the beam divergence. One may note that requirements for field homogeneity are very high and it is a kind of art and glass alchemy to make cells with small depolarization all determining the lifetime of ^3He polarization. The neutron polarization P raises with increasing ^3He cell size or pressure, while the transmission T decreases. The optimum in efficiency is usually chosen by the maximum of a quality factor P^2T .

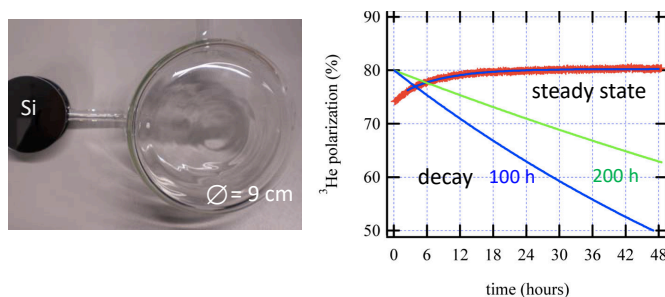


Fig. 8.4: (left) ^3He -cells made of Si-crystal (avoiding small angle scattering background) and of glass (for wide angle diffraction). ^3He in-situ polarization of a SEOP He-3 cell and measured polarization of neutron beam in transmission. (from Babcock et al. [15])

Guide-fields

A magnetic *guide field* is used to maintain the direction of the spin and the polarization of the neutron beam. The guide field preserves the quantization axis to which the neutron moments have to align either parallel or anti-parallel. Typical guide fields in the order of 10 G are strong compared to earth field and other possible stray fields and usually sufficient to prevent depolarization along the beam path. Such guide fields are usually too weak to have any significant impact on the sample magnetization.

Depolarization effects may occur for an inhomogeneous distribution of field directions over neutron beam cross-section, which is typically a few cm^2 . This can easily occur if a ferromagnetic material is used close to the beam or if the sample itself is ferromagnetic. A neutron beam passing through a ferromagnet is usually completely depolarized by differently oriented ferromagnetic domains in the beam path, unless a saturating magnetic field is used to align the domains. Depolarization will depend also on the path length through the sample, therefore, usually such effects are negligible in *neutron reflectometry* of thin ferromagnetic films.

XYZ-coils

In order to probe the orientation of the magnetic moments in the sample, it is desirable to align the polarization to any desired direction at the sample position. This can be done with a set-up of three orthogonal pairs of so-called xyz-coils. Fig. 8.5 illustrates the field setting along x-direction. In the example, one can see that the z-coil has been used to compensate the guide field at the sample position, and that the x-coils produce a field of a few Gauss. The field needs to be sufficiently strong so that the neutron polarization can follow the smooth variation of the field direction adiabatically, finally turning back into the z-direction of the guide field outside the xyz-coils.

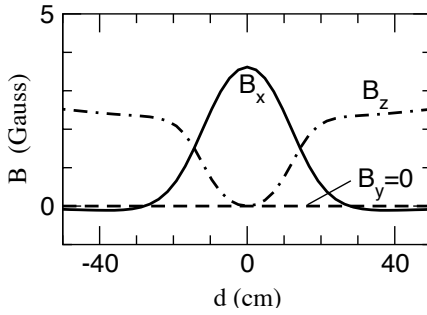


Fig. 8.5: (left) Magnetic field setting in a xyz-coil system for an adiabatic nutation of the polarization of cold neutrons in horizontal x-direction at the sample turning to a vertical (guide) field B_z at further distance from the sample. (right) A photo of the xyz-coil system in the DNS instrument at the FRM-2.

Flipper

The purpose of a π -flipper is to reverse the polarization and to detect whether the sample causes spin-flip scattering.

When applying a magnetic field perpendicular to the polarized neutron beam, the polarization immediately starts its Larmor precession. A flipper that reverses the neutron polarization with respect to the guide field has to induce a well-defined field pulse so that the polarization precesses by an angle π . For this purpose one can use the homogeneous field of a *Mezei* flipper, a long rectangular coil, see Fig. 8.6. Neutrons see a sudden field change when they enter and exit the coil, in between they precess around the perpendicular flipping field, whose magnitude is tuned with respect to the time of flight that the neutrons spend inside the coil. Therefore, the device is λ -dependent and currents (fields) need to be properly tuned for a π -flip.

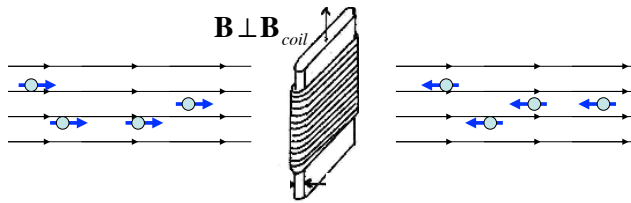


Fig. 8.6: Principle of a neutron π -spin flipper. The neutrons perform a Larmor-precession of 180° inside a long rectangular coil. The field B is perpendicular to spin orientation and adjusted to the speed of the neutrons.

The purpose of a $\pi/2$ -flipper is to set the polarization in precession mode by turning the polarization perpendicular to the guide field. A precessing polarization is used for instance in high resolution *Neutron Spin Echo spectroscopy* and for *Larmor diffraction*, see below. Both methods use the property of the neutron spin as an internal clock independent of the

scattering process itself and achieve highest resolution.

The above principle works for a monochromatic beam or when a wavelength spectrum is sorted in time of flight, as it is the case at pulsed neutron sources. However, it is also possible to change the neutron spin with respect to the magnetic field by using a *radio-frequency (RF) flipper* inducing a transition between the Zeeman splitting shown in Fig. 8.1. The operating frequency for the resonance is strictly tied to the strength of the static magnetic field B by the neutron's gyromagnetic ratio with $\hbar\omega = hf = h \cdot 29165s^{-1} \times B/\text{mT}$.

The classical experimental set-up of Moon, Riste and Koehler (1969) combines the above discussed devices for polarized neutron scattering with so-called longitudinal polarization analysis. Principles and examples from this study [4] will be discussed in the following section.

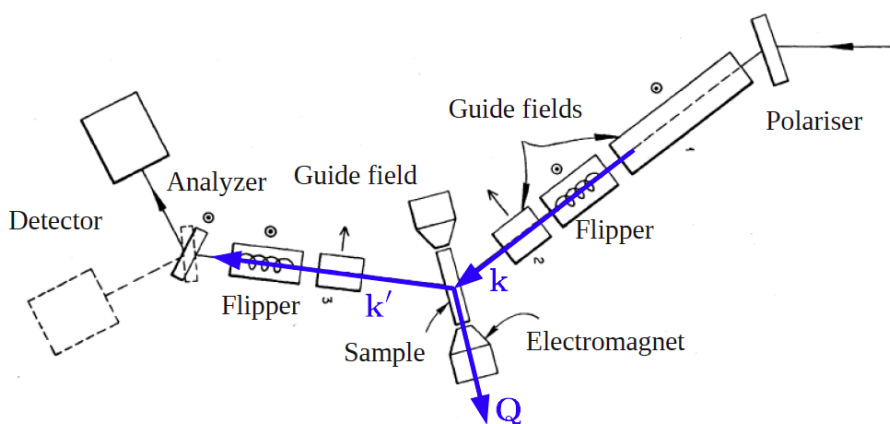


Fig. 8.7: The scheme of the triple axis instrument equipped for polarization analysis as used by Moon, Riste and Koehler (1969). Reprinted from [4]. Copyright (1969) by the American Physical Society.

8.3 Polarized neutron scattering and applications

8.3.1 Nuclear interaction of neutrons with matter

For thermal and cold neutrons, the range of the nuclear interaction is small compared to the neutron wavelength and can be described by a point-like and isotope-specific Fermi potential, which is proportional to the scattering length b ,

$$V(r) = \frac{2\pi\hbar^2}{m_n} b \delta(r - R) \quad (8.7)$$

The scattering amplitude $N_{\mathbf{Q}}$ for an ensemble of nuclei is determined by the transition matrix elements for the scattering potential $V_{\mathbf{Q}}$

$$N_{\mathbf{Q}} = \langle \mathbf{k}'\mathbf{S}' | V_{\mathbf{Q}} | \mathbf{k}\mathbf{S} \rangle \quad (8.8)$$

which in general depends on the scattering vector $\mathbf{k} - \mathbf{k}' = \mathbf{Q}$, the related energy transfer, and the spin states before and after the scattering process.

First, we consider the scattering of nuclei of one element only and assume further that these nuclei have zero spin (*e.g.* ^{12}C , ^{16}O ..., and typically "gg" isotopes with even number of protons and neutrons). The scattering length operator $\hat{b}$ is a scalar and the scattering will be independent of the neutron spin orientation. This leads to the scattering intensity, where we replace the actual scattering length by the average $\bar{b}_l$ and deviations, by including the mean square deviations

$$\frac{d\sigma}{d\Omega} = N \sum_l b_l b_{l'} e^{i\mathbf{Q}(\mathbf{R}_l - \mathbf{R}_{l'})} = N(\bar{b}^2 - \bar{b}^2) + \bar{b}^2 \sum_l e^{i\mathbf{Q}(\mathbf{R}_l - \mathbf{R}_{l'})}. \quad (8.9)$$

The first term on the right side is the isotopic incoherent scattering, it relates to random fluctuations in the scattering length. In contrast, the second term, the coherent nuclear scattering, is proportional to $\bar{b}^2$ and contains phase information.

Next we consider that scattering nuclei may have a spin $I \neq 0$ and that the interaction is spin-dependent. There are two possible spin states of the compound, coupling the neutron spin with the spin of a nucleus, which are either $J = J_+ = I + 1/2$ or $J = J_- = I - 1/2$, associated with different scattering lengths b_+ and b_- . The multiplicity of the spin states $2J + 1$ equal $2I + 2$ and $2I$ for parallel and anti-parallel spin alignment respectively. For an equiprobable occupation of all states, the probabilities for the J_+ and J_- states are

$$p_+ = \frac{I + 1}{2I + 1}, \quad p_- = \frac{I}{2I + 1}, \quad (8.10)$$

defining the weights for the average coherent scattering length and its mean square average

$$\bar{b} = p_+ b_+ + p_- b_-, \quad \bar{b}^2 = p_+ b_+^2 + p_- b_-^2. \quad (8.11)$$

Again this will lead to a scattering intensity as given by Eq.(8.9), only that the **spin-incoherent scattering** term is now related to the randomness of spin states.

In order to understand what will happen to the spin states of neutron and nuclei, we consider the transition matrix element Eq. (8.8) for the scattering length operator, which is the sum of the average, coherent part, $A (= \bar{b})$, and the fluctuating spin-dependent part, $B = \frac{b_+ - b_-}{2I+1}$,

$$\hat{\mathbf{b}} = A + B \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{I}}. \quad (8.12)$$

Here, $\hat{\boldsymbol{\sigma}}$ is the Pauli spin operator given by **Pauli spin matrices**

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (8.13)$$

We choose the quantization axis z for the neutron polarization $\mathbf{P} = 2\langle\hat{\mathbf{S}}\rangle = \langle\hat{\boldsymbol{\sigma}}\rangle$, with spin-up states $|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and spin-down states $|-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. With

$$\begin{aligned} \hat{\sigma}_x|+\rangle &= |-\rangle, & \hat{\sigma}_y|+\rangle &= i|-\rangle, & \hat{\sigma}_z|+\rangle &= |+\rangle \\ \hat{\sigma}_x|-\rangle &= |+\rangle, & \hat{\sigma}_y|-\rangle &= -i|+\rangle, & \hat{\sigma}_z|-\rangle &= -|-\rangle \end{aligned} \quad (8.14)$$

we obtain the transition matrix elements

$$\begin{aligned} \langle +|\hat{\mathbf{b}}|+\rangle &= (A + BI_z) \langle +|+\rangle \quad \text{nsf} \\ \langle -|\hat{\mathbf{b}}|-\rangle &= (A - BI_z) \langle -|-\rangle \quad \text{nsf} \\ \langle +|\hat{\mathbf{b}}|-\rangle &= B(I_x - iI_y) \langle +|+\rangle \quad \text{sf} \\ \langle -|\hat{\mathbf{b}}|+\rangle &= B(I_x + iI_y) \langle -|-\rangle \quad \text{sf} \end{aligned} \quad (8.15)$$

for the non-spinflip (nsf) and spinflip (sf) scattering amplitudes, respectively. The non-spinflip scattering is given by the coherent scattering and one third of the spin-incoherent scattering, while two thirds of the spin-incoherent scattering is spinflip scattering. If we consider only coherent scattering, the final polarisation $\mathbf{P}' = \mathbf{P}$, whereas in case of only spin-incoherent scattering $\mathbf{P}' = -\frac{1}{3}\mathbf{P}$. The combination of coherent and spin-incoherent scattering may result in a change of magnitude and sign of polarization, however, the final polarization will not deviate from the initial polarization axis. Furthermore, the obtained result is simply independent of the direction of $\mathbf{P}$ with respect to $\mathbf{Q}$. This is an important feature, which is in contrast to the dipolar magnetic interaction that will be discussed below.

In summary, we can distinguish three contributions to the nuclear scattering $|N_{\mathbf{Q}}|^2$ arising from the total nuclear scattering amplitude $N_{\mathbf{Q}} = \sum_j b_j e^{i\mathbf{Q}\cdot\mathbf{R}_j}$, the average coherent scattering, the isotopic, non-spin dependent part of the incoherent scattering, and the spin-incoherent scattering

$$\frac{d\sigma^N}{d\Omega_{\mathbf{Q}}} = |N_{\mathbf{Q}}|^2 = \frac{d\sigma^N}{d\Omega_{\text{spin-inc}}} + \frac{d\sigma^N}{d\Omega_{\text{isotope-inc}}} + \frac{d\sigma^N}{d\Omega_{\mathbf{Q},\text{coh}}}. \quad (8.16)$$

The sum of the coherent and isotopic incoherent nuclear scattering can be separated from the spin-incoherent scattering by measuring spin-flip and non-spin-flip scattering.

$$\frac{d\sigma}{d\Omega_{\text{spin-inc}}} = \frac{3}{2} \frac{d\sigma^{SF}}{d\Omega} \quad (8.17)$$

$$\frac{d\sigma^N}{d\Omega_{\mathbf{Q},\text{coh}}} + \frac{d\sigma^N}{d\Omega_{\text{isotope-inc}}} = \frac{d\sigma^{NSF}}{d\Omega} - \frac{1}{2} \frac{d\sigma^{SF}}{d\Omega} \quad (8.18)$$

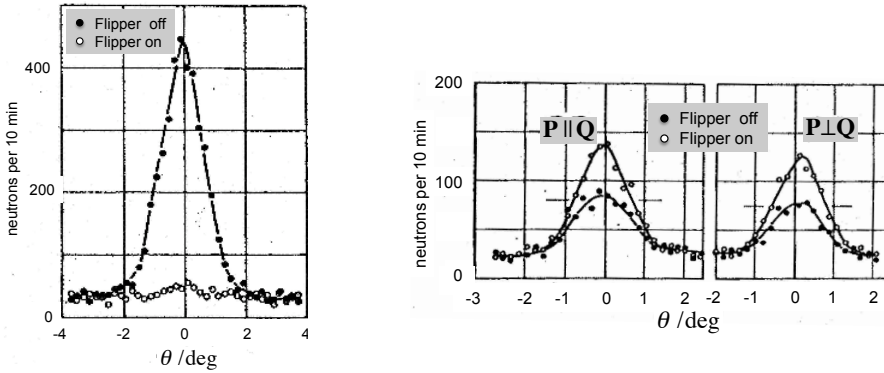


Fig. 8.8: *Left:* Nuclear isotopic incoherent scattering from nickel obtained by rocking the analyzer crystal through the elastic position, which is essentially all non-spin-flip scattering.

Right: Nuclear spin-incoherent scattering from vanadium show 2/3 and 1/3 contributions in the spin-flip and non-spin-flip channel respectively. There is no dependence on the direction of $\mathbf{P}$ relative to $\mathbf{Q}$ for all nuclear scattering. Reprinted from [4]. Copyright (1969) by the American Physical Society.

There are two good examples of isotope and spin-incoherent scattering, Nickel and Vanadium respectively. Because Vanadium has essentially no coherent scattering, it is often used as a reference sample to calibrate data for detector efficiencies. It consists to 99.75% of the stable isotope ^{51}V with a nuclear spin $I = 7/2$. Polarization analysis reveals that 2/3 of the spin-incoherent scattering is spinflip and 1/3 is non-spinflip scattering, see Fig. 8.8. The second example Nickel consists of various isotopes, mostly with $I = 0$. As expected, the related isotope incoherent scattering is purely non-spinflip scattering, as also shown in Fig. 8.8. Note, the magnetic scattering vanishes for applying a saturating field $H \parallel Q$, see also Fig. 8.7.

Applications to local order in disordered hydrogenous materials

Typical soft matter samples contain hydrogen which causes a huge spin-incoherent background ($\sigma_{inc}(H) = 80 \text{ b}$) in the wide-angle scattering that contains information about local correlations ($\sigma_{coh}(H) = 1.76 \text{ b}$). Here, a precise determination of coherent scattering can be achieved by measuring spin-flip and non-spin-flip scattering. It is particularly valuable to combine this further with the method of contrast variation using H and D isotopes, having rather distinct scattering lengths, $b_{coh}(H) = -0.374 \cdot 10^{-12} \text{ cm}$ and $b_{coh}(D) = 0.667 \cdot 10^{-12} \text{ cm}$. Fig. 8.9 shows the separated coherent scattering of a polymer glass. Such results provide most useful information about local order that can be compared to molecular dynamics simulations of theoretical polymer models [17].

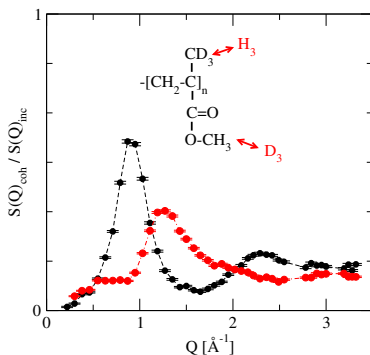


Fig. 8.9: Neutron polarisation analysis separates coherent scattering from spin-incoherent scattering, which is typically a disturbing large background in materials that contain hydrogen, while here it provides a precise intrinsic calibration. In addition, H/D contrast varies the coherent scattering of a polymer glass PMMA. [17]

Applications to dynamics in liquids

Since in a liquid all atoms are moving around, the scattering is not elastic as in the case of Bragg peaks from a solid, single crystal. Diffraction - the energy integrated scattering - provides us with structural properties from a snap-shot of typical atomic configurations. Since neutron energies are comparable to thermal energies involved in atomic motions, it is relatively simple to achieve an adequate energy resolution to study the dynamics for instance in liquids, see example in Fig. 8.10.

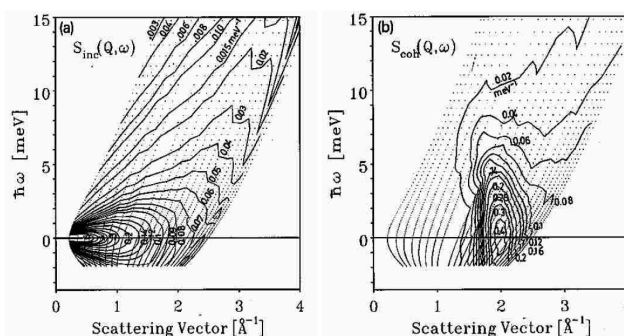


Fig. 8.10: Time-of-flight spectra of a) spin-incoherent and b) coherent scattering of liquid sodium at $T=840$ K separated by polarization analysis (from O. Schärpf. [18]). The dotted mesh corresponds to the coordinates of time-of-flight and scattering angles.

Therefore, a typical instrument set-up uses the time-of-flight technique: the monochromatic beam is pulsed by a mechanical chopper and the measured *time-of-flight* of the neutrons can be related to an energy transfer in the sample. Note, the separation by polarization analysis in *coherent* scattering and *spin-incoherent* scattering distinguishes *pair-correlations* from *single particle correlations*, respectively. The study of liquid sodium [18], see Fig. 8.10, demonstrates instructively the complementary information that can be obtained. From simple liquid models one expects that the incoherent scattering has a Lorentzian shape in energy at constant Q , related to exponential relaxations in time, with a width that for the macroscopic limit, $Q \rightarrow 0$, is related to the diffusion constant. In contrast, the coherent scattering very differently exhibits a pronounced peak related to typical nearest neighbor distances reflecting precursors of Bragg peaks and crystalline order.

8.3.2 Magnetic interaction of neutrons with matter

Spin and orbital moments exert dipolar fields

$$\mathbf{B}_S = \nabla \times \left(-\frac{\boldsymbol{\mu}_e \times \mathbf{R}}{R^3} \right), \quad \mathbf{B}_L = \frac{e}{c} \left(\frac{\mathbf{v}_e \times \mathbf{R}}{R^3} \right) \quad (8.19)$$

and result in a dipolar **magnetic interaction potential** for the neutron

$$V_m = -\boldsymbol{\mu} \cdot (\mathbf{B}_S + \mathbf{B}_L). \quad (8.20)$$

The derivation of the scattering law is lengthy and can be found in [16]; it leads to

$$\frac{d\sigma}{d\Omega_{\text{mag}}} = (\gamma_n r_0)^2 \left| \frac{1}{2\mu_B} \langle S'_Z | \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{M}}_Q^\perp | S_Z \rangle \right|^2, \quad (8.21)$$

where r_0 is the classical electron radius. $\hat{\mathbf{M}}_Q^\perp$ is the operator of the magnetic interaction vector, defined in units of μ_B ,

$$\mathbf{M}_Q^\perp = \mathbf{e}_Q \times \mathbf{M}_Q \times \mathbf{e}_Q \quad (8.22)$$

which is reduced to only the perpendicular components of $\mathbf{M}_Q$ with respect to $\mathbf{Q}$. $\mathbf{M}_Q$ represents the total Fourier transform of the spin and orbital contribution to the magnetization density. Consequently, and in fundamental contrast to nuclear scattering, the magnetic scattering depends on a **form factor**, similarly to x-ray scattering. Because unpaired electrons are typically in the outer shells, such as the $3d$ or $4d$ shell of transition elements or the $4f$ shell of rare earth elements, the form factor drops typically faster than for the total electron cloud as seen in the x-ray form factor. Measuring the form factor in detail can reveal the relevant spin and orbital contributions to the magnetic moments.

The anisotropy of the interaction is due to the dipolar interaction of the neutron spin with the magnetic moments, which is illustrated in Fig. 8.11. The components of a magnetic dipole field parallel to the scattering vector $\mathbf{Q}$ cancel out. Therefore, in contrast to the spin-incoherent scattering, magnetic scattering is anisotropic with respect to $\mathbf{Q}$ and only $\mathbf{M}_Q^\perp$, the components perpendicular to $\mathbf{Q}$ can be observed.

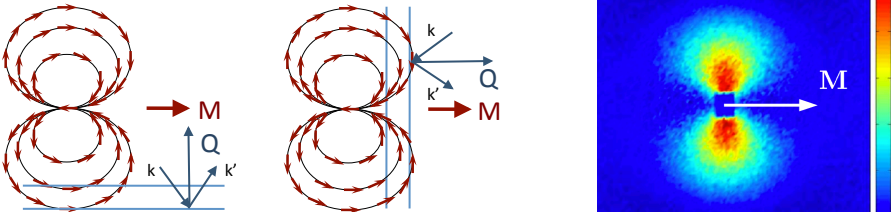


Fig. 8.11: Illustration why only $M_Q^\perp$ is measured. For $M \perp Q$, magnetic dipole field amplitudes show constructive interference, for $M \parallel Q$ destructive interference. *Right:* Polarized small angle scattering ($Q = 0$ in centre) probing the magnetization of iron oxide nanoparticles. [19]

In analogy to the spin-dependent nuclear interaction, we obtain the transition matrix elements for the magnetic interaction, choosing z-polarization and x parallel to Q , $M_{x,Q}^\perp = 0$, and

$$\begin{aligned}
 \langle + | \hat{\sigma} \cdot \hat{M}_Q^\perp | + \rangle &= M_{z,Q}^\perp, \text{ nsf} \\
 \langle - | \hat{\sigma} \cdot \hat{M}_Q^\perp | - \rangle &= -M_{z,Q}^\perp, \text{ nsf} \\
 \langle + | \hat{\sigma} \cdot \hat{M}_Q^\perp | - \rangle &= -iM_{y,Q}^\perp, \text{ sf} \\
 \langle - | \hat{\sigma} \cdot \hat{M}_Q^\perp | + \rangle &= iM_{y,Q}^\perp, \text{ sf}
 \end{aligned} \tag{8.23}$$

Hence, as illustrated in Fig. 8.12, the component of P parallel to $M_Q^\perp$ remains unchanged,

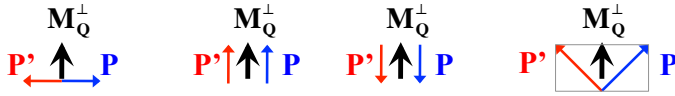


Fig. 8.12: Change of initial polarization P to final polarization P' : the component perpendicular to $M_Q^\perp$ reverses sign, the parallel component of P is invariant.

while the component of P perpendicular to $M_Q^\perp$ reverses its sign. This selection rule combined with the Q -dependence provides another simple rule: If $P \parallel Q$, the total magnetic scattering will be spin-flip.

Therefore, as exemplified in Moon, Riste, Koehler's seminal paper [4] nuclear and magnetic Bragg peaks can be separated from non-spin-flip and spin-flip scattering respectively by scanning with $P \parallel Q$, see the separation for Fe_2O_3 in Fig. 8.13.

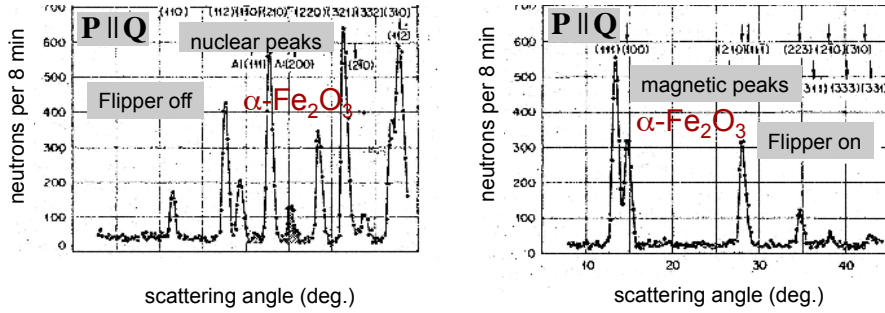


Fig. 8.13: Separation of magnetic and nuclear Bragg peaks for powder diffraction from Fe_2O_3 by non-spin-flip and spin-flip scattering with $\mathbf{P} \parallel \mathbf{Q}$. Reprinted from [4]. Copyright (1969) by the American Physical Society.

8.3.3 Scattering and polarization analysis, the Blume-Maleyev equations

However, turning from the individual expressions for the scattering amplitudes to scattering and interference of nuclear and magnetic scattering amplitudes, we have to face more complex expressions. A complete description of magnetic and nuclear neutron scattering has been given by Blume [2] and Maleyev [3] by two master equations. The first equation gives the scattering cross-section $\sigma_{\mathbf{Q}}$, the second one describes the final polarization $\mathbf{P}'$,

$$\sigma_{\mathbf{Q}} = |N_{\mathbf{Q}}|^2 + \sigma_{\text{isotope,inc}} + \sigma_{\text{spin,inc}} + |\mathbf{M}_{\mathbf{Q}}^{\perp}|^2 + \mathbf{P}(N_{-\mathbf{Q}}\mathbf{M}_{\mathbf{Q}}^{\perp} + \mathbf{M}_{-\mathbf{Q}}^{\perp}N_{\mathbf{Q}}) + i\mathbf{P}(\mathbf{M}_{-\mathbf{Q}}^{\perp} \times \mathbf{M}_{\mathbf{Q}}^{\perp}) \quad (8.24)$$

$$\begin{aligned} \mathbf{P}'\sigma_{\mathbf{Q}} = & |N_{\mathbf{Q}}|^2\mathbf{P} + \sigma_{\text{isotope,inc}}\mathbf{P} - \frac{1}{3}\sigma_{\text{spin,inc}}\mathbf{P} \\ & + \mathbf{M}_{\mathbf{Q}}^{\perp}(\mathbf{P}\mathbf{M}_{-\mathbf{Q}}^{\perp}) + \mathbf{M}_{-\mathbf{Q}}^{\perp}(\mathbf{P}\mathbf{M}_{\mathbf{Q}}^{\perp}) - \mathbf{P}\mathbf{M}_{\mathbf{Q}}^{\perp}\mathbf{M}_{-\mathbf{Q}}^{\perp} \\ & + \mathbf{M}_{\mathbf{Q}}^{\perp}N_{-\mathbf{Q}} + \mathbf{M}_{-\mathbf{Q}}^{\perp}N_{\mathbf{Q}} + i\mathbf{M}_{\mathbf{Q}}^{\perp} \times \mathbf{M}_{-\mathbf{Q}}^{\perp} + i(\mathbf{M}_{\mathbf{Q}}^{\perp}N_{-\mathbf{Q}} - \mathbf{M}_{-\mathbf{Q}}^{\perp}N_{\mathbf{Q}}) \times \mathbf{P} \end{aligned} \quad (8.25)$$

The notation uses $-\mathbf{Q}$ to denote the complex conjugate. Here, for simplicity only the $\mathbf{Q}$ -dependence is specified for Bragg scattering or diffuse scattering. However, in the more general form the scattering cross sections apply to inelastic scattering and can be related to van Hove correlation functions in space and time.

These equations readily show the different information that can be obtained from an unpolarized with respect to a polarized experiment. While unpolarized neutrons only measure the sum of nuclear and magnetic intensities, for polarized neutrons additional intensity may arise first, due to possible structural-magnetic (NM-terms) interference and second, due to cross products of the magnetic interaction vector $i\mathbf{M}_{\mathbf{Q}}^{\perp} \times \mathbf{M}_{-\mathbf{Q}}^{\perp}$ describing chiral correlations in non-collinear spin systems. A look at the second equation for the final polarization reveals that we can identify such terms "NM" and " $\mathbf{M} \times \mathbf{M}$ " even with unpolarized neutrons, because they may create final polarization (set $\mathbf{P} = 0$).

Eq. 8.25 can be written as a tensor equation [8] (neglecting for brevity the incoherent parts)

$$\mathbf{P}'\sigma = (|N|^2\mathbf{1} + \mathcal{R})\mathbf{P} + \mathbf{P}'' \quad (8.26)$$

in which the first term ($|N|^2 \mathbf{1} + \mathcal{R}$) $\mathbf{P}$ consists of the scalar nuclear scattering $|N|^2$, $\mathbf{1}$ is the unity matrix, the matrix $\mathcal{R}$ describes the rotation of $\mathbf{P}$, and $\mathbf{P}''$ is the created polarization.

Using the common convention for the specific orthogonal setting $\mathbf{x}$ parallel to $\mathbf{Q}$, and $\mathbf{y}$ and $\mathbf{z}$ perpendicular to $\mathbf{Q}$, horizontally and vertically set to the scattering plane respectively, $\mathcal{R}$ and $\mathbf{P}''$ are obtained as

$$\mathcal{R} = \begin{pmatrix} -|M_y|^2 - |M_z|^2 & 2 \operatorname{Im}[NM_z] & 2 \operatorname{Im}[NM_y] \\ -2 \operatorname{Im}[NM_z] & +|M_y|^2 - |M_z|^2 & 2 \operatorname{Re}[M_y M_z] \\ -2 \operatorname{Im}[NM_y] & 2 \operatorname{Re}[M_z M_y] & -|M_y|^2 + |M_z|^2 \end{pmatrix} \quad (8.27)$$

$$\mathbf{P}'' = (-2 \operatorname{Im}[M_y M_z], 2 \operatorname{Re}[NM_y], 2 \operatorname{Re}[NM_z]) \quad (8.28)$$

The diagonal elements can be obtained by **longitudinal polarization analysis**, in which we consider spin-flip and non-spinflip for either x , y or z direction of initial and final polarization. For measuring the off-diagonal elements, for example R_{yz} obtained by $\mathbf{P} = (0, P_y, 0)$ and $\mathbf{P}' = (0, 0, P'_z)$, the magnetic field needs to switch from y to z -direction, which can be achieved by a zero-field at the sample. Alternatively, but so far not much used in practice, one can work with precessing neutron polarization [20,21]. The conventional approach, however, is to access all elements of the tensor $\mathcal{R}$ by **spherical neutron polarimetry** (SNP). Experimentally, a zero-field can be achieved with a CryoPad or MuPad device [22] using superconducting material or a μ -metal [23] to shield the sample area from magnetic fields. In particular, SNP allows to distinguish a rotation of $\mathbf{P}'$ from a depolarization of the beam. Depolarization may occur due to an incoherent superposition of intensities with different polarization, this includes spin-incoherent scattering, and more important for determining magnetic structures, intensity from different magnetic domains. See Ref. [8] for detailed examples and analysis. The interested reader is also referred to the recent user software Mag2Pol: a versatile program, which also includes the analysis of spherical neutron polarimetry data [24].

It is noteworthy that the information in the off-diagonal elements, related to nuclear-magnetic interference and chirality, reappears in the diagonal elements in $\mathbf{P}''$ and can therefore also be obtained by conventional longitudinal polarization analysis. Polarization reversal and considering the sum and differences of intensities will separate $\mathbf{P}''$ from the trace of $\mathcal{R}$ [25].

Next we consider two important cases, the so called (i) "flipping ratio" or "half-polarized" experiments to determine the magnetic structure or spin density, and (ii) XYZ polarization analysis with multi-detectors.

Magnetization and spin density distribution. The usual approach [26] is to measure the "flipping ratio" of Bragg reflection, defined as the intensity ratio between spin-up and spin-down neutrons with respect to a vertical applied magnetic field

and is given by

$$R = \frac{I^+}{I^-} = \frac{N_{\mathbf{Q}} N_{-\mathbf{Q}} + (N_{\mathbf{Q}} \mathbf{M}_{-\mathbf{Q}}^\perp + N_{-\mathbf{Q}} \mathbf{M}_{\mathbf{Q}}^\perp) + \mathbf{M}_{\mathbf{Q}}^\perp \mathbf{M}_{-\mathbf{Q}}^\perp}{N_{\mathbf{Q}} N_{-\mathbf{Q}} - (N_{\mathbf{Q}} \mathbf{M}_{-\mathbf{Q}}^\perp + N_{-\mathbf{Q}} \mathbf{M}_{\mathbf{Q}}^\perp) + \mathbf{M}_{\mathbf{Q}}^\perp \mathbf{M}_{-\mathbf{Q}}^\perp}. \quad (8.29)$$

To illustrate the advantage of polarized neutrons consider the case of a weak magnetic amplitude, $M_z = 0.1N$. For unpolarized neutrons the interference term NM_z vanishes. Therefore, the unpolarized intensity I is less interesting, but in contrast the ratio I^+/I^- is very sensitive:

$$I = 1.01|N|^2, \quad \text{and} \quad \frac{I^+}{I^-} = \frac{(1 + 0.1)^2 N^2}{(1 - 0.1)^2 N^2} = \frac{1.21}{0.81} \approx 1.5. \quad (8.30)$$

In order to solve Eq. 8.29 for the magnetic amplitudes and the magnetic structure, we need *a priori* an accurate crystallographic structure determination for the nuclear amplitudes N .

In the experiment a flipper is used to switch the polarization with respect to the applied field, which led to the name "flipping ratio". The term could be misleading, since the scattering process is purely non-spinflip as $\mathbf{P} \parallel \mathbf{M}_Q^\perp \parallel z$. In such an experiment one uses polarized neutrons without polarization analysis, which has led to another deceptive term, describing this as a "half-polarized" set-up. Still, P is favorably large, close to one, just P' does not matter and is not measured.

With respect to applications, the samples could be ferromagnets, where the magnetization is best near saturation using a strong field. However, one can also study paramagnets, and the induced magnetic moments will represent the spin density distribution. An example is given in Figure 8.3.3 for the organic compound $[\text{Cu}_2(t\text{-Bupy})_4(\text{N}_3)_2](\text{ClO}_4)_2$. Here, the two Cu spins are in the triplet ground state, and a part of the spin density is spreading from the Cu sites to ligands. The contours of the map start at a level of $0.01 \mu_B$, which nicely demonstrates the sensitivity of such measurements.

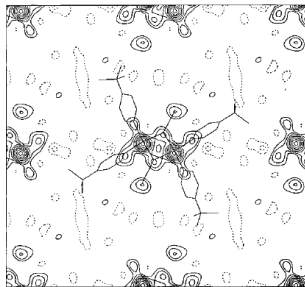


Fig. 8.14: $[\text{Cu}_2(t\text{-Bupy})_4(\text{N}_3)_2](\text{ClO}_4)_2$ spin density map (unit cell in ab , integration ± 0.25 in c), adapted with permission from [27]. Copyright 1998 American Chemical Society.

One may also study the response with respect to different field directions, which yields the susceptibility tensor on atomic scale. Strong anisotropies can be found for f -electrons of rare earth ions. It is noteworthy that such information can be obtained also from powder samples, when using a 2D detector which identifies the actual inclination of the Bragg planes with respect to the applied vertical magnetic field [28]. These are typical applications using Bragg intensities providing local information on atomic scale. If we turn to low Q and small angle neutron scattering, the intensities relate to the morphologies of magnetic structures, which refers to an example discussed already before: Fig. 8.11 shows the interference pattern $MN(\mathbf{Q})$ and contains the information on the magnetic morphology of iron oxide nanoparticles [19].

XYZ Polarization analysis with multi detectors

So far it has been implicitly assumed that the data are measured with a single detector related to a single $\mathbf{Q}$ set parallel to x . Multi-detector systems can collect scattering data in a much more efficient way and were used also for the previous example Fig. 8.18. The instrument D7 at ILL in Grenoble [30] was pioneering with covering a wide angle range with supermirror

based polarization analyzers in front of a multi-detector. A similar instrument DNS [31] is operated by JCNS at the MLZ and FRM-2 in Munich, see Fig. 8.15.

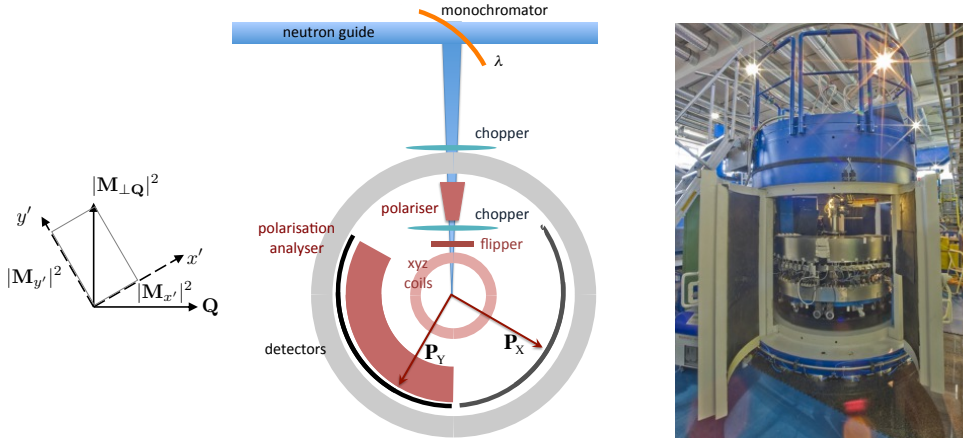


Fig. 8.15: Polarization analysis on a time-of-flight multi-detector instrument, the DNS instrument at FRM-2, see Ref. [25] for the specific setting of polarization.

Instead of measuring each data point with $\mathbf{P} \perp \mathbf{Q}$, using Pythagoras' theorem, we can construct the parallel and perpendicular components to $\mathbf{Q}$ from any two orthogonal settings (x', y') in-plane and measure simultaneously with a multi-detector. Assuming isotropy, *e.g.* for powders and paramagnets, the pure magnetic scattering contribution separated from nuclear scattering can be obtained by either of the two combinations of spin flip and non-spinflip scattering, which is the "XYZ-method" introduced by Otto Schärpf [33]:

$$\frac{d\sigma}{d\Omega_{\text{mag}}} = 2 \left(\frac{d\sigma^{SF}}{d\Omega_x} + \frac{d\sigma^{SF}}{d\Omega_y} - 2 \frac{d\sigma^{SF}}{d\Omega_z} \right) = -2 \left(\frac{d\sigma^{NSF}}{d\Omega_x} + \frac{d\sigma^{NSF}}{d\Omega_y} - 2 \frac{d\sigma^{NSF}}{d\Omega_z} \right), \quad (8.31)$$

The magnetic contribution is separated by the directional dependence with respect to $\mathbf{P}$ and identifies the magnetic contribution, while all nuclear scattering is independent of the direction of $\mathbf{P}$.

An application example for the XYZ-separation is given in Fig. 8.16 and identifies the weak magnetic diffuse scattering from a Keplerate, a molecular magnet $\text{Mo}_{72}\text{Fe}_{30}\text{X}$ of high symmetry with 30 magnetic vertex sites of Fe (X represents a larger number of H, C, and N atoms). The magnetic intensity (right figure) agrees favorably with the predicted structure resulting from a model with antiferromagnetic exchange between the Fe moments.

Of course, single crystals can be also measured efficiently with multi-detectors by rotating the sample, *i.e.* by rotating the Ewald circle in the scattering plane. In the following example, see also Fig. 8.17, a study [35] on the "spin-ice" system $\text{Ho}_2\text{Ti}_2\text{O}_7$, a cubic pyrochlore structure, the horizontal scattering plane has been mapped with measuring spin flip scattering and $\mathbf{P}$ vertical, obtaining the in-plane magnetic scattering (plus some weak flat background from spin-incoherent scattering). The tetrahedral network and Ising $\langle 111 \rangle$ spin-anisotropy leads to strong frustration for ferro-type exchange. In the ordered state the local spin-correlations can

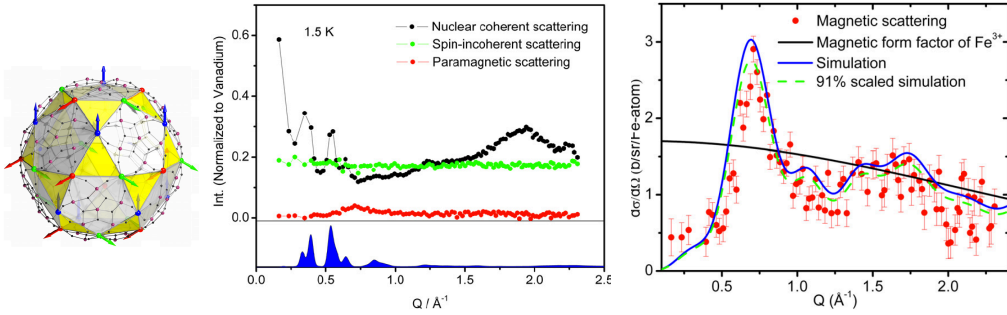


Fig. 8.16: $\text{Mo}_{72}\text{Fe}_{30}\text{X}$ molecule (magnetic Fe-ions at vertices, Mo-purple; X: O-black, H, C not shown) and a 3-sublattice non-collinear spin model resulting from AF Heisenberg exchange (*left*). XYZ-separation of weak magnetic intensities (*middle*). Comparison of the magnetic intensity and the spin-model calculation (*right*). [34]

be described for each tetrahedra by a simple rule: two spins are pointing along the $\langle 111 \rangle$ cube diagonals towards the center of the tetrahedra and two spins point outwards. Actually this rule is the perfect analogue to the ice rules in hexagonal ice, describing the hydrogen bonds around the tetrahedral environment of the O ions.

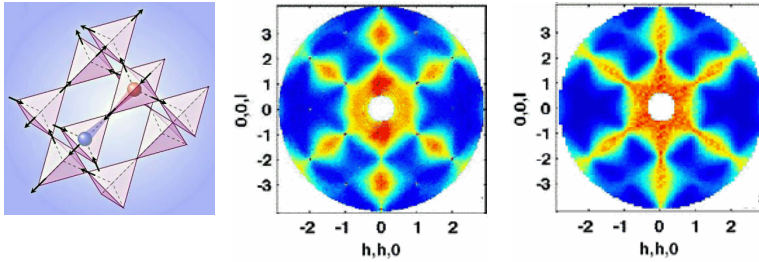


Fig. 8.17: Spin-ice. *left*: Topological magnetic monopoles, *middle*: measured diffuse scattering from $\text{Ho}_2\text{Ti}_2\text{O}_7$ at $T=1.7\text{K}$ with $\mathbf{P} \parallel z$ in spin-flip mode; note pinch points at (002) and (111); *right*: Monte Carlo simulations of based on a nearest neighbor exchange model. From [35]. Reprinted with permission from AAAS.

Hence Pauling's famous ice model also explains why there should be a residual entropy due to remaining disorder in spin-ice, which is the origin of the broad diffuse scattering at low temperatures.

The extraordinary features of this diffuse scattering are so-called pinch-points, the saddle-points in intensity at (111) and (200) positions; on one hand the intensity variation radially, along the modulus of $\mathbf{Q}$, is rather smooth, involving short-range correlations, on the other hand the transverse variation at constant $\mathbf{Q}$ is almost discontinuous and singular, which in-

volves many Fourier coefficients and long-range correlations. The explanation is that the ice-topology creates effectively long-range interactions, – any local decision for a specific two-in two-out spin configuration imposes far-reaching constraints for the other tetrahedra –, an effective interaction that can be mapped to Coulomb interaction between monopoles and provides a picture, where the dipole moments in their local sums over four tetrahedral sites can be viewed as two separated monopoles. [35]

From the methodological point of view, for the case above, polarization analysis with measuring spin flip intensities for $\mathbf{P} = P_z$ is simple and most appropriate to access correlation of spin components in the scattering plane. However, for a rigorous and systematic separation the interested reader is referred to two important recent extensions of the classical XYZ-method of Schärpf [33]: (i) for single crystals and multi-detectors separating all magnetic and nuclear contributions by including polarization reversal [25], (ii) for a separation of out-of-plane scattering using 2D detector systems using two additional measurements with orthogonal in-plane polarizations. [36]

Chirality. The last term in Eq. 8.24 refers to the vector product of spin components perpendicular to $\mathbf{Q}$, and therefore, $i\mathbf{M}_{\perp\mathbf{Q}} \times \mathbf{M}_{\mathbf{Q}}^{\perp}$ itself points in $\mathbf{Q}$ -direction. The magnetic moments in real space are real quantities and the imaginary sign i says that this term is antisymmetric in $\mathbf{Q}$ and relates to the sin-Fourier transform of chiral pair correlations $S_y(\mathbf{R})S_z(\mathbf{R}')$, which also implies the characteristic chiral feature of point inversion symmetry. A beautiful example depicted in Fig. 8.18 shows the antisymmetric chiral scattering from a spin liquid obtained by polarization reversal with respect to $\mathbf{Q}$ and taking the difference of the intensities [29]. The antisymmetry perpendicular to $\mathbf{Q}$, reveals that $\mathbf{C} = \mathbf{S} \times \mathbf{S}'$ is perpendicular to the propagation, i.e. a cycloidal chirality. In contrast for a helix, the antisymmetry and $\mathbf{C}$ would be in $\mathbf{Q}$ direction.

Depending on the propagation direction parallel or perpendicular to $\mathbf{Q}$, we can distinguish a helix from a cycloid spin structure, respectively. The chiral intensity can be separated by polarized neutron scattering with measuring the intensity difference for $\mathbf{P}$ parallel and antiparallel to $\mathbf{Q}$, which cancels out other nuclear and magnetic intensities, while there are no NM terms parallel to $\mathbf{Q}$. The chiral interference is purely spinflip scattering and it can be separated without applying polarization analysis like the NM interference.

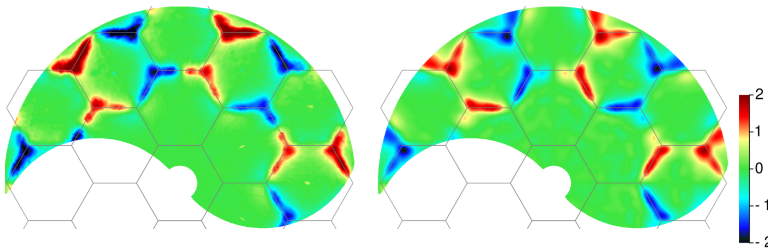


Fig. 8.18: Chiral spin liquid ground state in $\text{YBaCo}_3\text{FeO}_7$ [29].
 (left) Chiral scattering measured with polarization reversal along $\mathbf{Q}$.
 (right) Fourier analysis modeling based on purely cycloidal chiral correlations.

8.4 Final remarks and outlook

Polarized neutrons certainly prove to be very useful and may reveal structural and dynamic properties that are hidden to conventional neutron scattering. Applications are growing, slowly, since experimental techniques are more challenging and also because of the additional time requests for experiments. While there has been little gain in the average brightness of neutron sources since the early days, instrumentation has become much more efficient. Looking at count rates of Ni of MRK in Fig.8.8 a comparison to the instrument DNS using multiple detectors shows a gain of about three orders of magnitude.

The most modern and intense neutron sources are the MW pulsed spallation sources SNS in the USA, JPARC in Japan and in near future the **European Spallation Source ESS**. There is a great challenge and potential gain in using a pulsed beam with wide wavelength band rather than a monochromatic beam.

At ESS, there is currently a dedicated polarized instrument under construction called MAGIC. Its scheme is depicted in Fig. 8.19. Based on a **time-of-flight Laue technique** combined with position sensitive area detectors, it gives access to large volumes in reciprocal space with favorable resolution. Characteristic features are a 1.7 Å bandwidth of highly polarized neutrons within a spectrum of 0.6 to 6 Å wavelength from the peak fluxes of the thermal and cold moderators.

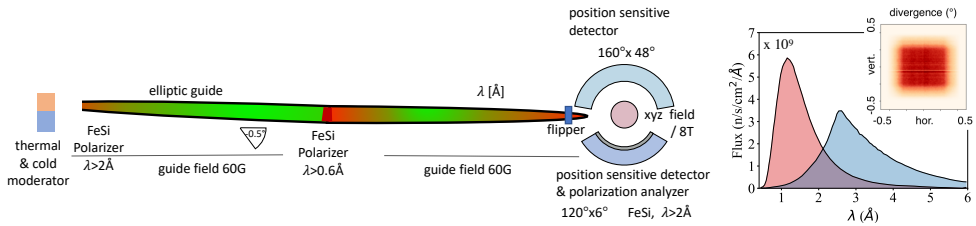


Fig. 8.19: Scheme of the ESS instrument MAGIC

In virtual experiments, simulating instrument, sample and scattering, the performance of this instrument has been studied and optimized [37]. A few examples are shown in Fig. 8.20.

The first one shows a Laue pattern from a small mm³ crystal (C₆₀). In contrast to normal Laue diffraction, with measuring the time-of-flight of the pulsed white beam all Bragg peaks are separated with a 3D access to reciprocal space. The gain compared to a conventional monochromatic instrument with a single detector is of course very high. Considering the determination magnetic structures with spin densities and weak moments, see Fig. 8.3.3 for comparison, it took two weeks counting with a single detector, while the best current instrumentation with a multi-detector and monochromatic beam would require two days, and the simulations, see middle of Fig. 8.20, show this will be possible with the same high quality already in 15 minutes. The example Fig. 8.20 (right) shows the simulation of the spin-ice scattering of Ho₂Ti₂O₇ based on the model of [38]. Here, with shorter wavelength a larger Q-range can be seen, compare Fig. 8.17 and again, with white beam and position sensitive detectors the Q-space is explored in 3D. The gain in efficiency, which is about three orders

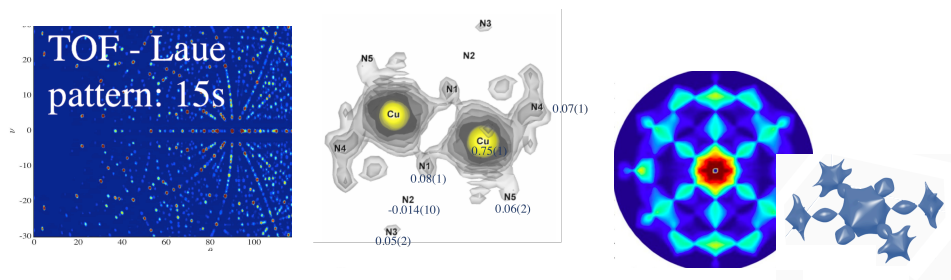


Fig. 8.20: Virtual experiments on the ESS instrument MAGIC [37].

left: time-of-flight Laue diagram from a 1mm^3 sample of C_{60} ;

middle: reconstructed spin density map (in μ_B) from a molecular nano-magnet

right: $\text{Ho}_2\text{Ti}_2\text{O}_7$ spin-ice scattering with 3 dim mapping in $\mathbf{Q}$ space..

of magnitude will open capabilities to measure even very small samples and weak magnetic features.

References

- [1] Halpern and Johnson, Phys Rev **55**, 898 (1939).
- [2] M. Blume, Phys. Rev. **130**, 1670 (1963).
- [3] S. V. Maleyev, V. G. Baryakhtar P. A. and Suris, Fiz. Tv. Tela **4**, 3461 (1962); Soviet Phys. Solid State **4**, 2533 (1963).
- [4] R.M. Moon, T. Riste, W.C. Koehler, *Polarization analysis of thermal neutron scattering*, Phys. Rev. **181**, 920 (1969).
- [5] F. Mezei, Z. Phys. Rev. **255**, 146 (1972).
- [6] Otto Schärpf, AIP Conf. Proc. **89**, 175 (1982).
- [7] Tasset *et al.*, J. Appl. Phys. **63**, 3606 (1988).
- [8] P. J. Brown, J. B. Forsyth, and F. Tasset, Proc. Roy. Soc. London A **442**, 147 (1993); P.J. Brown, *Polarimetric Neutron Scattering*, in lecture notes on *Polarized Neutron Scattering* (Eds. Th. Brückel and W. Schweika), Schriften des Forschungszentrums Jülich, Series Matter and Materials Vol.**12**, Forschungszentrums Jülich (2002).
- [9] Alvarez, L. W., F. A. Bloch, *Quantitative determination of the neutron magnetic moment in absolute nuclear magnetons*, Phys. Rev. **57**, 111 (1940). negative sign of γ_n : P.N. Powers, *The magnetic scattering of neutrons*, Phys. Rev. **54**, 827 (1938).
- [10] Charles M. Sommerfield, Phys. Rev. **107**, 328 (1957). Magnetic Dipole Moment of the Electron: Julian Schwinger, Phys. Rev. **73**, 416 (1948).
- [11] O. Schärpf, in *Neutron Spin Echo Lecture Notes in Physics* **128**, Ed. F. Mezei, Springer, pp. 27-52 (1980).
- [12] F. Klein, *The mathematical theory of the top*, Princeton 1897; see also H. Goldstein, *Klassische Mechanik*, Akademische Verlagsges. Frankfurt am Main (1974).
- [13] O. Schärpf, J. Physics E: Sci. Instrum. **8**, 268 (1975); F. Mezei, Commun. Phys. **1**, 81 (1976); P. Böni, J. Neutron Research **5**, 63 (1996).
- [14] <http://www.swissneutronics.ch/products/coatings.html>
- [15] E. Babcock *et al.*, Journal of Physics: Conference Series 711 (2016) 012008.
- [16] G.L. Squires, *Introduction to the theory of thermal neutron scattering*, Cambridge University Press, Cambridge (1978).
- [17] A. C. Genix *et. al.* Macromolecules **39**, 3947 (2006).
- [18] O. Schärpf, *The spin of the neutron as a measuring probe*, Chapter 11, p. 228, <http://82.135.31.182/neutronpol.pdf>
- [19] S. Disch, PhD thesis, RWTH Aachen (2010); New Journal of Physics **14**, 013025 (2012).

- [20] W. Schweika, *Physica B* **335** (1-4), 157 (2003).
- [21] W. Schweika, S. Easton, and K.-U. Neumann, *Neutron News* **16**, 14 (2005).
- [22] F. Tasset *et al.*, *Physica B* **267** (1-4) 69-74 (1999).
- [23] M. Janoschek *et al.* Spherical neutron polarimetry with MuPAD, *Physica B* **397** (1-2), 125-130 (2007).
- [24] N. Qureshi, *J. Appl. Cryst.* **52**, 175 (2019), arXiv:1801.08431v2 (2018).
- [25] W. Schweika, *J. Phys. Cons. Ser.* **211**, 012026 (2010).
- [26] J. Schweizer, *Magnetic Form Factors and Magnetization Densities Investigated by Polarized Neutron Diffraction* in lecture notes on *Polarized Neutron Scattering* (Eds. Th. Brückel and W. Schweika), Schriften des Forschungszentrums Jülich, Series Matter and Materials Vol.**12**, p. 291, Forschungszentrums Jülich (2002).
- [27] M. A. Aebersold *et al.* *J. Am. Chem. Soc.* **120**, 5238 (1998).
- [28] I. A. Kibalin and A. Gukasov, *Phys. Rev. Research* **1**, 033100 (2019).
- [29] W. Schweika *et al.* *Phys. Rev. X* **12**, 021029 (2022).
- [30] O. Schärpf, *Physica B* **182**, 376 (1992).
- [31] W. Schweika and P. Böni, *Physica B* **297**, 155 (2001).
- [32] J. R. Stewart *et al.*, *J. Appl. Cryst.* **42**, 69 (2009).
- [33] O. Schärpf, H. Capellmann, *Phys. Stat. Sol. (a)* **135**, 359 (1993).
- [34] Z. Fu *al.*, *New Journal of Physics* **12**, 083044 (2010).
- [35] T. Fennell *et al.* *Science* **326**, 415 (2009).
- [36] G. Ehlers *et al.* *EPL Web of Conferences* **83**, 03004 (2015).
- [37] https://indico.ess.eu/event/723/attachments/5647/7744/magic_proposal_0.pdf
- [38] C. Henley, *The Coulomb phase in frustrated systems* *Ann. Rev. Condens Matter Phys.* **1** 179-210 (2010).

Exercises

Exercise 1: How good is the polarization? Consider a few cases:



(i) Spins are evenly distributed within a cone of $\pm\pi/4$ around z . Make first a good estimate and calculate P_z .

(ii) An initially ideally polarized beam scatters from a Vanadium sample. What is the polarization after scattering? Next, looking more closely, if the sample is relatively thick and has a 20% scattering probability, calculate the polarization for two consecutive scattering events.

(iii) Among the isotopes of Ni (see <https://ncnr.nist.gov/resources/n-lengths/elements/nl.html>), you find few, which give spin-incoherent scattering causing a bit of spin-flip scattering. What is the polarization after scattering from natural Ni?

(iv) Actually, Ni is a ferromagnet, so how can we explain the figure 7.8 (left) and would one not expect also magnetic scattering and spin-flip scattering? However, by applying a magnetic field, how could you avoid magnetic scattering?

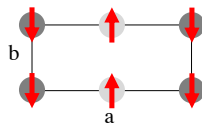
Exercise 2: Which is the required field in a flipper coil to rotate the polarization by π with respect to a external guide field H_z . Consider neutrons of 4 Å wavelength and a path of 1 cm in the flipper.

Exercise 3: Sprint competition of spin up and spin down neutrons. The course is 1 m and neutrons start with a speed of 4000 m/s. Immediately after the start a field of 1 T is switched on, when do the spin-up and spin-down neutrons arrive at the goal?

Exercise 4: Recall the rules about magnetic scattering:

- (i) which component of the magnetic moments with respect to Q are not scattering?
- (ii) which components with respect to P cause spinflip and non-spinflip scattering, respectively.

Exercise 5:



The unit cell displays two sites of different atoms, whose spins are antiferromagnetically ordered. This is an example of a so-called $q=0$ structure, where magnetic and the nuclear crystallographic Bragg peaks coincide. a) How to distinguish the contributions with polarization analysis and which Bragg peaks would you measure? b) Do you see a possibility to distinguish magnetic from nuclear scattering without polarization analysis?

9 Reflectometry and grazing incidence small angle scattering

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9.1 Introduction

Neutron reflectometry is a very efficient tool to determine the nuclear and magnetic density profiles along the depth of nanometric thin films. It has been used a lot to solve soft matter problems like the self organization of diblock copolymers, the structure of liquid-liquid interfaces or the structure of biomembranes [1]. Those studies benefit a lot from the possibility of contrast variation, i.e. the exchange of hydrogen by deuterium.

In the mid 1980's a new field of application of neutron reflectometry emerged. Following the discoveries of interlayer exchange coupling and giant magnetoresistance effect in magnetic multilayers [2], there has been an interest to determine, depth-resolved, the magnetic profile (see lecture 10 of this book).

More recently, the interest evolved towards the determination of the correlations of in-plane fluctuations in thin films. Those fluctuations can be nuclear or magnetic, in the bulk of the layers or at their interfaces, or nanometric objects deposited on a surface. The breaking of in-plane invariance introduced by those fluctuations produce scattering of radiation out of the specular direction, called grazing incidence small angle scattering (GISAS).

In this lecture, we will concentrate on neutron and x-ray reflectometry and GISAS for the determination of nuclear and chemical profiles. Section 9.2 shows the calculation of specular reflection at flat and homogeneous surfaces, introducing the concepts of scattering length density, index of refraction and total external reflection. It then describes the reflectivity from various types of layered structures and the effect of interfacial roughness and interdiffusion. Finally, an example of the application of grazing incidence small angle x-ray scattering (GISAXS) for the depth-resolved investigation of the lateral arrangement of nanoparticles is depicted (section 9.3).

9.2 Description of specular reflection¹

A monochromatic, well collimated beam impinges under a well defined, small angle $\alpha_i = \theta$ (in most cases $\theta \ll 5^\circ$) onto the surface of the sample. It is then partly reflected specularly from the surface, i.e. the outgoing angle $\alpha_f = \theta$ as well, and partly refracted into the material (See Fig. 9.1). As we will derive below, the reflection from a laterally homogeneous medium can be treated according to classical optics. Only the proper index of refraction n has to be used.

For most material, the index of refraction for neutrons is slightly smaller than 1, leading to total external reflection for small angles of incidence $\theta < \theta_c$, where θ_c depends on the material.

In the case of a single layer on the substrate, reflection and refraction take place at both the surface and the interface (Fig. 9.2). Then, the reflected beams from the different interfaces interfere with each other. Maximum intensity is received, when the path length difference between the two reflected beams is an integer multiple of the wavelength.

¹ A large part of this section is taken from Ref. [3–5].

For the case of perfectly smooth surface and interfaces, an exact description of the reflected and transmitted intensity can be deduced from quantum theory, as will be shown in the next subsections.

When the in-plane invariance of the layers or interfaces is broken, some diffuse signal can be observed out of the specular direction (Fig. 9.3). This is grazing incidence small angle scattering (GISAS). Its theoretical description goes beyond the scope of this lecture [6, 7].

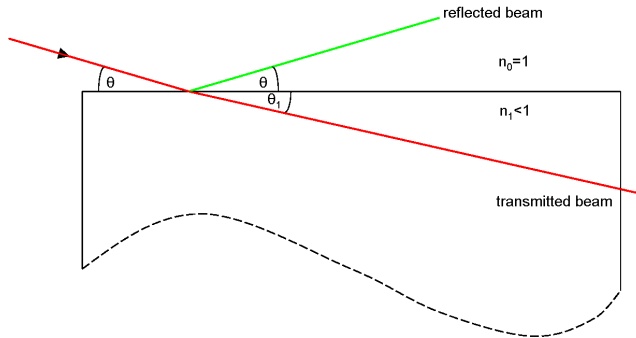


Fig. 9.1: Reflection and refraction from a free surface

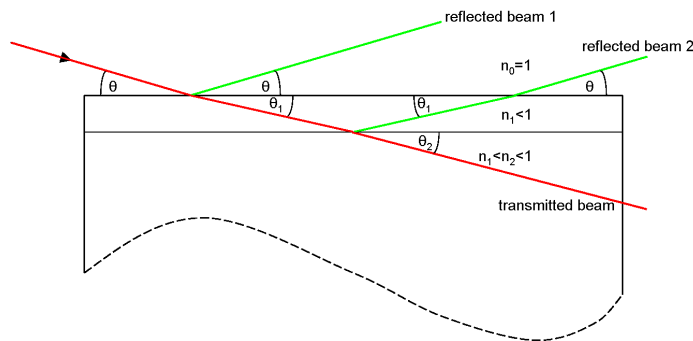


Fig. 9.2: Reflection and refraction from a single layer on a substrate

9.2.1 Wave equation in homogeneous medium. Optical index

The starting point is the Schrödinger equation for the wave function of the neutron:

$$\left[-\frac{\hbar^2}{2m} \Delta + V(\mathbf{r}) \right] \psi(\mathbf{r}) = E \psi(\mathbf{r}) \quad (9.1)$$

The kinetic energy of the neutron is given by $E = \hbar^2 k^2 / (2m)$ with the modulus $k = 2\pi / \lambda$ of the wave vector $\mathbf{k}$.

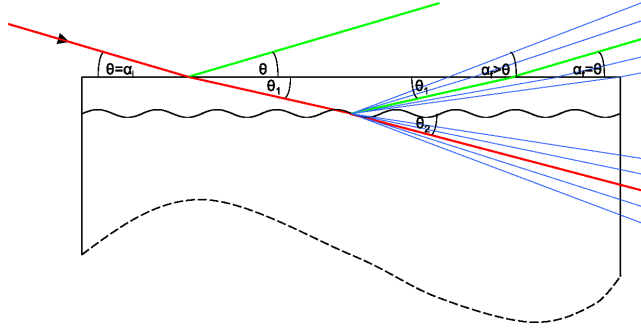


Fig. 9.3: Reflection, refraction and grazing incidence small angle scattering (GISAS) from a single layer on a substrate showing broken in-plane invariance

Due to the small $|\mathbf{Q}|$ values that are probed, a reflectometry experiment does not resolve the atomic structure of the sample in any of the three directions. Therefore, it is a valid approximation to describe the potential V_1 of the homogeneous material as

$$V_1 = \frac{2\pi\hbar^2}{m}\rho \quad (9.2)$$

where ρ is the scattering length density (SLD) defined by

$$\rho = \sum_j N_j b_j \quad (9.3)$$

where N_j is the number of nuclei per unit volume and b_j is the coherent scattering length of nucleus j . With that we receive

$$[\Delta + (k^2 - 4\pi\rho)] \psi(\mathbf{r}) = \left[\Delta + k^2 \left(1 - \frac{\lambda^2}{\pi} \rho \right) \right] \psi(\mathbf{r}) = [\Delta + k_1^2] \psi(\mathbf{r}) = 0 \quad (9.4)$$

with the wave vector k_1 inside the medium. From this equation, it is justified to introduce the index of refraction in the material

$$n = \frac{k_1}{k} \quad n \simeq 1 - \frac{\lambda^2}{2\pi} \rho \quad (9.5)$$

It is a number very close to 1 for thermal and cold neutrons. The quantity $1-n$ is of the order of 10^{-6} to 10^{-5} . For most materials it is positive (because the coherent scattering length b_j is positive for most isotopes), so that n is smaller than 1. This means that the transmitted beam is refracted towards the sample surface, which is opposite to the daily experience with light refracted at a glass or liquid surface.

9.2.2 Solution for a sharp surface. Fresnel's formulas

In analogy to classical optics, we can derive e.g. Fresnel's formulas. For the solution of the wave equation at a sharp surface between air and a semi-infinite medium, we assume the surface of the sample to be at $z = 0$. The potential is then

$$V(z) = \begin{cases} 0 & \text{for } z < 0 \\ V_1 & \text{for } z \geq 0 \end{cases} \quad (9.6)$$

As the potential V is independent of the in-plane coordinates x and y , the wave function in the Schrödinger equation (9.4) is of the form

$$\psi(\mathbf{r}) = e^{i(k_x x + k_y y)} \psi_z(z) \quad (9.7)$$

with the in plane components k_x and k_y of $\mathbf{k}$ independent of z . The Schrödinger equation then reduces to the one dimensional equation

$$\frac{d^2 \psi_z(z)}{dz^2} + k_z^2(z) \psi_z(z) = 0 \quad (9.8)$$

with $k_z(z)$ depending on the medium. The general solution is given by

$$\psi_{zl}(z) = t_l e^{ik_{zl}z} + r_l e^{-ik_{zl}z}, \quad (9.9)$$

where the index l distinguishes between vacuum ($l=0$) and medium ($l=1$) and where

$$k_{z0} = \frac{2\pi}{\lambda} \sin(\theta) \quad \text{and} \quad k_{z1}^2 = k_{z0}^2 - 4\pi\rho. \quad (9.10)$$

The unique solution is determined by the boundary conditions. The incoming wave in the vacuum before interaction with the sample is a plane wave of norm 1, i.e. t_0 is equal to 1. In a half-infinite medium, there is no reflected wave, because there is nothing to reflect from, i.e. r_1 vanishes. In addition, the wave function and its first derivative must be continuous at the interface. So we receive the following boundary conditions:

$$t_0 = 1 \quad ; \quad r_1 = 0 \quad ; \quad \psi_{z0}(z=0) = \psi_{z1}(z=0) \quad ; \quad \frac{d\psi_{z0}}{dz}(z=0) = \frac{d\psi_{z1}}{dz}(z=0). \quad (9.11)$$

When we insert (9.9) into (9.11) we receive the continuity equations for the wave function:

$$1 + r_0 = t_1 \quad ; \quad k_{z0}(1 - r_0) = k_{z1}t_1. \quad (9.12)$$

t_1 is the amplitude of the transmitted wave and r_0 is the amplitude of the reflected wave. The reflectivity R is defined as the modulus squared of the ratio of the amplitudes of reflected and

incoming waves, the transmissivity T is defined as the modulus squared of the ratio of the amplitudes or transmitted and incoming waves.

$$R = |r_0|^2 \quad ; \quad T = |t_1|^2 \quad (9.13)$$

In conclusion, we arrive at the Fresnel's formulas for the reflection and the refraction at a flat interface

$$\text{Reflectivity :} \quad R = \left| \frac{k_{z0} - k_{z1}}{k_{z0} + k_{z1}} \right|^2 \quad (9.14)$$

$$\text{Transmissivity :} \quad T = \left| \frac{2k_{z0}}{k_{z0} + k_{z1}} \right|^2 \quad (9.15)$$

The reflectivity and transmissivity are plotted below as a function of θ .

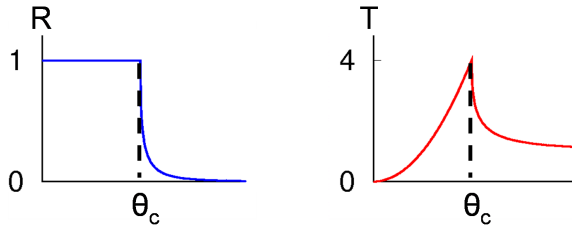


Fig. 9.4: Reflectivity and transmissivity of a substrate as a function of the angle of incidence

9.2.3 Total external reflection

For $k_{z1}^2 < 0$ in Eq. (9.10) i.e. for angles of incidence θ below the so called critical angle θ_c with

$$\theta_c \simeq \lambda \sqrt{\frac{\rho}{\pi}} \quad (9.16)$$

total reflection is observed, i.e. all intensity is reflected and no wave propagating in z -direction exists in the sample. Only an evanescent wave in the z -direction with propagation parallel to the surface is induced (k_{z1} is purely imaginary). For an angle of incidence above θ_c , the beam can partially penetrate the sample and is only partly reflected. Fig. 9.5 provides a calculation of the penetration depth Λ , defined as the inverse of the imaginary part of k_{z1} . Λ is equal to 10 nm at $\theta = 0$ and increases sharply (be attentive to the logarithmic scale) when θ crosses θ_c . It stays finite above θ_c because of absorption (ρ has actually an imaginary part).

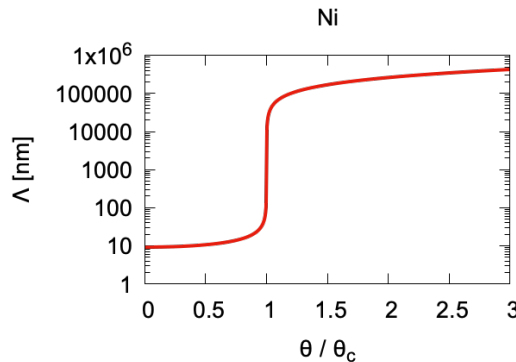


Fig. 9.5: Penetration depth of 6 Å wavelength neutrons in a nickel substrate

Note also in Fig. 9.4 that the transmissivity increases monotonously up to a value of 4 at θ_c and decreases to 1 at large angles. This result might look very surprising at first sight. The value of 4 for the transmissivity comes from the fact that the incident and the reflected waves in vacuum superpose to form a stationary wave of amplitude exactly equal to 2 at the interface with the medium. For the intensity, we obtain a factor of 4.

9.2.4 Reflectivity from layered systems

In a layered system, the same Ansatz as in Eq. (9.9) can be written in each layer l . The coefficients of reflection r_l and transmission t_l can be deduced recursively from the continuity relations of the wave function and its derivative at each interface. If N is the number of layers, and considering the vacuum on top of the multilayer and the substrate below, $2(N+2)$ coefficients have to be calculated. The number of interfaces being $N+1$, the continuity relations lead to $2(N+1)$ equations. Two other equations are obtained considering that the transmission into the vacuum is equal to one ($t_0 = 1$) and that, in the substrate, there is no reflected wave ($r_{N+1} = 0$), leading in total to a number of equations equal to the number of coefficients to determine. The calculation of the coefficients of reflection and transmission in each layer and, in particular, the calculation of the reflectivity in air are therefore possible [9].

Here we just want to demonstrate with very simple arguments how interference effects from layered structures arise and how the intensity modulations in Q-space are related to real space length scales.

Fig. (9.2) shows how interference can occur in a system composed of a single layer of thickness d deposited on a substrate. Interference occurs between beams reflected from the surface and those first transmitted in the layer, reflected from the interface between layer and substrate and then leaving the layer into vacuum. To a good approximation, refraction at the top surface can be neglected for incident angles twice the critical angle or total reflection. In this case $\theta = \theta_1$ in Fig. (9.2) holds. Since the index of refraction of the neutrons is very

close to one, this approximation is valid even for rather small angles of incidence. Then the optical path length difference between the two beams is:

$$\Delta = 2d \sin \theta \quad (9.17)$$

We can now determine the distance between interference maxima from the condition that the path length difference has to differ by one wavelength: $\lambda = 2d \cdot \delta(\sin \theta) \simeq 2d \cdot \delta\theta$. With $Q = \frac{4\pi}{\lambda} \sin \theta \simeq \frac{4\pi}{\lambda} \theta$ we finally obtain:

$$\delta Q \simeq \frac{2\pi}{d} \quad (9.18)$$

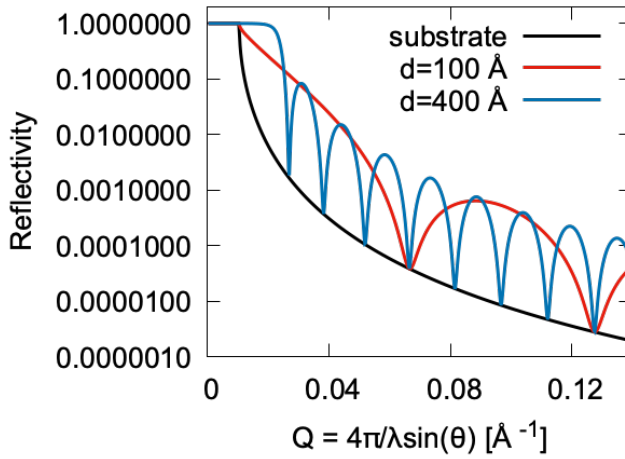


Fig. 9.6: Reflectivity of a Si substrate and reflectivity of a Ni layer ($\rho = 9.41 \times 10^{-6} \text{ \AA}^{-2}$) on Si substrate ($\rho = 2.15 \times 10^{-6} \text{ \AA}^{-2}$). Simulations are performed for two layer thicknesses d .

We can see that the interference phenomena in Q -space are connected with real space length scales in a reciprocal way. (9.18) tells us that there will be a number of interference maxima at a distance in Q of $\frac{2\pi}{d}$. These interference phenomena are called “Kiessig fringes”. Fig. 9.6 shows calculations of the reflectivity of a Ni layer deposited on a Si substrate. One observes that the reflectivities above the critical angle for total reflection decrease rapidly, therefore the ordinate is on a logarithmic scale. The oscillations of the reflectivity due to the above described interference effect can be observed. At small angles, due to the effect of refraction, the interference maxima are a bit denser distributed than at higher angles where formula (9.18) can be used to determine the layer thickness from the distance between the interference maxima. The thinner layer corresponds to an interference scheme with a bigger period. In both cases the minima of the interference scheme lay on the reflectivity of the Si substrate.

Note that for a 100 Å thick layer of Ni, that has a scattering length density (SLD) approximately 4 times larger than the one of Si, the critical angle of total reflection is determined by the SLD of Si and not by the one of Ni. This comes from the penetration depth of the neutrons that is bigger than 100 Å. For a 400 Å thick Ni layer, the θ_c approaches the one of Ni and the total reflection plateau is somewhat rounded.

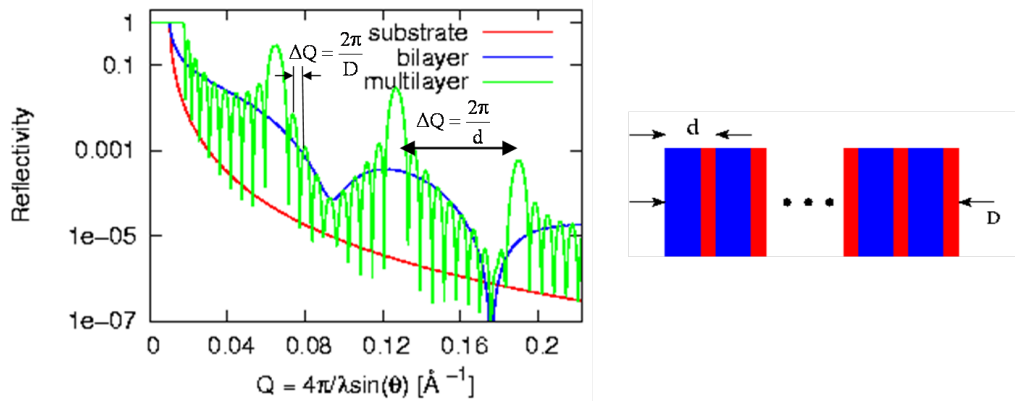


Fig. 9.7: Reflectivities of a Ni/Ti bilayer and of a Ni/Ti multilayer on Si substrate. Simulations are performed for Ni and Ti thicknesses of 70 and 30 Å respectively.

Fig. 9.7 shows the simulation of the neutron reflectivity from a multilayer on a Si substrate. This multilayer is composed of 10 double layers of 70 Å Ni and 30 Å Ti. One can clearly see the pronounced maxima due to the periodicity of the Ni/Ti double layer of thickness 100 Å. In between, one observes many weaker oscillations (be attentive to the logarithmic scale) with a period given by the total thickness of the multilayer.

9.2.5 Roughness and interdiffusion

Until now we assumed perfectly flat interfaces. A real interface will, however, always show a certain roughness at the atomic level, as shown in Fig. 9.8. The height profile of the interface is completely described by the parametrization $z(x, y)$. Such a detailed information is not at all interesting. Much more interesting are parameters that statistically describe the interface, such as the mean squared deviation from an ideally flat interface, or the lateral correlation length. Those parameters can be determined from reflectometry and scattering under grazing incidence [6].

As simplest model, we assume that the height coordinate z follows a random distribution of values around the nominal value z_j of the flat interface. The random distribution being described by a Gaussian function

$$P(\Delta z) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{\Delta z^2}{2\sigma^2}\right), \quad (9.19)$$

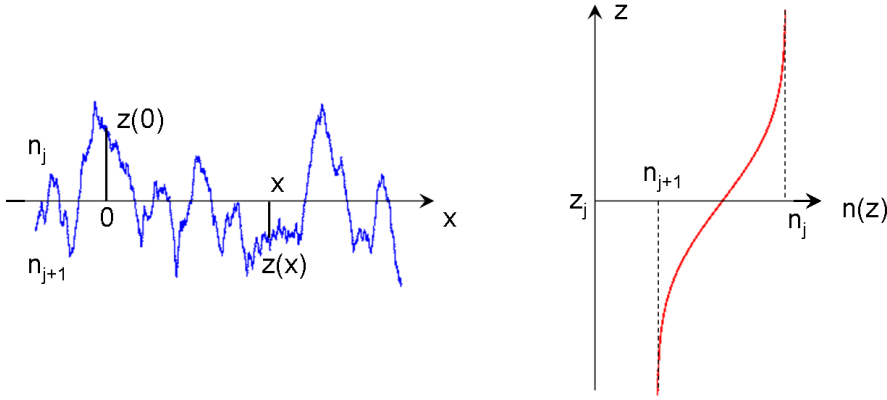


Fig. 9.8: Roughness of a real interface, characterized by the parametrization $z(x, y)$ and dependency of the refractive index on z .

the profile of index of refraction between layers j and $j + 1$ takes the form:

$$n(z) = \frac{n_j + n_{j+1}}{2} - \frac{n_j - n_{j+1}}{2} \operatorname{erf}\left(\frac{z - z_j}{\sqrt{2}\sigma_j}\right) \quad (9.20)$$

with the “Error” function:

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt. \quad (9.21)$$

The reflectivity from such a rough interface is obtained from the average of the reflectivities from a sequence of layers that describe the profile of refraction index. This average is performed in detail in Ref. [10,11]. As a result one obtains that the Fresnel coefficient for an ideally flat interface has to be modified by an exponential damping factor in the following way:

$$R_{\text{rough}} = R_{\text{flat}} \cdot \exp\left(-4\sigma_j^2 k_{zj} k_{zj+1}\right). \quad (9.22)$$

In this equation, σ_j is the root mean squared deviation from the nominal position of the flat interface.

The effects of interfacial roughness on the neutron reflectivity from a Si substrate and from a Ni layer on Si substrate have been simulated in Fig. 9.9. On the left side of Fig. 9.9 one can observe that the effect of roughness is to decrease the reflectivity at large wave vector transfers. The effect of roughness will be seen if the value of the scattering wave vector gets bigger than $1/\sigma$. Therefore, if one wants to determine very small roughness amplitudes, one has to measure the reflectivity till very large reflection angles and over a large dynamical range.

The right side of Fig. 9.9 shows the effect of the roughness of a single layer. The simulations have been performed for ideally flat interfaces, for a rough surface of the layer, for a rough interface between layer and substrate and for the case where both interfaces are rough. One can see that the four cases can be well differentiated. When only one of the two interfaces is rough, the interference pattern due to the reflection on the top and bottom interfaces is suppressed at large wave vectors. If both interfaces are rough, a faster decrease of the averaged reflectivity takes place.

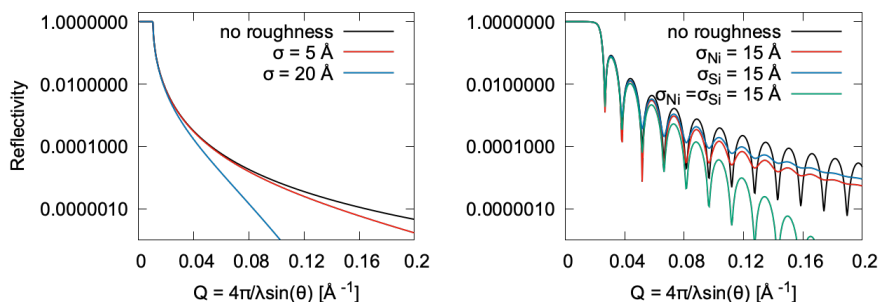


Fig. 9.9: Left: Neutron reflectivity at the interface between vacuum and Si. Right: Neutron reflectivity from a 400 Å thick Ni layer on Si substrate. Effect of interfacial roughness.

Finally, one should point out that a specular reflectivity measurement can only describe the profile of scattering length density normal to the interface. This means that a reflectivity measurement can not differentiate between interfacial roughness and interdiffusion, as interdiffusion will induce the same profile of refraction index as in Fig. 9.8. But what happens to the intensity loss described by the exponential factor of Eq. (9.22)? In the case of a diffuse interface, this intensity goes into the transmitted beam because there is no potential gradient in a direction different than the one normal to the interface. On the other hand, in the case of a rough interface, the intensity loss comes from scattering by lateral fluctuations of the potential, leading to intensities that can be observed in directions other than the specular direction: this is off-specular diffuse scattering. A statistical function like the height-height pair correlation function can be determined from the measurement of off-specular scattering [6].

9.3 Crystallography at the nanoscale: GISAXS from a nanoparticle assembly

The prime aim of this section is to emphasize on the added information provided by Grazing Incidence Small Angle Scattering (GISAS) with respect to other surface characterization techniques like Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). AFM and SEM give information on the in-plane fluctuations of the order parameter, while GISAS allows a full 3 dimensionnal investigation, i.e. gives depth-resolved information on those in-plane fluctuations.

The study reported here [12] concerns the investigation of the ordering in an assembly of magnetic nanoparticles deposited on a surface. Those nanoparticles, of truncated cubic shape, were deposited under an applied magnetic field, leading to the formation of mesocrystals, i.e. columns (see Fig. 9.10), several hundreds nanometres high and several micrometres diameter, composed of a single crystalline arrangement of nanoparticles (see insert of Fig. 9.11). The whole assembly is a 2 dimensional orientational average of such mesocrystals.

The in-plane arrangement of the nanoparticles in each mesocrystal has been determined by SEM and consists of a square lattice (see insert of Fig. 9.11) of lattice parameter 13.1 nm. Only five different cubic and tetragonal Bravais lattices are compatible with this 2 dimensional arrangement: simple cubic (sc), simple tetragonal (st), body centred cubic (bcc), body centred tetragonal (bct) and face centred cubic (fcc). Two (bcc and fcc) of those five lattices can be excluded from packing and geometrical conditions.

The actual three-dimensional Bravais lattice has been determined by GISAXS, the geometry of the experiment being depicted in Fig. 9.10: a beam of x-rays, well collimated in both directions perpendicular to $\mathbf{k}_i$, impinges on the surface under an angle of incidence α_i and the scattered x-rays are collected on a position sensitive detector. Each detector pixel is defined by the values of the angles θ and α_f . Taking into account the smallness of those three angles, the components of the scattering wave vector along the three axes depicted in Fig. 9.10 are given by:

$$Q_x = k (\alpha_i^2 - \alpha_f^2 - \theta^2) / 2, \quad Q_y = k\theta, \quad Q_z = k(\alpha_i + \alpha_f), \quad \text{with} \quad k = \frac{2\pi}{\lambda}. \quad (9.23)$$

The thus obtained GISAXS pattern at a certain angle of incidence α_i of the incoming beam close to the critical angle of total reflection is given in Fig. 9.11. This pattern shows a whole bunch of local intensity maxima at positions in Q_y and Q_z that are characteristic of the crystalline stacking respectively in-plane and out-of-plane. A relation connecting all the Q_z coordinates of the local maxima to their Q_y coordinates is obtained by a combination of Snell's law and Bragg's law leading to an extinction rule and an out-of-plane lattice parameter (17.8 nm) characteristic of a bct packing of the nanoparticle lattice.

9.4 Conclusion

This chapter has given an overview of reflectometry and GISAS as a tool for the investigation of thin films, their interfaces or mesoscopic objects deposited on a surface. We have presented a formalism which makes it possible to describe the specular reflectivity on non-magnetic systems. The formalism of neutron reflectometry for the investigation of the magnetic moment orientations in magnetic multilayers is presented in the next chapter of this book, together with several application examples.

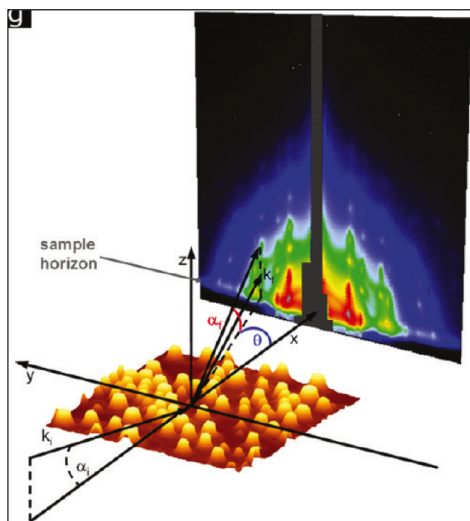


Fig. 9.10: Atomic Force Microscopy (AFM) image of the assembly of magnetic nanoparticles and geometry of the GISAXS experiment. GISAXS signal is collected on a 2 dimensional position sensitive detector. Taken from [12].

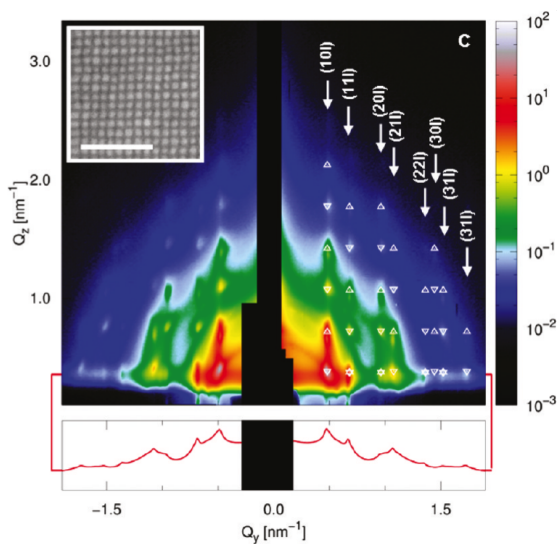


Fig. 9.11: GISAXS pattern of the assembly of magnetic nanoparticles. Insert: Scanning Electron Microscopy (SEM) image of the top of a mesocrystal of nanoparticles; scale bar represents 100 nm. Taken from [12].

9.5 Take-Home Message

Reflectometry of X-rays and neutrons from thin films with thicknesses in the mesoscopic range gives access to the scattering length density profile along their depth. The information is an average over the in-plane coordinates. With GISAS, in-plane correlations of the scattering length density can be investigated. Moreover, depth resolution is accessed by interpreting the GISAS signal as a function of α_i or α_f .

References

- [1] A special issue of *Langmuir* covers a broad range of applications of this technique for the characterization of surfaces and interfaces in the fields of soft matter and biology: *Langmuir* **25**(7), (2009).
- [2] P. Grünberg, *J. Phys. Condens. Matter* **13**, 7691 (2001). See also the web site of the European Magnetism Association, <https://magnetism.eu>
- [3] U. Rücker and E. Kentzinger in *Probing the Nanoworld, 38th IFF Springschool* (Schriften des Forschungszentrum Jülich, Materie und Material, Band 34, 2007). Lecture D4
- [4] Th. Brückel and E. Kentzinger in *Magnetische Schichtsysteme, 30. Ferienkurs des IFF* (Schriften des Forschungszentrum Jülich, Materie und Material, Band 2, 1999). Kapitel B3
- [5] Th. Brückel in *Laboratory course, Neutron Scattering* (Schriften des Forschungszentrum Jülich, Reihe Schlüsseltechnologien, Band 39, 2012). Lecture 14
- [6] S.K. Sinha, E.B. Sirota, S. Garoff, H.B. Stanley, *Phys. Rev. B* **38**:4, 2297 (1988).
- [7] G. Pospelov, W. Van Herck, J. Burle, J.M. Carmona Loaiza, C. Durniak, J.M. Fisher, M. Ganeva, D. Yurov and J. Wuttke, *J. Appl. Cryst.* **53**, 262 (2020). See also <https://www.bornagainproject.org>
- [8] M. Born and E. Wolf, *Principles of Optics* (Pergamon Press, Oxford, 1989).
- [9] L.G. Parratt, *Phys. Rev.* **95**, 359 (1954).
- [10] L. Névot, P. Croce, *Rev. de Phys. Appl.* **15**, 761 (1980).
- [11] J. Als-Nielsen and D. McMorrow, *Elements of Modern X-ray Physics. Second Edition* (Wiley, Chichester, 2011).
- [12] S. Disch, E. Wetterskog, R.P. Hermann, G. Salazar-Alvarez, P. Busch, Th. Brückel, L. Bergström, S. Kamali *Nano Letters* **11**, 1651 (2011). [dx.doi.org/10.1021/nl200126v](https://doi.org/10.1021/nl200126v)

Exercises

In the following the nuclear scattering length densities (in $10^{-6} \text{ \AA}^{-2}$) of several elements are displayed:

Cu: 6.53; Ag: 3.5; Si: 2.15; Au: 4.5

E9.1 * Reflection and transmission by a flat substrate

The following figure shows the neutron reflectivity from a flat substrate.

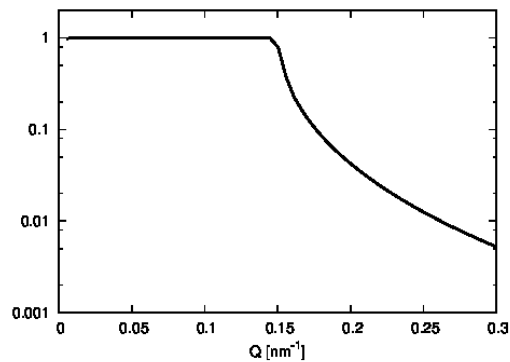


Fig. 9.12: Reflectivity from a substrate.

- Determine the element of which this substrate is made of
- Explain why the amplitude of the wave transmitted in the substrate is equal to 2 at an angle of incidence equal to the critical angle of total reflection

E9.2 * Layers on substrate

The figure below shows two simulations of reflectivity from a Cu layer deposited on Ag substrate. Determine for both cases (red and blue curves) the thickness of the Cu layer.

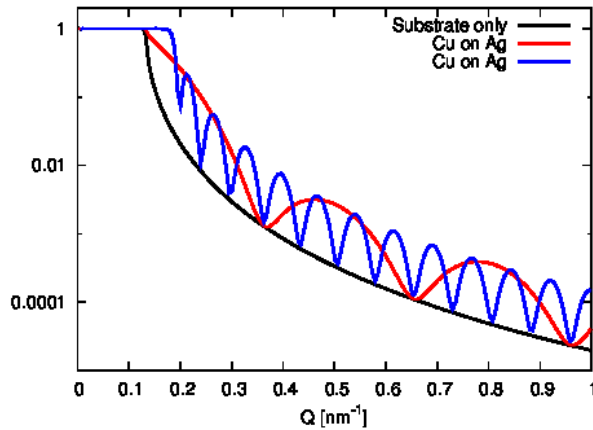


Fig. 9.13: Layer of Cu on Ag substrate

In the next figure, the reflectivity from a $[\text{Cu}/\text{Au}] \times n$ multilayer is depicted. Determine the $[\text{Cu}/\text{Au}]$ thickness, the total thickness of the multilayer and the number n of bilayers the multilayer is composed of.

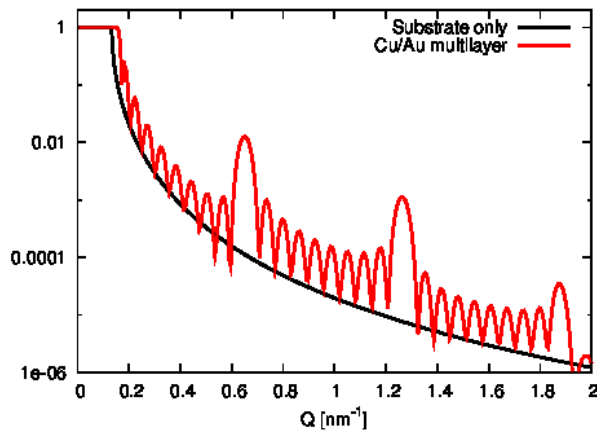


Fig. 9.14: Cu/Au multilayer on Ag substrate

E9.3 * GISAXS from nanoparticles on surface

The figure below shows a simulation of GISAXS from a square lattice of cubic nanoparticles of 5 nm edge length. The radiation wavelength is $1 \text{ \AA}$ and the plane of incidence of the X-rays is parallel to one edge of the cubes. Determine the lattice parameter.

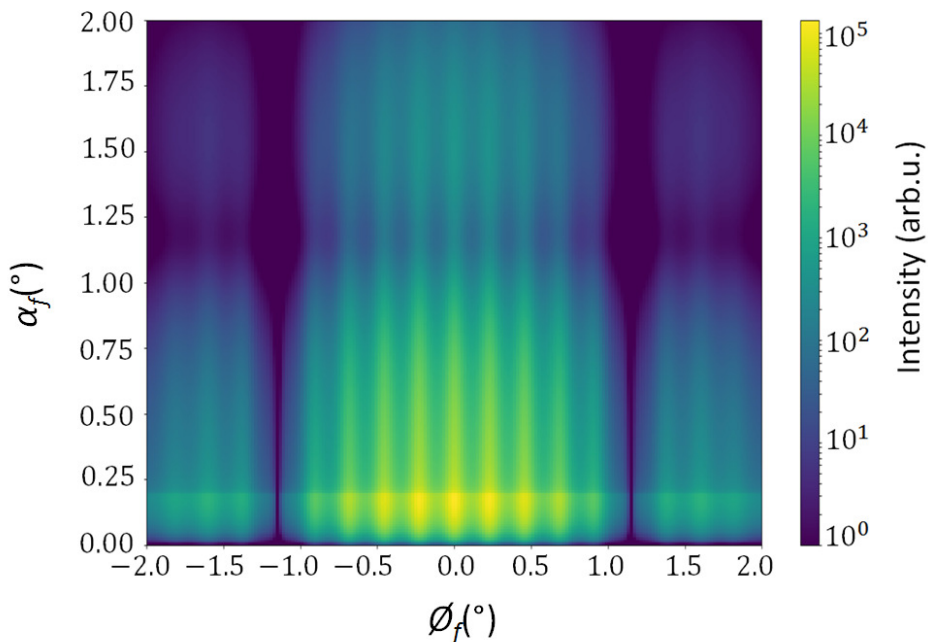


Fig. 9.15: GISAXS from a square lattice of cubic nanoparticles. The horizontal axis shows θ and the vertical one α_f as defined in Fig. 9.10. This simulation was performed by Asma Qdemat (JCNS-2) using the BornAgain software [7].

10 **Magnetic Nanostructures**

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10.1 Introduction

The physical properties of a layered structure of nanometer size, as it is shown schematically in Fig. 10.1, differ from the bulk properties of the constituents. There are several origins of new emerging effects due to miniaturization.

First, the ratio between surface and volume is much higher than in bulk. Therefore, the number of atoms with reduced coordination is significant and can change the crystalline structure as well as the electronic structure of the whole layer. Second, boundary conditions, e.g. for the magnetic induction $\mathbf{B}$ become important, introducing shape anisotropies. The magnetization of most materials in thin layer form tends to align along the long edges of the magnetic nanostructure because the dipolar fields are smaller there. Third, at the interface between two layers the electronic structures and the crystal lattices have to be matched, which leads to structural stress, interfacial disorder and electronically to charge transfer (e.g. a Schottky barrier in semiconductor heterostructures) or splitting of the layers' band structure.

Nanostructures can be prepared in several dimensions: thin films with a thickness in the nm range are 2D nanostructures, stripes with thickness and width in the nm range are 1D nano-structures, and dots or nanoparticles with all three dimensions in the nm range are 0D nano-structures. The dimension number indicates, in how many directions the dimension remains macroscopic.

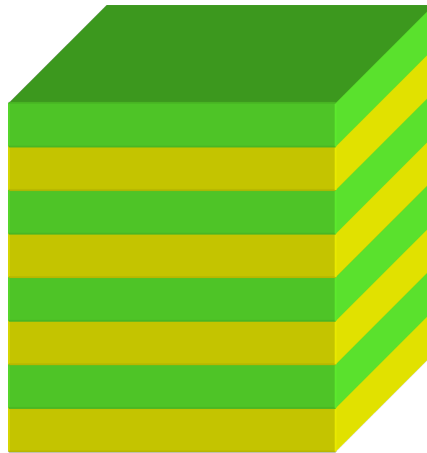


Fig. 10.1: Sketch of a layered structure of two materials

Magnetic nanostructures are nanostructures which contain at least one magnetic constituent. Typical systems are multi-layered structures with ferromagnetic and nonmagnetic layers or arrays of ferromagnetic dots on a nonmagnetic substrate. One interesting and well-studied aspect of 2D magnetic nanostructures is the fact that two ferromagnetic (FM) layers with a nonmagnetic (NM) spacer in between have a connection between their electronic systems across the spacer layer. This connection influences the magnetic behaviour as well as the electron transport through the system.

The first fundamental phenomenon found in magnetic layered structures has been the os-

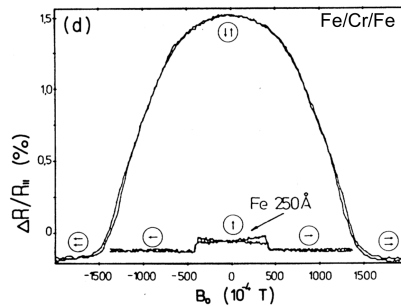


Fig. 10.2: Giant Magnetoresistance effect in an Fe/Cr/Fe trilayer compared to the anisotropic magnetoresistance effect in a single Fe layer. Reprinted figure with permission from [3]. Copyright 1989 by the American Physical Society.

cillating magnetic interlayer coupling in FM / NM / FM trilayer structures. Depending on the NM interlayer thickness, the magnetizations of the two FM layers tend to align parallel or antiparallel to each other [1]. The coupling is mediated by electronic states in the NM interlayer close to the Fermi surface [2].

Subsequently, the Giant Magnetoresistance Effect (GMR) was discovered [3,4]. For this discovery, P. Grünberg and A. Fert were awarded the Nobel Prize for Physics 2007. They found that the resistivity of a layered structure containing more than one ferromagnetic layer depends on the mutual orientation of the magnetization directions in each layer, see Fig. 10.2. They used the antiferromagnetic coupling in Fe / Cr / Fe trilayer structures to influence the mutual orientation of the magnetization of the Fe layers by changing the applied magnetic field.

Resistivity, in this case, is highest for the antiparallel alignment of the two magnetization directions. This effect is much stronger and much more sensitive to changes in the magnetization direction of each ferromagnetic layer than the already known and understood anisotropic magnetoresistance effect in single ferromagnetic layers. The microscopic origin of the GMR effect is the matching between the spin-split bandstructures of the two ferromagnetic layers. The conductivity of the entire structure is the sum of the conductivities for the two spin channels. As the Fermi surface is different for the two spin channels, the matching between the FM and the NM layer is different.

As shown in Fig. 10.3, in the case of parallel alignment, the scattering probability of a conduction electron is the same at both interfaces. For one spin channel, the scattering probability is high while for the other one it is low. The conductivity is then dominated by the spin channel with the smaller scattering probability. The resistivity of the entire structure, which is analogous to two resistors wired in parallel, is small.

In the case of antiparallel alignment, the scattering probability for each spin channel is high in one of the FM layers. This results in a relatively low conductivity for both spin channels, so that the resulting resistivity is much higher compared to the case of parallel magnetization.

As GMR structures are easy to prepare and easy to use, the sensor technology based on this effect quickly became standard in the readout system of computer hard disks and many other

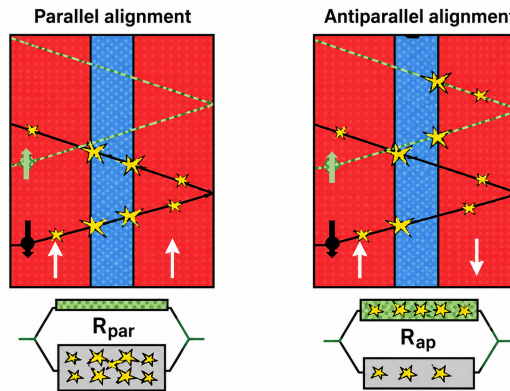


Fig. 10.3: Different matching of the band structure between ferromagnetic and nonmagnetic layers changes the resistivity for the different spin channels

applications. Today, it has been replaced by Tunneling Magnetoresistance (TMR), where the nonmagnetic interlayer is insulating and electrons travel across this tunneling barrier while preserving their spin state. Then, the height of the tunneling barrier depends on the spin of the electron and the magnetization direction of both ferromagnetic layers. TMR, using the electron spin rather than charge alone, is also the basis of modern MRAM including Race-track Memory and Spin-Orbit-Torque (SOT) MRAM. Furthermore, it is the principle behind modern magnetic position and current sensors that are used in industrial, automotive and consumer products. A detailed overview over the field of spin transport in layered systems is given in [5].

10.2 Neutrons for investigating magnetic nanostructures

For the investigation of magnetism, many methods are available: Vibrating Sample Magnetometer (VSM), SQUID Magnetometer, Hall Effect Sensor, Flux Gate Magnetometer, etc. Most of these methods directly measure the magnetization (usually over the entire volume) of a sample. A more indirect approach is to measure spin-dependent band structures by absorption and photoemission spectroscopy of polarized light or x-rays.

The simplest (and oldest) approach is to measure the integral magnetization of a sample by classical magnetometry, e.g. by using a Vibrating Sample Magnetometer (which measures induction when moving the magnetic sample in a coil), a Faraday balance (which measures the force on the magnetic sample in a field gradient), or more recently a SQUID magnetometer (which measures the magnetic flux inside a superconducting loop). In case of magnetic nanostructures deposited on any macroscopic substrate, the small signal coming from the nanostructure is always superimposed by the signal from the substrate which is typically 10000 times larger in volume. Even if the nanostructure is ferromagnetic and the substrate only diamagnetic, the correction due to the substrate is in most cases much stronger than the signal itself.

Better adapted to thin-film structures are methods that are surface sensitive. The magneto-optical Kerr effect (MOKE) measures magnetization with polarized light reflected from a magnetic surface. Due to the magnetization of the sample the polarization direction of the light is modified. This method is surface sensitive in the range of the penetration depth of the light used (typically some 10 nanometers). At synchrotron x-ray sources one can use X-ray Magnetic Circular Dichroism (XMCD). The energy dependence of the absorption of circularly polarized (soft) x-rays is measured at the absorption edges of the magnetic materials. *Again: the information is integrated over the penetration depth of the x-ray photons used*, however it is element specific due to the choice of the x-ray energy in resonance with the magnetic orbitals of a certain element.

Magnetic domains can be imaged using:

- *Magnetic Force Microscopy* (MFM) – a surface sensitive technique that uses a magnetized tip to measure the stray fields above the surface of the sample.
- *Nitrogen vacancy scanning probe microscopy* - also surface sensitive technique using a specially prepared diamond tip and optically detected magnetic resonance (ODMR) to sense the stray fields. The method is extremely sensitive and can also be used for antiferromagnetic domains.
- *Lorentz TEM* – in transmission the field sensitivity of the electrons being deviated by Lorentz forces is observed. Special sample preparation is time consuming and required.
- *Kerr Microscopy* – using an optical microscope to observe the magneto-optical Kerr effect (MOKE). The lateral resolution here is limited to that of the optical microscope.
- *Photoemission electron microscopy* (PEEM) – Soft X-rays ($\sim$ (keV)) are used to give an overview of the density of certain electronic states. The lateral resolution is in the nanometer range with time resolution down to nanoseconds, very useful for studying magnetic domain formation and dynamics.
- *XMCD-PEEM* – perhaps the most complementary method to PNR – can image the evolution of magnetic domains under varying magnetic fields. However, the depth resolution is limited to the penetration depth of the X-rays and the element specific absorption of the X-rays.
- Other techniques are SPLEEM (*spin-polarized low energy electron microscopy*) and SEMPA (SEM with *polarization analysis*). SPLEEM is limited to large domains sizes - on the order of microns. Similarly SEMPA uses a spin-filter in an SEM to sense the change in polarization of the secondary electrons. Both of these techniques are surface sensitive and useful for investigations of 2-D materials, and the top few layers of thin films.

Missing is a method that can access the magnetism of buried layers and correlate it with the penetration depth. Ideally we need a probe that is sensitive to magnetic fields and has a spatial resolution (at least in depth) in the nm regime. Cold neutrons are such a probe, having a wavelength appropriate for resolving nm length scales and carrying a spin that interacts with magnetic fields. Generally, it is useful to know the initial spin state of the

neutrons, so we prepare the neutrons that will interact with the sample by polarizing them and use these polarized neutrons for the investigation of magnetic nanostructures.

Polarized neutron reflectometry (the incoming beam is polarized, also sometimes called *half-polarized PNR*) with *polarization analysis* (the polarization change after sample interaction is measured) is a method for depth-resolved investigation of magnetic layered structures. Together with the analysis of *off-specular scattering*, lateral structures in the μm range can be investigated, allowing access to magnetic domains in buried layers. *Polarized SANS* reveals information about magnetic structures in the nm range perpendicular to the beam direction, while *polarized GISANS* (Grazing Incidence Small Angle Neutron Scattering) combines the possibilities of both methods and allows access to lateral buried magnetic structures in the nm range. These last two methods can also be used with polarization analysis.

It's important to keep in mind that although PNR can probe magnetic periodicities at nm length scales, it only gives the average magnetic moment in the probed layer. In other words, as you probe through the sample, what you measure is an 'averaged laterally over the nm layer' magnetic moment. The area being averaged over is the coherent beam 'footprint' on the sample, which is usually very elongated in the propagation direction due to the small incidence angle. Integrating along the depth of the sample, then gives a volume averaged magnetic moment which can and should be measured and compared with the moment measured using standard laboratory techniques.

10.3 Specular reflectivity of polarized neutrons

The previous lecture introduced specular reflectivity of neutrons on layered structures with nuclear scattering contrast. For the investigation of magnetic layered structures, remember that the neutron is a spin 1/2 particle and therefore interacts with the magnetic induction $\mathbf{B}$. To treat the neutron's spin properly, use the wave functions in the 2-dimensional quantum mechanical spin space, where the usual space-dependent functions, e.g. the potential, become operators on the neutron's spin. In analogy to equation (9.2), the potential of a homogeneous magnetic material in layer number l can be separated into two parts

$$\hat{V}_l = V_l^N \hat{\mathbf{1}} + \hat{V}_l^M \quad (10.1)$$

where V_l^N is the nuclear interaction potential known from equation (9.2), and $\hat{\mathbf{1}}$ is the unity operator, which does not affect the spin state, so that the nuclear interaction is described independently of the neutron spin. The magnetic dipole interaction is described by the operator $\hat{V}_l^M = -\mu_n \hat{\sigma} \cdot \mathbf{B}_l$, a scalar product of the neutron magnetic moment operator and the magnetic induction $\mathbf{B}_l$ inside the layer.

For coordinate representation, we need to define a coordinate system which is convenient to the experiment. Typically, the magnetic field $\mathbf{H}$ is applied in the plane of the sample. We choose this direction to be the x-direction of the coordinate system $\mathbf{H} = H\mathbf{e}_x$ and also as the quantization axis for the neutron spin. Under this assumption, the spin operator $\hat{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ is written as

$$\sigma_x = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (10.2)$$

In analogy to section 9.2, the Schrödinger equation can be solved in coordinate and spin space, where the eigenvectors $|+\rangle$ and $|-\rangle$ of the operator $\hat{\sigma} \cdot \mathbf{b}_0 = \sigma_x$ with the eigenvalues $+1$ and -1 , respectively, define states of the neutron with “spin up” and “spin down”. The solution of the Schrödinger equation is the neutron wave function $|\Psi(\mathbf{r})\rangle$, which is again a linear combination of those two spin states.

$$|\Psi(\mathbf{r})\rangle = \Psi^+(\mathbf{r})|+\rangle + \Psi^-(\mathbf{r})|-\rangle = \begin{pmatrix} \Psi^+(\mathbf{r}) \\ \Psi^-(\mathbf{r}) \end{pmatrix} \quad (10.3)$$

After some calculation which you can find in [6] we end up with a set of two coupled one-dimensional linear differential equations for every layer, which are the analog to equation (9.8).

$$\frac{\partial^2 \Psi_l^+(z)}{\partial z^2} + [k_{zl}^2 - 4\pi(\rho_l^N + \rho_l^M m_{xl})] \Psi_l^+(z) - 4\pi\rho_l^M m_{yl} \Psi_l^-(z) = 0 \quad (10.4)$$

$$\frac{\partial^2 \Psi_l^-(z)}{\partial z^2} + [k_{zl}^2 - 4\pi(\rho_l^N - \rho_l^M m_{xl})] \Psi_l^-(z) - 4\pi\rho_l^M m_{yl} \Psi_l^+(z) = 0 \quad (10.5)$$

In these formulas, you find the nuclear scattering length density, ρ^N , familiar from eq. (9.3) together with its magnetic analog, ρ^M , the magnetic scattering length density. ρ^M is proportional to the net magnetization M of the material. In ferromagnetic materials, the magnetization vector $\mathbf{M}$ typically is aligned in some direction, which is described by the unit vector $\mathbf{m} = \mathbf{M}/M$.

We can have a closer look at the different terms in equation (10.4) and (10.5). As Non-Spinflip (NSF) interaction, one finds in (10.4) for spin $+$ (“spin up”) the sum of the nuclear interaction and the magnetic interaction with the magnetization along the quantization direction and in (10.5) for spin $-$ (“spin down”) the difference. In the case of a magnetically saturated layer (all the magnetization is aligned with the external field), the scattering length density for spin $+$ neutrons is enhanced and for spin $-$ neutrons it is reduced, both compared to the nonmagnetic case.

This influences the index of refraction, the total reflection angle, and of course the reflectivity, which is a function of the change of the index of refraction at a certain interface. Essentially you have two split reflectivity curves for magnetic materials (with a magnetic SLD), depending on if $\mathbf{M}$ is parallel or anti-parallel to $\mathbf{H}$. Fig. 10.4 shows schematically the splitting of the total reflection angle. This splitting and how it changes is representative as to how the magnetization is changing as you probe deeper into the material. In addition, analogous to eq. (9.14), if you put a second polarizer into your experiment to polarize the reflected beam before it hits the detector, four channels of reflectivity can be measured, being the squares of the projections of the reflection amplitude onto spin up or spin down neutron states:

$$\mathbf{R}^{\pm\pm} = |\langle \pm | (\hat{r}_0) | \pm \rangle|^2 \quad (10.6)$$

Importantly, when the magnetization is not fully aligned with the field, the component along the field direction influences the scattering length density for the NSF channels. The in-plane magnetization component perpendicular to the field induces a spin-flip (SF) interaction

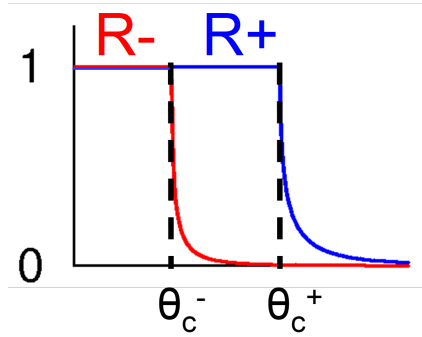


Fig. 10.4: The total reflection angle θ_c of the surface of a magnetized material is different for both spin directions

by applying a torque to the polarized neutron that is equally strong for both spin-flip channels R^{+-} and R^{-+} , as is described in the last term of eq. (10.5) (10.4), respectively. To measure the SF channels, a spin-analyzer (essentially another polarization of the outgoing beam before it hits the detector) is necessary. This is called PNR with *polarization analysis*. N.B. Every instrument scientist that runs a PNR beam-line will be very quick to inform you that measurements with polarization analysis are extremely time-consuming - requiring count times up to 16x longer to obtain equivalent statistics to NR measurements - and thus should be well-thought out and the necessity of the measurement well-justified when writing experiment proposals, as it requires such long measurement times. On the other hand, there currently exists no other technique that can gently probe the depth-dependant spin arrangement of layered systems as effectively.

To summarize: R^{++} and R^{--} indicate that incident and scattered neutrons have the same spin and are the non-spin flip channels. Whereas, R^{+-} and R^{-+} indicate the spin has flipped its orientation during the scattering process and are called the spin flip (SF) channels. If no polarization analysis is performed, R^{++} and R^{--} are often abbreviated to R^+ and R^- , and the SF channels are ignored.

In addition, *specular reflectivity of polarized neutrons is not sensitive to any magnetization component perpendicular to the layer plane* [7]. This means that components of the magnetization out of the plane of the film are not easily accessible via PNR. For the beamline ESTIA at ESS, a polarizing supermirror analyzer has been developed that thorough clever optics simultaneously allows two spin states (up and down) to reach different areas on the detector, thus cutting the measurement time in half, but this still only gives information about the in-plane moment [10]. For current analyzers, there are 'tricks' that have been developed to determine the presence and magnitude of out-of-plane magnetic moment from a very fundamental understanding of polarized reflectivity and a thorough analysis of the reflectivity curves by measuring at saturating and very tiny in-plane fields, respectively [9]. True 3D magnetometry in neutron reflectometry is only possible with a combined analysis of specular, off-specular and grazing incidence scattering [11]. There are some limitations as to what magnetic samples can be probed this way. This point is discussed in more detail in the following sections.

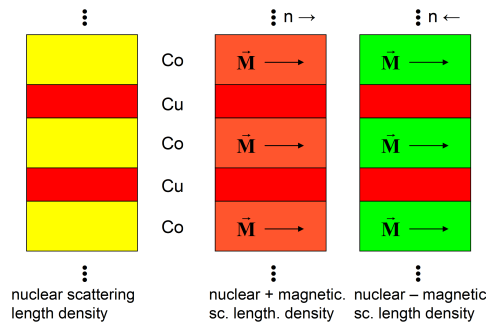


Fig. 10.5: The contrast between Co and Cu depends on the magnetization state. It almost vanishes for spin up neutrons, but is strong for spin down.

10.3.1 Polarized neutron reflectivity of Co/Cu multilayers

A first simple example is the polarized neutron reflectivity of a [Co/Cu] multilayer. The respective nuclear and magnetic scattering length densities are:

$$\begin{aligned} \text{Co: } \rho_N &= 2.30 \cdot 10^{-6} \text{ \AA}^{-2} & \rho_M &= 4.24 \cdot 10^{-6} \text{ \AA}^{-2} \\ \text{Cu: } \rho_N &= 6.53 \cdot 10^{-6} \text{ \AA}^{-2} & \rho_M &= 0 \end{aligned}$$

The sum of the magnetic and the nuclear scattering length density of Co is almost equal to the scattering length density of Cu. In the case of magnetic saturation, spin + neutrons will not feel any contrast at the Co / Cu interfaces because they see the sum of nuclear and magnetic scattering length density in the Co layer. The multilayer structure is invisible for spin + neutrons. In contrast, spin – neutrons experience the difference of nuclear and magnetic scattering length density (which is in fact negative), so the contrast is huge.

Fig. 10.5 illustrates the difference in contrast by using colours representing the different scattering length densities.

Fig. 10.6 shows the measured polarized neutron reflectivity of such a multilayer. The total reflection edge is identical for both spin channels, because the penetration depth of the neutrons is larger than the total thickness of the multilayer stack, so both polarizations penetrate equally into the substrate, resulting in the same critical angle. However, the multilayer Bragg peaks at $2\theta = 3^\circ$ and $2\theta = 6^\circ$ are strongly spin split. For spin – neutrons, the Bragg peak is about 30 times stronger than for spin + neutrons. The contrast is responsible for the reflectivity, not the strength of the scattering potential, as the scattering length density (which describes the scattering potential) is higher for spin +, but the contrast between the layers is much stronger for spin –.

For this example, the splitting is very large, and quite visible in the specular reflectivity. Often the effects or differences in magnetism are much more subtle and thus it is helpful to plot the spin asymmetry ratio:

$$SA = \frac{R^{++} - R^{--}}{R^{++} + R^{--}} \quad (10.7)$$

The spin asymmetry is directly proportional to the magnitude of the magnetization that is

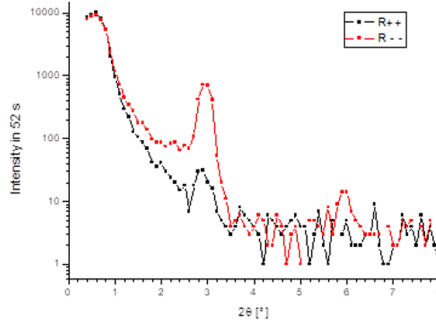


Fig. 10.6: Specular reflectivity of polarized neutrons from a [Co / Cu] multilayer with 20 periods at magnetic saturation.

parallel (or anti-parallel) to the direction of beam polarization or the applied field.

10.4 Off-specular scattering of neutrons

As discussed at the end of section (9.2), real interfaces have roughness, also magnetic roughness where $\mathbf{m}$ may correlate to the structural roughness or may be periodic due to anisotropy in the layer and the formation of magnetic domains in the layer. The effects are seen in the exponential decay of the specular signal. These lateral fluctuations of the potential lead to off-specular diffuse scattering.

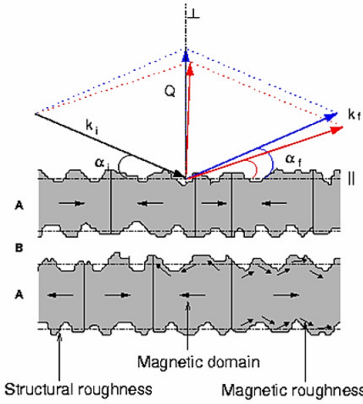
In specular scattering, as shown in Fig. 10.8 the entire wavevector $\mathbf{Q}$ is in the z -direction, perpendicular to the sample surface, and its magnitude is expressed as¹

$$Q_z = |\mathbf{k}_f - \mathbf{k}_i| = \frac{2\pi}{\lambda}(\sin \alpha_i + \sin \alpha_f) = \frac{4\pi}{\lambda} \sin \omega \quad (10.8)$$

where the angle ω is exactly half the reflected angle, 2θ , and $\alpha_i = \alpha_f = \omega$. This scattering geometry is thus sensitive to structural and magnetic differences perpendicular to the plane of the sample, i.e. within the layers, but not to those in the plane of the film [12]. Stated differently, it reveals only an *average* in density and magnetism in the plane, and nothing about inhomogenities or periodicities in the plane.

The off-specular component arises from the roughness. In Fig. 10.7 the effect on $\mathbf{Q}$ is shown. The angle of the incident neutron wavevector, $\mathbf{k}_i$ is no longer exactly half of the reflected angle, $\omega \neq \theta$ or $\alpha_i \neq \alpha_f$. This results in a $\mathbf{Q}$ that contains a component, Q_x that is sensitive to structural and magnetic inhomogenities in the plane of the film. There is now a diffuse scattering signal outside of the specular signal - hence off-specular diffuse scattering [12].

¹ In keeping with grazing incidence notation found in the literature, we use here $\mathbf{k}_i$ and $\mathbf{k}_f$ (*initial* and *final*) instead of $\mathbf{k}$ and $\mathbf{k}'$, as well as α_i and α_f instead of α and α' .



If $\alpha_f = \alpha_i$ then $Q_{\parallel} = 0$:

- specular reflectivity
- average over the lateral coordinates

If $\alpha_f \neq \alpha_i$ then $Q_{\parallel} \neq 0$:

- off-specular scattering
- probing of lateral correlations

Fig. 10.7: General geometry of reflectivity and off-specular scattering, showing magnetic domains in the cross-section and structural and magnetic roughness. From [6].

Following the geometry, this leads to expressions for Q_x and Q_z as follows from Fig. 10.8(b)

$$Q_x = \frac{2\pi}{\lambda} (\cos \theta_y \cos \alpha_f - \cos \alpha_i) \quad (10.9)$$

$$Q_z = \frac{2\pi}{\lambda} (\sin \alpha_i + \sin \alpha_f) \quad (10.10)$$

As a check, substituting in $\alpha_i = \alpha_f = \omega$ gives the specular case: (10.9) reduces to zero and we are left with eq. (10.8).

Larger lateral structures ($\sim 400\text{nm}$ to $100\mu\text{m}$), such as magnetic domains or roughness can be resolved by an examination of the off-specular scattering. The off-specular scattering is very sensitive to the size of magnetic domains. This is directly related to the coherence volume, or more specifically, the coherent footprint of the neutron beam on the sample [14, 15].

10.5 Grazing incidence small angle neutron scattering (GISANS)

When the in-plane invariance of the layers or interfaces is broken, some diffuse signal can be observed outside of the specular direction (Fig. 9.3). This is grazing incidence small angle scattering (GISAS) from sec. 9.2.1. For neutrons, the geometry is shown in Fig. 10.8(c) where now there is a component of the scattering vector in the y-direction

$$Q_y = \frac{4\pi}{\lambda} (\sin \theta_y \cos \alpha_f) \quad (10.11)$$

In the small angle approximation, equations (10.9), (10.10), and (10.11) can then be represented (using the angle notation from Fig. 10.11a) for GISANS geometry as

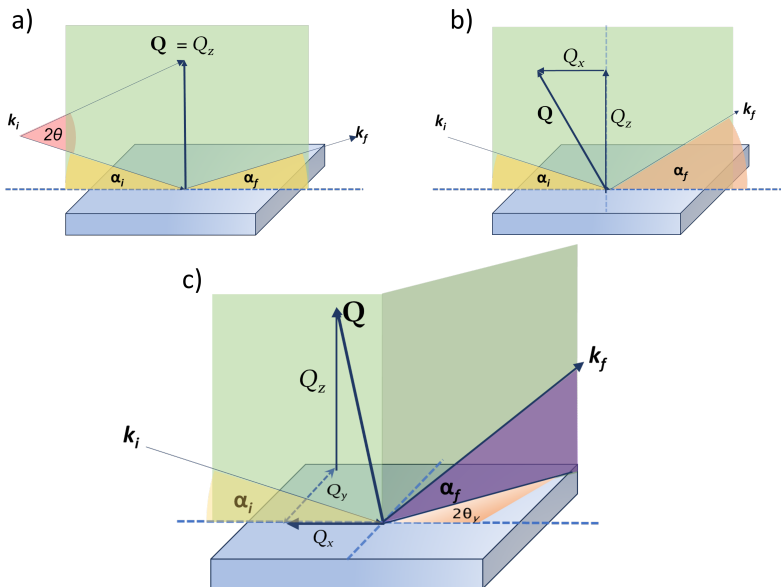


Fig. 10.8: The different geometries of PNR and GISANS. (a) Specular scattering has an angle of incidence, ω that is exactly half that of the reflected angle 2θ (where $\omega = \theta$) and the entire magnitude of Q is in the z -direction. (b) Off-specular scattering in the x -direction where $\alpha_i \neq \alpha_f$. (c) Grazing incidence geometry where there is an additional angle $2\theta_y$ in the y -direction. Size of $2\theta_y$ is exaggerated here for clarity.

$$\begin{pmatrix} Q_x \\ Q_y \\ Q_z \end{pmatrix} = \frac{2\pi}{\lambda} \begin{pmatrix} \theta_i \Delta\theta_x + \frac{(\Delta\theta_x)^2}{2} + \frac{(\Delta\theta_y)^2}{2} \\ \Delta\theta_y \\ 2\theta_i + \Delta\theta_x \end{pmatrix} \quad (10.12)$$

Analogously to X-rays as described in sec 9.3, neutrons can be used at grazing incidence to measure this diffuse signal aside the specular peak. Whereas off-specular scattering can resolve larger features or magnetic texture, in the plane of the film (in the x -direction), it is limited by the neutron coherence length and additionally has no resolution in the y -direction [14]. This is due to the relaxed collimation of the beam along that direction. Grazing incidence scattering, on the other hand, uses collimation in both directions (or a pin-hole geometry) and thus can detect features from ~ 1 to 200 nm, the range necessary for many structures and magnetic textures including domain walls, skyrmion bubbles, or nanoparticles arrayed on a substrate. The only caveat is that the scattering intensity is dependent on a lateral coherence of the signal, i.e a lattice or repeating lateral pattern in real space which shows up as the Fourier transform in Q -space [13]. This means that a single domain structure, or nanometer sized physical structure, such as a nanodot, will not have any scattering intensity. However, a pattern of domain walls, or an array of magnetic nanodots will [11].

10.5.1 GISANS with polarization analysis on FePd thin films

An example of such a system is the $L1_0$ -ordering magnet FePd. Grown epitaxially on MgO substrates the thin film alloy exhibits a controllable strength of perpendicular magnetic anisotropy (PMA) through controlled growth conditions, which manifests in tuneable magnetic texture from stripes to maze domains [16]. These domains have lateral dimensions ~ 200 nm, with domain walls and closure domains commensurately smaller and well-resolvable with GISANS. Shown in Fig. 10.9(b) is an MFM image of the domain structure on FePd grown to have a maze-like structure, (c) shows the accompanying hysteresis curves for in- and out-of- plane magnetism. Clearly the out-of-plane axis is the easy axis in these thin films, as most of the domains have a moment pointing out of the film. As can be seen in the MFM image domains are well separated by domain walls that have an inverse direction of moment showing up as inverse contrast in the image. What is not well understood is how the magnetism looks within the walls as it inverts from up to down from one side of the wall to the other. Measuring these films in GISANS was undertaken to learn more about the in-depth domain wall structure [16]. GISANS without PA can already give us information on the size and depth extension of the domains or if there are closure domains present. Using polarization analysis can help us then to uncover the internal magnetic structure of the domains. By flipping spins in small magnetic fields carefully aligned along and perpendicular to the polarization direction, it reveals the chirality (exactly how the spins are changing) of the domain walls and closure domains. Preference in chirality shows up as an asymmetry (or imbalance) in the SF channels in polarized analysis of GISANS. For these films, as well as in heterostructures with a thin film of superconducting Nb on top - to make things more interesting and technologically relevant - it was found that a definite preferred chirality is present [17].

From theory [18–20], the atomistic magnetic interactions in a thin film can be written down

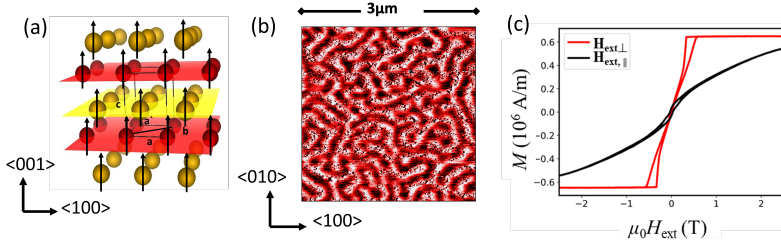


Fig. 10.9: Structure and magnetism of L₀ FePd. (a) Atomic structure model showing the layer arrangement of Fe (red) and Pd (gold) atoms and the alignment of moments in the <001> direction (out-of-plane). (b) MFM scan of high-PMA FePd showing maze domain formation. Scan is of the [100] plane. (c) Magnetometry hysteresis curve for FePd with high-PMA.

in the Hamiltonian as

$$\hat{\mathcal{H}} = - \sum_{\langle i,j \rangle} J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j - \sum_{\langle i,j \rangle} \mathbf{d}_{ij} \cdot (\hat{\mathbf{S}}_i \times \hat{\mathbf{S}}_j) - \sum_{\langle i,j \rangle} K_i (S_z)_i^2 \quad (10.13)$$

where the indices i and j indicate atoms A and B. The first term comes from direct energy exchange due to Pauli and Coulomb interactions. The last term contains the shape anisotropy and spin orbit coupling. The middle term contains the DMI vector, $\mathbf{d}_{ij}$, which is due to interactions of the spins in forming and stabilizing helical structures in the domain walls. These structures can have a preferred chirality or 'handedness'.

Possible chiral orientations of the domains and domain walls are shown in Fig. 10.10. In principle, perfectly L₁₀-ordered films should not have any DMI contributions, i.e the domain walls should be randomly oriented and any chirality should cancel itself out by balancing with an adjacent wall. However, it is already well-known that an interface-driven DMI can lead to chiral and helical structures, such as chiral N  el-walls or even N  el-type skyrmions, and that these spin structures can be stabilized and even moved around (spintronics) [21]. Furthermore, structural or chemical inhomogeneities in grown films due to strain, formation of antiphase boundaries and layer intermixing can also lead to the broken inversion symmetry necessary for DMI to occur, and would manifest itself as an imbalance in chirality of the domain walls.

Measuring GISANS with uniaxial polarization analysis, the direction, chirality and nuclear-magnetic interactions of the magnetic moments can be determined for specific polarization directions [17]. Example detector maps corrected for polarization efficiency are shown in Fig. 10.11 along with a sketch of the geometry with the small angles from (10.12). Analysis for this measurement requires simulation of the scattering data in the DWBA (Distorted Wave Born Approximation), beyond the scope of this chapter, and other simulations and modelling of the system, as well as analysis of integrated intensity over the area defined by the grey boxes in the detector maps of Fig. 10.11 using (10.12). Although minute, a definite preferred chirality is measurable for both a simple FePd thin film and the SC/FM system (Nb/FePd).

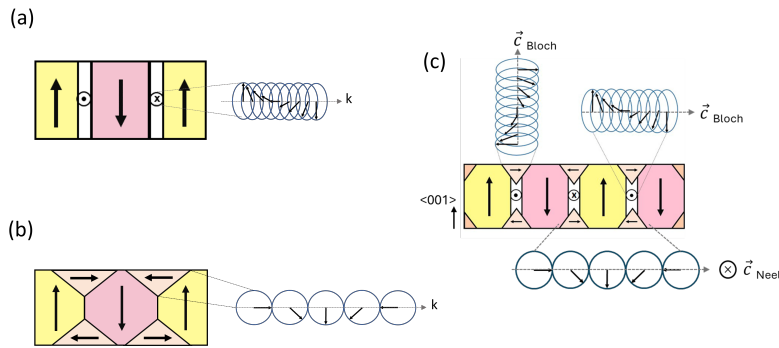


Fig. 10.10: Chirality of magnetic domains postulated in FePd thin films. (a) Bloch-type - favored by high PMA systems. (b) Néel-type - favored by low PMA systems with surface or interface 'closure domains'. (c) A combination of Bloch and Néel types may be found in systems with intermediate PMA.

10.6 Conclusions

Neutron reflectometry with polarized neutrons and polarization analysis is a tool to determine depth-dependent magnetization in layered magnetic nanostructures.

Non-Spinflip (NSF) reflectivity contains information about the magnetization components along the field direction of the different layers inside the structure. As (in magnetic saturation) the spin + neutrons are sensitive to $\rho_N + \rho_M$ and the spin - neutrons to $\rho_N - \rho_M$, the contrast seen by the neutrons with different spin is different due to the magnetized layers.

Spinflip (SF) reflectivity is purely induced by magnetization components perpendicular to the field direction. This makes it a very sensitive tool to determine magnetization rotation or tilting processes in magnetic structures and even in determining the presence of perpendicular magnetic anisotropy or a preferred chirality. Together with a quantitative modeling of the four reflectivity components, the size and direction of the in-plane components of the magnetization vector can be determined in all layers of a layered magnetic structure.

Off-specular and grazing incidence scattering are two ways to measure and characterize lateral correlations in a sample. Combined with neutron scattering and polarization analysis, these methods give powerful insight into the magnetic nanotexture of thin films and nanomaterials.

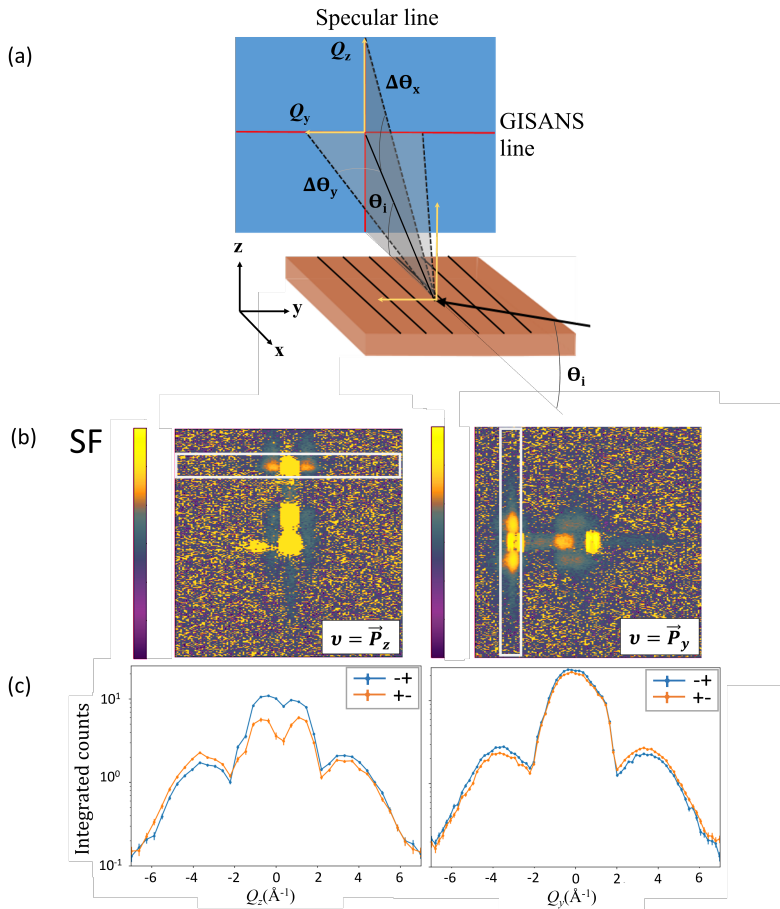


Fig. 10.11: a) A sketch of the GISANS geometry referring to the small angle approximations in equation (10.12). b) Detector maps of the GISANS signal for the polarization SF channels in the z - and y -directions. The grey boxes highlight the area of the GISANS signal. c) Integrated count plots of the area defined by the grey boxes showing a slight preference in chirality.

References

- [1] P. Grünberg, R. Schreiber, Y. Pang, M.B. Brodsky, and H. Sowers, *Phys. Rev. Lett.* **57**, 2442 (1996).
- [2] P.H. Dederichs: “Interlayer Exchange Coupling”, *chapter C3 in “Magnetism goes Nano”* (36th IFF Spring School, Forschungszentrum Jülich, Series Matter and Materials, Vol. 26, 2005).
- [3] G. Binasch, P. Grünberg, F. Saurenbach, and W. Zinn, *Phys. Rev. B* **39**, 4828 (1989).
- [4] M.N. Baibich, J.M. Broto, A. Fert, F. Nguyen Van Dau, et al., *Phys. Rev. Lett.* **61**, 2472 (1988).
- [5] D.E. Bürgler, “Spin-Transport in Layered Systems”, *chapter E5 in “Magnetism goes Nano”* (36th IFF Spring School, Forschungszentrum Jülich, Series Matter and Materials, Vol. 26, 2005).
- [6] U. Rücker, E. Kentzinger, “Thin Film Systems: Scattering under Grazing Incidence”, *chapter D4 in “Probing the Nanoworld”* (38th IFF Spring School Forschungszentrum Jülich, Series Matter and Materials, Vol. 34, 2007).
- [7] C. Fermon, *Physica B* **213-214**, 910 (1995).
- [8] B. Toperverg, O. Nikonov, V. Lauter-Pasyuk, and H. J. Lauter, *Physica B: Condensed Matter* **297**, 169 (2001).
- [9] O.A. Vail, S-W. Wang, Y. Hou, et al., *ACS Nano* **20**, 10737 (2026).
- [10] J. Stahn and A. Glavic, *J. Phys.: Conf. Ser.* **862**, 012007 (2017).
- [11] C. Fermon, F. Ott, B. Gilles, A. Marty, et al, *Physica B: Condensed Matter* **267-268**, 162 (1999).
- [12] G.L. Causer, L. Guasco, O. Paull, and D. Cortie, *physica status solidi (RRL) – Rapid Research Letters* **17**, 2200421 (2023).
- [13] S.J. Callori, T. Saerbeck, D.L. Cortie, K.W. Lin: “Chapter Three - Using polarized neutron reflectometry to resolve effects of light elements and ion exposure on magnetization” in: R.L. Stamps, editor, *Solid State Physics* (Academic Press, Cambridge, MA, 2020).
- [14] B. Toperverg and H. Zabel: “Neutron Scattering in Nanomagnetism” in F. Fernandez-Alonso and D. Price (eds.), *Experimental Methods in the Physical Sciences* (Academic Press, London, 2015).
- [15] E. Kentzinger, U. Rücker, B. Toperverg, F. Ott, and T. Brückel, *Phys. Rev. B* **77**, 104435 (2008).
- [16] A. Stellhorn, A. Sarkar, E. Kentzinger, M., Waschk, P. Schöffmann, S. Schröder, et al., *Journal of Magnetism and Magnetic Materials* **476**, 483 (2019).

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- [17] A. Stellan, J.G.C. Palma, A. Backs, A. Bergman, A.B. Klautau AB, E. Kentzinger, et al., *preprint arXiv*, 2604.02824 (2026).
 - [18] S. Blundell *Magnetism in Condensed Matter* (Oxford Academic, Oxford, 2001).
 - [19] M. Getzlaff *Fundamentals of Magnetism* (Springer, Berlin, 2008).
 - [20] J. Liang, M. Chshiev, A. Fert, H. Yang, *Nano Lett.* **24**, 10128 (2022).
 - [21] S.H. Yang, R. Naaman, Y. Paltiel, S.S.P. Parkin, *Nat Rev Phys.* **5**, 328 (2021).

Exercises

E10.1 Magnetic Contrast

We measure the polarized neutron reflectivity of a $[\text{Ni}_2\text{Fe}/\text{Pt}]_N$ multilayer structure in magnetic saturation. The Ni_2Fe alloy is ferromagnetic.

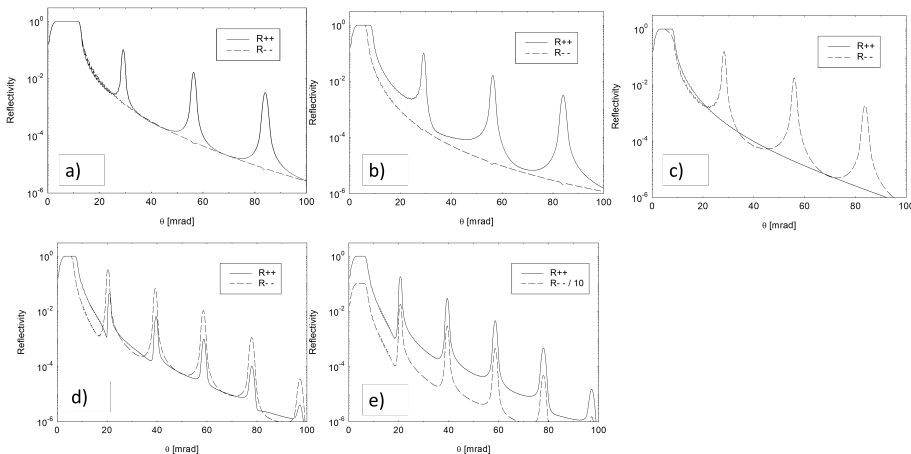
- a) Calculate the nuclear and magnetic scattering length densities for the two constituents of the multilayer:

	Ni	Fe	Pt
density (g/cm^3)	8.90	7.86	21.4
atomic weight (g/mol)	58.71	55.85	195.09
nuclear scattering length (10^{-14}m)	1.03	0.954	0.95
magnetic scattering length density ($10^{-6}\text{\AA}$)	1.52	5.12	0

If you don't want to calculate all the values yourself, you may continue with the tabulated values of the nuclear scattering length densities:

Ni: $9.41 \times 10^{-6} \text{\AA}^{-2}$, Fe: $8.09 \times 10^{-6} \text{\AA}^{-2}$, Pt: $6.29 \times 10^{-6} \text{\AA}^{-2}$.

- b) Which of the 5 reflectivity curves presented below is the one measured on this alloy? Think about the critical angle (has to do with the highest scattering length density in all layers) and the contrast between adjacent layers (influences the height of the diffraction peaks) for both spin directions parallel (R^{++}) and antiparallel (R^{--}) to the applied magnetic field (saturation!).



- c) The other 4 curves have been measured on different samples. Which curve belongs to which sample?

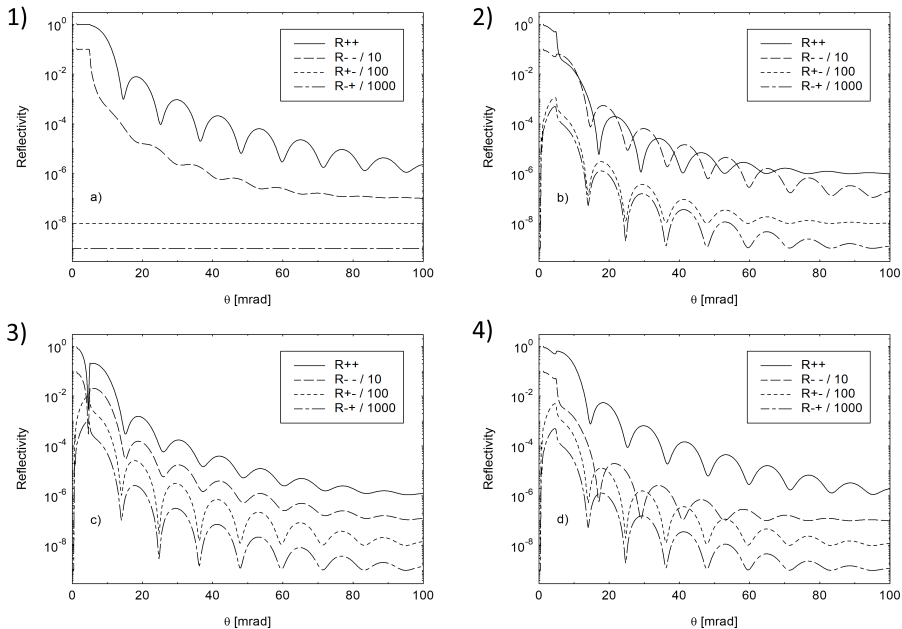
- i) The sum of nuclear and magnetic scattering length density of the magnetic layers is equal to the nuclear scattering length density of the nonmagnetic layers

- ii) The sample contains an additional nonmagnetic layer with a scattering length density higher than the sum of the magnetic and nuclear scattering length densities of Ni_2Fe on top of the $[\text{Ni}_2\text{Fe}/\text{Pt}]_N$ multilayer
- iii) No layer is magnetic
- iv) The nuclear scattering length density of the nonmagnetic layers is somewhere between the sum and the difference of nuclear and magnetic scattering length density of the magnetic layers

E10.2 Vector magnetometry

The following figures show polarized neutron reflectivity measurements with polarization analysis from a ferromagnetic single layer on a nonmagnetic substrate. Find out which figure belongs to which magnetization state:

- i) The sample is magnetized perpendicular to the field direction
- ii) The sample is magnetized parallel to the field direction
- iii) The magnetization of the sample is inclined by 45° against the field direction
- iv) This set of curves shows a chirality preference



11 Inelastic Neutron Scattering

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11.1 Introduction

One of the most important benefits of neutron scattering is the possibility to do inelastic scattering and by this way gain insight into the dynamics of materials as well as the structure. Neutrons tell us where the atoms are *and how they move* [1]. Although this feature is shared with inelastic x-ray scattering and dynamic light scattering, there is still a considerable range of slow dynamics in molecular systems which can be studied exclusively by inelastic neutron scattering.

This lecture can only present a short glimpse on the theoretical foundations and instrumental possibilities of inelastic neutron scattering. For those who are interested in more details, several textbooks can be recommended [2–6]. Also supplementary information on correlation functions [7] and Fourier transforms [8] may be found in earlier editions of this school.

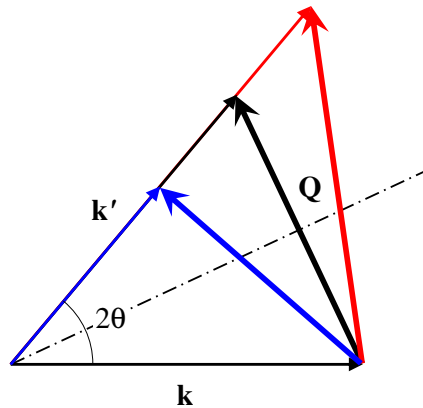


Fig. 11.1: Definition of the scattering vector Q in terms of the incident and final wave vectors k and k' . The black (isosceles) triangle corresponds to elastic scattering. The blue and red ones correspond to inelastic scattering with energy loss or gain of the scattered neutron, respectively.

11.2 Theory

11.2.1 Kinematics of neutron scattering

Up to this lecture it has always been tacitly assumed that the wavelength (or wave vector, or energy) of the neutrons is the same before and after scattering. The defining quality of *inelastic neutron scattering* is that this is not anymore the case. The neutrons may lose or gain energy in the collision with the nuclei. The characteristic quantity for the inelasticity is the energy transfer,

$$\hbar\omega = \Delta E = E' - E. \quad (11.1)$$

Here, E and E' are the energies of the neutron before and after the scattering. In the following, the notation $\hbar\omega$ will be used preferentially because it reveals the meaning of the energy transfer controlling the time scale of the observed dynamics, $1/\omega$.

Note that in some books E and E' represent the energy of the scattering system. This leads to a change of sign in ΔE . Even the wording “energy gain/loss” becomes ambiguous and should always be supplemented by “of the neutron” or “of the system”. Also, some authors prefer to write $E = E_{\text{final}} - E_{\text{initial}}$. So, it should always be checked whether E denotes the incident energy or the energy transfer.

$\hbar\omega \neq 0$ implies $k' \neq k$. As a consequence, Q now does not anymore result from the isosceles construction drafted in black in Fig. 11.1 but from scattering triangles as those in blue and red. Application of the cosine theorem leads to the following expression for Q in the inelastic situation:

$$Q = \sqrt{k^2 + k'^2 - 2kk' \cos(2\theta)} \quad (11.2)$$

$$= \sqrt{\frac{8\pi^2}{\lambda^2} + \frac{2m\omega}{\hbar} - \frac{4\pi}{\lambda} \sqrt{\frac{4\pi^2}{\lambda^2} + \frac{2m\omega}{\hbar}} \cos(2\theta)}. \quad (11.3)$$

Note that there is a fundamental difference to the simpler expression for elastic scattering,

$$Q_{\text{el}} = \frac{4\pi}{\lambda} \sin \theta, \quad (11.4)$$

used in the preceding lectures. Q now also depends on the energy transfer $\hbar\omega$ implying that Q is not anymore constant for a single scattering angle. Fig. 11.2 shows the magnitude of this effect for typical parameters of a neutron scattering experiment. It can be seen that it is by no means negligible for typical thermal energies of the sample even at temperatures as low as 100 K.

The other fundamental difference to elastic scattering to be considered is that the total scattering cross section is not identical anymore to the bound scattering cross section read from tables. In the extreme case of a free nucleus the scattering cross section is reduced to

$$\sigma = \frac{4\pi b^2}{(1 + m/M)^2} \quad (11.5)$$

where M is the mass of the scattering nucleus [2]. It can be seen that in the worst case (scattering from a gas of atomic hydrogen) this is a reduction by $1/4$.

11.2.2 Scattering from vibrating atoms

The most important case of inelastic neutron scattering from vibrating atoms is that of scattering from phonons in crystals. For the study of phonons, inelastic neutron scattering is the most important tool of research. At first, a short recapitulation of the phonon picture will be presented [9, 10].

As a simplified model for the crystal one can consider a chain of N atoms with mass M regularly spaced by a distance a and connected by springs with the spring constant K . For

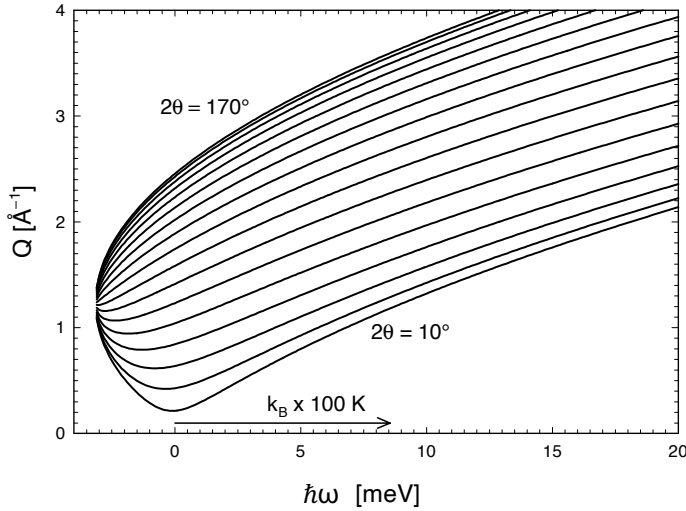


Fig. 11.2: Scattering vectors Q accessed by a neutron scattering experiment with the detector at scattering angles $2\theta = 10 \dots 170^\circ$ vs. the energy transfer $\hbar\omega$ (incident wavelength $\lambda = 5.1 \text{ \AA}$). For comparison the thermal energy $k_B T$ corresponding to 100 K is indicated by an arrow.

this system the equations of motion can readily be written down:

$$\frac{d^2 u_j}{dt^2} = \frac{K}{M} (u_{j+1} - 2u_j + u_{j-1}) . \quad (11.6)$$

In addition, it has to be specified what the equations of motions are for the first and the last atom (boundary condition). This is usually done by identifying the left neighbour of the first atom with the last and vice versa, $u_0 = u_N$ and $u_{N+1} = u_1$, as in a closed necklace rather than an open chain. This is the most natural choice for large N and called the Born-von-Kármán boundary condition. The equation system (11.6) can be solved by the ansatz

$$u_j(t) = \sum_k U_k(t) \exp\left(i \frac{kj}{N}\right) \quad (11.7)$$

with integer k ($k \in \mathbb{Z}$). Here, U_k are the *normal coordinates* and each of them fulfils the equation of motion of a single harmonic oscillator:

$$\frac{d^2 U_k}{dt^2} = \frac{2K}{M} \left(\cos \frac{2\pi k}{N} - 1 \right) U_k . \quad (11.8)$$

By introducing these *normal coordinates*, the system of differential equations (11.6) can be *decoupled* into a set of differential equations which can be solved separately. The solutions are

$$U_k(t) = A_k \exp(i\Omega_k t) \text{ with} \quad (11.9)$$

$$\Omega_k = \sqrt{\frac{2K}{M} \left(1 - \cos \frac{2\pi k}{N} \right)} = 2\sqrt{\frac{K}{M}} \left| \sin \frac{\pi k}{N} \right| . \quad (11.10)$$

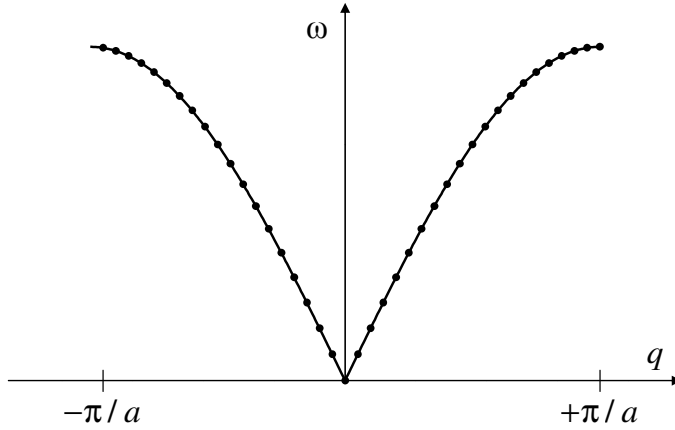


Fig. 11.3: Dispersion relation in a linear chain with $N = 40$ atoms (Born-von-Kármán boundary condition).

The second equation gives a relation between the index of the oscillator k and the frequency. On the other hand, the index determines via equation (11.7) the wavelength of the vibration. One wavelength covers N/k lattice positions, corresponding to $\lambda_{\text{vib}} = Na/k$ in actual length. The corresponding wave ‘vector’ is $q = 2\pi/\lambda_{\text{vib}} = 2\pi k/Na$ ¹. This implies that there is a relation between the wave vector and the frequency called the *dispersion relation* (Fig. 11.3):

$$\Omega(q) = 2\sqrt{\frac{K}{M}} \left| \sin \frac{qa}{2} \right|. \quad (11.11)$$

This relation does not contain the number of atoms anymore. For large N the points constituting the curve in Fig. 11.3 will get closer and closer, finally leading to the continuous function (11.11). The individual positions of these points depend on the boundary condition. But because they are getting infinitely dense for $N \rightarrow \infty$ the exact boundary conditions do not matter for a large system.

It can be seen that the dispersion relation (11.11) is periodic in q . On the other hand, there are only N normal coordinates necessary to solve the N original equations of motion. This is exactly the number of wave vectors found in a q interval of length $2\pi/a$. The usual choice is $-\pi/a \dots \pi/a$ as a representative zone for the dispersion relation.

There are two modifications necessary when considering a real three-dimensional crystal instead of this simplified model: (1) The crystal is periodic in three dimensions. (2) The vibrations are governed by quantum mechanics. The first requirement leads to the consequence that instead of a scalar, one has to use a real wave *vector*, $q \rightarrow \mathbf{q} = (q_x, q_y, q_z)$ in reciprocal space. The interval defined in Fig. 11.3 changes into a polyhedron called the first Brillouin zone (Fig. 11.4) [9, 10]. It is constructed in the same way as the Wigner-Seitz cell in real space: The Brillouin zone contains all points which are closer to the origin than to any other

¹ As will be seen later, there is a close connection between this lower case q and the scattering vector upper case Q . Nevertheless, they are not the same and care has to be taken not to mix up both q -s.

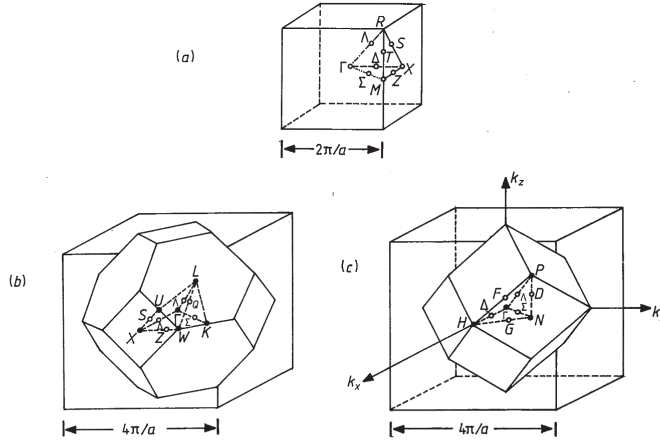


Fig. 11.4: Brillouin zones for cubic lattices: (a) simple cubic, (b) face-centred cubic, (c) body-centred cubic. From [10].

lattice point. Its surfaces are the bisecting planes between the origin and its neighbours (in reciprocal space).

For every amplitude A_k equation (11.9) gives a valid solution of the equations of motion. This means that in the classical picture the vibrations can have any energy. The quantum mechanical treatment (which is too complex to be treated here in detail) leads to the result that only certain energies with a distance of $\hbar\Omega_k$ are allowed. This quantisation implies that the vibrations can be treated as *quasiparticles* with the energy $\hbar\Omega_k$ called *phonons*. The increase of the vibrational amplitude corresponding to an energy change of $+\hbar\Omega_k$ is then seen as a creation, the inverse process as an annihilation of a phonon. Then it makes sense to define $\hbar\mathbf{q}$ as the momentum of the phonon. In this way the dispersion relation $\Omega(\mathbf{q})$ is similar to the relations shown in Fig. 4.2 of lecture 4 for real particles.

The introduction of the quasiparticle (phonon) concept leads to a simple interpretation of inelastic neutron scattering by vibrating lattices: The scattering process can be viewed as a collision between phonons and neutrons. In this process the energy as well as the momentum has to be conserved:

$$E' - E = \hbar\omega = \pm\hbar\Omega(\mathbf{q}), \quad (11.12)$$

$$\mathbf{k}' - \mathbf{k} = \mathbf{Q} = \pm\mathbf{q} + \mathbf{G}. \quad (11.13)$$

The second equation shows that the analogy with a two-particle collision is not complete. A wave vector, changed by a lattice vector $\mathbf{G}$ in reciprocal space, corresponds to the *same* phonon. In the one-dimensional case, this can be seen from equation (11.7): If one adds an integer multiple of N to k (corresponding to a multiple of $2\pi/a$ in q) all values of the complex exponential remain the same. Analogously, in the three dimensional case adding a lattice vector

$$\mathbf{G} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (h, k, l \in \mathbb{Z}) \quad (11.14)$$

does not change anything and momentum has only to be conserved up to an arbitrary reciprocal lattice vector. The condition (11.13) can also be visualised by the Ewald construction

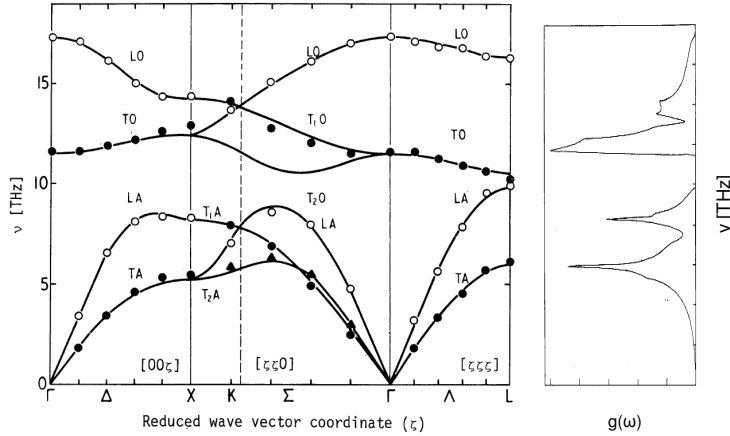


Fig. 11.5: Left: Phonon dispersion of NiO measured by inelastic neutron scattering. Frequencies are expressed as $\nu = \omega/2\pi$ and the wave vector is expressed in units of $\zeta = \pi/a$. The lattice is simple cubic, thus the symbols below the abscissa correspond to those in Fig. 11.4(a). Right: Phonon density of states (see section 11.2.3) of NiO plotted to the same scale in frequency. From [11].

as done in lecture 4 for elastic scattering.

From the conservation laws (11.12) and (11.13) one expects that the scattering intensity has sharp peaks at the positions where both conditions are fulfilled and is zero everywhere else. This is indeed so for coherent scattering, unless effects as multi-phonon scattering and anharmonicity are strong (usually at higher temperatures). Therefore, inelastic scattering allows the straightforward determination of the phonon dispersion relation as shown in Fig. 11.5.

In this figure, it can be seen that some of the phonon ‘branches’ start at the origin (*acoustic phonons*), as in the simple calculation of the one-dimensional chain. Others are ‘floating’ around high frequencies (*optical phonons*). The latter occur in materials with atoms of different weight or bond potential. (The one-dimensional chain would also produce these solutions if the masses were chosen differently for even and odd j .) In this case, a mode where all atoms of a unit cell move roughly in phase has the usual behaviour expected from the monatomic chain. In particular the dispersion relation at low q is a proportionality:

$$\Omega(q) = vq. \quad (11.15)$$

This relation is typical for sound waves. v is the sound velocity, longitudinal or transverse according to the type of phonons considered. In the polyatomic crystal or chain, there are additional modes where the atoms move in anti-phase. This implies a much higher deformation of the bonds. These vibrations constitute the optical phonon branches.

There is another difference between the one-dimensional chain and the three-dimensional crystal visible. The atomic displacements are not simply scalars u_j but vectors $\mathbf{u}_j$ which have a direction. This direction can be either parallel or perpendicular to the wave vector $\mathbf{q}$. Depending on this, one speaks of *longitudinal* and *transverse* phonons. The usual notation is LA, TA, LO, TO, where the first letter indicates the phonon polarisation and the

second whether it is acoustic or optical. An additional index as T_1A is used for $\mathbf{q}$ directions where the symmetry allows a distinction between the perpendicular orientations of $\mathbf{u}_j$. The full mathematical expression for the phonon scattering [2] includes an intensity factor proportional to $|\mathbf{Q} \cdot \mathbf{u}_j|^2$. This factor obviously vanishes if $\mathbf{Q}$ and $\mathbf{u}_j$ are perpendicular, implying that purely transverse modes are unobservable in the first Brillouin zone where $\mathbf{Q} = \mathbf{q}$.

It has to be noted, that the above arguments only hold for *coherent neutron scattering* (see equation (11.22) below) from crystalline materials. If the material is amorphous the coherent scattering will be diffuse (as it is for incoherent scattering always). The readily understandable reason for this is that the definition of the phonon wave vector $\mathbf{q}$ requires a lattice.

Finally, an indirect effect of vibrations on the elastic scattering should be mentioned. The elastic scattering (also for x-ray scattering) is reduced by the *Debye-Waller factor*. This reduction can be understood from a ‘hand-waving’ argument: Due to the thermal vibrations, atoms are displaced by $\mathbf{u}_j$ from their nominal lattice position. Although on the average $\langle \mathbf{u} \rangle$ is zero, there will be a finite *mean-square displacement* $\langle u^2 \rangle$. The Debye-Waller factor can be shown [2, 9] to be

$$\exp(-\langle (\mathbf{Q} \cdot \mathbf{u}) \rangle) = \exp(-Q^2 \langle u^2 \rangle / 3) \quad (11.16)$$

where the second expression is only valid for isotropic conditions. It can be seen that the attenuation of diffraction peaks increases with increasing Q and increasing mean-square displacement, that is at higher temperature. Note, that this does *not* mean that elastic scattering can observe dynamics, because a permanent static displacement of the atoms would have the same effect.

The treatment of inelastic scattering by spin waves is very similar to that of deformation waves above. In analogy to the phonon the quasiparticle “magnon” is introduced. For this purpose, the displacement $\mathbf{u}_j$ is replaced by the orientation of the spin. The construction of normal modes (Bloch waves) and the quantisation proceeds in the same way as for phonons. As explained in lecture 7 neutrons interact with the nuclei as well as with the magnetic moments of nuclei and electrons. Therefore, inelastic neutron scattering is also a tool for the detection of magnons and this has been one of its first applications [12].

11.2.3 Scattering from diffusive processes

For the inelastic scattering from vibrational motions it was practical to consider the scattering as a process between (quasi)particles, neutrons and phonons/magnons. But there are many types of molecular motions, mostly irregular and only statistically defined, which cannot be treated in this concept, e.g. thermally activated jumps or Brownian motion. For these motions it is more adequate to use a concept of *correlation functions* to calculate the scattering.

Because these ‘diffusive’ processes are usually much slower than phonon frequencies it is in most cases not necessary to treat them quantum-mechanically. Therefore, in this section, a picture of the scattering material will be used where the positions of all scatterers are given as functions of time $\mathbf{r}_j(t)$ (trajectories)². In this picture the *double differential cross-section*, defined as the probability density that a neutron is scattered into a solid angle element $d\Omega$

² This treatment also ignores that in the scattering process the trajectories of the scattering particles are modified, i.e. recoil effects. The consequences of this approximation are outlined by the end of this section.

with an energy transfer $\hbar\omega \dots \hbar(\omega + d\omega)$, is

$$\frac{d\sigma}{d\Omega d\omega} = \frac{1}{2\pi} \frac{k'}{k} \int_{-\infty}^{\infty} e^{-i\omega t} dt \sum_{j,k=1}^N b_j^* b_k \langle e^{i\mathbf{Q} \cdot (\mathbf{r}_k(t) - \mathbf{r}_j(0))} \rangle. \quad (11.17)$$

In order to derive a quantity similar to the structure factor $S(\mathbf{Q})$ in lectures 6 and 15, one assumes again a system of N *chemically* identical particles. Because the neutron scattering length is a nuclear property, there may still be a variance of scattering lengths. And even in monoisotopic systems, there may be such a variance due to disorder of the nuclear spin orientations, since the scattering length also depends on the combined spin state of the scattered neutron and the scattering nucleus³. Therefore, it is assumed that scattering lengths are randomly distributed with the average $\bar{b} = (1/N) \sum_j b_j$ and the variance $\overline{|b|^2} - |\bar{b}|^2 = \overline{|b - \bar{b}|^2} = (1/N) \sum_i |b_i - \bar{b}|^2$. As will be seen later, this gives rise to the *incoherent scattering* contribution which is usually found in neutron scattering (in contrast to x-ray scattering). The sum in expression (11.17) can be decomposed into one over different indices and one over identical indices:

$$\sum_{j,k=1}^N b_j^* b_k e^{i\mathbf{Q} \cdot (\mathbf{r}_k(t) - \mathbf{r}_j(0))} = \sum_{j \neq k=1}^N b_j^* b_k e^{i\mathbf{Q} \cdot (\mathbf{r}_k(t) - \mathbf{r}_j(0))} + \sum_{j=1}^N |b_j|^2 e^{i\mathbf{Q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))}. \quad (11.18)$$

They have to be averaged in different ways with respect to the distribution of scattering lengths. In the first term b_j^* and b_k can be averaged separately because the different particle scattering lengths are uncorrelated: $\overline{b^* b} = \overline{b^*} \overline{b} = |\bar{b}|^2$. In the second term one has to average *after* taking the absolute square:

$$= \sum_{j \neq k=1}^N |\bar{b}|^2 e^{i\mathbf{Q} \cdot (\mathbf{r}_k(t) - \mathbf{r}_j(0))} + \sum_{j=1}^N \overline{|b|^2} e^{i\mathbf{Q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))}. \quad (11.19)$$

In order to avoid the sum over distinct particles, the first sum is complemented by the $j = k$ terms, $|\bar{b}|^2 e^{i\mathbf{Q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))}$, and to compensate, these terms are subtracted in the second sum:

$$= \sum_{j,k=1}^N |\bar{b}|^2 e^{i\mathbf{Q} \cdot (\mathbf{r}_k(t) - \mathbf{r}_j(0))} + \sum_{j=1}^N \left(\overline{|b|^2} - |\bar{b}|^2 \right) e^{i\mathbf{Q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))}. \quad (11.20)$$

With this result it is possible to express the double differential cross section as

$$\frac{\partial \sigma}{\partial \Omega \partial \omega} = N \frac{k'}{k} \left(|\bar{b}|^2 S_{\text{coh}}(\mathbf{Q}, \omega) + \left(\overline{|b|^2} - |\bar{b}|^2 \right) S_{\text{inc}}(\mathbf{Q}, \omega) \right) \quad (11.21)$$

with

$$S_{\text{coh}}(\mathbf{Q}, \omega) = \frac{1}{2\pi N} \int_{-\infty}^{\infty} e^{-i\omega t} dt \sum_{j,k=1}^N \langle e^{i\mathbf{Q} \cdot (\mathbf{r}_k(t) - \mathbf{r}_j(0))} \rangle \quad (11.22)$$

and

$$S_{\text{inc}}(\mathbf{Q}, \omega) = \frac{1}{2\pi N} \int_{-\infty}^{\infty} e^{-i\omega t} dt \sum_{j=1}^N \langle e^{i\mathbf{Q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))} \rangle. \quad (11.23)$$

³ In this section only nuclear non-magnetic scattering will be considered. For a full treatment of magnetic scattering see lecture 7 or vol. 2 of ref. 2.

The quantities defined by (11.22) and (11.23) are called *coherent* and *incoherent scattering function* or *dynamic structure factors*. It is a peculiarity of neutron scattering that there is also the incoherent term, which solely depends on the *single particle dynamics* due to the variance of the scattering lengths.

The prefactors of the scattering functions in expression (11.21) are often replaced by the scattering cross sections

$$\sigma_{\text{coh}} = 4\pi |\bar{b}|^2, \quad \sigma_{\text{inc}} = 4\pi \left(\overline{|b|^2} - |\bar{b}|^2 \right). \quad (11.24)$$

They give the scattering into all directions, i.e. the solid angle 4π (for the incoherent part in general and for the coherent in the limit $Q \rightarrow \infty$).

As demonstrated in ref. 2, it is also possible to use the concept of correlation functions for phonons. In this way it is possible to calculate the scattering from phonons in terms of $S_{\text{coh}}(\mathbf{Q}, \omega)$ and $S_{\text{inc}}(\mathbf{Q}, \omega)$. The result for the coherent scattering gives non-vanishing contributions only for $(\mathbf{Q}, \omega)$ combinations which fulfil the conservation laws (11.12) and (11.13). This was already shown in section 11.2.2 but the explicit calculation gives also the intensity of the phonon peaks, e.g. the mentioned result that transverse phonon peaks vanish in the first Brillouin zone. But with this mathematical approach it is also possible to calculate the incoherent scattering which is not bound to the momentum conservation (11.13). The result is for inelastic incoherent neutron scattering from cubic crystals in the one-phonon approximation [2]:

$$S_{\text{inc}}(\mathbf{Q}, \omega \neq 0) = \frac{\hbar Q^2}{2M} \exp(-2W(\mathbf{Q})) \frac{g(|\omega|)}{\omega} \frac{1}{\exp(\hbar\omega/k_{\text{B}}T) - 1} \quad (11.25)$$

$$\xrightarrow{\text{high } T \text{ limit}} \exp(-2W(\mathbf{Q})) \frac{Q^2 k_{\text{B}} T}{2M} \frac{g(|\omega|)}{\omega^2}. \quad (11.26)$$

(Here, $\exp(-2W(\mathbf{Q}))$ is a shorthand for the Debye-Waller factor (11.16).) From this expression it can be seen that the incoherent scattering is determined by the *phonon density of states* $g(\omega)$ alone and does not depend on the full details of the phonon dispersion. The density of states $g(\omega)$ is the projection of the phonon dispersion curves onto the frequency axis, as demonstrated in Fig. 11.5. Besides nuclear inelastic scattering, which requires Mößbauer-active nuclei, inelastic incoherent neutron scattering is the most important method to determine $g(\omega)$.

In some cases it is interesting to consider the part of expression (11.22) before the time-frequency Fourier transform, called *intermediate coherent scattering function*:

$$I_{\text{coh}}(\mathbf{Q}, t) = \frac{1}{N} \sum_{jk} \langle e^{i\mathbf{Q} \cdot (\mathbf{r}_k(t) - \mathbf{r}_j(0))} \rangle. \quad (11.27)$$

Its value for $t = 0$ expresses the correlation between atoms *at equal times*. A theorem on Fourier transforms tells that this is identical to the integral of the scattering function over all energy transfers:

$$I_{\text{coh}}(\mathbf{Q}, 0) = \frac{1}{N} \sum_{jk} \langle e^{i\mathbf{Q} \cdot (\mathbf{r}_k - \mathbf{r}_j)} \rangle = S(\mathbf{Q}) = \int_{-\infty}^{\infty} S_{\text{coh}}(\mathbf{Q}, \omega) d\omega. \quad (11.28)$$

($S(\mathbf{Q})$ is the structure factor as derived in lecture 5 for the static situation.) This integral relation has a concrete relevance in diffraction experiments. There, the energy of the neutrons is not discriminated: The diffraction experiment implicitly integrates over all $\hbar\omega$ ⁴. Equation (11.28) shows that this integral corresponds to the instantaneous correlation of the atoms. The diffraction experiment performs a ‘snapshot’ of the structure. All dynamic information is lost in the integration process and therefore it is invisible in a diffraction experiment.

Similarly the *incoherent intermediate scattering function* is

$$I_{\text{inc}}(\mathbf{Q}, t) = \frac{1}{N} \sum_{j=1}^N \langle e^{i\mathbf{Q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))} \rangle \quad (11.29)$$

with

$$I_{\text{inc}}(\mathbf{Q}, 0) = \frac{1}{N} \sum_{j=1}^N \langle e^{i\mathbf{Q} \cdot (\mathbf{r}_j - \mathbf{r}_j)} \rangle = 1 = \int_{-\infty}^{\infty} S_{\text{inc}}(\mathbf{Q}, \omega) d\omega. \quad (11.30)$$

Note that this result is independent of the actual structure of the sample. Integration of the double-differential cross section (11.21) over ω shows that also the static scattering contains an incoherent contribution. But because of (11.30), this term is constant in Q . It contributes as a flat background in addition to the $S(Q)$ -dependent scattering. In some cases (e.g. small-angle scattering) it may be necessary to correct for this, in other cases (e.g. diffraction with polarisation analysis) it may even be helpful to normalise the coherent scattering.

In the paragraphs before it was shown, that the value of the intermediate scattering functions at $t = 0$ corresponds to the integral of the scattering function over an infinite interval. This is a consequence of a general property of the Fourier transform. There is also the inverse relation that the value of $S(\mathbf{Q}, \omega)$ at $\omega = 0$ is related to the integral of $I(\mathbf{Q}, t)$ over all times. The most important case is here when $I(\mathbf{Q}, t)$ does not decay to zero for infinite time, but to a finite value $f(\mathbf{Q})$. In that case the integral is infinite, implying that $S(\mathbf{Q}, \omega)$ has a delta function contribution at $\omega = 0$. This means that the scattering contains a strictly elastic component. Its strength can be calculated by decomposing the intermediate scattering function into a completely decaying part and a constant for the coherent and the incoherent scattering:

$$I_{[\text{coh}|\text{inc}]}(\mathbf{Q}, t) = I_{[\text{coh}|\text{inc}]}^{\text{inel}}(\mathbf{Q}, t) + f_{[\text{coh}|\text{inc}]}(\mathbf{Q}). \quad (11.31)$$

Because the Fourier transform of constant one is the delta function this corresponds to

$$S_{[\text{coh}|\text{inc}]}(\mathbf{Q}, \omega) = S_{[\text{coh}|\text{inc}]}^{\text{inel}}(\mathbf{Q}, \omega) + S_{[\text{coh}|\text{inc}]}^{\text{el}}(\mathbf{Q})\delta(\omega), \quad (11.32)$$

where $S_{[\text{coh}|\text{inc}]}^{\text{el}}(\mathbf{Q}) = f_{[\text{coh}|\text{inc}]}(\mathbf{Q})$, the *elastic coherent/incoherent structure factor* (EISF), can

⁴ Strictly speaking, this is only an approximation. There are several reasons why the integration in the diffraction experiment is not the ‘mathematical’ one of (11.28): (1) On the instrument the integral is taken along a curve of constant 2θ in Fig. 11.2 while constant Q would correspond to a horizontal line. (2) The double differential cross-section (11.21) contains a factor k'/k which depends on ω via (11.2). (3) The detector may have an efficiency depending on wavelength which will introduce another ω -dependent weight in the experimental integration. All these effects have been taken into account in the so-called Placzek corrections [8, 13, 14].

be written as

$$S_{\text{coh}}^{\text{el}}(\mathbf{Q}) = \frac{1}{N} \sum_{j,k=1}^N \langle e^{i\mathbf{Q} \cdot (\mathbf{r}_k(\infty) - \mathbf{r}_j(0))} \rangle, \quad (11.33)$$

$$S_{\text{inc}}^{\text{el}}(\mathbf{Q}) = \frac{1}{N} \sum_{j=1}^N \langle e^{i\mathbf{Q} \cdot (\mathbf{r}_j(\infty) - \mathbf{r}_j(0))} \rangle. \quad (11.34)$$

Here, $t = \infty$ indicates a time which is sufficiently long that the correlation with the position at $t = 0$ is lost. For the EISF this lack of correlation implies that the terms with initial and final positions can be averaged separately:

$$\begin{aligned} S_{\text{inc}}^{\text{el}}(\mathbf{Q}) &= \frac{1}{N} \sum_{j=1}^N \langle e^{i\mathbf{Q} \cdot \mathbf{r}_j} \rangle \langle e^{-i\mathbf{Q} \cdot \mathbf{r}_j} \rangle \\ &= \frac{1}{N} \sum_{j=1}^N |e^{-i\mathbf{Q} \cdot \mathbf{r}_j}|^2 \end{aligned} \quad (11.35)$$

$$= \frac{1}{N} \sum_{j=1}^N \left| \int_V d^3r \exp(i\mathbf{Q} \cdot \mathbf{r}) \rho_j(\mathbf{r}) \right|^2. \quad (11.36)$$

Here, $\rho_j(\mathbf{r})$ denotes the ‘density of particle j ’, i.e. the probability density of the individual particle j being at $\mathbf{r}$. From (11.35) one can see that the normalisation of the EISF is $S_{\text{inc}}^{\text{el}}(0) = 1$ (in contrast to that of the structure factor, $\lim_{Q \rightarrow \infty} S(Q) = 1$). One can say that the EISF is the form factor of the volume confining the motion of the particles. E.g. for particles performing any kind of motion within a sphere, the EISF would be $S_{\text{inc}}^{\text{el}}(Q) = 9(\sin(QR) - QR \cos(QR))^2 / Q^6 R^6$ as derived in lecture 5.

As in the static situation, the scattering law can be traced back to distance distribution functions. These are now (in the treatment of inelastic scattering) time-dependent. They are called *van Hove correlation functions*:

$$G(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{j,k=1}^N \delta(\mathbf{r} - \mathbf{r}_k(t) + \mathbf{r}_j(0)) \right\rangle, \quad (11.37)$$

$$G_s(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j(t) + \mathbf{r}_j(0)) \right\rangle. \quad (11.38)$$

Insertion into

$$I_{\text{coh}} = \int_{V_d} G(\mathbf{r}, t) \exp(i\mathbf{Q} \cdot \mathbf{r}) d^3r \quad \text{or} \quad (11.39)$$

$$I_{\text{inc}} = \int_{V_d} G_s(\mathbf{r}, t) \exp(i\mathbf{Q} \cdot \mathbf{r}) d^3r \quad (11.40)$$

directly proves that the spatial Fourier transforms of the van Hove correlation function are the intermediate scattering functions.

The two particle version can be reduced to the microscopic density,

$$\rho(\mathbf{r}, t) = \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j(t)). \quad (11.41)$$

Its autocorrelation function in space and time is

$$\langle \rho(\mathbf{0}, 0) \rho(\mathbf{r}, t) \rangle. \quad (11.42)$$

The $\mathbf{0}$ is showing that translational symmetry is assumed. So the correlation function can be replaced by its average over all starting points $\mathbf{r}_1$ in the sample volume:

$$\langle \rho(\mathbf{0}, 0) \rho(\mathbf{r}, t) \rangle = \frac{1}{V} \int_V d^3r_1 \langle \rho(\mathbf{r}_1, 0) \rho(\mathbf{r}_1 + \mathbf{r}, t) \rangle. \quad (11.43)$$

Insertion of (11.41) gives

$$\langle \rho(\mathbf{0}, 0) \rho(\mathbf{r}, t) \rangle = \frac{1}{V} \left\langle \sum_{j,k=1}^N \int_V d^3r_1 \delta(\mathbf{r}_1 - \mathbf{r}_k(t)) \delta(\mathbf{r}_1 + \mathbf{r} - \mathbf{r}_j(t)) \right\rangle \quad (11.44)$$

$$= \frac{1}{V} \left\langle \sum_{j,k=1}^N \delta(\mathbf{r}_k(t) + \mathbf{r} - \mathbf{r}_j(t)) \right\rangle. \quad (11.45)$$

Together with (11.37) this implies

$$G(\mathbf{r}, t) = \frac{1}{\rho_0} \langle \rho(\mathbf{0}, 0) \rho(\mathbf{r}, t) \rangle. \quad (11.46)$$

Again setting $t = 0$ results in the static scattering situation:

$$G(\mathbf{r}, 0) = \frac{\langle \rho(\mathbf{0}, 0) \rho(\mathbf{r}, 0) \rangle}{\rho_0} = \delta(\mathbf{r}) + \rho_0 g(\mathbf{r}) \quad (11.47)$$

with $g(\mathbf{r})$ as defined in lecture 5.

As in the case of static scattering there is an alternative way to derive the scattering function by Fourier-transforming the density

$$\rho_{\mathbf{Q}}(t) = \int d^3r e^{i\mathbf{Q} \cdot \mathbf{r}} \rho(\mathbf{r}, t) = \sum_{j=1}^N e^{i\mathbf{Q} \cdot \mathbf{r}_j(t)} \quad (11.48)$$

and then multiplying its conjugated value at $t = 0$ with that at t :

$$I_{\text{coh}}(\mathbf{Q}, t) = \frac{1}{N} \langle \rho_{\mathbf{Q}}^*(0) \rho_{\mathbf{Q}}(t) \rangle \quad (11.49)$$

(This is a consequence of the Wiener-Khintchine theorem.) and

$$S_{\text{coh}}(\mathbf{Q}, \omega) = \frac{1}{2\pi N} \int_{-\infty}^{\infty} e^{-i\omega t} \langle \rho_{\mathbf{Q}}^*(0) \rho_{\mathbf{Q}}(t) \rangle dt. \quad (11.50)$$

Note that a reduction of the self correlation function $G_s(\mathbf{r}, t)$ to the density is *not* possible in the same way. The multiplication $\rho(\mathbf{0}, 0)\rho(\mathbf{r}, t)$ in equation (11.46) inevitably includes all combinations of particles j, k and not only the terms for identical particles j, j . Therefore, the incoherent scattering cannot be derived from the density alone but requires the knowledge of the motion of the individual particles.

From the definitions (11.37) and (11.38) it is immediately clear that the van Hove correlation functions (as defined here) are symmetric in time

$$G(\mathbf{r}, -t) = G(\mathbf{r}, t), \quad G_s(\mathbf{r}, -t) = G_s(\mathbf{r}, t) \quad (11.51)$$

if the system is dynamically symmetric to an inversion of space. From (11.51) and general properties of the Fourier transform it follows that $I(\mathbf{Q}, t)$ is real and that it is also symmetric in time:

$$I(\mathbf{Q}, -t) = I(\mathbf{Q}, t) \quad (11.52)$$

(here and in the following for both the coherent and incoherent versions). In turn this implies that the scattering functions are real and symmetric in energy transfer $\hbar\omega$:

$$S(\mathbf{Q}, -\omega) = S(\mathbf{Q}, \omega). \quad (11.53)$$

It can be seen that this identity violates the principle of detailed balance. Up- and downscattering should rather be related by

$$S(\mathbf{Q}, -\omega) = \exp\left(\frac{\hbar\omega}{k_B T}\right) S(\mathbf{Q}, \omega). \quad (11.54)$$

The reason for this is that (as mentioned in footnote 2) the influence of the neutron's impact on the motion of the system particles is neglected. This would be included in a full quantum-mechanical treatment as carried out in ref. 2 or ref. 8 where the detailed balance relation (11.54) emerges in a natural way. Note that equation (11.54) implies that both $I(\mathbf{Q}, t)$ and $G(\mathbf{r}, t)$ are complex functions. (This is not 'unphysical' because they are no directly measurable quantities in contrast to $S(\mathbf{Q}, \omega)$ which is proportional to $d\sigma/d\Omega d\omega$. Even neutron spin-echo measures only the real part of $I(\mathbf{Q}, t)$, see equation (11.71).)

Because the detailed balance relation (11.54) is also valid in classical thermodynamics (and also recoil can be understood in the framework of classical mechanics) there should be a way to derive a correct result from a classical treatment of the system too. This task is important because only rather simple systems can be treated quantum-mechanically. Especially, results from molecular dynamics computer simulations are classical results. The result for $S(\mathbf{Q}, \omega)$ derived here is obviously only a crude approximation. Better approximations can be obtained by applying correction factors restoring (11.54) [16–18]. The 'exact classical' calculation is rather complicated [19] and requires knowledge of the system beyond just the trajectories of the particles.

Inelastic scattering is often also called neutron (scattering) spectroscopy. That there is indeed a relation to better-known spectroscopic methods as light spectroscopy, can be seen from the dependence of the scattering function on a frequency ω . It can be said that inelastic neutron scattering, for every $\mathbf{Q}$, produces a spectrum, understood as the frequency dependence of a quantity, here the scattering cross section. The optical methods Raman- and Brillouin spectroscopy are completely analogous in this respect, yielding the same $S(\mathbf{Q}, \omega)$ but different

measured double-differential cross-sections because photons interact with matter differently. Other methods, as absorption spectroscopy, impedance spectroscopy or rheology do not yield a Q dependence and are thus insensitive to the molecular structure. They provide only information about the overall dynamics. The deeper reason for this analogy is that scattering experiments as well as ‘ordinary’ spectroscopy can be explained by linear response theory (appendix B of ref. 2 or ref. 15).

Example: diffusion

For simple diffusion the density develops in time following Fick’s second law,

$$\frac{\partial \rho}{\partial t} = D \Delta \rho \equiv D \left(\frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial y^2} + \frac{\partial^2 \rho}{\partial z^2} \right). \quad (11.55)$$

The underlying mechanism is Brownian motion, i.e. random collisions with solvent molecules. Therefore, it can be concluded from the central limit theorem of statistics that the density of particles initially assembled at the origin is a Gaussian in all coordinates:

$$\begin{aligned} \rho_1 &= \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{x^2}{2\sigma^2}\right) \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{y^2}{2\sigma^2}\right) \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{z^2}{2\sigma^2}\right) \\ &= \frac{1}{(2\pi)^{3/2}\sigma^3} \exp\left(-\frac{r^2}{2\sigma^2}\right). \end{aligned} \quad (11.56)$$

The index 1 should remind that the prefactor is chosen such that the total particle number $\int \rho_1 d^3r$ is normalised to one. The width of the distribution, σ has the dimension length. The only way to construct a length out of D (dimension length²/time) and time is $\sigma = c\sqrt{Dt}$ where c is a dimensionless constant. Inserting this into (11.56) yields:

$$\rho_1 = \frac{1}{c^3(2\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{2c^2 Dt}\right). \quad (11.57)$$

The derivatives of this expression with respect to t and x, y, z can be calculated and inserted into (11.55):

$$\frac{\sqrt{2}(r^2 - 3c^2 Dt)}{8\pi^{3/2}c^5 D^{5/2}t^{7/2}} \exp\left(-\frac{r^2}{2c^2 Dt}\right) = \frac{\sqrt{2}(r^2 - 3c^2 Dt)}{4\pi^{3/2}c^7 D^{7/2}t^{7/2}} \exp\left(-\frac{r^2}{2c^2 Dt}\right). \quad (11.58)$$

One can see that the right- and left-hand side are identical if $c = \sqrt{2}$. This proves that the ‘guess’ (11.56) is indeed a solution of Fick’s second law and also determines the unknown c . With the value of c substituted, the ‘single particle density’ is

$$\rho_1 = \frac{1}{(8\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right). \quad (11.59)$$

Diffusion-like processes are often characterised by the *mean-square displacement* $\langle r^2 \rangle$ ⁵. Because of the statistical isotropy, the average displacement $\langle r \rangle$ is always zero. Therefore, the

⁵ Here, the definition is “displacement from the position at $t = 0$ ” rather than “displacement from a potential minimum” on page 8. This is an obvious choice because the diffusing particle is not subjected to a potential as the atom in a crystal. Therefore, there is nothing like an ‘equilibrium position’. This difference is indicated by the usage of $\langle r^2 \rangle$ instead of $\langle u^2 \rangle$. Because in the case of motion in a potential the displacement between time zero and time t can be understood as the difference of the displacements at time zero from the equilibrium position and that at time t , it follows that $\langle r^2 \rangle = 2\langle u^2 \rangle$

characterisation of the mobility of a diffusional process has to be done using the second moment, which is the average of the square of the displacement. For the simple Fickian diffusion this can be calculated from (11.59):

$$\langle r^2 \rangle = \int \rho_1 r^2 4\pi r^2 dr = 6Dt. \quad (11.60)$$

For incoherent scattering the starting position $\mathbf{r}(0)$ is irrelevant. Therefore, expression (11.59) is also $G_s(r, t)$. Because the Fourier transform of a Gaussian function is a Gaussian itself, the corresponding incoherent intermediate scattering function is

$$I_{\text{inc}}(Q, t) = \exp(-DQ^2t), \quad (11.61)$$

and because the Fourier transform of an exponential decay is a Lorentzian the incoherent scattering function is

$$S_{\text{inc}}(Q, \omega) = \frac{1}{\pi} \frac{DQ^2}{\omega^2 + (DQ^2)^2}. \quad (11.62)$$

This function is centred around $\omega = 0$, and for that reason the scattering is called *quasielastic*. This is typical for diffusionlike processes in contrast to vibrational processes which yield (phonon) peaks at finite energy transfers. For this reason, many textbook authors distinguish between inelastic and quasielastic neutron scattering instead of subsuming the latter under the former as done here⁶.

From expression (11.61) one can see that $I_{\text{inc}}(Q, t)$ decays faster with time for larger Q and from (11.62) that $S_{\text{inc}}(Q, \omega)$ is getting broader. This is understandable because Q defines the spatial resolution of a neutron scattering experiment in a reciprocal way. So a larger Q means observation on shorter distances which can be travelled faster by the diffusing particle.

Finally, one can see that

$$I_{\text{inc}}(Q, t) = \exp\left(-\frac{Q^2 \langle r^2 \rangle}{6}\right). \quad (11.63)$$

Because this expression is derived independently of the specific form of $\sigma(t)$ in (11.56) it is generally valid if the distribution of displacements $G_s(r, t)$ is a Gaussian. Even if this is not the case, equation (11.63) is often a good low- Q approximation called the *Gaussian approximation*⁷ and is the dynamical analogue of to the Guinier approximation of static scattering.

In general, the incoherent intermediate scattering function cannot be derived from the mean-square displacement alone. Because equation (11.63) is the first term of the cumulant expansion $\exp(aQ^2 + bQ^4 + \dots)$ of $I_{\text{inc}}(Q, t)$ [20] the mean-square displacement can be calculated

⁶ There are two reasons for the choice made here: (1) The correlation function approach is also applicable to phonons. So, if this method is used, there is no conceptual difference between the treatment of vibrations and diffusion. (2) There are models as the damped harmonic oscillator which yield a continuous transition between inelastic scattering in the underdamped case and quasielastic scattering in the overdamped case.

⁷ In the literature, denominators 1, 2, and 3 are also found in this expression. Most of these formulae are nevertheless correct. Some authors use $\langle r^2 \rangle$ as mean-square displacement from an average position (what is called $\langle u^2 \rangle$ here). Then, 3 is the correct denominator because of $\langle r^2 \rangle = 2\langle u^2 \rangle$ (footnote 5). If the displacement is considered only in one coordinate ($\langle x^2 \rangle$), then 2 is the right denominator.

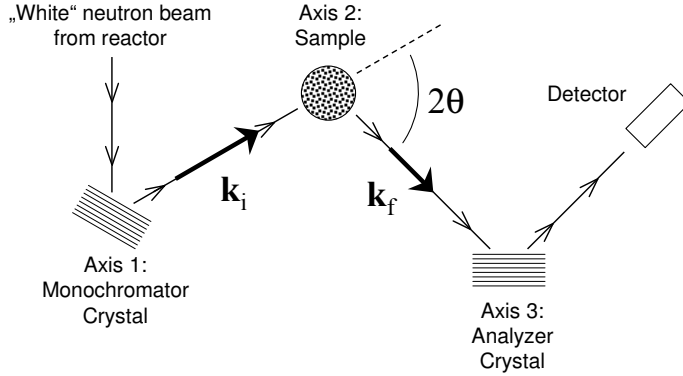


Fig. 11.6: Schematic setup of a triple-axis spectrometer.

as

$$\langle r^2 \rangle = - \lim_{Q \rightarrow 0} \frac{6}{Q^2} \ln I_{\text{inc}}(Q, t) \quad \text{or} \quad (11.64)$$

$$\langle r^2 \rangle = - \left. \frac{d \ln I_{\text{inc}}(Q, t)}{dQ^2} \right|_{Q=0}. \quad (11.65)$$

By replacing $I_{\text{inc}}(Q, t)$ by its value at infinite time, the EISF $S_{\text{inc}}^{\text{el}}(Q)$, the limiting mean-square displacement of a confined motion can be obtained. This is the principle of the *elastic scan* technique often used on neutron backscattering spectrometers [21].

11.3 Instrumentation

11.3.1 Triple axis spectrometer

The basic objective of inelastic neutron scattering is to measure the momentum transfer $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ and the energy transfer $\hbar\omega = E' - E$. This task in general requires a monochromator for the incoming neutron beam and an analyzer for the scattered neutrons. In the most straightforward setup, the triple-axis spectrometer (3AX), one uses the Bragg planes of crystals similar to the diffracting grids in an optical spectrometer (figure 11.6).

Axis 1 turns the monochromator crystal. By doing this the neutron wavelength fulfilling the Bragg condition can be changed. In this way the wave vector $k = 2\pi/\lambda$ of the neutrons impinging on the sample is determined. Axis 2 turns the arm carrying the analyser crystal around the sample position. This defines the scattering angle 2θ . Finally, axis 3 turns the analyser crystal around its own axis such that only the desired k' is admitted to the detector.

For a given setting of axis 1 all points in the kinematically allowed (Q, ω) area (see Fig. 11.2) can be addressed by suitable settings of axis 2 and 3. E.g., for the study of phonons usually a 'constant- Q scan' is performed where $\mathbf{Q} = \mathbf{k}' - \mathbf{k}$ is held constant and only $\hbar\omega = E' - E$

is varied. For this purpose a coordinated change of the angles of axis 2 and 3 is required which is accomplished by computer control.

Historically, the triple-axis spectrometer is the first inelastic neutron scattering instrument. The first prototype was constructed in 1955 by Bertram N. Brockhouse. In 1994, Brockhouse received the Nobel prize for this accomplishment (together with Clifford G. Shull for the development of neutron diffraction).

The 3AX spectrometer is still widely in use for purposes where a high Q resolution is necessary and only a small region in the (Q, ω) plane has to be examined. This is mostly the study of phonons and magnons in crystals. In other fields, e.g. for ‘soft matter’ systems, it has been replaced by instruments showing better performance. The most important ones will be discussed here: time-of-flight (TOF) spectrometer, backscattering (BS) spectrometer, inverse TOF spectrometer, and neutron spin echo (NSE) spectrometer.

11.3.2 Time-of-flight spectrometer

The main disadvantage of the 3AX spectrometer is that it can only observe one (Q, ω) point at a time. While for samples where the scattering is concentrated into Bragg peaks this may be acceptable, for systems with diffuse scattering a simultaneous observation of a range of Q vectors and energy transfers $\hbar\omega$ is desired. This is accomplished by surrounding the sample position with an array of detectors (figure 11.7). In addition the energy of the scattered neutrons E' is here measured by their time of flight: A chopper in the incident beam defines the start time of the neutrons. The electronic pulse from their registration in the detector gives the end of their flight through the spectrometer. From the time difference the velocity of the neutrons can be calculated and from this in turn the energy transfer. The relation between time-of-flight and energy transfer is given by

$$\hbar\omega = \left(\frac{l_1^2}{\left(l_0 - \sqrt{2E/m_n} t_{\text{flight}} \right)^2} - 1 \right) E. \quad (11.66)$$

As in all inelastic neutron scattering experiments, the lower limit of the energy transfer is $-E$. (The neutrons cannot lose more than their incident energy.) Because scattered neutrons with arbitrary high energies arrive at the detector in a finite time there is no principal upper limit. Nevertheless, at high energy transfers the time-of-flight scale gets so compressed that energy resolution worsens. This sets a practical upper limit at $5 \dots 10 E$.

The monochromatization of the incoming neutron beam can either be done by Bragg reflection from a crystal or by a sequence of choppers which are phased in order to transmit a single wavelength only. The former principle usually yields higher intensities while the latter is more flexible for the selection of the incident energy E and attains better energy resolution.

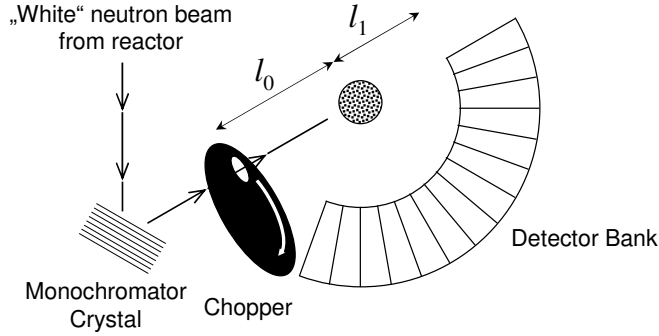


Fig. 11.7: Schematic setup of a time-of-flight spectrometer with crystal monochromator.

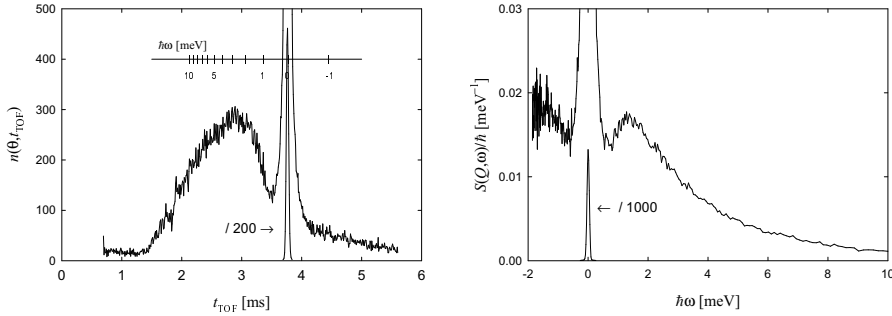


Fig. 11.8: Left: raw data from TOF spectrometer: neutron counts in a time channel of $10 \mu\text{s}$ during one hour registration time. The sample is a mesoscopically confined glass-forming liquid. The floating non-linear axis indicates the energy transfers calculated by equation (11.66). Because of the strength of the elastic scattering that part of the spectrum has been reduced by a factor of 200. Right: the same TOF data converted to $S(Q, \omega)$, elastic line reduced by factor 1000. The characteristic vibrational modes of the material at $\hbar\omega \approx 1.7 \text{ meV}$ (14 cm^{-1}) become only visible after the transformation.

Table 11.1 shows some representative TOF instruments with their basic specifications. Depending on the desired incident wavelength the instruments are constructed either using neutrons directly from the reactor moderator (thermal neutrons, $\lambda_{\text{max}} \approx 1.8 \text{ \AA}$) or a cold source, where an additional moderation, e.g. by liquid hydrogen, takes place ($\lambda_{\text{max}} \approx 4 \text{ \AA}$). Thermal neutrons make a larger Q range accessible while cold neutrons yield better energy resolution. Therefore, the choice of the instrument depends on the system to be observed but in general ‘cold neutron’ instruments are preferred for inelastic neutron scattering in soft matter systems while ‘thermal neutron’ instruments are used for studies of phonons and magnetism.

Instrument	Type	λ_i [Å]	$Q_{\max}$ [Å ⁻¹]	$\Delta\hbar\omega$ [meV]
PANTHER (ILL)	TX	0.86–3.3	3.5–14	0.4–6
IN5 (ILL)	CC	2–15	0.8–5.7	0.01–6
SHARPER (ILL)	CX	1.5–6	2.0–7.9	0.055–3
TOFTOF (MLZ)	CC	1.4–14	0.8–8	0.002–3

Table 11.1: Basic specifications of representative neutron time-of-flight spectrometers. Instrument types: TX–thermal, crystal; CX–cold, crystal; CC–cold, chopper. The maximal Q and the energy resolution $\Delta\hbar\omega$ depend on the incident wavelength; the upper limits of their ranges correspond to the lower limit of the incident wavelength λ_i and vice versa. Institutions: ILL–Institut Laue-Langevin, MLZ–Maier-Leibnitz Zentrum.

11.3.3 Backscattering spectrometer

A recurring problem of inelastic neutron scattering investigations is that processes are too slow to be observed. Without resorting to extreme setups which lead to a loss of intensity, the energy resolution of TOF spectrometers is limited to about $10\ \mu\text{eV}$, which corresponds to a maximal timescale of 200 ps. This is often not sufficient for e.g. the large scale motions in polymers, biological systems, or glass-forming materials. Therefore, instruments with highest energy resolution are often needed, the backscattering (BS) and neutron spin echo (NSE) spectrometer.

The energy resolution of a TOF spectrometer is limited by the selectivity of the monochromator crystal⁸. If perfect crystals are used the spread of the selected wavelengths $\Delta\lambda/\lambda$ is determined by the uncertainty of the scattering angle α at the monochromator and analyser, $\Delta\alpha$. Differentiating the Bragg condition $\lambda = 2 \sin(\alpha/2)/d$ one obtains

$$\Delta\lambda/\lambda = \cot \alpha \cdot \Delta\alpha/2. \quad (11.67)$$

This expression becomes zero for $\alpha = 180^\circ$. In practice this means that the wavelength spread becomes minimal if the neutron beam is reflected by 180° , i.e. in backscattering condition.

Figure 11.9 shows schematically the instrument based on this principle. The first crystal in the beam is only a deflector with low wavelength selectivity. The actual monochromatization takes place upon the second reflection by the crystal in backscattering position. The monochromatized neutrons are then scattered by the sample which is surrounded by analyzer crystals placed on a spherical surface. There they are again scattered under backscattering condition. The reflected neutrons pass once more through the sample and finally reach the detector.

It can be seen that the backscattering condition leads to technical problems in several places: (1) The deflector must not accept all neutrons otherwise the monochromatized beam would be scattered back into the source. This can be solved by reducing its size deliberately below

⁸ For chopper spectrometers the limit is given by the pulse length which could in principle be arbitrary small. But since the counted intensity decreases quadratically with pulse length the resolution limit of an efficient experiment is in the same range.

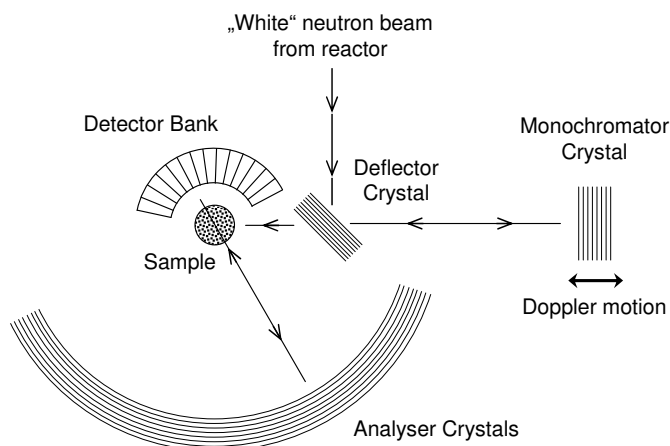


Fig. 11.9: Schematic setup of a backscattering spectrometer.

the neutron beam area or putting it on a rotating disk which removes it at the moment when the neutrons come back from the monochromator. Of course all these measures are taken at the expense of intensity. (2) The second passage of the scattered neutrons through the sample causes additional multiple scattering and absorption. Both problems can be avoided by leaving exact backscattering condition but with the consequence that the energy resolution degrades.

So far it seems that the backscattering instrument can only observe elastic scattering ($E' = E$) if the same crystals are used for monochromator and analyzer. In order to do inelastic scattering one has to change either E or E' . It turns out that this is much easier for the incident energy by either using a moving monochromator (Doppler effect) or a heated monochromator (thermal expansion modifying the lattice plane distance d). The latter technique usually allows larger energy transfers. For very large energy transfers, different crystals are used for monochromator and analyzer, yielding an offset of the whole $\hbar\omega$ range. Table 11.2 comprises specifications of representative BS spectrometers.

11.3.4 Inverse TOF spectrometer

The inverse TOF spectrometer is a kind of hybrid between the TOF spectrometer and the backscattering spectrometer. Usually, such instruments are built at spallation sources which produce short pulses of neutrons. If the neutrons are produced in pulses one can use their creation time to start the TOF clock and in principle there is no need for a chopper. In this way, on a pulsed source, all neutrons can be used in contrast to conventional TOF spectrometers which use only a few percent. The principle can also be realised by chopping a continuous beam into pulses on reactors with a loss of intensity comparable to that of an ordinary TOF instrument (e.g. BATS in Table 11.3). Because the energy resolution depends on the length of the pulses this 'pulse shaping' may also be necessary on a long-pulse spallation source.

Instrument	Type	λ [Å]	$Q_{\max}$ [Å ⁻¹]	$\Delta\hbar\omega$ [μeV]	$\hbar\omega_{\max}$ [μeV]
SPHERES (JCNS)	CD	6.27	1.8	0.7	30
HFBS (NIST)	CD	6.27	1.7	0.9	30
IN16B (ILL)	CD	3.23–6.27	1.8–3.5	0.3–2.0	31–59
IN13 (ILL)	TH	2.23	5.5	8	300

Table 11.2: Basic specifications of representative neutron backscattering spectrometers. Instrument types: CD–cold, Doppler monochromator; TH–thermal, heated monochromator. The maximal Q and the energy resolution $\Delta\hbar\omega$ depend on the incident wavelength; the upper limits of their ranges correspond to the lower limit of the incident wavelength λ_i and vice versa. Institutions: JCNS–Jülich Centre for Neutron Science, NIST–National Institute of Standards and Technology, ILL–Institut Laue-Langevin

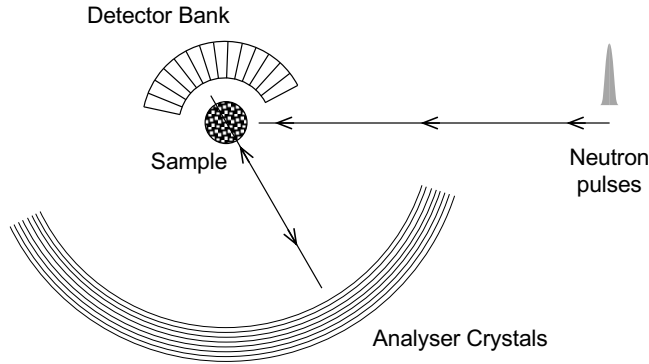


Fig. 11.10: Schematic setup of an inverse time-of-flight spectrometer.

For inverse TOF instruments, the incident energy E is variable and measured by the time-of-flight and the final energy E' is kept constant by a fixed set of analyser crystals. This is often called “inverse geometry” or “inverse time-of-flight”. By putting the analyser crystals into near backscattering position it is possible to obtain a very good energy resolution already close to true backscattering spectrometers and combine it with the large energy range of a TOF instrument. Because of the analyser positioning these instruments are sometimes also called “backscattering” although the way the energy transfer is measured is completely different from that of the instruments described in section 11.3.3.

11.3.5 Neutron spin echo spectrometer

In order to access even slower processes a very high resolution technique is needed allowing to reach more than 100 nanoseconds corresponding to energy transfers in the neV range.

Instrument	Source	λ [Å]	$Q_{\max}$ [Å ⁻¹]	$\Delta\hbar\omega$ [μeV]	$\hbar\omega_{\max}$ [meV]
IRIS (RAL)	S	6.7–20	0.6–1.9	1–18	0.4
BATS (ILL)	R	3.3–6.3	1.8–3.5	1.2–59	0.34–1.1
DNA (J-PARC)	S	3.3–6.3	2.0–3.4	1.4–19	0.08–1.5

Table 11.3: Basic specifications of representative inverse time-of-flight spectrometers. The maximal Q and the energy resolution $\Delta\hbar\omega$ depend on the incident wavelength; the upper limits of their ranges correspond to the lower limit of the incident wavelength λ_i and vice versa. R—reactor source, S—pulsed spallation source. Institutions: RAL—Rutherford-Appleton Laboratory, ILL—Institut Laue-Langevin, J-PARC—Japan Proton Accelerator Research Complex.

Such a technique is provided by neutron spin echo (NSE) spectrometers [22] which are able to measure directly energy *changes* of the neutron due to scattering.

This distinguishes NSE from conventional inelastic neutron scattering techniques which proceed in two steps: (1) monochromatization of the incident beam to E , (2) analysis of the scattered beam (E'). The energy transfer is then determined by taking the difference $E' - E$. In order to achieve high energy resolutions with these conventional techniques a very narrow energy interval must be selected from the relatively low-intensity neutron spectrum of the source. Conventional high-resolution techniques therefore inevitably run into the problem of low count rates at the detector.

Unlike these methods, NSE measures the individual velocities of the incident and scattered neutrons using the Larmor precession of the neutron spin in a magnetic field. The neutron spin vector acts as the hand of an internal clock, which is linked to each neutron and connects the result of the velocity measurement to the neutron itself. Thereby the velocities before and after scattering on one and the same neutron can be compared and a direct measurement of the velocity difference becomes possible. The energy resolution is thus decoupled from the monochromatization of the incident beam. Relative energy resolutions in the order of 10^{-5} can be achieved with an incident neutron spectrum of 20% bandwidth.

The motion of the neutron polarization $\mathbf{P}(t)$ —which is the quantum mechanical expectancy value of the neutron spin—is described by the Bloch equation

$$\frac{d\mathbf{P}}{dt} = \frac{\gamma\mu}{\hbar}(\mathbf{P} \times \mathbf{B}) \quad (11.68)$$

where γ is the gyromagnetic ratio ($\gamma = -3.82$) of the neutron, μ the nuclear magneton and $\mathbf{B}$ the magnetic field. Equation (11.68) is the basis for manipulation of the neutron polarization by external fields. In particular, if a neutron of wavelength λ is exposed to a magnetic field B over a length l of its flight path, its spin is rotated by

$$\phi = \left(\frac{2\pi|\gamma|\mu\lambda m}{\hbar^2} \right) Bl. \quad (11.69)$$

The basic setup of an NSE spectrometer is shown in figure 11.11. A velocity selector in the primary neutron beam selects a wavelength interval of 10–20% width. In the primary and secondary flight path of the instrument precession fields B and B' parallel to the respective

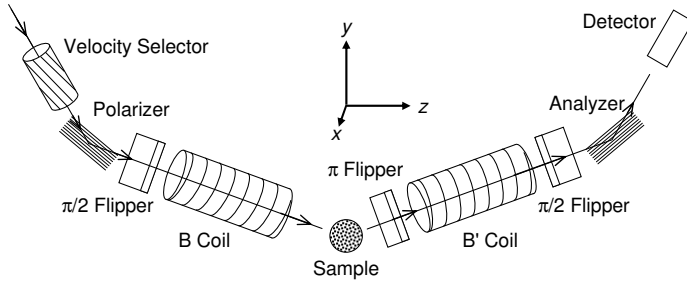


Fig. 11.11: Schematic setup of a neutron spin echo spectrometer.

path are generated by cylindrical coils. Before entering the first flight path the neutron beam is polarized in forward direction⁹. Firstly, a $\pi/2$ flipper rotates the polarization to the x direction perpendicular to the direction of propagation (z). This is done by exposing the neutrons to a well defined field for a time defined by their speed and the thickness of a flat coil (Mezei coil). Beginning with this well-defined initial condition the neutrons start their precession in the field B . After being scattered by the sample the neutrons pass a π flipper and then pass the second precession field B' . Finally, the neutrons pass another $\pi/2$ coil which, under certain conditions, restores their initial polarization parallel to their flight direction. In order to understand what that condition is, one has to trace the changes of the spin vector (z always denoting the direction parallel to neutron propagation):

(n_x, n_y, n_z)	neutronic device
$(0,0,1)$	
$(1,0,0)$	$\pi/2$ flipper
$(\cos \phi, \sin \phi, 0)$	field B
$(\cos \phi, -\sin \phi, 0) =$ $(\cos(-\phi), \sin(-\phi), 0)$	π flipper
$(\cos(\phi' - \phi), \sin(\phi' - \phi), 0)$	field B'
$(0, \sin(\phi - \phi'), \cos(\phi - \phi'))$	$\pi/2$ flipper

In total, the spin is rotated by $\phi - \phi'$ around the x axis when a neutron passes through the spectrometer. This means that the final polarization is identical to the incident if $\phi = \phi' (+2\pi n)$, especially if $\lambda_i = \lambda_f$ (elastic scattering) and $\int_0^l B dz = \int_0^{l'} B' dz$ (for homogeneous fields: $Bl = B'l'$) as follows from (11.69). This condition is called “spin echo” and is independent of the individual velocities of the neutrons because their difference alone determines $\phi - \phi'$.

Leaving spin echo condition the probability of a single neutron to reach the detector is reduced due to the polarization analyzer by $\cos(\phi' - \phi)$. If we keep the symmetry of the

⁹ This is done by a “polarizing supermirror” which only reflects neutrons of that spin—similar to the Nicol prism in optics.

instrument, $Bl = B'l'$, but consider inelastic scattering the precession angle mismatch can be approximated by

$$\begin{aligned}\phi' - \phi &= \left(\frac{2\pi|\gamma|\mu m}{h^2} \right) Bl(\lambda_f - \lambda_i) \\ &\approx \underbrace{\frac{|\gamma|\mu m_n^2 \lambda^3 Bl}{h^3}}_{=t_{\text{NSE}}(B)} \omega\end{aligned}\quad (11.70)$$

for small energy transfers where $\Delta\lambda \approx \hbar\omega / \frac{dE}{d\lambda}$ can be used. Because the energy transfer for inelastic scattering is not fixed but distributed as determined by the scattering function $S(Q, \omega)$ we have to average the factor $\cos(\phi' - \phi)$ weighted by $S(Q, \omega)$ to get the reduction of count rate at the detector, the effective polarization

$$P(Q, t_{\text{NSE}}) = \frac{\int_{-\infty}^{\infty} S(Q, \omega) \cos(\omega t_{\text{NSE}}) d\omega}{\int_{-\infty}^{\infty} S(Q, \omega) d\omega}. \quad (11.71)$$

Expression (11.71) reverses the temporal Fourier transform of equation (11.22) and therefore the result of the NSE experiment

$$P(Q, t_{\text{NSE}}(B)) = \frac{I(Q, t_{\text{NSE}}(B))}{I(Q, 0)} \quad (11.72)$$

is the normalised *intermediate* scattering function. This function is often more understandable and easier to interpret than the frequency dependent scattering function.

In order to estimate typical Fourier times t_{NSE} which can be accessed by NSE we consider maximum fields of $B = B' = 500 \text{ Gauss}$ in precession coils of $l = l' = 2 \text{ m}$ length operating at $\lambda = 8 \text{ \AA}$. Then (11.70) results in a time of about 10 ns which can be reached.

From this equation it also becomes clear that the most efficient way to enlarge this time is to use longer wavelengths because λ enters in the third power. This in turn reduces the accessible Q range which constitutes a drawback for studies on low molecular materials but not for the large scale properties of polymers which have to be observed at low Q anyway.

Because NSE works in time domain, there is no well-defined way to relate the maximum Fourier time t_{max} of an NSE spectrometer to the resolution $\Delta\hbar\omega$ of one of the instruments mentioned before. A rule of thumb would be that 1 ns corresponds to $1 \mu\text{eV}$, thus $\Delta\hbar\omega / \mu\text{eV} = \text{ns} / t_{\text{max}}$. Because of the inverse relation between time and frequency, the corresponding limit to $\hbar\omega_{\text{max}}$ on backscattering and inverse TOF, on an NSE spectrometer is the smallest time accessible, t_{min} . This time depends strongly on the technical set-up of the spectrometer. In most cases it is about three orders of magnitude below t_{max} .

There are two restrictions of the application of NSE which may impede its use even if the dynamical range is adequate for the system to be studied:

- If the sample changes the polarisation of the beam the information encoded in the neutron spins gets ‘scrambled’. This is the case for magnetic samples but also for systems with spin-incoherent scattering. Because ^1H hydrogen is a spin-incoherent

scatterer this often makes chemical deuteration necessary. Nowadays, NSE experiments are often still feasible because there may be a stochastic relation between the numbers of neutrons scattered. This would be 1/3 ‘up’ and 2/3 ‘down’ in the case of pure spin-incoherent scattering. Nevertheless, there are combinations of nuclei which bring the probabilities close to 1/2 or uncontrollable situations as in ferromagnets where NSE measurements are impossible.

- Similar complications arise if magnetic scattering is happening in the sample [23]. Depending on the orientation of the magnetic fluctuations, a π flip may occur, making the instrumental π flipper (Fig. 11.11) unnecessary. The most complicated situation arises for ferromagnetic samples where a uncontrollable phase shift occurs due to domain sizes and orientations. In that situation, only NSE variants which are immune to spin changes at the sample (e.g. MIEZE [24] or IMNSE [25]) will work.
- Because the value of λ in equation (11.70) varies by 10...20% from neutron to neutron the relation between the phase difference and the energy transfer is somewhat ‘blurred’. For processes like diffusion which have a broad distribution of ω (see (11.62)) this is usually not important. But for mechanisms which produce well-defined energy transfers $\hbar\omega$ this is problematic and neutron backscattering is preferable.

Exemplary NSE spectrometers with their specifications are listed in table 11.4. NSE spectrometers are very flexible instruments often used with different setups of which only “typical” ones have been included. As special features have to be mentioned that IN11 and WASP have one-dimensional detector arrays which span 60° and 130° degrees respectively, allowing the simultaneous observation of a range of Q values. The instruments IN15 and J-NSE have two-dimensional detector arrays which can be used for studying anisotropies but cover a smaller angular range. IN15 uses a focusing mirror in order to increase neutron flux which would be otherwise very low due to its long precession coils.

A straightforward optimisation is the use of multidetectors covering a large angular range as in TOF or BS spectrometers. This is indeed possible by adopting a radial magnetic field configuration. The drawback is that the field integral is less well defined in this setup. This leads to a reduction of the time range by a factor of about 10 compared to a conventional NSE spectrometer.

Also for NSE it is possible to optimise the instrument for pulsed sources by using time-of-flight. The idea is that one omits the velocity selector and uses the fact that the neutrons arrive ‘sorted’ by velocity at the instrument. So one works with a very large wavelength range. But still individual wavelengths can be identified from the time of registration in the detector. The different wavelengths generate different Q values at the same detection angle. This saves the often necessary step to vary either the scattering angle or the wavelength to collect several Q values.

Instrument	λ [Å]	$Q_{\max}$ [Å ⁻¹]	$t_{\max}$ [ns]	features	options
IN11 [†] (ILL)	4.5–12	0.9–2.4	2–45		multidetector, three-axes
J-NSE (JCNS)	4.5–16	0.4–1.5	10–350	multidetector, superconducting coils	
IN15 (ILL)	8–25	0.13–0.4	30–1000	mirror optics	time-of-flight
WASP (ILL)	3–12	1.0–3.9	0.6–18	radial geometry	
NSE (ORNL)	2–14	0.4–3.1	1–280	time-of-flight, superconducting coils	

Table 11.4: Basic specifications of representative neutron spin echo spectrometers. The maximal Q and the maximal Fourier time $t_{\max}$ depend on the incident wavelength; the upper limit of the Q range and the lower limit of $t_{\max}$ correspond to the lower limit of the incident wavelength λ and vice versa. Institutions: ILL—Institut Laue-Langevin, JCNS—Jülich Centre for Neutron Science, ORNL—Oak Ridge National Laboratory. [†]IN11 is not in operation anymore but included for historical reasons.

References

- [1] This dictum is usually attributed to the Nobel prize winners B. N. Brockhouse and/or C. G. Shull. But to the knowledge of the author, no reliable quotation clarifying its true origin exists.
- [2] S. W. Lovesey: “Theory of Neutron Scattering from Condensed Matter” (Clarendon Press, Oxford, 1984).
- [3] G. L. Squires: “Introduction to the theory of thermal neutron scattering” (Cambridge University Press, Cambridge, 1978).
- [4] G. E. Bacon: “Neutron Diffraction” (Clarendon Press, Oxford, 1975).
- [5] G. E. Bacon (ed.): “Fifty Years Of Neutron Diffraction: The Advent Of Neutron Scattering” (Adam Hilger, Bristol, 1986).
- [6] M. Bée: “Quasielastic neutron scattering” (Adam Hilger, Bristol, 1988).
- [7] R. Zorn: “Fourier Transforms” in T. Brückel, G. Heger, D. Richter, R. Zorn (eds.): “Neutron Scattering” (Forschungszentrum Jülich, 2008, <http://hdl.handle.net/2128/37180>), chapter I.
- [8] R. Zorn, D. Richter: “Correlation Functions Measured by Scattering Experiments”, *ibidem*, chapter 4.
- [9] N. W. Ashcroft, N. D. Mermin: “Solid State Physics” (Holt-Saunders, New York, 1976).
- [10] G. P. Srivastava: “The physics of phonons” (Adam Hilger, Bristol, 1990).

- [11] H. Bilz, W. Kress: “Phonon dispersion relations in insulators”, Solid-state sciences, Vol. 10 (Springer, Berlin, 1979).
- [12] B. N. Brockhouse, *Phys. Rev.* **106** 859 (1957).
- [13] G. Placzek, *Phys. Rev.* **86** 377 (1952).
- [14] J. L. Yarnell, M. J. Katz, R. G. Wenzel, S. H. Koenig, *Phys. Rev. A* **7** 2130 (1973).
- [15] R. Zorn: “Correlations and Response of Matter to Probes” in K. Urban, C. M. Schneider, T. Brückel, S. Blügel, K. Tillmann, W. Schweika, M. Lentzen, L. Baumgarten: “Probing the Nanoworld” (Forschungszentrum Jülich, 2008).
- [16] P. Schofield, *Phys. Rev. Lett.* **4** 239 (1958)
- [17] R. Aamodt, K. M. Case, M. Rosenbaum, P. F. Zweifel, *Phys. Rev.* **126** 1165 (1962)
- [18] Eq. 5.98 in volume 1 of ref. 2.
- [19] Chapter 3.5 in volume 1 of ref. 2.
- [20] A. Rahman, K. S. Singwi, A. Sjölander, *Phys. Rev.* **126**, 986 (1962).
- [21] R. Zorn, *Nucl. Instr. Meth. A* **603**, 439 (2009)
- [22] Mezei, F. (ed.) (1980): *Neutron spin echo*, Springer, Heidelberg.
- [23] T. Keller, H. Trepka, K. Habicht, B. Keimer, *Phys. Status Solidi B* **259**, 2100164 (2022).
- [24] R. Gahler, R. Golub, T. Keller, *Physica B* **180–181**, 899 (1992).
- [25] B. Farago, F. Mezei, *Physica B+C* **136**, 100 (1986).

Exercises

Note: Exercises are labelled by stars (* through ***) indicating the level of difficulty. Try to solve the easier ones first.

E11.1 Scattering triangle*

For the feasibility of an inelastic neutron scattering experiment it is essential that the desired $Q, \hbar\omega$ combination (in the scattering function $S(Q, \omega)$) can be reached at a certain combination of incident neutron wavelength λ and angle 2θ .

1. $\lambda = 5.1 \text{ \AA}$, $2\theta = 90^\circ$ and $\hbar\omega = 5 \text{ meV}$, which value has Q ? Which value would Q have calculated from the formula for elastic scattering?
2. $\lambda = 5.1 \text{ \AA}$, $Q = 1 \text{ \AA}^{-1}$, what is the largest energy gain and largest absolute energy loss one can reach? What do you have to do if you need larger values of $|\hbar\omega|$?

Hints: $\hbar = 1.0546 \times 10^{-34} \text{ Js}$, neutron mass: $m = 1.6749 \times 10^{-27} \text{ kg}$, $1 \text{ eV} = 1.6022 \times 10^{-19} \text{ J}$.

E11.2 Q dependence of characteristic time***

In many cases, the incoherent intermediate scattering function can be written in the form $I_{\text{inc}}(Q, t) = \exp(-(t/\tau(Q))^\beta)$ with $\tau(Q) \propto Q^{-x}$. E.g. in the lecture diffusion ($x = 2$, $\beta = 1$) and the ideal gas ($x = 1$, $\beta = 2$) were presented. In a later lecture you will learn that for polymers in the melt $x = 4$, $\beta = 1/2$ holds. For polymers in solution the Zimm model predicts $x = 3$, $\beta = 2/3$. In all cases $x \cdot \beta = 2$. What is the reason for this nearly universal relation?

E11.3 Choice of instruments**

The most important aspect of planning an inelastic neutron scattering experiment is the choice of the right instrument matching the time scale of the process to be observed.

1. What is the range of energy transfers corresponding to the right-hand side of Fig. 11.5 in meV? Which instrument would you chose?
2. The diffusion coefficient of benzene at room temperature is about $2 \times 10^{-5} \text{ cm}^2/\text{s}$. Which instrument would you use to study this diffusion on the length scale of 0.5 nm ? (Hints: As you may know from the lectures of diffraction and SANS, the lengths are related roughly roughly by $Q = 2\pi/l$. From that value calculate the width of the quasielastic scattering in (11.62) and convert it to meV.)
3. The diffusion coefficient of the protein alcohol dehydrogenase in water is $23.5 \mu\text{m}^2/\text{s}$. Which instrument would you use to study this diffusion on the length scale of 3 nm ?

4. When molecules containing methyl groups are cooled down to near absolute zero, their rotation does not completely stop because quantum tunnelling between the energy minima is possible. This leads to a splitting of the ground state, which can be very different in chemically similar molecules: methane (CH_4): $142 \mu\text{eV}$, methyl fluoride (CH_3F): $23.1 \mu\text{eV}$, methyl iodide (CH_3I): $2.44 \mu\text{eV}$. Which instrument may be used for which compound?

12 Virtual Neutron Scattering Experiments

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12.1 Introduction

Mankind faces several challenges these days: it is necessary to stop the climate change, fight diseases, keep the biodiversity and reach a sustainable economy and ecological food and water supply for everybody. To achieve all that, new technologies and materials are needed, which require research to understand the processes underlying the problem and to find and test new materials. This requires a variety of methods to investigate matter.

Neutron scattering is an important method for this research, especially to study biological systems, magnetic materials and energy materials, because it makes magnetic structures and light atoms visible (especially H atoms) and can distinguish atoms close to each other in the periodic system and is even isotope sensitive.

Dedicated instruments were built to determine atomic structures or structures in the nm-scale, to study inelastic processes in a certain time and length range, to take images of the interior of objects or to analyse their atomic compositions.

Practically all neutron scattering instruments are prototypes, adapted to the source and the planned scientific applications. The construction is expensive, and the flux is lower than that of other beams. This results in long measuring times and makes beamtime precious. As a consequence, it is necessary to build optimized instruments and use beamtime efficiently. To build optimized instruments, they are first designed analytically and then simulated by Monte Carlo simulations. This allows comparing different setups and parameter choices and even enables numerical optimization.

Usually, the simulations include scattering of neutrons in known samples and determining the distribution of neutrons on the detector. They are then called virtual experiments. Often, the simulated spectra are evaluated using the data evaluation software foreseen for the real experiments.

Virtual experiments are also useful for teaching purposes, training to handle the instrument, preparation of the real experiment and even for testing the data evaluation software.

12.2 Simulation of neutron scattering instruments

12.2.1 Monte Carlo simulations

If the dependence of a measurement on one or two parameters shall be studied, it is straightforward to scan this/these parameter(s) and measure all these points. As an example, we might scan over the surface of the neutron source to see which part of it contributes to the signal on the detector (cf. Fig. 12.1). That can also be done in a simulation. However, this does not work anymore, if the number of parameters having effect on the signal is large, because we either need a very large measurement/computation effort, or the number of different parameter values is very low. In the example shown in Fig. 12.1 with 8 parameters, we would need 100 million calculations for only 10 different values for each parameter. If we choose wavelengths of 1, 2, ... 10 Å, peaks caused by neutrons of e.g. 2.45 or 3.6 Å will not be visible. The idea of the Monte Carlo (MC) method is therefore to choose randomly any

value of each parameter (in a given range) for each of these 100 million calculations, so that the calculation is performed for 100 million different wavelength values λ , 100 million different horizontal positions y of the surface, ... So, one does not calculate all combinations of parameters, but gets a 'dense' distribution of each parameter in the simulation.

Monte Carlo simulations are used in many fields, e.g. traffic simulations, telecommunication or physics. The basic idea is to create a large number of events by random number choices. As an example, in a simulation of the traffic in a town, an 'event' is the ride from point A to B in the town, e.g. a commute to work in the morning. The random number choices would be: the home address (mainly in living area), work address (usually in the city centre or a business park) and the starting time.

Similarly, in a virtual neutron scattering experiment, the events are the possible trajectories of a neutron through the instrument including the scattering possibilities in the sample. Accordingly, the parameters determined by random choices for each event are: the starting position (on the surface of the source), the flight direction from the moderator, the neutron wavelength, the starting time at the source (for pulsed sources) and the scattering in the sample (see Fig. 12.1). Dependent on the instrument, additional choices may be needed, e.g. in a monochromator.

The trajectory of each neutron through the instrument is then calculated treating it as a classical particle usually under the influence of gravity until it is absorbed, misses a component or reaches the sample. Here, the neutrons are scattered, and if they hit the detector, they are counted there.

It is possible to perform the simulation of a virtual experiment with individual neutrons. If there is a transmission or reflection of 80% at any point of the instrument, 20% of them will then be removed by a random number choice. For efficiency reasons, this is not done in current simulation programs. Instead, trajectories, also called 'rays', are seen as the events in the simulation. Each trajectory is given a weight (in neutrons per second), which is reduced by 20% in the case presented above, but none of them is taken out of the calculation.

Name and history of simulation programs

First Monte Carlo simulations were performed within the Manhattan Project to develop the atomic bomb; they called it Monte Carlo method as it reminded them of gambling in a casino. It was also the start of the MCNP program, which is still used today. It is one of a few programs to simulate shielding and the target-moderator-reflector system, where neutrons are generated and slowed down.

A branch of the MCNP program was converted to NISP [1] to simulate neutron scattering instruments with the idea to accelerate simulation by only considering neutrons on their way to sample and detector. As it was difficult to use, it was only continued as long as the author supported the simulations. In the late 90s, new programs were developed (e.g. VITESS[2], McStas [3]). They were designed for a broad user community, are easy to use and can be employed for all kinds of instruments at all kinds of neutron sources.

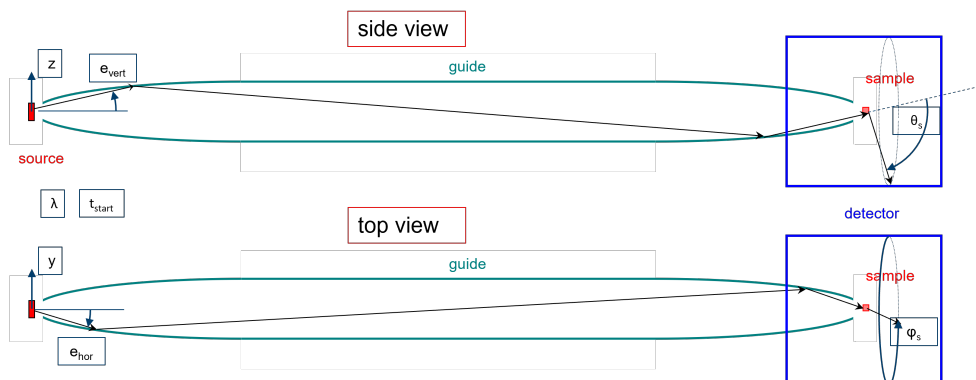


Fig. 12.1: Concept of Monte Carlo simulations as used in virtual experiments on neutron scattering instruments showing the 8 parameters determined by random choices to simulate the diffraction pattern of a time-of-flight diffractometer at a pulsed source: wavelength λ , starting time t_{start} , starting position y , z , flight direction from the source e_{hor} , e_{vert} and scattering direction Θ_s , Φ_s .

12.2.2 Instrument design

A new instrument first needs a design concept and analytical calculations starting from the scientific applications foreseen for the instrument. The analytical calculations allow already an estimation of its resolution and the flux at the sample.

Then it is simulated to see the beam properties (at the sample) and get more precise values for flux and resolution. It can be optimized for highest flux, highest resolution, best peak shape, highest signal to noise ratio or any other figure-of-merit. Therefore, many simulations are necessary comparing different parameter settings or even using numerical optimisation to find the best parameter set.

When instruments are upgraded, both, the old and the new setup are simulated and compared. The simulation of the old version should reflect the experimental results. If that is the case and the simulation of the new setup gives a better performance, e.g. a higher flux or a better resolution, that can also be expected for the real instrument (one example is the upgrade of D11 at ILL, where the flux at the sample could be increased by more than 40% by a new guide system [4]).

12.2.3 Example: A diffractometer for the High Brilliance neutron Source (HBS)

As an alternative to fission or spallation neutron sources, Compact Accelerator-driven Neutron Sources (CANS) have been developed, in which protons with energies of less than 100 MeV cause the release of neutrons by nuclear reactions in neutron-rich isotopes of some elements (e.g. ^7Li , ^9Be , or ^{181}Ta). CANS sources are scalable by adapting proton energy and current to the needed source strength. At the upper end, High-Current Accelerator-driven Neutron Sources (HiCANS) allow instrument performances as those of current medium sized reactor and spallation sources.

The Jülich High Brilliance neutron Source (HBS) is one of these HiCANS sources. It has been developed over the last years at Forschungszentrum Jülich. The Technical Design Report [5], released in 2023 contains not only a description of the facility as a whole, of the accelerator and the target-moderator-reflector system, but also a suggestion for the instrument suite, which covers all scientific applications using neutrons. It comprises SANS instruments and reflectometers for large scale structure studies, spectrometers to study dynamics of materials, imaging instruments for 'photos' of the interior of objects and analytics instruments for the determination of element or isotope composition by analytics instruments and six diffractometers to determine atomic positions.

One of them is the Thermal Powder Diffractometer (TPD), a time-of-flight powder diffractometer. It allows a large variation in flux and resolution so that it can be used for high-resolution measurements as well as low-resolution time-resolved measurements [6]. It has been simulated in detail three different setups - high resolution, medium resolution and high intensity. The results show promising beam properties at the sample position (see Fig. 12.2).

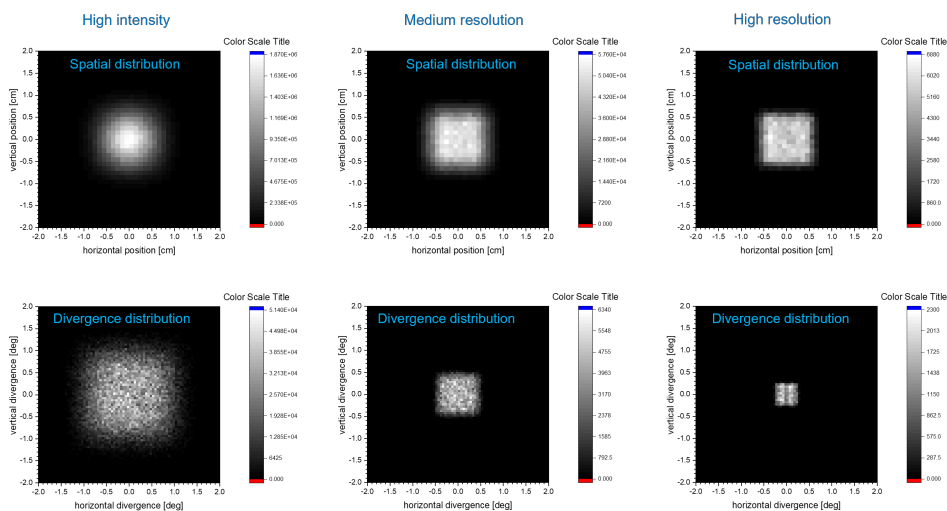


Fig. 12.2: Spatial (top) and divergence (bottom) distribution of the beam of the thermal powder diffractometer of the HBS at the sample position for the three different setups as obtained by MC simulations using the VITESS program [1]

12.3 Virtual experiments

In the next step, a sample is added to the simulation. The sample scatters the neutrons, and their distribution on the detector is simulated – this is the diffraction pattern. For time-of-flight instruments, it is converted into a function $I(Q)$ or $I(d)$, the intensity as a function of the momentum transfer Q or the d-spacing d . (see Fig. 12.3). This allows to calculate the linewidth and check the line shape. The diffraction pattern can now be used for data evaluation, e.g. by using the same software as for real experiments. This enables to check the instrument performance in terms of the final output.

In our example, a virtual experiment of the Thermal Powder Diffractometer was performed using the standard sample $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ (NAC) for powder diffractometers. It revealed a symmetric linewidth, and a resolution and detector count rate comparable to diffractometers on current neutron sources (see Fig. 12.3).

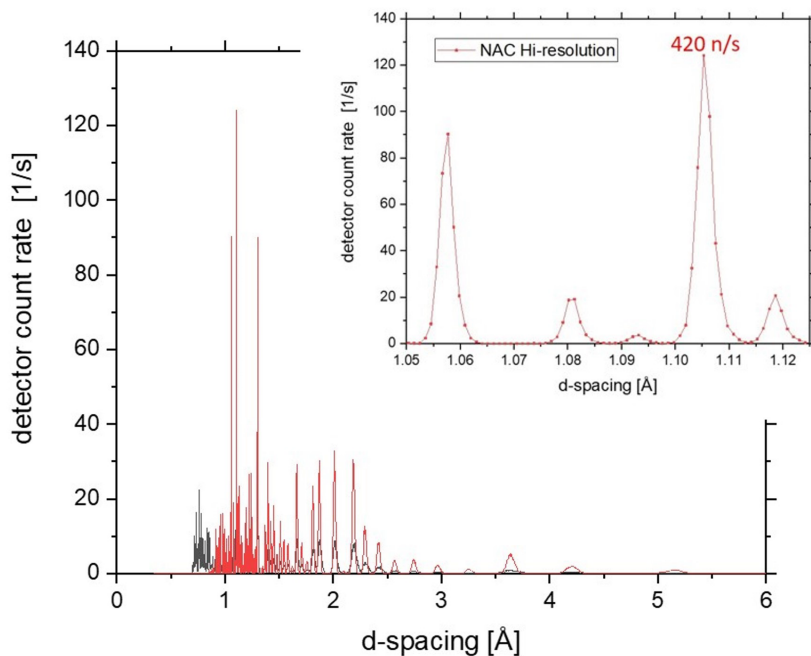


Fig. 12.3: Diffraction pattern of a NAC sample obtained by simulation of the thermal powder diffractometer of the HBS in the high-resolution setup. The red curve shows the pattern of the long wavelength frame (1.65 – 2.7 Å), the black curve that of the short wavelength frame (0.6 – 1.65 Å). The inset shows the range around 1.1 Å of the red curve stretched by a factor of about 50. (The pattern is cut at $d=0.7$ Å by a limit in the input data of the NAC sample.)

12.4 Digital twins

Simulations of the diffraction patterns have been performed for many years already. The current goal is to emulate the real neutron scattering experiment by a simulation, in which the simulated system reacts just like the real system. Ideally, the graphical user interface that is used for the real instrument is also used for the virtual experiments. It is then called a digital twin of the instrument. This is realized for several instrument at neutron facilities to enable experiment preparation or virtual experiments for courses, when the real experiments cannot be performed (see section 12.5).

While most components in a real instrument have their counterpart in the virtual experiment, the neutron beam is usually treated differently: So far, it has been common practice to take all neutrons out of the consideration that are not on the way to sample and detector anymore. In a digital twin, we have to treat also neutrons scattered in the sample environment, passing through the sample without reacting with it, or interacting with the sample environment (cf. Fig. 12.4).

In a second step, the absorption of neutrons in the different components could be used to simulate the radiation background. It is also required for a digital twin to enable a visualization of the detector screen (or the monitors) and to update this output every few seconds in order to show the advance of the (virtual) measurement.

For some instruments, it is a challenge to get the simulation as fast as the experiment. In such a case, the simulation can be accelerated by running in advance the (fixed,) first part of the instrument, which takes most of the time, and save the neutron data in a file. During the virtual experiment, these data are read, and the simulation is only carried out for the (variable,) second part of the instrument.

The final step to a digital twin is then to have an 'endless' simulation that reacts instantaneously on parameter changes. This has been realized for the first time in a simulation of the reflectometer MARIA at the Maier-Leibnitz Zentrum in Garching (close to Munich) using the simulation program VITESS [1].

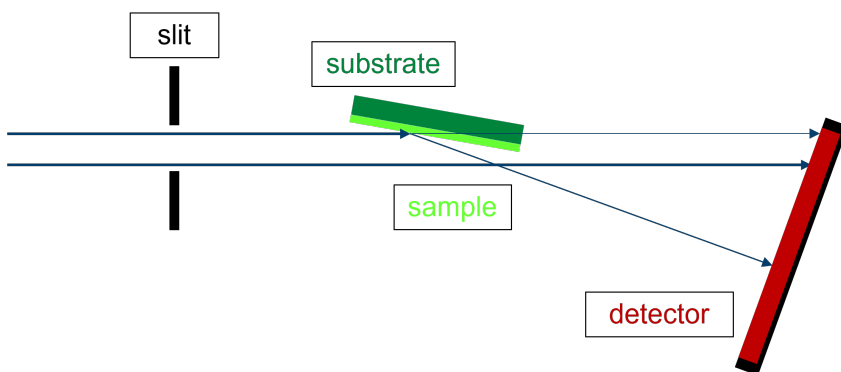


Fig. 12.4: Neutron trajectories being reflected on the sample surface, transiting the sample or passing by it in a digital twin of a neutron reflectometer.

12.5 Applications of virtual experiments

12.5.1 Training and experiment preparation

If a digital twin of an instrument with the same GUI exists, it can be used to learn how to set up the instrument and to conduct an experiment. For this purpose, the simulation should be available as a web application enabling the scientist to control the (virtual) instrument before he gets beamtime on the real instrument (cf. Fig. 12.5). That will save him time at the facility so that he can use the beamtime more efficiently.

Even without the same GUI, virtual experiments can be used to prepare experiments. Using a sample similar to the one to be measured, instrument settings can be varied to find out the best compromise between high resolution and high counting rate. It also gives an estimation of the beamtime needed for each experiment, which will allow to set up a realistic measurement plan.

12.5.2 Teaching

Virtual experiments can also be used to learn about neutron scattering. Independent of a real measurement, one can exchange samples and vary instrument settings and view the results. One only needs a simple PC for that, install a freely available software (VITESS, McStas, ...) and get results after some seconds or a few minutes of simulation time.

12.5.3 Test of data evaluation software

One advantage of virtual experiments over real experiments is that the sample parameters are exactly known, because they are input parameters. So, it is possible to compare the result of the data evaluation with the true parameters.

This does not only allow to check the influence of the instrument on the final result, but also to check the data evaluation software.

Another possibility is to mark neutron trajectories in the simulation, e.g. where they are scattered. Thus, you can separate contributions from the sample environment or from multiple scattering from the real signal.

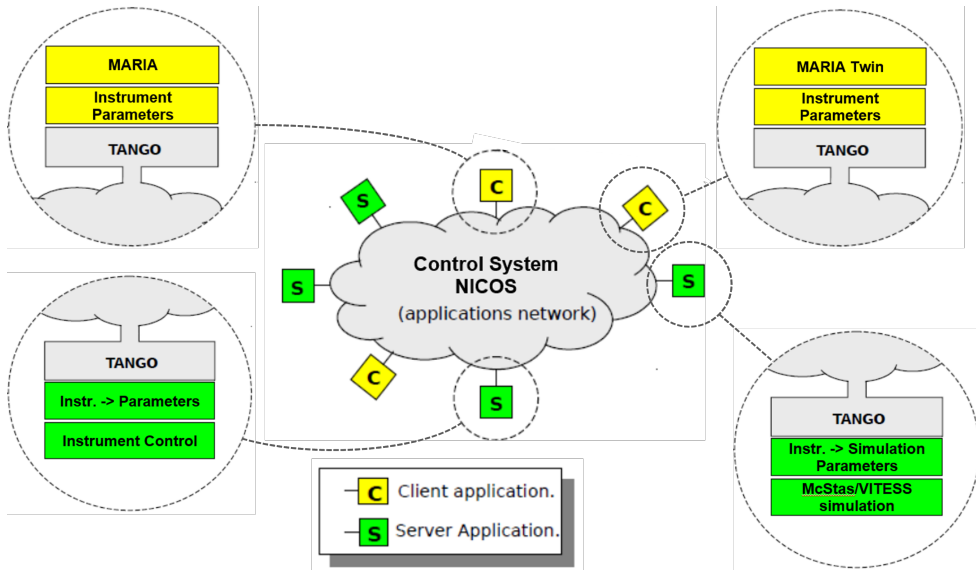


Fig. 12.5: Integration of a program for virtual neutron scattering instruments into the NICOS operating system for instrument control of the MLZ instruments in a client-server-application, which creates a digital twin of the real instrument.

References

- [1] P.A. Seeger and L.L. Daemen, *Proc. SPIE* **5536**, 109 (2004).
- [2] C. Zendler et al., *J. Phys.:Conf.Ser.* **528**, 012036 (2014).
<https://vitess.fz-juelich.de/>
- [3] P. K. Willendrup and K. Lefmann, *J. Neutron Res.* **22**, 1 (2020).
mcstas.org
- [4] K. Lieutenant et al., *J. Appl. Cryst.* **40**, 1056 (2007).
- [5] Th. Brückel, Th. Gutberlet, eds., *Technical Design Report HBS*, Vol. 9 of *Schriften des Forschungszentrums Jülich*, General (Forschungszentrum Jülich GmbH, Jülich, 2023).
- [6] K. Lieutenant et al., submitted for publication

Exercises

Preparation

- Download the current version of the program VITESS by going to the homepage <https://vitess.fz-juelich.de> or directly to the Git site for the downloads <https://iffgit.fz-juelich.de/vitess/vitess/-/releases>
- Start the program and prepare a new instrument simulation by defining a parameter directory, where the simulation is executed

E12.1 Source and sample illumination*

- Use 'source' as the first module and create neutrons in the wavelength range 4.5 to 5.5 Ang.
- Choose a cold moderator of the ILL source (from InstallDirectory/FILES/moderators/...)
- Illuminate a 2 x 2 cm² large area in 10 meters distance.
- Put a 2D monitor there to show the divergence distribution
- Put a 1D monitor there to show the wavelength distribution
- Run the simulation using 1 Mio and 100 Mio 'trajectories' (= 'rays') and compare

E12.2 SANS spectrum**

- Add a 2 x 2 x 0.1 cm SANS sample of spheres of 100 nm diameter shortly behind the monitors
- Add a 1 m² detector of 5 x 5 mm² cell size (using the modules 'screen') in 4 m distance from the sample
- Run the simulation and monitor the intensity distribution on the detector
- Use the module 'eval_sans' to generate the spectrum $I(Q)$

E12.3 Resolution***

- Look at the spectrum $I(q)$. Is it in agreement with your expectations for a spherical sample?
- Which parameters contribute to the Q resolution?
- Which parameter is dominating here?
- What can be done to improve the resolution e.g. to half the value in $\delta Q/Q$?

13 **Strongly correlated electrons**

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13.1 Introduction

Materials with *strong electronic correlations* are materials, in which the movement of one electron depends on the positions and movements of all other electrons due to the long-range Coulomb interaction. With this definition, one would naively think that all materials show strong electronic correlations. However, in purely ionic systems, the electrons are confined to the immediate neighborhood of the respective atomic nucleus. On the other hand, in ideal metallic systems, the other conduction electrons screen the long-range Coulomb interaction. Therefore, while electronic correlations are also present in these systems and lead for example to magnetism, the main properties of the systems can be explained in simple models, where electronic correlations are either entirely neglected (e.g. the free electron Fermi gas) or taken into account only in low order approximations (Fermi liquid, exchange interactions in magnetism etc.). In highly correlated electron systems, simple approximations break down and entirely new phenomena and functionalities can appear. These so-called *emergent* phenomena cannot be anticipated from the local interactions among the electrons and between the electrons and the lattice [1]. This is a typical example of *complexity*: the laws that describe the behavior of a complex system are qualitatively different from those that govern its units [2]. This is what makes highly correlated electron systems a research field at the very forefront of condensed matter research. The current challenge in condensed matter physics is that we cannot reliably predict the properties of these materials. There is no theory, which can handle this huge number of interacting degrees of freedom. While the underlying fundamental principles of quantum mechanics (Schrödinger equation or relativistic Dirac equation) and statistical mechanics (maximization of entropy) are well known, there is no way at present to solve the many-body problem for some 10^{23} particles. Some of the exotic properties of strongly correlated electron systems and examples of emergent phenomena and novel functionalities are:

- *High temperature superconductivity*; while this phenomenon was discovered in 1986 by Bednorz and Müller [3], who received the Nobel Prize for this discovery, and since then has continually attracted the attention of a large number of researchers, there is still no commonly accepted mechanism for the coupling of electrons into Cooper pairs, let alone a theory which can predict high temperature superconductivity or its transition temperatures. High temperature superconductivity has already some applications such as highly sensitive magnetic field sensors, high field magnets, and power lines, and more are likely in the future.
- *Colossal magnetoresistance* effect CMR, which was discovered in transition metal oxide manganites and describes a large change of the electrical resistance in an applied magnetic field [4]. This effect can be used in magnetic field sensors and could eventually replace the giant magnetoresistance [5,6] field sensors, which are employed for example in the read heads of magnetic hard discs.
- The *magnetocaloric* effect [7], a temperature change of a material upon applying a magnetic field, can be used for magnetic refrigeration without moving parts or cooling fluids.
- *Metal-insulator-transitions* as observed e.g. in magnetite (Verwey transition [8]) or certain vanadites are due to strong electronic correlations and could be employed as

electronic switches.

- *Multiferroicity* [9], the simultaneous occurrence of various ferroic orders, e.g. ferromagnetism and ferroelectricity, in one material. If the respective degrees of freedom are strongly coupled, one can switch one of the orders by applying the conjugate field of the other order. Interesting for potential applications in information technology is particularly the switching of magnetization by an electric field, which has been proposed to be used for easier switching of magnetic non-volatile memories [10]. Future applications of multiferroic materials in computer storage elements are apparent. One could either imagine elements, which store several bits in form of a magnetic- and electric polarization, or one could apply the multiferroic properties for an easier switching of the memory element.
- *Negative thermal expansion* [11] is just another example of the novel and exotic properties that these materials exhibit.

It is likely that many more such emergent phenomena will be discovered in the near future. This huge potential is what makes research on highly correlated electron systems so interesting and challenging: this area of research is located right at the intersection between fundamental science investigations, striving for basic understanding of the electronic correlations, and technological applications, connected to the new functionalities [12].

13.2 Electronic structure of solids

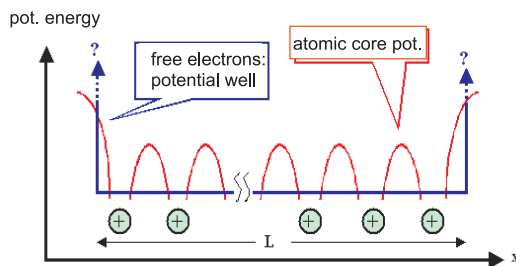


Fig. 13.1: Potential energy of an electron in a solid.

In order to be able to discuss the effects of strong electronic correlations, let us first recapitulate the textbook knowledge of the electronic structure of solids [13,14]. The description of the electron system of solids usually starts with the adiabatic or Born-Oppenheimer approximation: The argument is made that the lighter electrons are moving so quickly compared to the nuclei that the electrons can instantaneously follow the movement of the much heavier nuclei and thus see the instantaneous nuclear potential. This approximation serves to separate the lattice- and electronic degrees of freedom. Often one makes the further approximation to consider the nuclei to be at rest in their equilibrium positions. The potential energy seen by a single electron in the averaged field of all other electrons and the atomic core potential is depicted schematically for a one dimensional system in Fig. 13.1.

The following simple models are used to describe the electrons in a crystalline solid:

- *Free electron Fermi gas*: here a single electron moves in a 3D potential well with infinitely high walls corresponding to the crystal surfaces. All electrons move completely independent, i.e. the interaction between the electrons is considered only indirectly by the Pauli exclusion principle.
- *Fermi liquid*: here the electron-electron interaction is accounted for in a first approximation by introducing *quasiparticles*, so-called dressed electrons, which have a charge e , and a spin $\frac{1}{2}$ like the free electron, but an effective mass m^* , which can differ from the free electron mass m . Other than this renormalization, interactions are still neglected.
- *Band structure model*: this model takes into account the periodic potential of the atomic cores at rest, i.e. the electron moves in the average potential from the atomic cores and from the other electrons.

Considering the strength of the long-range Coulomb interaction, it is surprising that the simple models of Fermi gas — or better Fermi liquid — already are very successful in describing some basic properties of simple metals. The *band structure model* is particularly successful in describing semiconductors. But all three models have in common that the electron is described with a single particle wave function and electronic correlations are only taken into account indirectly, to describe phenomena like magnetism due to the exchange interaction between the electrons or BCS superconductivity [15], where an interaction between electrons is mediated through lattice vibrations and leads to Cooper pairs, which undergo a Bose-Einstein condensation.

What we have sketched so far is the textbook knowledge of introductory solid state physics courses. Of course there exist more advanced theoretical descriptions, which try to take into account the electronic correlations. The strong Coulomb interaction between the electrons is taken into account in density functional theory in the so-called “LDA+U” approximation or in the so-called dynamical mean field theory DMFT or a combination of the two in various degrees of sophistication [16]. Still, all these extremely powerful and complex theories often fail to predict even the simplest physical properties, such as whether a material is a conductor or an insulator.

Let us come back to the *band structure* of solids. In the so-called tight-binding model one starts from isolated atoms, where the energy levels of the electrons in the Coulomb potential of the corresponding nucleus can be calculated. If N such atoms are brought together, the wave functions of the electrons from different sites start to overlap so that electrons can hop between neighboring atoms. This leads to a broadening of the atomic energy levels, which eventually will give rise to the electronic bands in solids, each of which is a quasi-continuum of $2N$ electronic states (N possible values of $\mathbf{k}$, spin $\sigma = \uparrow$ or $\downarrow$). The closer the atoms are brought together, the more the wave functions overlap, the more the electrons will be delocalized, and the broader in energy are the corresponding bands (Fig. 13.2).

If electronic correlations are not too strong, the electronic properties can be described by a band structure, which allows one to predict whether a material is an insulator or a metal. This is shown in Fig. 13.3. At $T = 0$ all electronic states are being filled up to the Fermi

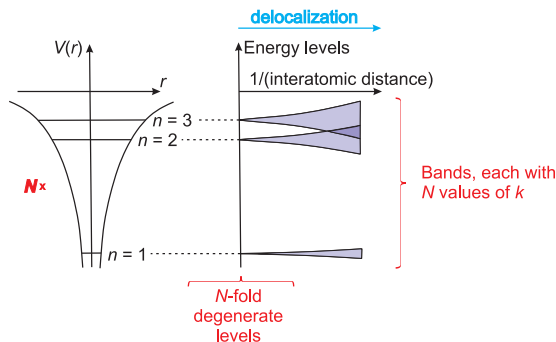


Fig. 13.2: *Left:* Atomic potential of an electron interacting with the atomic core and the corresponding level scheme of sharp energy levels. *Right:* Broadening of these levels into bands upon increase of the overlap of the wave functions of neighboring atoms. After [13].

energy, taking into account the Pauli principle. If there is an even number of electrons per atom (or more generally per primitive unit cell), say $2m$, these will fill up exactly the first m bands, and the higher energy bands are empty. Unless there is band-overlap between the highest occupied (valence) band and the lowest unoccupied (conduction) band (which may accidentally happen in 3D) any electron transport would require the bump of an electron from the valence to the conduction band, and consequently the material is an insulator (at non-zero T some electrons may be thermally excited to the conduction band if the band gap is small, one calls the material then a semi-conductor rather than an insulator). If there is an odd number of electrons per primitive unit cell, say $2m + 1$, the first $2m$ bands will be completely full, but the band $2m + 1$ will be half-filled. In a partially filled band electrons easily move in response to a voltage, hence the material is a metal – within the model described so far always. However, as mentioned above this *band structure model* describes the electrons with single particle wave functions. Where are the electronic correlations?

13.3 Strong electronic correlations: the Mott transition

It turns out that *electronic correlations* are particularly important in materials that have some very narrow bands. This occurs for example in transition metal oxides or transition metal chalcogenides as well as in some light rare earth intermetallics (heavy fermion systems). Consider CoO as a typical and simple example of a transition metal oxide. CoO has the rock-salt structure shown in Fig. 13.4, with a face-centered cubic (fcc) unit cell containing four formula units. The primitive unit cell of the fcc lattice, however, is spanned by the basis vectors $\mathbf{a}' = \frac{1}{2}a(\mathbf{e}_x + \mathbf{e}_y)$, $\mathbf{b}' = \frac{1}{2}a(\mathbf{e}_y + \mathbf{e}_z)$, and $\mathbf{c}' = \frac{1}{2}a(\mathbf{e}_z + \mathbf{e}_x)$, where a is the lattice constant, and $\mathbf{e}_x$, $\mathbf{e}_y$, and $\mathbf{e}_z$, are the unit basis vectors of the original fcc unit cell. The primitive unit cell contains only one cobalt and one oxygen atom. The electronic configurations of these atoms are: Co: $[\text{Ar}]3d^74s^2$; O: $[\text{He}]2s^22p^4$. In the solid, the atomic cores of Co and O have the electronic configuration of Ar and He, respectively. These electrons are very strongly bound to the nucleus and we need not consider them on the usual energy scales for

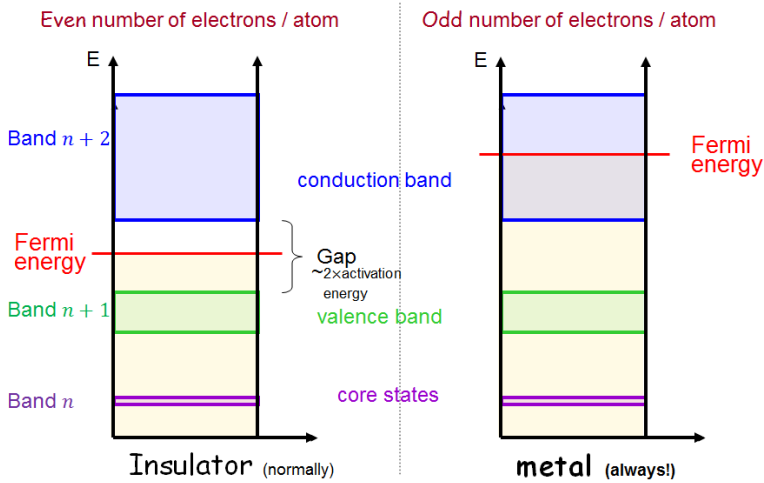


Fig. 13.3: Band structure of insulators and metals.

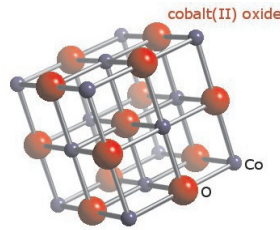


Fig. 13.4: Rock-salt (NaCl)-type structure of CoO.

excitations in the solid state. We are left with nine outer electrons for the Co and six outer electrons for the O atom in the solid, so that the total number of electrons per primitive unit cell is $9 + 6 = 15$, i.e. an odd number. According to our considerations in the last section, we must have at least one partially filled band and CoO *should* be a metal.

What does the experiment tell us? Well, in fact, CoO is a very good insulator with a room-temperature resistivity $\rho(300\text{ K}) \sim 10^8 \Omega\text{cm}$ (For comparison, the good conductor iron has $\rho(300\text{ K}) \sim 10^{-7} \Omega\text{cm}$). The resistivity of CoO is exponentially decreasing with increasing temperature T , and the T -dependence corresponds to activation energies of about 0.6 eV or a temperature equivalent of 7000 K, which means there is a huge band gap making CoO a very good insulator. To summarize these considerations: the band theory breaks down already for a very simple oxide consisting of only one transition metal and one oxygen atom!

In order to understand the reason for this dramatic breakdown of band theory, let us consider an even simpler example: the alkali metal sodium (Na) with the electronic configuration $[\text{Ne}]3s^1 = 1s^2 2s^2 2p^6 3s^1$. Following our argumentation for CoO, sodium obviously has a half-filled 3s band and is therefore a metal. This time our prediction was correct: $\rho(300\text{ K}) \sim 5 \times 10^{-6} \Omega\text{cm}$. However, what happens if, hypothetically, we pull the atoms further apart

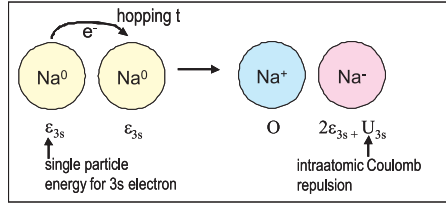


Fig. 13.5: Illustration of (electron) hopping between two neutral Na atoms - involving charge fluctuations.

and increase the lattice constant continuously? Band theory predicts that for all distances sodium remains a metal, since the 3s band will always be half-filled. This contradicts our intuition: at a certain critical separation of the sodium atoms, there must be a transition from a metal to an insulator. This metal-to-insulator transition was predicted by Sir Nevill Mott (physics Nobel price 1977); it is therefore called the *Mott transition* [17]. The physical principle is illustrated in Fig. 13.5: On the left, two neutral Na atoms are depicted. The atomic energy levels of the outer electrons correspond to an energy ε_{3s} . The wave functions of the 3s electrons will overlap giving rise to a finite probability that an electron can hop from one sodium atom to the other one. Such a delocalization of the electrons arising from their possibility to hop is favored because it lowers their kinetic energy. This can be seen for example by generalizing the “particle in a box” problem: $E_{\text{kin}} \propto p^2 = \hbar^2/\lambda^2$ (de Broglie) and $\lambda \sim \text{box size}$, and it is consistent with the uncertainty principle $\Delta p \cdot \Delta x \geq \frac{\hbar}{2}$. Fig. 13.5 on the right shows the situation after the electron transfer. Instead of neutral atoms, we have one Na^+ and one Na^- ion. However, we have to pay a price for the double occupation of the 3s states on the Na^- ion, namely the intra-atomic Coulomb repulsion between the two electrons denoted as U_{3s} . While this is a very simplistic picture, where we assume that the electron is either located on one or the other Na atom, this model describes the two main energy terms by just two parameters: the hopping matrix element t , connected to the kinetic energy, and the intra-atomic Coulomb repulsion U , connected with the potential energy due to the Coulomb interaction between the two electrons on one site. In this simple model, we have replaced the long range Coulomb potential proportional to $1/r$ with its leading term, an on-site Coulomb repulsion U . More realistic models would have to take higher order terms into account but already such a simple consideration leads to very rich physics. We can see from Fig. 13.5 that electronic conductivity is connected with charge fluctuations and that such charge transfer costs energy, where U is typically of the order of 1 or 10 eV. Only if the gain in kinetic energy due to the hopping t is larger than the penalty in potential energy U can we expect metallic behavior. If the sodium atoms are now being separated more and more, the intra-atomic Coulomb repulsion U will maintain its value while the hopping matrix element t , which depends on the overlap of the wave functions, will diminish. At a certain critical value of the lattice parameter a , potential energy will win over kinetic energy and conductivity will be suppressed. This is the physical principle behind the *Mott transition*.

More formally, this model can be cast into a model Hamiltonian, the so-called *Hubbard model* [18]. In second quantization of quantum-field theory, the corresponding Hamiltonian is

$$\hat{\mathcal{H}} = -t \sum_{j,l,\sigma} (\hat{c}_{j\sigma}^\dagger \hat{c}_{l\sigma} + \hat{c}_{l\sigma}^\dagger \hat{c}_{j\sigma}) + U \sum_j \hat{n}_{j\uparrow} \hat{n}_{j\downarrow}, \quad (13.1)$$

where the operator $\hat{c}_{j\sigma}^\dagger$ creates an electron in the atomic orbital $\Phi(\mathbf{r} - \mathbf{R}_j)|\sigma\rangle$, j runs over all atomic sites, and l on nearest neighbors of j . The first term is nothing but the tight-binding model of band structure (in second quantization), where t is the hopping amplitude depending on the overlap of the wavefunctions from nearest-neighbor atoms at $\mathbf{R}_1$ and $\mathbf{R}_2$:

$$t = \int \Phi(\mathbf{r} - \mathbf{R}_1) \frac{e^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{R}_2|} \Phi(\mathbf{r} - \mathbf{R}_2) d\mathbf{r}. \quad (13.2)$$

It describes the kinetic energy gain due to electron hopping.

The second term is the potential energy due to doubly-occupied orbitals. Here, $\hat{n}_{j\sigma} = \hat{c}_{j\sigma}^\dagger \hat{c}_{j\sigma}$ is the occupation operator of the orbital $\Phi(\mathbf{r} - \mathbf{R}_j)|\sigma\rangle$ and U is the Coulomb repulsion between two electrons in this orbital,

$$U = \int \frac{e^2 |\Phi(\mathbf{r}_1 - \mathbf{R}_j)|^2 |\Phi(\mathbf{r}_2 - \mathbf{R}_j)|^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \quad (13.3)$$

The *Hubbard model* is a so-called *lattice fermion model*, since only discrete lattice sites are being considered. It is the simplest way to incorporate correlations due to the Coulomb interaction since it takes into account only the strongest contribution, the on-site Coulomb interaction. Still there is very rich physics contained in this simple Hamiltonian like the physics of ferromagnetic- or antiferromagnetic metals and insulators, charge- and spin density waves and so on [18]. A realistic Hamiltonian should contain many more inter-site terms due to the long-range Coulomb interaction likely to contain additional new physics.

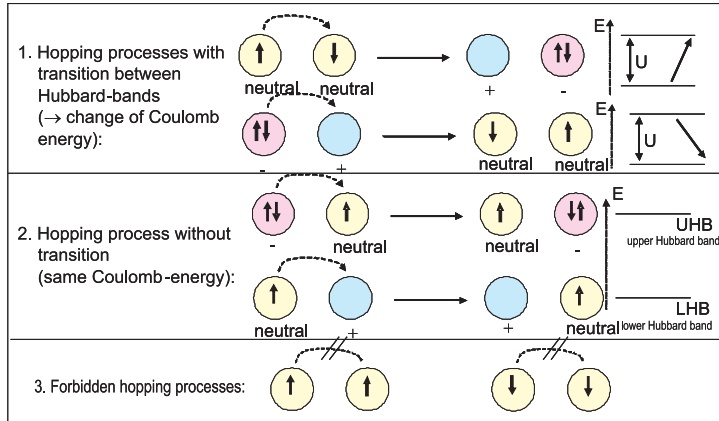


Fig. 13.6: Illustration of hopping processes between neighboring atoms together with their corresponding energy scales.

The most direct consequence of the on-site Coulomb interaction is that additional so-called Hubbard bands are created due to possible hopping processes, illustrated in Fig. 13.6: The first row shows hopping processes involving a change of the total Coulomb energy. The second row shows hopping processes without energy change. The last row shows hopping processes forbidden due to the Pauli principle (here, the spin enters the model, giving rise to magnetic order). From Fig. 13.6 we can identify two different energy states. Configurations

for which the on-site Coulomb repulsion comes into play have an energy which is higher by the on-site Coulomb repulsion U as compared to such configurations where the electrons are not on the same atom. In a solid these two energy levels will broaden into bands (due to the delocalization of the electrons on many atoms driven by the hopping matrix element t), which are called the lower Hubbard band and the upper Hubbard band. If these bands are well separated, i.e. the Coulomb repulsion U dominates over the hopping term t , we will have an insulating state (only the lower Hubbard band is occupied). If the bands overlap, we will have a metallic state. Note that lower and upper Hubbard bands are totally different from the usual band structure of solids as they do not arise due to the interaction of the electrons with the atomic cores but due to electronic correlations. As a result the existence of the Hubbard bands depends on the electronic occupation: the energy terms for simple hopping processes depend on the occupation of neighboring sites. The apparently simple single electron operator gets complex many body aspects.

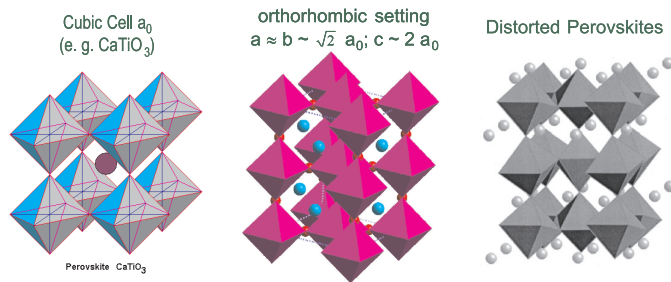


Fig. 13.7: Perovskite structures. The A-site atoms are shown as spheres, octahedra have Mn (or Ti) at their center and O at their corners. Left: Ideal (cubic) structure. Middle: cubic structure in orthorhombic setting. Right: distorted structure with rotated and tilted oxygen octahedra.

13.4 Complex ordering phenomena: perovskite manganites as example

The correlation-induced localization leads to atomic-like *electronic degrees of freedom* that can (because the possible hopping of electrons between sites means that different sites interact with one another) order in complex ways. The electronic degrees of freedom include charge (or ion valence), orbital (which atomic orbitals are occupied, what is the shape of the electron cloud), and magnetic moment. In the following we will discuss these ordering processes, taking as an example, because of their particularly simple basic structure, *perovskite manganites* (see e.g. [19]). Their stoichiometric formula is $A_{1-x}B_x\text{MnO}_3$, where A is a trivalent cation (e.g. $A = \text{La, Gd, Tb, Er, Y, Bi}$) and B is a divalent cation ($B = \text{Sr, Ca, Ba, Pb}$). The doping with divalent cations leads to a mixed valence on the manganese sites. In a purely ionic model (neglecting covalency) charge neutrality requires that manganese exists in two valence states: Mn^{3+} (electronic configuration $[\text{Ar}]3d^4$, note that the 4s electrons are lost first upon positive ionization in a solid; the reason is that the 4s orbitals have electron density extending much further from the nucleus, which leads to a Coulomb

penalty given nearby negative ions) and Mn^{4+} ($[\text{Ar}]3d^3$) according to the respective doping levels: $A_{1-x}B_x\text{MnO}_3 \rightarrow [A_{1-x}^{3+}B_x^{2+}] [\text{Mn}_{1-x}^{3+}\text{Mn}_x^{4+}] \text{O}_3^{2-}$. The structure of these mixed valence manganites is related to the perovskite structure (Fig. 13.7). Perovskite CaTiO_3 is a mineral, which has a cubic crystal structure, where the smaller Ca^{2+} metal cation is surrounded by six oxygen atoms forming an octahedron; these corner sharing octahedra are centered on the corners of a simple cubic unit cell and the larger Ti^{4+} metal cation is filling the interstice in the center of the cube. This ideal cubic perovskite structure is extremely rare. It only occurs when the sizes of the metal ions match to fill the spaces between the oxygen atoms ideally. Usually there is a misfit of the mean ionic radii of the A and B ions, which leads to sizeable tilts of the oxygen octahedra, described in larger cells (see Fig. 13.7). These tilt distortions are, however, not important for the following general considerations of the electronic degrees of freedom.

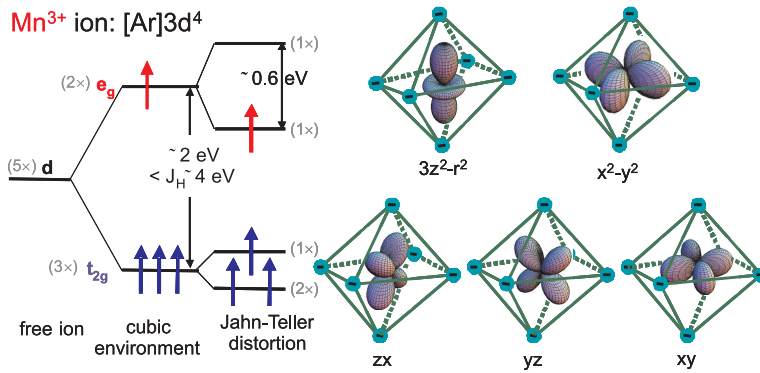


Fig. 13.8: Energy level diagram for a Mn^{3+} ion in an oxygen octahedron. For the free ion, the five 3d electron levels are degenerate. They split in a cubic environment into t_{2g} and e_g levels. If Hund's rule coupling is stronger than crystal field splitting, a high-spin state results. The degeneracy of the e_g level is lifted by a Jahn-Teller distortion resulting in an elongation of the oxygen octahedra. On the right of the figure, a basis set of 5 *real* 3d orbitals are depicted.

For an isolated manganese, or other transition metal, ion, the electrons are filled into the five d orbitals according to *Hund's rules*. The first, and dominant, Hund rule implies that electrons tend to maximize their total spin $S = \sum_j s_j$, avoiding in particular double occupation of any d orbital. In other words, the electrons occupy the orbitals in such a way that the spins of all electrons are parallel as far as the Pauli principle permits. This is a consequence of the intra-atomic Coulomb repulsion between electrons, in particular the exchange contribution to the Coulomb repulsion. The energy gained by fulfilling the first Hund rule is called the Hund's rule energy J_H . The second Hund rule, originating from direct intra-atomic Coulomb repulsion, states that the total angular momentum L is maximized, as far as consistent with the first Hund rule, i.e. orbitals are filled from high to low angular momentum. Finally, the third Hund rule, due to spin-orbit coupling, states that total spin and orbital momentum are (anti-)parallel for more (less) than half-filled shells. For the manganites the octahedral surrounding of the Mn ions leads to so-called *crystal field effects*. To explain these we stay in the ionic model and describe the oxygen atoms as O^{2-} ions. The outer electrons of the Mn ions, the 3d electrons, experience the electric field created by the surrounding O^{2-} ions of

the octahedral environment. This so-called crystal field leads to a splitting of the electronic levels by the crystal field as depicted in Fig. 13.8: The $3d$ orbitals with lobes of the electron density pointing towards the negatively charged oxygen ions ($3z^2 - r^2$ and $x^2 - y^2$; so-called e_g orbitals) will have higher energies compared to the orbitals with the lobes pointing in-between the oxygen atoms (xy , yz , and xz ; so-called t_{2g} orbitals). For the manganites this crystal-field splitting is typically ~ 2 eV. If we now consider a Mn^{3+} ion, how the electrons will occupy these crystal field levels depends on the ratio between the crystal-field splitting and the intra-atomic exchange J_H : If the crystal field splitting is much larger than Hund's coupling, a *low-spin state* results, where all electrons are in the lower t_{2g} level and two of these t_{2g} orbitals are singly occupied and one is doubly occupied. Due to the Pauli principle the spins in the doubly occupied orbital have to be antiparallel, giving rise to a total spin $S = 1$ for this low-spin state. Usually, however, in the manganites Hund's rule coupling amounts to ~ 4 eV, stronger than the crystal field splitting. In this case the *high spin state* shown in Fig. 13.8 is realized, where four electrons with parallel spin occupy the three t_{2g} orbitals plus one of the two e_g orbitals. The high spin state has a total spin of $S = 2$ and the orbital angular momentum is quenched, i.e. $L = 0$. This state has an orbital degree of freedom: the e_g electron can either occupy the $3z^2 - r^2$ or the $x^2 - y^2$ orbital. The overall energy can (and thus will) be lowered by a geometrical distortion of the oxygen octahedra that shifts the e_g levels, lifting their degeneracy. This so-called *Jahn-Teller effect* (Fig. 13.8) further splits the d-electron levels. For the case shown, the c -axis of the octahedron has been elongated, thus lowering the energy of the $3z^2 - r^2$ orbital with respect to the energy level of the $x^2 - y^2$ orbital. The Jahn-Teller splitting in the manganites has a magnitude of typically ~ 0.6 eV.

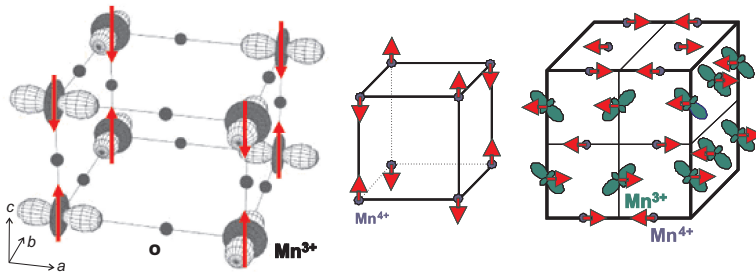


Fig. 13.9: *Left:* Orbital order in LaMnO_3 . Below the Jahn-Teller transition temperature of 780 K, a distinct long range ordered pattern of Jahn-Teller distortions of the oxygen octahedra occurs leading to orbital order of the e_g orbitals of the Mn^{3+} ions as shown. Also shown is the antiferromagnetic spin order which sets in below the Néel temperature $T_N \sim 145$ K. Oxygen atoms are represented by filled circles, La is not shown. *Center:* Distinct spin order of CaMnO_3 . *Right:* Charge-, orbital- and spin-order in half-doped manganite $\text{La}_{0.5}^{3+}\text{Sr}_{0.5}^{2+}\text{Mn}_{0.5}^{3+}\text{Mn}_{0.5}^{2+}\text{O}_3$.

The Jahn-Teller effect demonstrates nicely how in these transition metal oxides electronic and lattice degrees of freedom are coupled. Only the Mn^{3+} with a single electron in the e_g orbitals exhibits the Jahn-Teller effect, whereas the Mn^{4+} ion does not. A transfer of charge between neighboring manganese ions is accompanied with a change of the local distortion of the oxygen octahedron: a so-called lattice polaron. Due to the Jahn-Teller effect, charge

fluctuations and lattice distortions become coupled in these mixed-valence oxides.

Having explained the Jahn-Teller effect, we can now introduce an important type of electronic order occurring in these materials: *orbital order*. Consider the structure of LaMnO_3 : All manganese are trivalent and are expected to undergo a Jahn-Teller distortion. In order to minimize the elastic energy of the lattice, the Jahn-Teller distortions on neighboring sites are correlated. Below a certain temperature $T_{\text{JT}} \sim 780 \text{ K}$, a cooperative Jahn-Teller transition takes place, with a distinct pattern of distortions of the oxygen octahedra throughout the crystal lattice as shown in Fig. 13.9 left. This corresponds to a long-range orbital order of the e_g electrons, not to be confused with magnetic order of an orbital magnetic moment. In fact, the orbital magnetic moment is quenched, i.e. totally suppressed, by the crystal field surrounding the Mn^{3+} ions (this is always the case for non-degenerate states with real wave functions because such functions have pure-imaginary expectation values for an angular momentum operator). *Orbital ordering* instead denotes a long-range ordering of an anisotropic charge distribution around the nuclei. As the temperature is further lowered, magnetic order sets in at $T_N \sim 145 \text{ K}$. In LaMnO_3 the spin degree of freedom of the Mn^{3+} ion orders antiferromagnetically in so-called A-type order: spins within the a - b plane are parallel, while spins along c are coupled antiferromagnetically. The depicted antiferromagnetic ordering results from a complex interplay between structural-, orbital- and spin degrees of freedom and the relative strengths of the different coupling mechanisms in LaMnO_3 , as can be seen by comparing with the different magnetic order of CaMnO_3 , which does not have an orbital degree of freedom (Fig. 13.9 center).

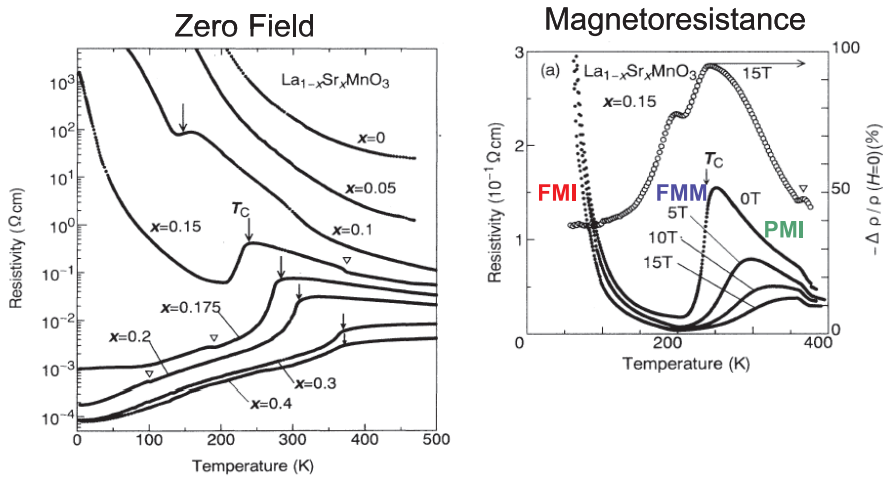


Fig. 13.10: Resistivity in the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ series [20]. *Left:* resistivity in zero field for various compositions from $x = 0$ to $x = 0.5$. *Right:* resistivity for $x = 0.15$ in different magnetic fields H , and magnetoresistance, defined as the change in resistivity relative to its value for $H = 0$. Reprinted with permission from [20]. © 1995 by the American Physical Society.

Doped manganites are even more complex, because the charge on the Mn site becomes an additional degree of freedom due to the two possible manganese valences Mn^{3+} and Mn^{4+} . In

order to minimize the Coulomb interaction between neighboring manganese sites, so-called *charge order* (or *ion valence order*) can develop. This is shown for the example of half-doped manganites in Fig. 13.9 on the right: These half-doped manganites show antiferromagnetic spin order, a checkerboard-type charge order with alternating Mn^{3+} and Mn^{4+} sites and a zig-zag orbital order of the additional e_g electron present on the Mn^{3+} sites. This is only one example of the complex ordering phenomena that can occur in doped mixed valence manganites. These ordering phenomena result from a subtle interplay between lattice-, charge-, orbital-, and spin degrees of freedom and can have as a consequence novel phenomena and functionalities such as *colossal magnetoresistance*.

How are these ordering phenomena related with the macroscopic properties of the system? To answer this question, let us look at the resistivity of doped Lanthanum-Strontium-Manganites (Fig. 13.10): The zero field resistance changes dramatically with composition. The $x = 0$ compound shows insulating behavior: the resistivity ρ increases with decreasing temperature T . The higher doped compounds, e.g. $x = 0.4$, are metallic with $\rho(T)$ decreasing. Note, however, that the resistivity of these compounds is still about three orders of magnitude higher than for typical good metals. At an intermediate composition $x = 0.15$, the samples are insulators at higher T down to about 250 K, then a dramatic drop of the resistivity indicating an insulator-to-metal transition and again an upturn below about 210 K with typical insulating behavior. The metal-insulator transition occurs at the temperature where ferromagnetic long-range order sets in. Around this temperature we also observe a very strong dependence of resistivity on external magnetic field. This is the so-called *colossal magnetoresistance* effect. In order to appreciate the large shift in the maximum of the resistivity curve with field (Fig. 13.10 right) one should remember that the energy scales connected with the Zeeman interaction of the spin $\frac{1}{2}$ electron in an applied magnetic field are very small: the energy equivalent of 1 Tesla for a spin $\frac{1}{2}$ system corresponds to 0.12 meV, which in turn corresponds to a temperature equivalent of 1.3 K. The strong dependence of the resistance on an external field is partly due to the so-called *double exchange* mechanism: the electron hopping from Mn^{3+} to Mn^{4+} (associated with metallicity) can occur only if the t_{2g} spins are parallel, which is automatically fulfilled (only) in the ferromagnetic state. This phase competition and consequent tunability by external parameters, such as temperature and field, is typical for correlated-electron systems.

It is clear that our entire discussion starting from ionic states is only a crude approximation to the real system. Therefore we now have to pose the question how can we determine the true valence state? Or more general, which experimental methods exist to study the complex ordering and excitations of the charge-, orbital-, spin- and lattice- degrees of freedom in these complex transition metal oxides?

13.5 Probing correlated electrons by scattering methods

How can these various ordering phenomena be studied experimentally? Obviously we need probes with atomic resolution, which interact with the spins as well as with the charges in the system. Therefore neutron and x-ray scattering are the ideal microscopic probes to study the complex ordering phenomena and their excitation spectra. The lattice and spin structure can be studied with neutron diffraction from a polycrystalline or single crystalline

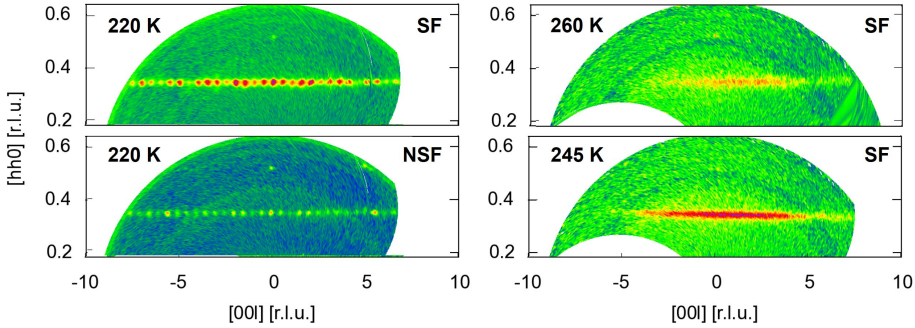


Fig. 13.11: Polarized single crystal neutron diffraction on LuFe_2O_4 . The $(\frac{1}{3}\frac{1}{3}\ell)$ line of spin and charge order superstructure reflections is shown. Left: magnetic reflections in the spin-flip channel (top) and charge order reflections in the non-spin-flip channel (bottom) at 220 K. Right: diffuse scattering in the spin-flip channel at two temperatures above T_N , revealing short-range magnetic correlations [21].

sample as detailed in chapter 5 of this course. Fig. 13.11 shows as an example of more recent research on a material with more complex (rhombohedral) crystal structure by polarized neutron diffraction on a single crystal of LuFe_2O_4 , a once-proposed charge-order-based multiferroic. Periodic arrangements of spins and/or Fe valence states in this material can be described by an enlarged cell, which corresponds to a smaller cell in reciprocal space and therefore leads to the emergence of *superstructure reflections* between the main nuclear reflections. Magnetic reflections in the spin-flip channel yield the spin structure, while the charge-order reflections show up in the non-spin-flip channel (c.f. chapter 8). For charge order and small structural distortions complementary synchrotron x-ray diffraction data is often useful because of the higher achievable q -resolution. It is beyond the scope of this lecture to discuss the experimental and methodological details of such a structure analysis or to present detailed results on specific model compounds. For this we refer to the literature, e.g. [21]. For the above example, we just want to mention that the refinement of spin and charge order showed strong spin-charge coupling, but the absence of a polar charge order, negating the proposed multiferroicity. At first sight it might be surprising that neutron diffraction is able to give us information about *charge order*. We have learnt in the introductory chapters that neutrons interact mainly through the strong interaction with the nuclei and through the magnetic dipole interaction with the magnetic induction in the sample. So how can neutrons give information about charge order? Obviously charge order is not determined directly with neutrons. However, the length of the transition metal-oxygen bond will depend on the charge (valence state) of the transition metal ion. The higher the positive charge of the transition metal, the shorter will be the bond to the neighbor-ing oxygen, just due to Coulomb attraction. This qualitative argument can be quantified in the so-called *bond-valence sum*. There is an empirical correlation between the valence V_i of an ion and the bond lengths R_{ij} to its neighbors:

$$V_i = \sum_{ij} s_{ij} = \sum_{ij} e^{\frac{R_0 - R_{ij}}{B}}. \quad (13.4)$$

Ions	La ³⁺	Pr ³⁺	Nd ³⁺	Sm ³⁺	Eu ³⁺	Gd ³⁺	Tb ³⁺	Dy ³⁺	Er ³⁺
R_0	2.172	2.138	2.105	2.090	2.074	2.058	2.032	2.001	1.988

Ions	Tm ³⁺	Yb ³⁺	Y ³⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺	Mn ³⁺	Mn ⁴⁺
R_0	1.978	1.965	2.019	1.967	2.118	2.285	1.760	1.753

Table 13.1: R_0 values of cation-oxygen bonds [22] in manganese perovskites needed for the bond valence calculation (13.4).

Here, the R_{ij} are the experimentally determined bond lengths, $B = 0.37$ is a constant, and R_0 are tabulated values for the cation-oxygen bonds, see, e.g., [22]. Table 13.1 reproduces some of these values. The sum over the partial “bond-valences” s_{ij} gives the valence state of the ion.

Even though this method to determine the valence state is purely empirical, it is rather precise compared to other techniques. The values of the valences found with this method differ significantly from a purely ionic model. Instead of integer differences between charges on different transition metal ions, one finds more likely differences of a few tenths of a charge of an electron, though rare exceptions, where near-integer valence differences were observed, exist [23].

Just like *charge order*, *orbital order* is not directly accessible to neutron diffraction since orbital order represents an anisotropic charge distribution and neutrons do not directly interact with the charge of the electron. However, we have seen in the discussion of the Jahn-Teller effect (Figs. 13.8 and 13.9) that an orbital order is linked to a distortion of the local environment visible in different bond lengths within the anion complex surrounding the cation. Thus, by a precise determination of the structural parameters from diffraction, one can determine in favorable cases the ordering patterns of all four degrees of freedom: lattice, spin, charge and orbitals.

Is there a more direct way to determine charge- and orbital order? The scattering cross section of x-rays contains the atomic form factors, which are Fourier transforms of the charge density around an atom. Therefore, one might think that charge and orbital order can be easily determined with x-ray scattering. However, as discussed in the last paragraph, usually only a fraction of an elementary charge contributes to charge- or orbital ordering. Consider the Mn atom: the atomic core has the Ar electron configuration, i.e. 18 electrons are in closed shells with spherical charge distributions. For the Mn⁴⁺ ion, three further electrons are in t_{2g} levels. Since in scattering, we measure intensities, not amplitudes, these 21 electrons contribute $21^2 r_0^2$ to the scattered intensity (the classical electron radius r_0 is the natural unit of x-ray scattering). If the difference in charge between neighboring Mn ions is $0.2e$, this will give an additional contribution to the scattered intensity of $0.2^2 r_0^2$. The relative effect of *charge order* in x-ray scattering is therefore only a tiny fraction $\frac{0.2^2}{21^2} \sim 10^{-4}$, even ignoring that scattering from all other atoms makes the situation worse. There is, however, a way to enhance the scattering from non-spherical charge distributions, the so-called *anisotropic anomalous x-ray scattering*, first applied for *orbital order* in manganites by Murakami *et*

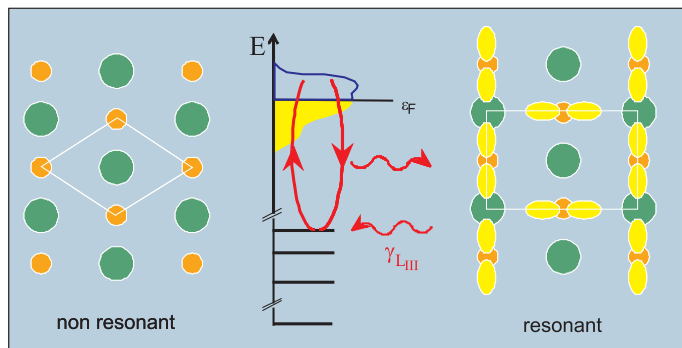


Fig. 13.12: Anisotropic anomalous x-ray scattering for a hypothetical diatomic 2D compound. *Left:* Reconstruction of the charge distribution from a laboratory x-ray source, sensitive mainly to the spherical charge distribution and corresponding unit cell (white lines). *Middle:* Principles of resonance x-ray scattering in an energy level diagram (see text). *Right:* Charge distribution deduced from such an anomalous x-ray scattering experiment. An orbital ordering pattern is apparent, which could not be detected with non-resonant x-ray scattering. The evidently larger unit cell gives rise to superstructure reflections (at resonance).

al. [24]. The principle of this technique is depicted in Fig. 13.12, showing scattering from a hypothetical diatomic 2D compound. Non resonant x-ray scattering is sensitive mainly to the spherical charge distribution. A reconstruction of the charge distribution done from such an experiment might look schematically as shown on the left. The corresponding crystal structure can be described with a primitive unit cell (white lines). To enhance the scattering from the non-spherical part of the charge distribution, an experiment can be done at a synchrotron source, with the energy of the x-rays tuned to the energy of an absorption edge (middle). Now, second order perturbation processes can occur, where a photon induces virtual transitions of an electron from a core level to empty states above the Fermi energy and back with re-emission of a photon of the same energy. As second-order perturbation processes have a resonant denominator, this scattering will be strongly enhanced near an absorption edge. If the intermediate states in this resonant scattering process are somehow connected to orbital ordering, scattering from orbital ordering will be enhanced. Thus in the resonant scattering experiment, orbital order can become visible as indicated on the right. With the shown arrangement of orbitals, the true primitive unit cell of this hypothetical compound is obviously larger than the unit cell that was deduced from the non resonant scattering experiment (left), which was not sensitive enough to determine the fine details of the structure. An increase of the unit cell dimensions in real space is connected with a decrease of the distance of the reciprocal lattice points, leading to additional *superstructure reflections*. The intensity of these reflections has the strong energy dependence expected for a second-order perturbation process. This type of experiment is called *anisotropic anomalous x-ray scattering*, because it is sensitive to the anisotropic charge distribution around an atom.

So far we have discussed some powerful experimental techniques to determine the various ordering phenomena in complex transition metal oxides. Scattering can give much more information than just on the time averaged structure. Quasi-elastic diffuse scattering gives

us information on fluctuations and short range correlations persisting above the transitions, e.g. short range correlations of polarons, magnetic correlations in the paramagnetic state (Fig. 13.11), local dynamic Jahn-Teller distortions etc. Studying these correlations and fluctuations helps to understand what drives the respective phase transitions into long-range order. The relevant interactions, which give rise to these ordering phenomena, can be determined from inelastic scattering experiments as learnt in the chapter “Inelastic neutron scattering”. For example, in a new class of iron-based high-temperature superconductors, the involvement in Cooper pairing of lattice vibrations or alternatively magnetic fluctuations is controversial, and both of these can be probed in-depth by inelastic neutron scattering (see, e.g., [25]). Since there is a huge amount of scattering experiments on highly correlated transition metal oxides and chalcogenides, a review of these experiments definitely goes far beyond the scope of this introductory lecture.

13.6 Summary

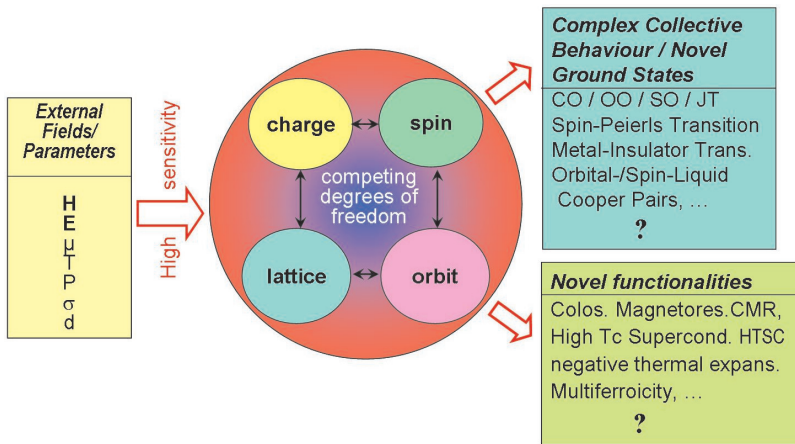


Fig. 13.13: Illustration of complexity in correlated electron systems. **H, E:** magnetic and electric field, respectively; μ : chemical potential (doping); T : temperature; P : pressure; σ : strain (epitaxial growth); d : dimensionality (e.g. bulk versus thin film systems); CO: charge order; OO: orbital order; SO: spin order; JT: Jahn-Teller transition.

This chapter gave a first introduction into the exciting physics of highly correlated electron systems, exemplified by transition metal oxides and chalcogenides. The main message is summarized in Fig. 13.13. The complexity in these correlated electron systems arises from the competing *degrees of freedom*: charge, lattice, orbit and spin. The ground state is a result of a detailed balance between these different degrees of freedom. This balance can be easily disturbed by external fields or other thermodynamical parameters, giving rise to new ground states or complex collective behavior. Examples are the various ordering phenomena discussed, Cooper pairing in superconductors, so-called spin-Peierls transitions in 1D systems etc. This high sensitivity to external parameters as well as the novel ground states of the systems give rise to novel functionalities, such as the colossal magnetoresistance effect, high temperature superconductivity, multiferroicity, and many more. A theoretical description of these complex systems starting from first principles, like Schrödinger equation in quantum mechanics or the maximization of entropy in statistical physics, is bound to fail due to the large number of strongly interacting particles. Entirely new approaches have to be found to describe the emergent behavior of these complex systems. Therefore highly correlated electron systems are a truly outstanding challenge in modern condensed matter physics. We have shown in this lecture that neutron and x-ray scattering are indispensable tools to disentangle this complexity experimentally. They are able to determine the various ordering phenomena as well as the fluctuations and excitations corresponding to the relevant degrees of freedom. No other experimental probe can give so much detailed information on a microscopic level as scattering experiments.

References

- [1] R. B. Laughlin and D. Pines, *Proc. Natl. Acad. Sci. USA* **97**, 28 (2000).
- [2] T. Vicsek, *Nature* **418**, 131 (2002).
- [3] J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189 (1986).
- [4] A.-M. Haghir-Gosnet and J.-P., *J. Phys. D: Appl. Phys.* **36**, R127 (2003).
- [5] G. Binasch, P. Grünberg, F. Saurenbach, and W. Zinn *Phys. Rev. B* **39**, 4828 (1989).
- [6] M. N. Baibich *et al.*, *Phys. Rev. Lett.* **61**, 2472 (1988).
- [7] M. H. Phan and S. C. Yu, *J. Magn. Magn. Mater.* **308**, 325 (2007).
- [8] E. J. W. Verwey, *Nature* **144**, 327 (1939).
- [9] M. Fiebig, *J. Phys. D: Appl. Phys.* **38**, R123 (2005).
- [10] M. Bibes and A. Barthélémy, *Nat.* **7**, 425 (2008).
- [11] G. D. Barrera *et al.*, *J. Phys.: Condens. Mat.* **17**, R217 (2005).
- [12] E. Dagotto, *Science* **309**, 257 (2005).
- [13] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Thomson Brooks/Cole, New York, 1976).
- [14] H. Ibach and H. Lüth, *Solid State Physics: An introduction to principles of materials science* (Springer, Berlin, 2010).
- [15] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Nobel Prize in Physics in 1972 for a microscopic theory of superconductivity (nowadays called BCS-theory.)*
- [16] K. Held *et al.*, *J. Phys.: Condens. Mat.* **20**, 064202 (2008).
- [17] N. F. Mott, *Rev. Mod. Phys.* **40**, 677 (1968).
- [18] P. Fazekas, *Lecture notes on electron correlation and magnetism* (World Scientific, Singapore, 2003).
- [19] T. Chatterji (Ed.), *Colossal magnetoresistive manganites* (Kluwer Academic Publishers, Dordrecht, 2004).
- [20] A. Urushibara *et al.*, *Phys. Rev. B* **51**, 14103 (1995).
- [21] J. de Groot *et al.*, *Phys. Rev. Lett.* **108**, 037206 (2012). *ibid.* **108**, 187601 (2012). For a general review see also M. Angst, *Phys. Status Solidi RRL* **7**, 383 (2013).
- [22] G. H. Rao, K. Bärner, and I. D. Brown, *J. Phys.: Condens. Mat.* **309**, 257 (2005).
- [23] M. Angst *et al.*, *Phys. Rev. Lett.* **99**, 086403 (2007).
- [24] Y. Murakami *et al.*, *Phys. Rev. Lett.* **81**, 582 (1998).
- [25] R. Mittal *et al.*, *Phys. Rev. Lett.* **102**, 217001 (2009).

Exercises

Note: ★ indicates an increased difficulty. Solve the easier problems first.

E13.1 Electronic structure and Mott transition

- a) In modeling the electronic structure of crystalline solids, what is the typical starting assumption to separate the electronic structure from the lattice dynamics, and why does it work?
- b) In which of the three simplest models of electrons in a solid are the electronic correlations taken into account at least approximately?
- c) Neglecting electronic correlations, would you predict NaCl to be an insulator or a metal? Why?
- d) The competition of which two contributions to the total energy of the electrons is crucial for the Mott-transition? Which further contributions to the total energy are neglected in the simplest model?
- e) Assume that a particular material is a Mott-insulator, but just barely so (i.e. the relevant energy contributions are almost equal). What would you predict to happen when sufficiently high pressure is applied, and why?

E13.2 Electronic ordering in correlated-electron materials

- a) List and very briefly explain three “electronic degrees of freedom”, which can become ordered.
- b) To order of which of the electronic degrees of freedom is neutron scattering *directly* sensitive, and to which not?
- c) For those electronic degrees of freedom, to which neutron is *not* directly sensitive, neutron scattering can still be used to deduce an ordered arrangement: How and why? Is there a more direct scattering method than neutron scattering?
- d) ★ What, if any, connection is there between orbital order and orbital magnetic momentum?
- e) ★ Discuss why electronic correlations favor ordering processes of electronic degrees of freedom.

E13.3 Crystal field

Fe has atomic number 26 and in oxides typically has valence states 2+ or 3+.

- a) Determine the electronic configuration of free Fe^{2+} and Fe^{3+} ions (hint: as for Mn the outermost *s*-electrons are lost first upon ionization).

b) From Hund's rules determine the values of the spin S , orbital angular momentum L , and total angular momentum J of Fe^{2+} and Fe^{3+} ions.

(Hund's rules:

1. S max.
2. L max consistent with 1.
3. $J = |L - S|$ for a less than half filled shell,
 $J = |L + S|$ for a more than half filled shell).

c) ★ The effective moment μ_{eff} of a magnetic ion can be determined experimentally by the Curie-Weiss law, and is given by $\mu_{\text{eff}} = g_J \sqrt{J(J+1)} \mu_B$, where the Landé factor is

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}. \quad (13.5)$$

Calculate the expected effective moment in units of μ_B of Fe^{2+} and Fe^{3+} ions, i) assuming S , L , and J as determined in b) and ii) setting $L = 0$ ('quenched orbital momentum'). Compare with the experimental values of $\sim 5.88 \mu_B$ for Fe^{3+} and $\sim 5.25 - 5.53 \mu_B$ for Fe^{2+} .

d) ★ The negatively charged oxygen ions surrounding the Fe ions in an oxide solid influence the energy of the different orbitals. Plot the expected energy level diagram for the case of an octahedral environment of nearest-neighbor O^{2-} (corresponding to the example in the lecture). How does the total spin moment of Fe^{2+} change between weak and strong crystal field splittings (relative to intra-atomic "Hund's" exchange)?

e) (optional) ★★ In a tetrahedral environment the energy levels of the orbitals are reversed compared to an octahedral environment. Determine the spin moment of Fe^{2+} in a tetrahedral environment with strong crystal field splitting. Is an orbital angular momentum possible in this case?

E13.4 Orbital and Magnetic order in LaMnO_3 (Optional!)

The orbital and magnetic order in LaMnO_3 is sketched in Fig. 13.9 (page 11 of the chapter) on the left. One crystallographic unit cell $a \times b \times c$ is shown.

- a) Why is there no charge order in LaMnO_3 ?
- b) What are the smallest unit cells (sketch in relation to the crystallographic cell) that can describe i) magnetic order, ii) ★ orbital order (*Hint: consider also centered cells, where the centering symmetry is broken by the orbital order*), iii) both magnetic and orbital order.
- c) Make a plot of reciprocal space in the a^*-c^* -plane indicating the positions, where you expect nuclear, orbital, and magnetic Bragg peaks to occur.
- d) ★ As c), but for the a^*-b^* -plane.

14 Dynamics of Polymers and Biological Macromolecules

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14.1 Introduction

A polymer is a chain of polyatomic units, called monomers, that are covalently bonded together. Since almost all molecules can act as monomers, differing only in the ways they can be bound together, a wide variety of synthetic and naturally occurring biopolymers with diverse properties are now known. They all belong to the polymer class. Synthetic polymers are materials without which modern technology cannot be imagined. In many places they have supplanted traditional materials as metals. One of the reasons for this is that polymers show unique mechanical properties which are desirable for engineering, e.g. high impact resistance at low specific mass. The polymer composition (specific monomers) and architecture (linear, branched ring) influence the material properties.

Biopolymers as proteins or DNA determine life. Biopolymers, in particular proteins, share similarities with polymers which allow to use polymer models to describe their structure and dynamics. Proteins are polymers with a specific sequence of the 22 (proteinogenic) amino acids which are charged, hydrophobic or hydrophilic. Intrinsically disordered proteins (IDP) sample a large conformational space similar to synthetic polymers. The structure of globular proteins is mainly stabilized by hydrophobic interactions but additionally via a hydrogen bond network and crosslinking by disulfide bonds. The protein structure and related conformational changes are often related to the function of the protein e.g. by arranging the active center after substrate binding or allowing transport and release of products. As larger domains contribute to configurational changes, the timescale of the motions involved is slowed down. The role of slow domain dynamics in understanding the function of proteins is increasingly recognised.

14.2 Coarse graining

Nowadays, the complexity of polymers and biopolymers can be covered by all-atom MD simulations, which require a huge amount of resources and computation time. The essential structure and dynamics can be examined since long time [1, 2, 3, 4] by coarse grained models that successfully describe all essential features of polymers within analytical theories and allow to understand all basic properties.

The basic assumption of the simplest bead-and-spring models is that the beads do not interact with each other except via springs connecting neighbouring beads. For linear polymers, the result is a Gaussian chain, which is the simplest model for chain relaxation. Such a chain is made up of N segments, each of which consists of a sufficient number of monomers for their end-to-end distance to follow a Gaussian distribution, with an average segment length of l . Coarse graining involves the segments consisting of several monomers and being longer than the Kuhn length, which describes the local stiffness of the chain structure. While the Rouse model assumes friction only with the surrounding medium, the Zimm model includes additional friction between beads, which is mediated by hydrodynamic interactions between all beads. Assuming friction between monomers results in additional internal friction within the chain. More structured objects like proteins or double stranded DNA can be described by networks of connected beads in a similar way describing also the 3D structure. Neutron scattering allows to study the microscopic structure and dynamics of polymer chains based on the existing theories.

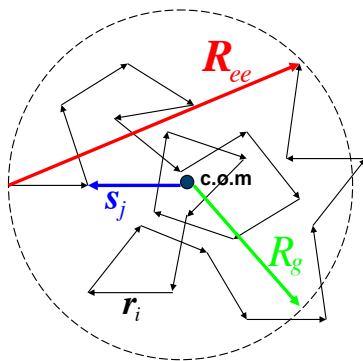


Fig. 14.1: A freely jointed chain and definitions: end-to-end distance R_{ee} , gyration radii R_g , segment vector $\mathbf{r}_i$ and $\mathbf{s}_j$ is a vector between the segment and centre-of-mass.

14.3 Conformation of linear chains

Polymers are often imagined as spaghetti-like or coiled molecules. Their stiffness can range from flexible to rigid, depending on the shape of the polymer. Their configuration, i.e., the spatial distribution of their monomer units or segments, changes constantly due to Brownian dynamics, leading to sampling over a vast configurational space. The simplest model is the freely jointed chain (FJC). Figure 14.1 shows an example of such a configuration and illustrates the idea that polymer chains consisting of equivalent segments perform random walks. With this model, the ensemble of systems can be characterized by average quantities. One such quantity is the end-to-end vector and its square.

$$\mathbf{R}_{ee} = \sum_{i=1}^N \mathbf{r}_i, \quad R_{ee}^2 = \sum_{i,j=1}^N \mathbf{r}_i \cdot \mathbf{r}_j \quad (14.1)$$

which is a scalar quantity. N is the number of segments in the polymer chain. The bond vector length (or step) $|\mathbf{r}_i|$, connecting 2 beads is l . A further important parameter which has its counterpart in classical mechanics is the radius of gyration R_g with

$$R_g^2 = \frac{1}{N} \sum_{i=1}^N (\mathbf{r}_i - \langle \mathbf{r}_i \rangle)^2 \quad (14.2)$$

where $\langle \mathbf{r}_i \rangle$ is the center of mass averaged over all i . The FJC model assumes an equal probability in all directions of all bond vectors, random bond rotation angles while keeping the bond length constant. The mean radius of gyration can then be obtained - using random walk statistics

$$\langle R_g^2 \rangle = \frac{1}{6} N l^2 \quad (14.3)$$

From both end-to-end distance and radius of gyration an important statement which applies to polymer chain is already observed: the size depends on the square root of the number of basic steps (number of segments), $\sqrt{N}$. Real polymer chains are not connected in this freely

jointed way. Instead, bond angles θ_{ij} assume well-defined values and correlations between bonds within the chain as well as from the environment will affect the size. Intuitively it can be understood that these correlations will vanish with increasing separation distance. Also, the flexibility of polymer chains is restricted by the fact that rotations with the so-called bond rotation angle are enabled within a certain range only due to steric reasons.

An important polymer model that includes interactions is the Flory theory [2], which incorporates intermolecular and solvent interactions. If the monomers like the solvent, they will try to have more contact, causing the polymer to swell (good solvent). This corresponds to a repulsive interaction between monomers, which includes non-overlapping volumes. If the monomers do not like the solvent, the polymer tries to avoid contact with the solvent and collapses (bad solvent), which corresponds to attractive monomer interactions. In between these two cases, when the interactions are balanced, they cancel each other out, resulting in an ideal configuration without interactions (theta solvent), which is close to the FJC. The end-to-end distance is

$$\langle R_{ee}^2 \rangle = N^\nu l^{2\nu} \quad (14.4)$$

The Flory exponent ν is 0.5 for ideal solvents and 0.588 for good solvent. Often the range of ν is increased to span from collapsed chains to highly swollen chains with repulsive interactions between monomers $1/3 < \nu < 1$.

The size of a polymer chain can be measured by various scattering experiments (light scattering, SAXS, SANS). The single chain normalized formfactor $P(Q)$ is:

$$P(Q) = \frac{1}{N^2} \sum_{k,j=1}^N \langle \exp(i\mathbf{Q} \cdot (\mathbf{r}_k - \mathbf{r}_j)) \rangle = \frac{1}{N^2} \sum_{k,j=1}^N \exp\left(-\frac{1}{6}Q^2 l^2 |k - j|^{2\nu}\right) \quad (14.5)$$

using $\langle r_k - r_j \rangle = l^2 |k - j|^{2\nu}$ [5]. For long chains ($Q^2 l^2 / 6 \ll 1$ and $N \gg 1$) and $\nu = 1/2$ $P(Q)$ is described by the Debye function [6] with

$$g_D(x) = \frac{2}{x^2} (e^{-x} - 1 + x) \quad (14.6)$$

and the argument $x = (QR_g)^2$. A SANS experiment with fit to the Debye function is presented in Fig. 14.2 in a linear scale and in the form of a second moment Kratky representation achieved when $g_D(x)$ is multiplied by Q^2 . The Kratky representation emphasises the high Q -regime. For Gaussian chains with an asymptotic Q^{-2} behaviour the high Q regime then assumes a plateau. As shown, the data are in perfect agreement with the Gaussian chain results derived above.

14.4 Separation of global and internal dynamics

The intermediate scattering function (ISF) measured e.g. by NSE has contributions from overall translational and rotational diffusion and from motions within the molecule that we call internal dynamics. In the general case, all motions might be coupled. In a simplifying assumption known as decoupling approximation we assume that the internal dynamics (int) does not alter the overall diffusion and that translational (trans) and rotational (rot) diffusion

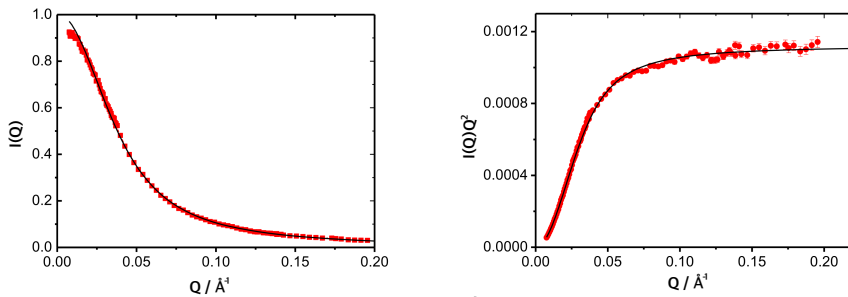


Fig. 14.2: SANS scattering intensity obtained for a poly(alkylene oxide) polymer and described by the Debye function (lines) [7]. On the left, the Debye curve fits ideally and the high Q -dependence shows Q^{-2} . On the right, the Kratky region (plateau) is highlighted.

are decoupled too. For the single particle pair correlation function $F(Q, t)$ or intermediate scattering function we assume

$$F(Q, t) = F_{\text{trans}}(Q, t) \cdot F_{\text{rot}}(Q, t) \cdot F_{\text{int}}(Q, t) \quad (14.7)$$

For spherical symmetric objects like spheres or Gaussian chains rotational contributions cannot be observed as there is no contrast change during rotation. On the other side proteins and DNA are asymmetric and have significant rotational contributions.

Diffusion of rigid objects

The diffusional term contributing to equation (14.7) for a rigid object has contributions from translational and rotational diffusion characterized by the respective diffusion coefficients D_T and D_R . These can be calculated from the atomic coordinates r_α or coarse grained bead models by HYDROPRO on basis of a protein data bank (PDB) conformation [8] or measured in dilute solutions. We yield

$$F_{\text{trans}}(Q, t) = \exp(-Q^2 D_T t) \quad (14.8)$$

$$F_{\text{rot}}(Q, t) = \sum_{l=0}^{\infty} S_l(Q) \exp(-l(l+1) D_R t) \quad (14.9)$$

$$\text{with} \quad S_l(Q) = \sum_m \left| \sum_{\alpha} b_{\alpha} j_l(Q r_{\alpha}) Y_{l,m}(\Omega_{\alpha}) \right|^2 \quad (14.10)$$

where $S_l(Q)$ are the coefficients of a multipole expansion of the asymmetric form factor with scattering length b_{α} of the atom α at position r_{α} and orientation Ω_{α} , $j_l(Qr)$ are the spherical Bessel functions and $Y_{l,m}(\Omega_{\alpha})$ the spherical harmonics [9, 10].

Concentration effects

At infinite dilution the measured intensity $I(Q, t)$ is independent of direct concentration effects and $I(Q, t)/I(Q, 0) = F(Q, t)/F(Q, 0)$. For larger concentrations c the interaction depends on the type of polymer and the solvent. Polymers in theta-solvent or in melt have virtually no interaction. Dependent on the solvent quality, as good or bad solvent, the interactions can be attractive or repulsive. Additional charges and excluded volume for globular particles contribute to the overall interaction. This leads to a spatial distribution describing spatial correlations between objects subsumed in the structure factor $S(Q, c)$ depending on the concentration c . The translational diffusion coefficient D_T is influenced by these direct interactions and hydrodynamic interactions (HI) described by the hydrodynamic function $H_T(Q)$. This is described by $D_T(Q) = D_{T0}H_T(Q, c)/S(Q, c)$ where the index 0 indicates the dilute limit (single particle limit, $c \rightarrow 0$). [10, 11].

The hydrodynamic function $H_T(Q)$ can be calculated within the $\delta\gamma$ expansion of Beenakker and Mazur [12, 13] for spherical objects which approximately holds also for polymers with a HI screening radius R_{HI} . [14] or proteins [9, 15, 16] and reduces the translational diffusion coefficient with $H_T(Q = \infty) = \eta_0/\eta < 1$ [17, 12, 13, 18]. η_0/η is measured as the ratio between solvent viscosity η_0 and protein solution viscosity at the measured concentration η . At low Q $H(Q)$ has similarities to $S(Q)$ and as a rule of thumb is approximately $H(Q) - H(\infty) \approx 0.5(S(Q) - 1)$ for hard spheres. Hydrodynamic effects also influence the rotational diffusion coefficient subsumed in the hydrodynamic factor H_R for rotational diffusion with $D_R = D_{R0}H_R$. According to ref. [4] for spherical particles this effect can be estimated as $1 - H_R = (1 - H_T(Q = \infty))/3$.

14.5 Linear polymers in melt

To describe the motion of a polymer, we start with the bead and spring model. Each bead undergoes friction $\zeta = 6\pi\eta l$ with the surrounding which can be a polymer melt or solvent of viscosity η . Hydrodynamic interactions are assumed screened and therefore neglected. It is assumed that the harmonic springs with an entropic origin have a spring constant of $\kappa = (k_B T)/l^2$. We can write down a Langevin equation for the segmental motion using $f_n(t)$ for the thermal random force acting on bead “ n ” within the Rouse model [1]:

$$\zeta \frac{dr_n}{dt} = \kappa (r_{n+1} - 2r_n + r_{n-1}) + f_n(t) \quad (14.11)$$

$$\zeta \frac{d\mathbf{r}}{dt} = \kappa \mathbf{k}\mathbf{r} + \mathbf{f}(t) \quad (14.12)$$

using vector notation $\mathbf{r} = (r_1, \dots, r_N)$ with the tri-diagonal connectivity matrix

$$\mathbf{k} = \begin{pmatrix} -1 & 1 & 0 & 0 & \dots \\ 1 & -2 & 1 & 0 & \dots \\ 0 & 1 & -2 & 1 & \dots \\ 0 & 0 & 1 & -2 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} \quad (14.13)$$

Microscopic dynamics on scales shorter than the segment or Kuhn length like dihedral rotations of bonds can lead to internal friction ζ_i between beads which can be included in the RIF model (Rouse with internal friction) as [19] :

$$\zeta \frac{d\mathbf{r}}{dt} = \kappa \mathbf{k} \mathbf{r} + \zeta_i \frac{d}{dt} \mathbf{k} \mathbf{r} + \mathbf{f}(t) \quad (14.14)$$

The coupled differential equations (14.12) and (14.14) can be solved using the eigenbasis of the connectivity matrix (14.13), i.e. normal mode decomposition. With the proper boundary conditions of force free ends $\partial r_n / \partial n (n=0, N) = 0$ the eigenmodes turn out as

$$\phi_p(n) = \frac{1}{N} \cos\left(\frac{p\pi}{N}n\right) \quad (14.15)$$

with a wavelength $\lambda_p = lN/p$ along the chain. The eigenmode p relaxes with the characteristic time τ_p where

$$\tau_p = \tau_R/p^2 + \tau_i, \quad \tau_R = \frac{N^2 l^2 \zeta}{3\pi^2 k_B T} = \frac{N^2 \zeta}{3\pi^2 \kappa} = \tau_0 N^2, \quad \tau_i = \zeta_i / \kappa \quad (14.16)$$

τ_R is the longest relaxation time also called the Rouse time without internal friction in the Rouse model. $\tau_0 = \frac{l^2 \zeta}{3\pi^2 k_B T} = \frac{1}{W\pi^2}$ is the segmental relaxation time where W is the Rouse rate which is related to monomer (bead) friction ζ . τ_i is the additional relaxation time due to internal friction ζ_i . At the time τ_p the chain subsection with N/p monomers moves over its own distance. Thus the mean square displacement msd ,

$$msd = \langle (r_n(\tau_p) - r_n(0))^2 \rangle = l^2 \frac{N}{p} = l^2 \left(\frac{\tau_p}{\tau_0} \right)^{\frac{1}{2}} \quad (14.17)$$

Since (14.17) holds for all p , the chain segments at times shorter than τ_R move in a subdiffusive way with $msd \propto t^{1/2}$. This is a basic prediction of the Rouse model. Performing the full calculation starting from (14.11)-(14.12), the final result for the time dependent msd is:

$$msd = \langle r_n^2(t) \rangle = \sqrt{\frac{12l^2 k_B T}{\pi \zeta}} t \quad (14.18)$$

For the single chain pair correlation function $F(Q, t)$, where we look on a labelled e.g. protonated chain in a deuterated environment, we have to deal with the interference of scattered waves originating from the different atoms or monomers of the same chain. The detailed calculations are given in reference [5]. The result may be expressed in terms of

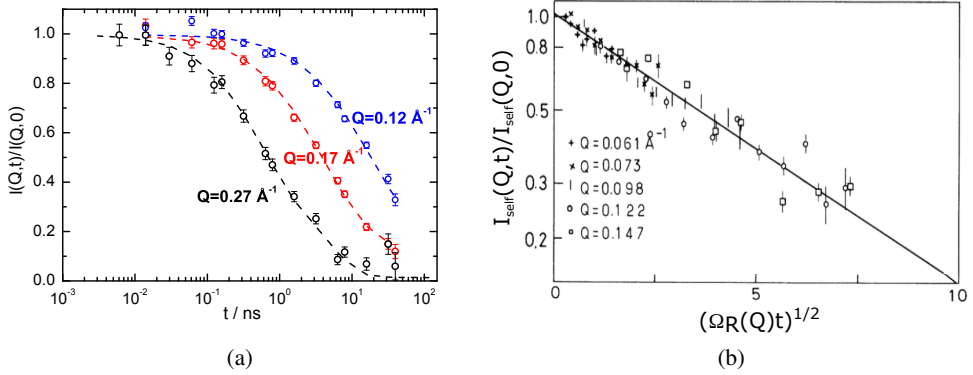


Fig. 14.3: (a) NSE data for the polydimethylsiloxane (PDMS) melt measured at different values of the momentum transfer Q [20]. Dashed lines present fitting curves obtained by using (14.19); (b) Dynamic structure factor for the segmental self motion in a PDMS melt at 100°C [21]. The data are scaled with the Rouse variable (14.20). The solid line shows the predicted $t^{1/2}$ relaxation by the Rouse model.

the Rouse modes Eq. (14.15) and corresponding relaxation times $\tau_p = \tau_R/p^2$ and amplitude factors $a_p = 1/p^2$ as

$$F_{\text{coh}}(Q, t) = \frac{1}{N} e^{-Q^2 D_R t} \sum_{n,m}^N e^{-\frac{1}{6} Q^2 B(n,m,t)} \quad (14.19)$$

$$B(n, m, t, \tau_p) = |n - m|^2 \nu l^2 + \frac{4R_e^2}{\pi^2} \sum_{p=1}^{N-1} a_p \cos(\pi p n / N) \cos(\pi p m / N) (1 - e^{-t/\tau_p})$$

The first part presents translational centre of mass diffusion, while the sum describes internal motions. For small Q ($QR_{\text{ee}} < 1$) the internal motions in $B(n, m, t)$ become negligible and $F_{\text{coh}}(Q, t)$ describes the centre-of-mass self diffusion of the chain with $D_R = k_B T / N \zeta$.

For $QR_{\text{ee}} > 1$ and $t < \tau_R$ the internal relaxation processes dominate. For $t = 0$ we have $F(Q, t = 0) = P(Q)$; *i.e.* and the form factor corresponds to a snapshot of the chain structure (14.5). By using a mixture of protonated ($\approx 10\%$) and deuterated chains, neutron spin echo (NSE) directly measures $F(Q, t)$ that is the spatial Fourier transform of the monomer-monomer dynamic pair correlation function. As an example, the NSE data for the bulk PDMS melt are shown in Fig. 14.3a.

Quasielastic incoherent neutron scattering directly measures the segment self correlation function with $n = m$ in (14.19). In Gaussian approximation we have for pure Rouse:

$$F_{\text{self}}(Q, t) = \exp\left(-\frac{Q^2}{6} \langle r^2(t) \rangle\right) = \exp(-D_R Q^2 t) \exp\left(-\frac{2}{\sqrt{\pi}} (\Omega_R(Q) t)^{\frac{1}{2}}\right) \quad (14.20)$$

$$\Omega_R(Q) = \frac{k_B T l^2}{12 \zeta} Q^4$$

The second part of this equation is obtained by inserting of Eq.(14.18). $\Omega_R(Q)$ is the characteristic relaxation rate, that increases with the momentum transfer as Q^4 .

Even though a clear cut prediction, experimentally the observation of the self correlation function of a Rouse chain is an important challenge. Neutron spin echo spectroscopy is necessary for the required resolution at low momentum transfers. [22, 23]. Here, incoherent experiments are difficult since incoherent scattering depolarises the neutron beam to a large extent (i.e. 2/3 of the spins are flipped). Therefore, the first successful experiments were carried out using a trick. The chemists produced deuterated PDMS in which short protonated sections were randomly copolymerised. These protonated sections, present in an otherwise deuterated environment, gave rise to coherent scattering. However, since the scattering from different labels was uncorrelated, the self-correlation function was measured.

Fig. 14.3b displays the obtained self correlation function for PDMS [21] in a presentation where the logarithm of the scattering function is plotted versus $(\Omega_R(Q)t)^{\frac{1}{2}}$, the scaling variable of Eq.(14.20). In this way all the data collapse on one single master curve that according to Eq.(14.20) should be a straight line. The experimental results beautifully verify the major prediction of the Rouse model and show that the simple approximation of the bead - spring model properly accounts for the segmental dynamics of the PDMS chain on the space time frame investigated.

14.6 Linear polymers in solution

In the above melt, we assume that polymer chains do not interact with each other; however, this is different in solution. In solution, polymers may interact depending on how they interact with the solvent (e.g., whether they like or dislike the solvent), and they may have direct interactions, such as coulomb interactions, if charges are present. Additionally, hydrodynamic interactions (HIs) must be considered. In the the Zimm model [3] this is done by using a preaveraging approximation using the equilibrium average

$$\mathbf{H}_{nm} \longrightarrow \langle \mathbf{H}_{nm} \rangle = \frac{\mathbf{I}}{2\pi^2 \zeta |n - m|^{1/2}} \quad (14.21)$$

The above equation (14.14) changes to

$$\frac{d\mathbf{r}}{dt} = \langle \mathbf{H} \rangle (\kappa \mathbf{kr} + \zeta_i \frac{d}{dt} \mathbf{kr} + \mathbf{f}(t)) \quad (14.22)$$

For $N \gg 1$ $\langle \mathbf{H} \rangle$ becomes diagonal in the eigenbasis of the connectivity matrix (14.13). The eigenmode p relaxes with the characteristic time τ_p where

$$\tau_p = \tau_Z / p^{3\nu} + \tau_i, \quad \tau_Z = \frac{\eta R_e^3}{(3\pi)^{1/2} k_b T} = \frac{N^{3\nu} \zeta}{6\pi (3\pi)^{1/2} \kappa}, \quad \tau_i = \zeta_i / \kappa \quad (14.23)$$

τ_Z is the longest relaxation time also called the Zimm time without internal friction in the Zimm model. τ_i is the additional relaxation time due to internal friction ζ_i in the corresponding ZIF model (Zimm with internal friction).

The single chain $F(Q, t)$ for the Zimm model is the same as (14.19) with the amplitude factor $a_p = 1/p^{3\nu+1}$ and the mode relaxation time τ_p of the Zimm respectively the ZIF model. Here $R_e = N^\nu l$ and $D_Z = \frac{8}{3(6\pi^3)^{1/2}} \frac{k_b T}{\eta R_e} = 0.196 \frac{k_b T}{\eta R_e}$ for $\nu = 0.5$. For $\nu = 0.6$ the prefactor is 0.203.

Fig. 14.4 shows an example for the polyelectrolyte (PE) polystyrene sulfonic acid (PSS)[14]. The SAXS data Fig. 14.4a decrease at low Q is due to the structure factor $S(Q)$ with increasing concentration. $S(Q)$ effects are reduced with increasing charge screening due to added salt. PE formfactor shows a more expanded chain with $\nu \gtrsim 0.6$ due to repulsion between charges. The minima around $Q = 3 - 4 \text{ nm}^{-1}$ are related to a disc like cross section of the chain from counter ion condensation. NSE spectra were fitted with a ZIF model complemented by $H(Q)/S(Q)$ correction for D_Z . Fig. 14.4b show effective diffusion extracted by fitting $\exp(-Q^2 D_{\text{eff}} t)$ to model and data to get an easier overview. At low Q the collective D_{eff} increases due to $H(Q)/S(Q)$ correction reflecting $S(Q)$ and hydrodynamic interactions. At larger Q above 0.5 nm^{-1} we observe self diffusion ($S(Q) \approx 1$) with an approximate linear increase as predicted for Zimm dynamics $D_{\text{eff}} \propto kT/\eta$ [5] of neutral chains. Above 1 nm^{-1} dynamics slows down due to internal friction. The charged chain behaves on segment length scale independently of charge or screening salt like a neutral chain expanded according to ν .

14.7 Protein domain motions

To explore the internal dynamics of fragments or domains we use a Langevin equation similar to (14.12). Unlike polymer models, we must consider all neighbors in direct contact with the beads representing amino acids, which can form hydrophobic contacts, for example. The connectivity matrix (14.13) contains more off-diagonal elements representing interacting beads. Tirion demonstrated that a simplified elastic force field is sufficient for describing the slowest large-scale motions. [4]. With this in mind we assume Brownian motion of the protein atoms in a harmonic potential around the equilibrium positions, a problem described by the Ornstein-Uhlenbeck process [24, 25]. The coherent intermediate scattering function is (for details see [26])

$$F_{\text{int}}(Q, t) = \left\langle \sum_{\alpha, \beta} b_\alpha b_\beta \exp(i\mathbf{Q} \cdot \mathbf{R}_\beta^{\text{eq}}) \exp(-i\mathbf{Q} \cdot \mathbf{R}_\alpha^{\text{eq}}) \cdot f_{\alpha\beta}(Q, \infty) \cdot f'_{\alpha\beta}(Q, t) \right\rangle. \quad (14.24)$$

Here $f_{\alpha\beta}(Q, \infty)$ is a time independent factor determined by the internal forces. The time dependent part is

$$f'_{\alpha\beta}(Q, t) = \exp \left(\sum_{j=1 \dots 3N} (\mathbf{v}_\alpha \cdot \mathbf{Q})(\mathbf{v}_\beta \cdot \mathbf{Q}) \exp(-\lambda_j t) \right) \quad (14.25)$$

with displacements $v_{j\alpha} = \sqrt{k_B T / (\lambda_j \Gamma_j)} \hat{b}_{j\alpha}$ in Brownian normal mode j with relaxation time $1/\lambda_j$ and friction Γ_j . The contribution of internal dynamics to the NSE signal is

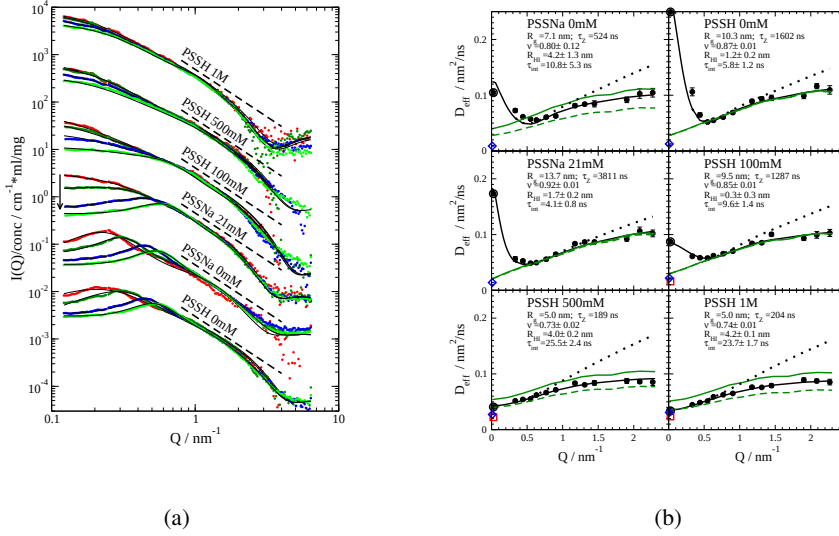


Fig. 14.4: (a) SAXS data for PSS MW=39k (c_{NaCl} shifted consecutively). A stronger $S(Q)$ with increasing c_p results mainly in the decreased intensity at a low Q . Concentrations were 5, 10, 20, 30 mg/mL except for 21 mM with 8.3, 16.6, 33.2 and 50 mg/mL (colors red to green, along arrow). Black lines correspond to fits using a generalised Gaussian worm as formfactor and a 2-Yukawa potential with attractive and repulsive components. Broken lines indicate the extension of a Q^{-2} power law to a high Q to demonstrate the deviation from a Gaussian chain. (b) Effective diffusion coefficients D_{eff} for PSS 39k $c_p M_w = 30$ mg/ml with respective parameters: experimental (points); ZIF with full $H(Q)/S(Q)$ correction (black line); ZIF only with self-part correction D_s/D_0 (green dashed); same but $\tau_{int} = 0$ (Zimm) (dotted); ZIF without correction (green line); DLS extrapolated concentration 0 mg/mL (red square), 30 mg/mL (circle); PFG-NMR self-diffusion D_s (blue diamond). It should be noted that the self-part corrected ZIF (green dashed line) fits well to D_s . The self-part D_s/D_0 correction is noticeable as a difference between solid and dashed green lines. Reprinted from ref [14] Licensed under CC-BY 4.0

$F_{int}(Q, t)/F_{int}(Q, 0)$. The dynamics of single independent particles or subunits can be described by the much simpler function

$$F_{int}(Q, t) = \exp(-Q^2 \langle u^2 \rangle (1 - \exp(-\lambda t))) \quad (14.26)$$

with the mean square displacement $\langle u^2 \rangle$ in the harmonic potential [27]. Nevertheless, in this simplification, the specific arrangement of the conformation is lost.

Looking at the time dependence we find again the pattern $\exp(\dots(1 - e^{-\lambda t}))$ observed in Rouse (14.19). Expanding the first exponential in equation (14.25) as $\exp(x) = 1 + x$ we get

a simplification for small displacements

$$f'_{\alpha\beta}(Q, t) = 1 + \sum_{j=1 \dots 3N} (\mathbf{v}_\alpha \cdot \mathbf{Q})(\mathbf{v}_\beta \cdot \mathbf{Q}) \exp(-\lambda_j t) \quad (14.27)$$

showing that the amplitude is directly related to the displacements of the modes. Using $F(Q, t)/F(Q, 0)$ for the measured NSE signal we find with $B = \sum_{j=1 \dots 3N} (\mathbf{v}_\alpha \cdot \mathbf{Q})(\mathbf{v}_\beta \cdot \mathbf{Q})$ and $A = B/(1 + B)$ assuming a single relaxation rate λ

$$\frac{F(Q, t)}{F(Q, 0)} = [(1 - A) + Ae^{-\lambda t}] \frac{F_{\text{trans}}(Q, t) \cdot F_{\text{rot}}(Q, t)}{F_{\text{trans}}(Q, 0) \cdot F_{\text{rot}}(Q, 0)} \quad (14.28)$$

14.8 Between chain dynamics and domain motions: intrinsically disordered proteins (IDP)

The biological role of the IPD is founded in their high conformational adaptivity, enabling them to respond rapidly to environmental changes, in the flexibility of their associative properties allowing them to fold into different states depending on partner molecules. For these properties the dynamics is essential. Myelin basic protein (MBP) is a major component of the Myelin sheets in the central nervous system [28]. The major human and bovine MBP variant, which has 18.5 kDa and 170 amino acids, was investigated. MBP is of significant importance in the human body because many neurological disorders, such as multiple sclerosis, are related to MBP malfunction. Lipid free MBP is not completely unfolded but retains some elements of the alpha helix and beta sheet (about 60 % of the protein is unfolded) [29].

Since the intrinsic disorder prevents crystallographic structure determination, only low-resolution SANS and SAXS information about the average structure in the disordered state exists. Figure 14.5A and B display X-ray and neutron form factors of MBP. Both data show a power law decay at $Q > 1.0 \text{ nm}^{-1}$ with power law coefficients of ≈ -2 , which is characteristic for Gaussian chain polymers in theta solvents. Figure 14.6 displays NSE spectra from 54 mg/ml solutions. Inspecting Figure 14.6A already with a naked eye the two-component structure of the NSE spectra at Q-values above 0.9 nm^{-1} is visible. Thus, we deal with long time rigid body motion augmented by internal dynamics with relaxation times below 10 ns.

As the SAS data could be reasonably well described by a Debye form factor, Gaussian chain statistics with $\nu = 0.5$ and an end-to-end distance $R_e = \sqrt{6}R_g = 8.08 \text{ nm}$ was employed. With this approach the first Zimm mode corresponding to the rotational relaxation time equals to $\tau_1 = 73.9 \text{ ns}$. Fig. 14.6B displays the results of the ZIF description – the translational diffusion coefficient was adapted to the experimental values from DLS. The solid lines in Figure Fig. 14.6B show the improved result of ZIF compared to Zimm model. A large amount of internal friction is imposed, with $\tau_1 = 81.6 \pm 4 \text{ ns}$, that exceeds the relaxation time of the first mode. Internal friction dominates all higher relaxation times to such an extent that the limiting value, τ_1 , is quickly approached. and the $\tau_p \sim p^{-3/2}$ signature of the Zimm model is lost. As a second approach a structural ensemble evaluated from a inverse Monte Carlo simulation (Ensemble Optimisation Method [31]) was used to interpret the full NSE spectra. We found elongated structures with a relatively compact core and flexible ends on both sites similar to Figure 14.5C. The most probable structure was used for normal mode

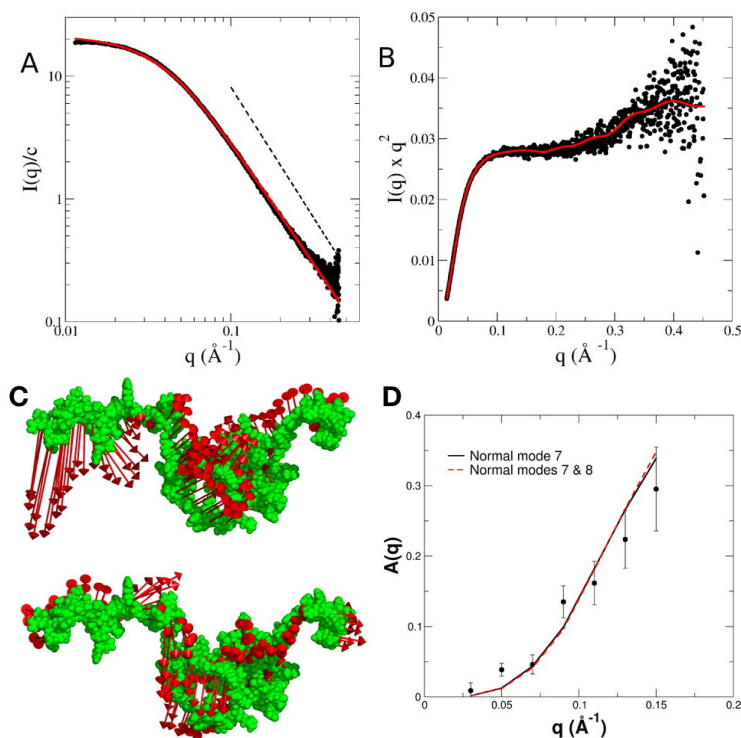


Fig. 14.5: Small angle scattering data from MBP (A) SAXS data at 4.5 mg/ml. (B) SANS results extrapolated to infinite dilution. The solid lines in (A) are fits with the Debye equation for a Gaussian chain with $R_g = 3.38$ nm. Power law scattering is indicated above $Q > 1 \text{ nm}^{-1}$ by dashed lines. (C) Kratky plot of the SAXS data. The line is a result of the scattering from the most probable conformational ensembles. (C) Displacement pattern of the normal modes 7 (upper part) and 8 (lower part) from a structural model. The lengths of the vectors are increased for better visibility. (C) Amplitude of the internal protein dynamics as obtained from the fit. The solid and dashed lines are the calculated mode amplitude according to equation 4. Reprinted with permission from ref. [30].

analysis as rigid protein. On this basis the Q -dependent effective diffusion coefficient D_0 was calculated. For the translational and rotational diffusion coefficients $D_T = 3.7 \pm 0.2 \text{ \AA}^2/\text{ns}$ and $D_R = 2.35 \pm 0.36 \times 10^6 \text{ s}^{-1}$ were found. The corresponding average rotational correlation time $\tau_R = 1/(6D_{R0}) = 70.9 \text{ ns}$. The calculated translational diffusion coefficients agree well with the DLS results at infinite dilution.

Using equation (14.28), a Q -dependent motional amplitude $A(Q)$ and an internal mode relaxation time were evaluated. The fit results from the structural model to the NSE spectra are displayed in Figure Fig. 14.6A up to 40 ns. The contribution of the internal protein motion to the spectra becomes directly visible. The results for the Q -dependent amplitude are displayed in Figure 14.5D. For the characteristic internal relaxation time $1/\lambda_{\text{int}} = 8.4 \pm 2.0 \text{ ns}$

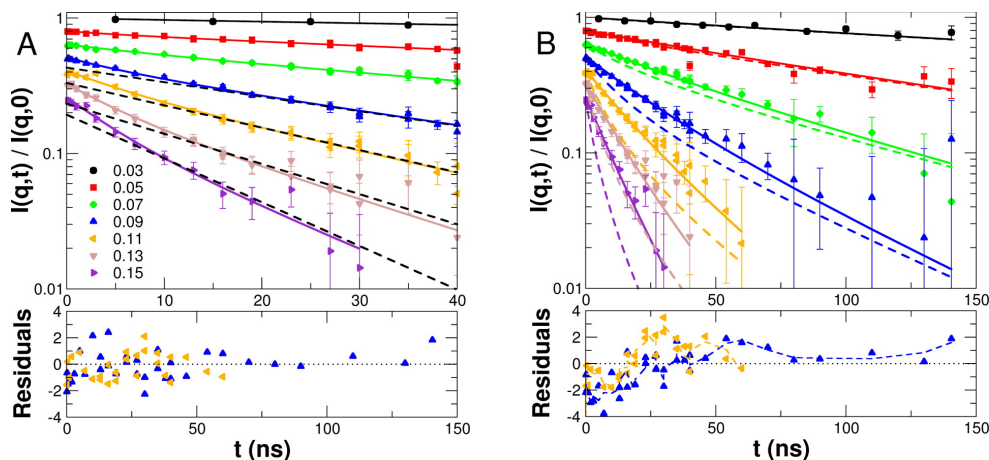


Fig. 14.6: NSE Data for MBP: All spectra start at unity but are shifted consecutively by a factor of 0.8 for clarity. The residuals of the displayed fits are given for $Q=0.9$ and 1.1 nm^{-1} below the graphs. (A) Solid lines are fits to the NSE data with the structural model. The dashed lines are exponential fits for $t > 20$ ns to extrapolate the long time rigid body dynamics. A clear separation between the internal and the global dynamics is obvious. (B) The dashed lines are a result of the Zimm model. The solid lines represent a fit with a ZIF model. Reprinted with permission from ref. [30].

is found for the whole structural ensemble.

Given the structural information and the spectral line shapes, it is not surprising that the polymer approach does not work. The motions of MBP are significantly slower than those of a Gaussian polymer of the same size in solution. Therefore, the structural ensemble provides a significantly better representation of MBP dynamics than the polymer model. The lowest soft collective excitations of the structural model, as they are revealed by the normal mode analysis, are displayed in Figure 14.5C. Normal mode 7 and 8 correspond to bending and stretching motions of the structural model. With these modes the internal dynamics amplitude $A(Q)$ was calculated and is compared with the experimental values in Figure 14.5D. As may be seen, mode 7 is dominating and fully reproduces the observed $A(Q)$. The displacement patterns indicate that the center part of MBP remains rather rigid, while the termini are flexible.

14.9 Domain dynamics of antibodies

Specificity and constancy cause the high potential of antibodies to be used in immunotherapy or to develop new specific drugs targeting specific cells for inhibition/activation of cell processes. IgG are the major antibody class, large molecules of 150 kDa composed of four peptide chains: two identical heavy chains of 50 kDa and two identical light chains of 25 kDa, in a Y-shaped structure (Figure 14.7). The conformational dynamics of IgG results from a functional important hinge region as a loose section of the polypeptide chain that links the Fc

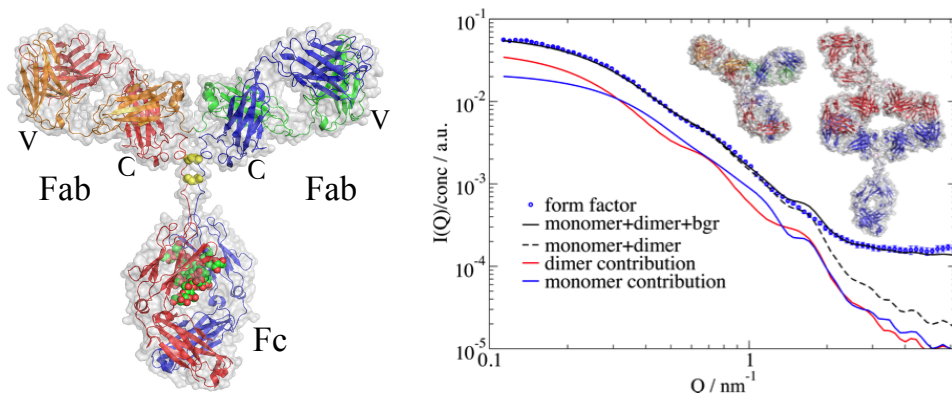


Fig. 14.7: Left: Immunoglobulin G1 with Fc and two Fab fragments with the van der Waals surface in grey. The Fc fragment is built from parts of the heavy chains (red and blue cartoon) and the glycans (red and green spheres) between the two heavy chains. Fab fragments are built from heavy and light chains (orange and green cartoon) with a hinge between the variable region (V) and the constant region (C) of the Fab fragment. The heavy chains are connected in the linker region by two disulfide bonds (yellow spheres). The structure displayed is based on the human IgG1 structure IgG-ALL.pdb of Padlan [33]. Right: The SAXS form factor with the fit result. The form factor fit includes $52 \pm 4\%$ monomer as monomer and $48 \pm 4\%$ monomer in dimers and a background contribution (bgr). The dashed line shows the combined monomer-dimer scattering, the red line shows the contribution of the dimer, while the blue line shows the monomer, all without the residual background. Reprinted from ref. [26] Licensed under CC-BY 4.0

and Fab domains.

We used X-ray scattering to investigate the configurations of IgG in solution at concentrations ranging from 3 to 26.4 mg/mL, as shown in Figure 14.7 right [26]. As confirmed by analytical ultracentrifugation, the solution contains monomers and dimers, which is common for antibodies in solution due to their tendency to form oligomers. Dimers with a head-head configuration are proposed [32]. Modeling of mixtures between monomers and dimers, including a flexible hinge region in the center, allows one to fit the SAXS form factor, as shown in the figure 14.7, right. The dimers show still flexibility in the hinge.

Figure 14.8 displays the intermediate scattering function $I(Q, t)/I(Q, t = 0)$ as measured by NSE. Already by simple inspection, a clear deviation from a simple diffusion process is observed on short times. Fitting the data by the corresponding single exponential decay $I(Q, t)/I(Q, t = 0) = \exp(-D_{\text{eff}}Q^2t)$ one can see a proper fit for long times t with an effective diffusion coefficient D_{eff} . The effective diffusion is shown on the right. On a ten-nanosecond scale, clear indications for a faster relaxation can be observed, which we attribute to motions within the molecule.

The 6×6 diffusion tensor $\mathbf{D}$ was calculated by HYDROPRO on basis of a valid PDB

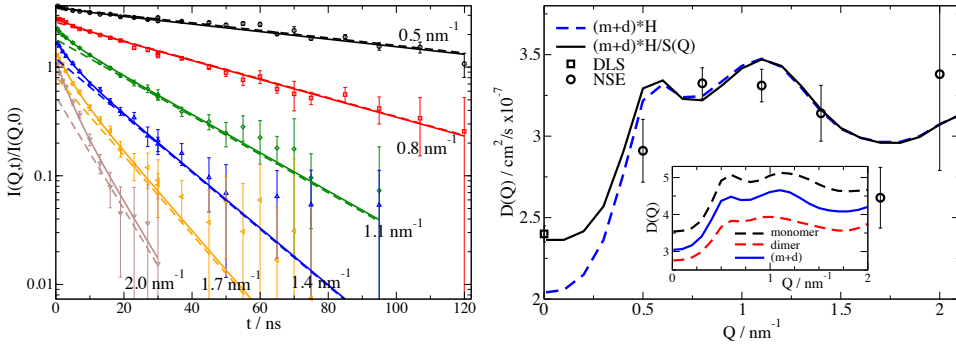


Fig. 14.8: $I(Q,t)/I(Q,0)$ of IgG. Spectra were shifted for clarity. Solid lines represent the fit by (14.7) with contributions from translational and rotational diffusion from (14.8) and internal dynamics described in section (14.7) using 3 degrees of freedom for each domain. Dashed lines correspond to the contribution of translational and rotational diffusion and are close to a single exponential for $t > 15$ ns. Right: Effective diffusion coefficient D_{eff} for long Fourier times at a concentration of 29 mg/ml for NSE and DLS. The dashed blue line shows the result for $D_{\text{eff}}(Q)$ as a mixture between monomer and dimer including $H(Q)$. The black solid line includes additionally the $1/S(Q)$ correction. The inset shows the diffusion coefficients for monomer and dimer with the intensity averaged $D_{\text{eff}}(Q)$. Reprinted from ref. [26] Licensed under CC-BY 4.0

conformation [8]. As result we get additionally the scalar diffusion coefficients D_{T0} and D_{R0} for the monomer and dimer. The rotational correlation times $\tau_r = 1/6D_{R0}$ for the monomer and dimer are on a scale of 260 ns^{-1} respectively 500 ns^{-1} and are longer than the translational diffusion times. Therefore, we can extract the effective diffusion $D_{\text{eff}}(Q)$ comprising translational and rotational contributions of the overall protein by applying a single exponential fit for times $t > 15$ ns. The result is shown in Figure 14.8 together with the DLS result for the same concentration as used for NSE measurement. We use equation (14.29) and the 6×6 diffusion tensor $\mathbf{D}$ together with the monomer and dimer structure to calculate $D_0(Q)$ of the rigid structures (see inset in Figure 14.8). The increase from low Q to the higher Q values results from the stronger visibility of the rotational diffusion if the observation length scale $2\pi/Q$ reaches the size of the protein. At low Q we see only the translational diffusion as measured by DLS. The expected diffusion $D_{\text{eff}}(Q)$ of the monomer/dimer mixture can be calculated as the average of monomer and dimer diffusion weighted by the scattering contribution to the form factor as shown in Figure 14.7. To include the hydrodynamic effects, the translational contribution $D_{\text{eff}}(Q=0)$ is corrected by $H_t(Q=\infty) = 0.66$ as calculated from viscosity and correspondingly the rotational diffusion contribution $D_{\text{eff}}(Q) - D_{\text{eff}}(Q=0)$ as described above by H_r . It needs to be emphasised that the excellent agreement is not a fit but based on additional measurement and model calculations. The specific structure of IgG, which has three nearly equal-sized fragments connected by flexible linkers, suggests a simple model of three fragments within a harmonic potential. These flexible linkers may act as springs, fixing the equilibrium positions of the fragments while allowing fluctuations

around these positions.

We use a reduced set of obvious displacement patterns and consider three perpendicular unit-length vectors for each of the three fragments. One vector is aligned parallel to the linker, from the IgG center of mass to a fragment center of mass, and two are aligned perpendicular to this vector. This represents nine degrees of freedom overall. Using equation (14.24)ff we find an excellent description of the data as shown in Figure 14.8 left. Beyond amplitude and relaxation time, the additional information is the force constant of the harmonic potential and the relevant friction for the Ornstein-Uhlenbeck process. We find a force constant of about 10 pN/nm and a friction of about 40000 g/ps/mol. The friction corresponds to the friction exerted by the water on a single free fragment. The force constant is comparable to that of an entropic spring of the same length as the linker from the center to the fragment (approximately eight amino acids). In conclusion, we observe that even short linkers act as an entropic spring for the fragments, allowing the highest degree of mobility and large configurational freedom.

14.10 Summary

The macroscopic properties of polymers and the function of biopolymers can be explained based on their microscopic dynamics. Inelastic neutron scattering is the most important experimental technique for exploring the latter because it covers the necessary length and time scales. In particular, neutron spin echo spectroscopy is useful because its time range allows one to observe the slow motions of polymer chains. Another advantage of neutron scattering is that it enables the selective study of polymer chain regions through isotopic labeling.

Appendices

A14.1 Diffusion of rigid globular macromolecules

The effective diffusion of rigid macromolecules like proteins can be calculated by [16]

$$D_0(Q) = \frac{1}{Q^2 F(Q)} \sum_{j,k} \langle b_j e^{-iQr_j} \begin{pmatrix} Q \\ r_j \times Q \end{pmatrix} D_{6 \times 6} \begin{pmatrix} Q \\ r_j \times Q \end{pmatrix} b_k e^{-iQr_k} \rangle \quad (14.29)$$

with $F(Q) = \langle \sum_{j,k} b_j b_k e^{-Q(r_j - r_k)} \rangle$ as formfactor of a atomic configuration with atom positions r_i and coherent scattering length b_i . $D_{6 \times 6} = \begin{pmatrix} D_{TT} & D_{TR} \\ D_{TR} & D_{RR} \end{pmatrix}$ is the 6×6 diffusion matrix.

References

- [1] P. E. Rouse. *A Theory of the Linear Viscoelastic Properties of Dilute Solutions of Coiling Polymers*. The Journal of Chemical Physics 21 (1953) 1272–1280. doi:10.1063/1.1699180.
- [2] Paul J. Flory. *Statistical Mechanics of Chain Molecules*. New York: Interscience.
- [3] B. H. Zimm. *Dynamics of Polymer Molecules in Dilute Solution: Viscoelasticity, Flow Birefringence and Dielectric Loss*. The Journal of Chemical Physics 24 (1956) 269–278. doi:10.1063/1.1742462.
- [4] M. M. Tirion. *Large Amplitude Elastic Motions in Proteins from a Single-Parameter, Atomic Analysis*. Physical Review Letters 77 (1996) 1905–1908. doi:10.1103/PhysRevLett.77.1905.
- [5] M. Doi and S. F. Edwards. *The Theory of Polymer Dynamics*. Clarendon Press. ISBN: 978-0-19-852033-7. doi:10.1016/S1359-0286(96)80106-9.
- [6] B. Hammouda. *SANS from Homogeneous Polymer Mixtures: A Unified Overview. Polymer Characteristics*. Vol. 106. Berlin, Heidelberg: Springer 87–133. ISBN: 978-3-540-47477-7. doi:10.1007/BFb0025862.
- [7] C. Gerstl et al. *Chain Conformation of Poly(Alkylene Oxide)s Studied by Small-Angle Neutron Scattering*. Macromolecules 44 (2011) 6077–6084. doi:10.1021/ma201288a.
- [8] A. Ortega et al. *Prediction of Hydrodynamic and Other Solution Properties of Rigid Proteins from Atomic- and Residue-Level Models*. Biophysical Journal 101 (2011) 892–898. doi:10.1016/j.bpj.2011.06.046.
- [9] R. Biehl and D. Richter. *Slow Internal Protein Dynamics in Solution*. Journal of Physics: Condensed Matter 26 (2014) 503103. doi:10.1088/0953-8984/26/50/503103.

- [10] H. M. Lindsay et al. *Effect of Rotational Diffusion on Quasielastic Light Scattering from Fractal Colloid Aggregates*. *Physical Review A* 38 (1988) 2614–2626. doi:10.1103/PhysRevA.38.2614.
- [11] P. N. Pusey. *The Dynamics of Interacting Brownian Particles*. *Journal of Physics A: Mathematical and General* 8 (1975) 1433–1440. doi:http://dx.doi.org/10.1088/0305-4470/8/9/012.
- [12] C. W. J. Beenakker and P. Mazur. *Self-Diffusion of Spheres in a Concentrated Suspension*. *Physica A: Statistical Mechanics and its Applications* 120 (1983) 388–410. doi:10.1016/0378-4371(83)90061-4.
- [13] C. Beenakker and P. Mazur. *Diffusion of Spheres in a Concentrated Suspension II*. *Physica A: Statistical Mechanics and its Applications* 126 (1984) 349–370. doi:10.1016/0378-4371(84)90206-1.
- [14] E. Buvalaia et al. *Interchain Hydrodynamic Interaction and Internal Friction of Polyelectrolytes*. *ACS Macro Letters* 12 (2023) 1218–1223. doi:10.1021/ACSMACROLETT.3C00409.
- [15] R. Inoue et al. *Large Domain Fluctuations on 50-ns Timescale Enable Catalytic Activity in Phosphoglycerate Kinase*. *Biophysical Journal* 99 (2010) 2309–2317. doi:10.1016/j.bpj.2010.08.017.
- [16] R. Biehl et al. *Direct Observation of Correlated Interdomain Motion in Alcohol Dehydrogenase*. *Physical Review Letters* 101 (2008) 138102. doi:10.1103/PhysRevLett.101.138102.
- [17] P. Mazur and W. V. Saarloos. *Many-Sphere Hydrodynamic Interactions and Mobilities in a Suspension*. *Physica A: Statistical Mechanics and its Applications* 115 (1982) 21–57. doi:10.1016/0378-4371(82)90127-3.
- [18] V. Degiorgio, R. Piazza, and R. B. Jones. *Rotational Diffusion in Concentrated Colloidal Dispersions of Hard Spheres*. *Physical Review E* 52 (1995) 2707–2717. doi:10.1103/PhysRevE.52.2707.
- [19] R. R. Cheng, A. T. Hawk, and D. E. Makarov. *Exploring the Role of Internal Friction in the Dynamics of Unfolded Proteins Using Simple Polymer Models*. *Journal of Chemical Physics* 138 (2013) 074112. doi:10.1063/1.4792206. PMID: 23445002.
- [20] M. Krutyeva et al. *Effect of Nanoconfinement on Polymer Dynamics: Surface Layers and Interphases*. *Physical Review Letters* 110 (2013) 108303. doi:10.1103/PhysRevLett.110.108303.
- [21] D. Richter et al. *Microscopic Dynamics and Topological Constraints in Polymer Melts: A Neutron-Spin-Echo Study*. *Physical Review Letters* 62 (1989) 2140. doi:10.1103/PhysRevLett.62.2140.
- [22] F. Mezei et al., eds. *Neutron Spin Echo Spectroscopy: Basics, Trends and Applications*. Vol. 601. *Lecture Notes in Physics*. Berlin, Heidelberg: Springer. doi:10.1007/3-540-45823-9.
- [23] D. Richter et al. *Neutron Spin Echo in Polymer Systems*. Vol. 174. Berlin, Heidelberg: Springer Berlin Heidelberg. doi:10.1007/b106578.
- [24] G. Uhlenbeck and L. Ornstein. *On the Theory of the Brownian Motion*. *Physical Review* 36 (1930) 823–841. doi:10.1103/PhysRev.36.823.

- [25] M. Wang and G. Uhlenbeck. *On the Theory of the Brownian Motion II*. Reviews of Modern Physics 17 (1945) 323–342. doi:10.1103/RevModPhys.17.323.
- [26] L. R. Stingaciu et al. *Fast Antibody Fragment Motion: Flexible Linkers Act as Entropic Spring*. Scientific Reports 6 (2016) 22148. doi:10.1038/srep22148.
- [27] G. R. Kneller. *Quasielastic Neutron Scattering and Relaxation Processes in Proteins: Analytical and Simulation-Based Models*. Physical Chemistry Chemical Physics 7 (2005) 2641–55. doi:10.1039/b502040a. PMID: 16189576.
- [28] G. Harauz et al. *Myelin Basic Protein—Diverse Conformational States of an Intrinsically Unstructured Protein and Its Roles in Myelin Assembly and Multiple Sclerosis*. Micron 35 (2004) 503–542. doi:10.1016/j.micron.2004.04.005.
- [29] E. Polverini et al. *Conformation of Bovine Myelin Basic Protein Purified with Bound Lipids*. European Biophysics Journal 28 (1999) 351–355. doi:10.1007/s002490050218.
- [30] A. M. Stadler et al. *Internal Nanosecond Dynamics in the Intrinsically Disordered Myelin Basic Protein*. Journal of the American Chemical Society 136 (2014) 6987–6994. doi:10.1021/ja502343b.
- [31] P. Bernadó et al. *Structural Characterization of Flexible Proteins Using Small-Angle X-ray Scattering*. Journal of the American Chemical Society 129 (2007) 5656–5664. doi:10.1021/ja069124n.
- [32] G. Deperalta et al. *Structural Analysis of a Therapeutic Monoclonal Antibody Dimer by Hydroxyl Radical Footprinting*. mAbs 5 (2012) 86–101. doi:10.4161/mabs.22964.
- [33] E. A. Padlan. *Anatomy of the Antibody Molecule*. Molecular Immunology 31 (1994) 169–217. doi:10.1016/0161-5890(94)90001-9.

Exercises

Note: Exercises are labelled by stars (* through ***) indicating the level of difficulty. Try to solve the easier ones first.

E14.1 Scaling arguments

(a **) You may have noticed that no firm definition of the average segment length l has been given. Related to this, there is no fixed relation between the number of segments N and well-defined quantities as the degree of polymerisation or the molecular weight. On the first thought, this casts some doubts on results as (14.30).

$$\eta = \frac{\zeta l^2 \rho N}{36} \propto N \quad (14.30)$$

$$D = \frac{k_B T}{\zeta N} \propto N^{-1} \quad (14.31)$$

But on a closer look it turns out that the limiting results of the Rouse model are independent of the choice of l . When l is replaced by $l' = \alpha l$, one can replace N , ζ , and ρ in such a way that all macroscopic results remain unchanged. Show this for the end-to-end distance $R_e^2 = Nl^2$ and equations (14.30), (14.31), and (14.18).

(b *) In the pre-CGI days of King Kong and Godzilla filmmakers sometimes used scaled-down mechanised models of the monsters for the scenes where these deal out destruction, e.g. by tearing down houses. These scenes were often taken in slow motion to make them look more realistic. Why? What slow-motion factor would be (theoretically) appropriate if the monster is scaled down 1 : 25.

E14.2 Internal friction

(c *) Assume we find in the ZIF model an internal friction time τ_i roughly equal to the Zimm time τ_Z for MBP with 170 residues and $\nu \approx 0.5$. Calculate the ratio of internal and solvent friction of a bead ζ_i/ζ for $\nu = 0.5$.

Discuss the case when $\zeta_i/\zeta = 1$. Can the internal friction time be measured? If yes where and why is this difficult?

E14.3 R_g/R_h

(d *) Dynamic light scattering measures the low Q diffusion coefficient which is often interpreted as hydrodynamic radius R_h of a sphere with same diffusion coefficient $D = k_B T / 6\pi\eta R_h$. SAXS or SANS result in R_g . What is R_h/R_g for a Gaussian chain in solvent? What is the ratio for a sphere with $R_g^2 = 3/5 R^2$. Are conclusions from R_h/R_g e.g. from DLS and SAXS unambiguous? How do you substantiate a statement?

15 Applications of Neutron Scattering

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15.1 Introduction

Neutron sources are built to enable a broad range of science that profits from the special properties of science. They are visited by thousands of users each year that come to study the structure and dynamics of their samples using the unique properties of the neutron as an agent in the pico- to micro-cosmos. These unique properties are:

1. The high penetration power, that enables an insight deep under the surface of things, e.g. inside running engines or archaeological artefacts. Furthermore it guarantees that the experiments probe the bulk structure and dynamics, to distinguish from and complement more surface sensitive microscopic probes such as x-ray, electrons or ions.
2. The contrast between chemically similar elements or even isotopes of the same element: Neutrons can distinguish neighboring elements in the periodic table, which is difficult to impossible for probes that scatter at the electron cloud of an atom. Even more, chemists can label certain positions with isotopes, in particular deuterium, which provides a spotlight to study that region for the function of a molecule e.g. in soft matter or life science.
3. Thermal and cold neutrons carry energy equivalent to temperatures from 10 to 1000 K. Therefore they are gentle to the sample giving hardly rise to radiation damage or beam heating. Therefore they can be used for studies at mK temperature probing fascinating properties of quantum materials.
4. The neutron carries a spin and hence it senses magnetic fields just like a microscopic compass needle. It can be used to study magnetic order and disorder in materials, which are tightly related to their electronic properties and the corresponding applications in devices. Furthermore, the relative orientation of the neutron spin and the nuclear spins in the samples strongly affects the interaction between neutron and nuclei. This can be used to extract very localized information about the motion of the respective nucleus, e.g. the diffusion of hydrogen in a storage material.

Therefore, neutron facilities are used from a very broad scientific community. Engineers study large devices in operation or explore how the microstructure affects the function of technical materials. Archaeologists and art experts look below the surface of precious artifacts or determine the age and origin by the isotopic composition. Crystal structures of novel materials and elementary excitations in condensed matter such as lattice vibrations or spin waves are investigated by material scientist, chemists or physicists to elucidate how the structure or the dynamic affects the function of a material. Life scientists determine the structure of proteins and enzymes with a high sensitivity to the hydrogen positions or watch the motion of large functional groups on their natural time scale from ns to μ s. In the remainder of this lecture, I will introduce the instruments that are employed for the different use cases, describe how they work and briefly explain what can be learned from the experiment.

15.2 Imaging

Neutron imaging and neutron radiography are powerful techniques used in various fields for non-destructive testing, material science, and imaging applications. Some of the most important applications include:

1. **Industrial Inspection:** Neutron imaging and radiography are used extensively in industrial settings for inspecting components, welds, and materials without damaging them. They can detect internal flaws, cracks, voids, and other defects in materials such as metals, ceramics, and composites. This includes parts under heavy loads, such as components in aerospace applications or nuclear engineering. The high penetration power of neutrons provides here an insight deep under surface of components .
2. **Archaeology and Cultural Heritage:** Neutron imaging has been employed to study artifacts and archaeological materials non-destructively. It can reveal hidden features within objects, such as the internal structure of ancient pottery or the composition of historical artifacts, without damaging them.
3. **Geological Studies:** Neutron imaging is used in geology to examine the internal structure and composition of rocks, minerals, and geological samples. It can provide valuable insights into pore structures, mineral distribution, and fluid flow within rocks, aiding in the understanding of geological processes.
4. **Biomedical Imaging:** Neutron imaging has potential applications in biomedical research for imaging soft tissues, bones, and organs. While it's less commonly used than techniques like X-ray imaging, neutron imaging offers unique advantages, such as enhanced contrast for certain soft tissue, complementary to X-ray radiography and the application of strongly neutron absorbing contrast agents.
5. **Fuel Cell and Battery Research:** Neutron imaging is valuable for studying the internal structure and performance of fuel cells and batteries. It can provide insights into electrode morphology, electrolyte distribution, and degradation mechanisms, aiding in the development of more efficient and durable energy storage devices.
6. **Environmental Science:** Neutron imaging can be used to study soil structure, water movement, and plant root systems in environmental science research. It allows researchers to visualize the distribution of water and nutrients in soil and to study the uptake of water by plants non-destructively.
7. **Aerospace and Defense:** Neutron imaging plays a role in the aerospace and defense industries for inspecting aerospace components, such as turbine blades, rocket engines, and composite materials. It helps ensure the integrity and safety of critical components without causing damage.
8. **Nuclear Engineering:** Neutron imaging is utilized in nuclear engineering for studying nuclear fuel rods, reactor components, and other nuclear materials. It can provide valuable information on fuel assembly geometry, fuel pellet distribution, and the integrity of reactor components.

Overall, neutron imaging and radiography offer unique capabilities for non-destructive testing and imaging across a wide range of applications, contributing to advances in materials science, engineering, archaeology, and other fields. Imaging or radiography relies on the transmission of radiation through a sample. The specimen is placed in the beam and a detector downstream the sample records the intensity that passed through the sample. The transmission is affected by the absorption of the neutrons within the sample, but also by scattering, which deflects neutrons from the straight path through the sample. The former allows, for example, to localize specific isotopes in specimen. The latter is used by the so-called Bragg imaging. For this one has to know the wavelength of the neutrons. If the wavelength λ becomes so long, that the Bragg condition for a given lattice spacing d cannot be fulfilled for any scattering angle

$$\lambda > 2d \sin(90^\circ) = 2d, \quad (15.1)$$

the transmission is increased and this allows to image regions of a specific crystal structure in a multicomponent sample.

15.3 Neutron analytics

While in an imaging experiment we probe how many neutrons are removed from their original path, neutron analytics methods detect the products of the nuclear reaction of the neutron with the nuclei within the sample. The reactions are specific for individual isotopes and therefore the analysis of the reaction products is a very sensitive measure of the composition of a specimen. Typically, the high penetration power of neutrons is used to detect small amounts of the isotopes of interest in bulky and crowded samples, that could be inspected only destructively otherwise. Thanks to the non-destructive nature of neutron analytics, they are often the method of choice for the study of precious or rare sample, e.g. from arts or archaeology. The high sensitivity to both light and heavy isotopes is the used in applications in material or environmental science.

While analytic methods can also be used in combination with laboratory scale neutron source such as neutron generators, at MLZ we operate two instruments for prompt gamma activation analysis and neutron depth profiling that benefit from the high intensity beam of neutrons that is only available at large scale facilities.

Prompt Gamma Neutron Activation Analysis When a sample is irradiated with neutrons, nuclear reactions between the nuclei and the neutrons may result in an emission of gamma photons, where the spectrum of the emitted gammas is specific for the isotope. Therefore the instruments use energy sensitive high purity Germanium detectors, which provide the sufficient energy resolution. They must be well shielded to detect only the gamma quanta created within the sample. The spectra are then analysed by mathematical models and compared against calibration standards to quantify the isotopes contained in the sample.

As both the neutrons and the gamma photons have a high penetration power, the analysis of the gamma spectrum yields information about the composition of large and bulky specimen with a detection limit down to the ng range for favourite isotopes, being typically in the μg range.

Neutron depth profiling The Neutron Depth Profiling (NDP) technique allows studying near-surface distributions of several light isotopes with relatively high neutron absorption cross-section (^3He , ^6Li , ^{10}B , ^{14}N and others) in solid materials. Absorption of a neutron results in a nuclear decay with emission of a mono-energetic charged particle (alpha particle, proton or triton) and a recoiling nucleus. Before escaping the sample surface, each particle loses a certain amount of energy depending on the stopping power of the host material. The detected energy spectrum depicts the in-depth distribution of a corresponding absorbing isotope. After deconvolving the spectra by an appropriate algorithm one obtains the concentration versus depth profile in absolute units, which is difficult for light elements by any other commonly used analytic technique (i.e. by different ion beam analysis techniques). Recently, NDP has gained a lot of interest due to its sensitivity to the isotope ^6Li , because Li is a key element of currently widely spread lithium-ion batteries. NDP provides insight on new developments in the field, i.e. rechargeable lithium-ion batteries with solid electrolytes. Because of its sensitivity to ^{22}Na isotope, NDP could also be applied to studies of the most promising competitor of commercial lithium-ion batteries – all-solid-state sodium-ion batteries. As NDP can be considered to be non-destructive, batteries can be explored *in situ* and *operando* for many cycles of battery charging and discharging, which is of high demand in the battery community.

15.4 Neutron scattering

While the neutron applications discussed so far track basically the fate of a single neutron to explore samples, a neutron scattering experiment in the sense of this lab course tracks how a thermal or cold neutron exchanges its momentum, energy or spin with the sample under investigation. These neutrons have kinetic energies in the order of meV and a wavelength in the order of Å. Hence they probe the structure of the sample with a resolution in the Å to several nm range and the dynamics from the μeV range to several hundreds of meV. These are the typical distances and energies of the motions, which atoms and molecules exhibit in the materials surrounding us.

In the remainder of this lecture, we want to explore, how one can determine the momentum and the energy of the neutrons before and after the interaction with the sample with sufficient resolution, to relate the momentum and energy transfer to the properties of the sample. In a scattering experiment, we measure, how neutrons have been deflected by the sample. To do so, we need to know the wave vector $\mathbf{k}$ of the neutrons that impinge on the sample and the final wave vector $\mathbf{k}'$ after the interaction between the neutrons and the atoms and spins in the sample. The difference between the wave vector before and after the interaction is called the scattering vector:

$$\mathbf{Q} = \mathbf{k}' - \mathbf{k} \quad (15.2)$$

For the case of elastic scattering, i.e. when the energy of the neutron has not changed and the wavelength λ, λ' are the same, we can express this as

$$Q = \frac{4\pi}{\lambda} \sin \theta, \quad (15.3)$$

where 2θ is the scattering angle as indicated in Fig. 15.1 So to analyze the scattering process, we

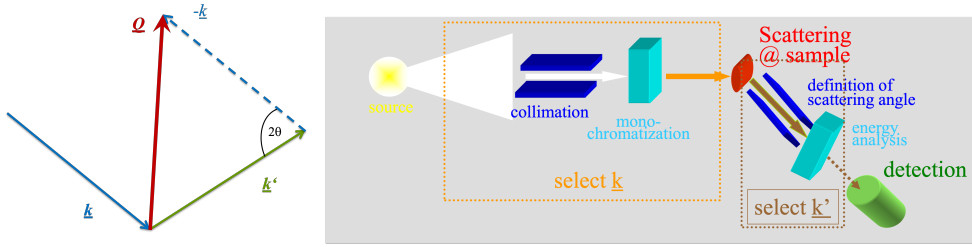


Fig. 15.1: Left: Scattering triangle: k, k' are the scattering angles before and after the interaction with the sample, Q is the momentum that is exchanged with the sample. Right: Generic layout of a neutron spectrometer.

- define the wavelength and direction to illuminate the sample.
- detect the neutrons after interaction in a well defined direction.
- (at an inelastic instrument) determine the wavelength of the neutrons after the interaction.

Depending on the resolution requirements of the experiment, we can choose between different methods to select or determine the wavelength or velocity of the neutrons. Making use of the wave property of the neutron we can employ the Bragg diffraction from a so-called monochromator crystal. Here a specific neutron wavelength is selected according to the Bragg equation eq. 15.6. The details are discussed in section 15.5.

As thermal and cold neutrons can be treated as non-relativistic particles (their speed varies between 100 and 10000 m/s), we can determine their velocity by a measurement of the time-of-flight along a well defined distance. This method is in particular useful at pulsed neutron sources, such as spallation sources or HiCANS, where all neutrons are born at a well defined time. Detecting the neutrons with a time stamp allows to deduce the neutron speed of all neutrons traveling from the source to the detector.

To analyze the neutron scattering, we need to measure the signal with reasonable statistics. Compared to x-ray sources, the number of neutrons emitted in the direction of the instrument within a certain energy interval is very small. The intensity of the neutron beam that illuminates the sample depends on the width of the angular, wavelength and space distributions that can be accepted to match the resolution requirements of the experiment:

$$I = T \times \iiint_{A, \Omega, \delta\lambda} \Phi dA d\Omega d\lambda \quad (15.4)$$

where A is the cross section of the sample, Ω two dimensional collimation of the beam, Φ the brightness of the moderator and T is the brilliance transfer of the optical system with $0 < T < 1$. The instrument design aims at pushing T close to 1, but as neutrons are difficult to manipulate typical values are below. The brightness of the source is optimized during the installation and later on can hardly be changed afterwards. So we can increase the intensity by illuminating larger samples, relaxing the collimation or monochromatization. The key task of the experimenter is to choose, where the resolution requirements can be relaxed to still answer the scientific question of the experiment.

15.5 How to localize spins and atoms

Many of the physical properties of crystals depend on how the atoms are arranged with respect to each other. Therefore the determination of the crystal structure is one of the first properties that is investigated, when a new compound is synthesized. In many cases, the explanation of a desired or interesting feature or function of a material depends on details of the structure. Hence neutron diffraction is applied in a very broad range of fields that require the special properties of the neutron:

- **Life sciences:** If one needs to determine the position in particular of Hydrogen in biological macromolecules, high resolution x-ray diffraction and neutron diffraction can be combined. The x-ray data determines the position of the heavy atoms with a very high precision, while the neutrons provide the information about the light elements
- **Chemistry:** Neutron scattering contributes the position of light elements and in case of magnetic order of the spins to elucidate the structure of newly synthesized compounds. As neutrons can also penetrate complex sample environments also kinetic measurements and in-situ measurements are possible.
- **Material Science:** As neutrons can penetrate steels and alloys cm deep, they are used to scan determine stress and strain in complete devices to understand how they work and eventually, why they failed. Also the texture of engineering alloys can be determined to optimize it for a specific application.
- **Geo science:** Phase and texture analysis from the earth's interior or from other planets and moons provides information about the formation of this regions. As specimens are often large and non-homogeneous a large penetration depth is crucial.
- **Solid state physics:** The atom and spin structure provides information about the lattice and spin interactions in a compound. It is often closely related to the function of the material, e.g. multiferroics or High T_C superconductors.

The diffraction of radiation with a wavelength of similar size to the distances found in the unit cell is employed to localize the position of atoms within the unit cell. While x-ray diffraction is available at many laboratories and therefore familiar to many scientists, neutrons are employed, when the specific properties of the neutron requested. One of these is the sensitivity to the arrangement of spins. While magnetic diffraction of x-ray is only a relativistic correction to the much stronger charge scattering, the unpaired electrons of an atom interact with the neutron in similar strength as the nuclei. Furthermore the scattering length of the different element and even isotopes varies randomly across the periodic table. This becomes important, if one needs to determine the position of light elements such as H, C, O or N in the vicinity of heavy atoms. Also, the neutron is a gentle probe to the sample causing basically no beam damage or beam heating beside activation. The latter is crucial for any measurement in the sub-Kelvin temperature regime, that is not accessible with the higher energy probes such as x-rays, electrons or ions. Finally, the high penetration power of neutrons enables the use of complex sample environments allowing the application of many different fields to manipulate the sample or investigations under in-situ or operando conditions.

The comparably big sample amount is the prize you have to pay to profit from the beneficial properties of the neutron. For the diffraction applications we discuss in this section, one provides ideally single crystals with a mass > 10 mg. In the case of protein diffraction, even smaller samples with a sample mass < 1 mg are feasible, but comparing to the sample size required e.g. for x-ray or electron diffraction they are still huge and extremely challenging to synthesize.

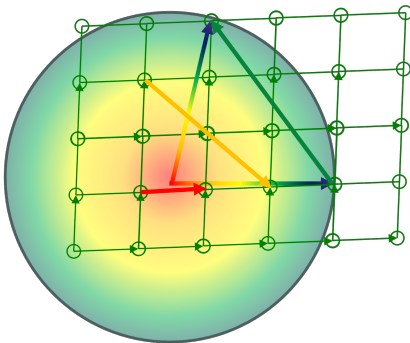
For a crystalline sample, the atom or spins are arranged on a regular lattice. You have learned in lecture 4, that the real space lattice is related to the reciprocal lattice, that describes the reciprocal of the distances between the lattice planes. Constructive interference of the neutron wave scattered at two different atoms of the lattices requires, that the scattering vector equals a reciprocal lattice vector

$$\mathbf{Q} = \boldsymbol{\tau}. \quad (15.5)$$

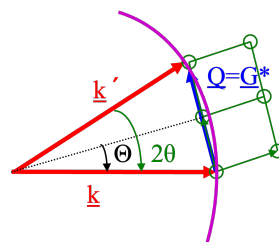
If we consider only the norm of this vector equation, we find the well known Bragg condition

$$n\lambda = 2d \sin \theta, \quad (15.6)$$

where n indicates, that you fulfil the Bragg condition at a given angle also for wavelength $\lambda = \lambda_0/n$, yielding so-called higher order reflections. In Fig. 15.2, the Laue condition is visualised in the so-called Ewald construction. You draw a circle (a sphere in 3 dimensions) with radius equal to the length of the initial scattering vector k around the tip. The origin of the reciprocal space is at the foot of the initial wave vector. So all radius vectors of the Ewald circle (sphere), that pass through a reciprocal lattice point, represent the Bragg reflections, that can be measured for a given initial wave vector and orientation of the crystal. If detectors cover only a reduced solid angle, one can measure only a fraction of the Ewald sphere. Varying the length of the wave vector and the orientation of the crystal one can measure the intensity of many reflections for a full structure refinement.



Time-of-flight diffraction



Monochromatic diffraction

Fig. 15.2: Ewald construction to visualise the Laue condition. To measure a Bragg peak, one has to tune the length of the scattering vector, the angle between initial and final neutron wave vector and the orientation of the crystal lattice

While the position of the Bragg reflections yields the information about the metric and the symmetry of the crystal lattice under investigation, the intensity of the reflections depends on the contents of the unit cell. You can determine the positions of the different atoms and spins, their thermal displacements factors, the size of the magnetic moment etc. Hence you have many degrees of freedom in your refinements and accordingly you need to measure the integrated intensity of thousands of reflections for a reliable data analysis.

Above we have sketched how one can extract the details of the atomic and magnetic structure of a single crystal. Practically, many and in particular new materials exist only in the form of crystalline powders, where the individual crystal grains have μm size or below and are randomly oriented. As all grains feature the same crystalline lattice, but are randomly oriented, any lattice distance d_{hkl} is scattered into a cone. All wave vectors in this cone are deflected by the same scattering angle 2θ with respect to the initial wave vector. So the intensity of a single Bragg peak is not concentrated in a one point on the detector but distributed over a ring, the so-called Debye-Scherrer ring. As different lattice vectors can have the same norm and hence correspond to the same lattice spacings, they all contribute intensity to the ring and hence the information contained in a powder diffraction pattern is reduced compared to a single crystal pattern. Still, it is possible to refine the structure from neutron powder diffraction making use of the Rietveld formalism [1], if the structure is known. Besides that, one can determine the lattice metric and symmetry from powder data patterns making use of the Le Bail method [2], which is often part of the software packages for the Rietveld method.

15.5.1 Components of a diffractometer

To perform a diffraction experiment we can see from Fig. 15.2 that we need to know the wavelength that we shine onto the sample and the direction into which the neutron are diffracted. For a neutron powder diffraction instrument this information is sufficient, in case of a single crystal measurement we need further the information about the orientation of the crystal.

In a monochromatic diffractometer we use a well defined single crystal to select a specific wavelength from the spectrum according to the Bragg equation 15.6. We can control, how precisely we select the wavelength by inspection of the differential of the Bragg equation

$$\frac{\delta\lambda}{\lambda} = \frac{\delta d}{d} + \frac{\delta\theta}{\tan\theta} \quad (15.7)$$

In the case of neutron scattering, the second term is usually the dominating contribution. This one can be controlled by the choice of the scattering angle, the collimation that we allow before and after the monochromator, and the width of the mosaic spread of the monochromator crystal, i.e. a measure of the quality of a single crystal. While one could assume, that one aims at the best possible resolution and hence chooses as perfect crystals as possible, one has to keep in mind, that neutron scattering is a flux limited method. Therefore the selection of the wavelength and the direction should only be as tight as needed for the requirements of the experiment. This is typically achieved, if one matches the different contributions to the resolution. Hence the collimation impinging on the crystal should be similar in size to the mosaic spread. A popular choice, in particular for instruments making use of cold neutrons, is highly oriented pyrolytic graphite (HOPG) with its (002) reflection. It features a lattice

spacing $d = 3.355 \text{ \AA}$ and can be procured with mosaic spread of approximately 0.5° . For typical Bragg angles ranging from 20° to 50° , a wavelength resolution $0.01 < \delta\lambda/\lambda < 0.03$ can be realized. As we can see from eq. 15.7, the angular contribution becomes smaller, when a larger scattering angle is chosen. Approaching the Bragg angle $\theta = 90^\circ$ and hence a scattering angle $2\theta = 180^\circ$ the angular term vanishes independent of the mosaic spread and the resolution depends then only on spread of the d-spacing in a crystal, which is 10^{-6} for Si or 10^{-4} for HOPG. The downside of the high resolution is the very low intensity that is reflected in this case. Therefore it is always important to consider the necessary resolution for an experiment and to relax then the resolution as much as possible to optimize the intensity to acquire the best statistics needed to analyze the data.

Alternatively, one can make use of the time-of-flight method to determine the neutron wavelength from the arrival time of the neutron at the detector. In this case, one needs to define the starting time of the neutrons and the length of the neutron flight path, to determine the neutron velocity and hence velocity from the arrival time of the neutron at the detector. The sample is then illuminated by a band of wavelengths, leading to a modified Ewald construction shown in Fig. 15.2. A Bragg reflection is now always measured, if the shell of the same color in Fig. 15.2 connects two reciprocal lattice points. This method allows the simultaneous recording of several reflections and a section of reciprocal space can be explored fully rotating the sample with less steps. At pulsed neutron sources, the starting point of the neutrons is precisely known, and all neutrons within a given band can be used. Therefore you find only time-of-flight diffractometers there. At continuous sources, one can use a chopper to impose a well defined time structure on the neutron beam. Here you can find both types of instruments.

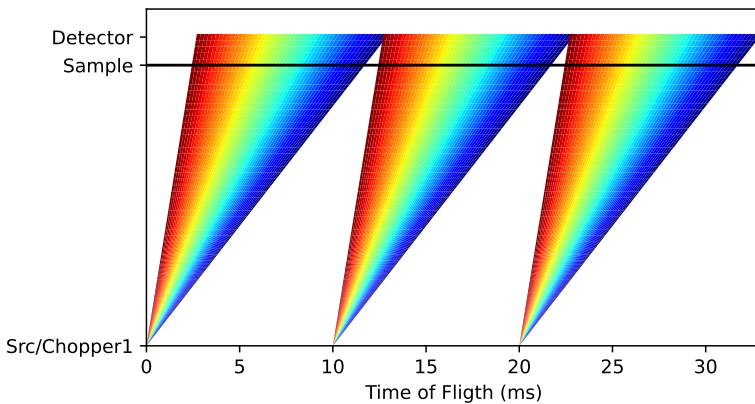


Fig. 15.3: Flight-path diagram of a diffractometer: The source/chopper emits/transmits a white neutron spectrum. At the sample, the scattering is predominantly elastic. Recording the time-of-flight at the detector, the neutron velocity/wavelength can be determined.

For the different types of instruments, one uses also different neutron detectors. A gallery of them is shown in Fig. 15.4. In the case of time-of-flight instruments one tries to maximize the solid angle coverage, building spherical or cylindrical detectors. For a monochromatic



Fig. 15.4: Neutron detectors for time-of-flight powder diffraction, monochromatic powder diffraction, monochromatic 2d detector and monochromatic single counter.

instrument, the resolution is anisotropic. It is narrow in the plane, that is spanned by the vectors $\mathbf{k}$ and $\mathbf{k}'$ and more relaxed in the direction perpendicular. The detectors are typically covering only a region close to this plane. Detectors of powder diffractometers have therefore often the shape of a banana to cover a large range of scattering angles close the horizontal scattering plane. In the case of four circle diffractometers sometimes even single counters are used, that are scanned to determine the integrated intensity of a reflection. While this requires time consuming scans to determine the integrated intensities of a Bragg reflection, the data reduction is very reliable and such small detectors can be very well shielded to realize an extremely low background.

15.6 Shapes and arrangements large scale structures

Often it is not the atomistic structure, that is key to the understanding of a material, but larger units of atoms have emergent properties and the correlations between these units are important for their function. Polymers are typical examples of large functional molecules. As light elements and their interactions play a crucial role here, the soft matter community

has a strong interest to use neutrons for structural investigations on the length scale from 1 to 1000 nm. Neutrons can provide information about polymer chain conformation, self assembly from block copolymers, colloids and suspensions and address also questions in complex fluids.

The functional groups in biological systems have also structure sizes in the nm range. Key questions are folding and unfolding of proteins, or the structure and functions of membranes or lipid bilayers. Even virus structures can be resolved. Naturally one is then also interested how drugs affect the biological tissue and how they interact with cell membranes. Recently, food science has started to use neutrons to study emulsions on the search for vegan alternatives to dairy products.

But also hard matter forms larger functional units. Novel nanoparticles with core-shell structures naturally fall into this category. But also porous structures, e.g. for catalysis or gas storage have nm structure size. In alloys and metals precipitation and phase separation have an impact on the mechanical properties. Neutrons are here used, if the different metals exhibit only small contrast for other probes. A special case in hard matter is the distribution of magnetization inside. The domain sizes in ferromagnets fall into the nm to μm range, but also objects like skyrmions or flux lines in superlattices extend over this length scale.

Furthermore, porous media are important in geological system or planetary systems, as they may store or transport gases or water and these questions can have a large societal impact, considering e.g. CO_2 sequestration or clean water provision.

15.6.1 Components of a SANS diffractometer

While the short distances between atoms correspond to large vectors in reciprocal space, the distances of several nm correspond to much shorter vectors in reciprocal space for a distance $D = 10\text{nm}$ we find $Q = \frac{2\pi}{D} \approx 0.6\text{nm}^{-1} = 0.06\text{\AA}^{-1}$. According to eq. 15.3, a small momentum transfer is probed using neutrons with a long wavelength and/or recording the scattering under small scattering angles. The spectrum of cold neutron moderators limits the wavelength range to $\lambda \leq 2\text{ nm}^{-1}$ and hence the scattering angle 2θ is typically smaller than 10° . The larger the structures become the narrower is the requested angular resolution. Therefore we talk about small angle neutron (or x-ray) scattering, when we investigate large scale structures with scattering methods.

The scattering triangle for small angle scattering is depicted in Fig. 15.5. As you can immediately see, the length of the scattering vector is affected strongly by the collimation in the incoming beam and the angular resolution of the scattered beam, while the length of the initial and final wave vector hardly changes the scattering vector. We can quantify this observation considering the differential of eq. 15.3:

$$\frac{\delta Q}{Q} = \frac{\delta \lambda}{\lambda} + \frac{\delta \theta}{\tan \theta} \approx \frac{\delta \lambda}{\lambda} + \frac{\delta \theta}{\theta}. \quad (15.8)$$

As the scattering angle approaches zero, the angular resolution term diverges. Referring to the figure, that means that the uncertainty on the scattering vector becomes much larger than the actual scattering vector.

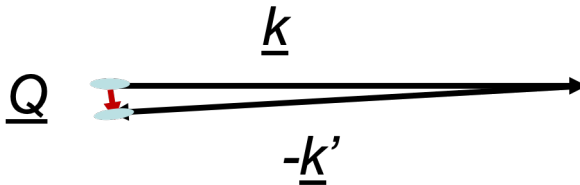


Fig. 15.5: Left: Scattering triangle for a small angle measurement. The ellipsoids represent the longitudinal and transverse uncertainties of initial and final wave vector $\mathbf{k}$ and $\mathbf{k}'$. The longitudinal uncertainty corresponds to the wavelength resolution, the transverse to the angular collimation. Right: Detector tank of D11 at the ILL

While the beam for a SANS experiment needs a narrow collimation matched to the structure size to be resolved, the wavelength resolution can be largely relaxed. Most SANS diffractometers use a so-called pin hole geometry to define the collimation, see Fig. 15.6. The two apertures at the end of the neutron transport system and in front of the sample define the initial collimation. In angle, they give rise to a trapezoidal intensity distribution downstream the second aperture. Mildner and Carpenter optimized the count rate on the detector at a fixed scattering vector Q [3]. As a result they find relations for the collimation length L_C and the detector distance L_D , as well as for the width of the entrance aperture D_E , the sample aperture D_S and the width of the detector element D_D :

$$L_C = L_D \quad (15.9)$$

$$D_E = D_D = 2D_S \quad (15.10)$$

To resolve a scattering vector $Q \leq 10^{-2} \text{ nm}^{-1}$, a collimation length of 20 m is requested yielding a total length of 40 m from the entrance aperture to the detector.

Modern SANS instrument allow the variation of the collimation and the detector distance over a wide range. The entrance aperture can be placed at different positions upstream the sample. Movable neutron guide elements assure, that the entrance aperture is always illuminated with a beam, that is more divergent than the requested collimation.

The detector can be moved inside huge evacuated flight tubes enabling a detector distance between 2m and 40 m (for the longest SANS instrument at ILL, D22). These tubes host position sensitive detectors that cover a area of typically a m^2 . A disordered sample, e.g. an emulsion produces a ring pattern on the detector. The rings can be integrated and the data is presented just as a function of the scattering vector norm. However, ordered nano structures, e.g. self organized nano particles or flux lines are explored using the 2d image of

the detector. Also aligned magnetic particles produce an anisotropic detector image that can be used to determine the orientation of the magnetic entities.

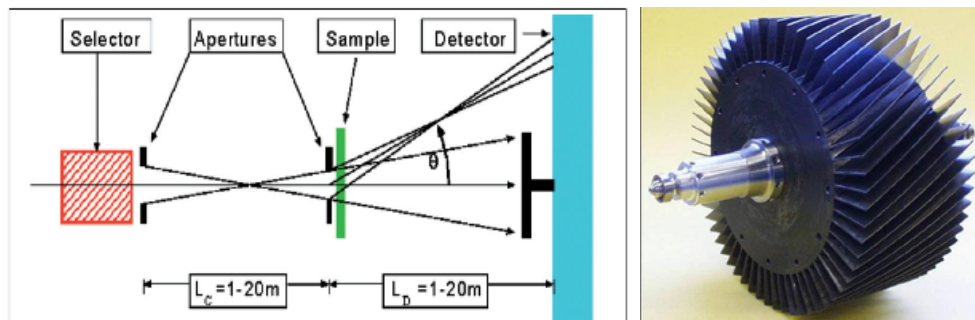


Fig. 15.6: Left: Schematics of a pin hole collimation system for a SANS instrument. Right: Photo of the velocity selector drum of the JCNS instrument KWS-3 showing the screw-like twisted channels separated by absorbing walls, which only neutrons of a certain wavelength band can pass when the drum is turning.

From eq. 15.8, we deduce, that the required wavelength resolution in a SANS experiment is relaxed. So we can compensate the requirements of a very narrow collimation by relaxing the wavelength resolution. The single crystal monochromators, we have discussed in section 15.5 provide typically a wavelength resolution $0.01 < \delta\lambda/\lambda < 0.05$. In the present case, we profit strongly, if we can allow a wavelength resolution $0.1 < \delta\lambda/\lambda < 0.2$. This can be realized making use of mechanical velocity selectors as shown in Fig. 15.6. The drum spins at a frequency of tens of kHz. For a specific neutron velocity and rotation speed, the walls of the selector move synchronized with the neutrons. Slower or faster neutrons collide with the walls and get absorbed. Changing the rotation velocity allows the selection of different wavelength bands.

15.6.1.1 Unique properties of SANS

The high collimation required for a SANS experiment results in a low flux, if you compare to other SAS variants. E.g. a synchrotron provides beams with a brilliance that is orders of magnitude larger than even the brightest neutron source. As such, typical SAXS experiments have illumination times in the ms range. The key argument for a SANS experiment is always the unique contrast properties and often the opportunity to tune this contrast via isotope substitution, which leaves the chemistry of the compound basically unchanged. The most important isotope is clearly the deuterium ^2H allowing the deuteration of many organic and biological molecules. This can be used, e.g. to match the scattering length density of a solvent to a certain part of a molecule. This part becomes then invisible and the remaining part can be studied more precisely. Due to the large difference between the scattering length of ^1H and ^2H the effect is huge and opens a huge playground in soft matter research and life science. The proton ^1H features a coherent scattering cross section $\sigma_{\text{coh}} \approx 1.8$ barn, while the coherent cross section of the deuterium ^2H is larger: $\sigma_{\text{coh}} \approx 5.6$ barn. So exchanging deuterons for protons changes the contrast to the surrounding elements, which enables to

highlight specific regions in large structures. The large incoherent scattering cross section of the proton ($\sigma_{\text{incoh}} \approx 80$ barn) to a background signal, which is weaker, if fully deuterated samples are studied ($\sigma_{\text{incoh}} \approx 2.05$ barn). As SANS experiments are performed typically in transmission geometry, the high penetration power allows to look into opaque materials, which is in particular important for studies on metals, e.g. functional alloys and steels or magnetic materials.

15.6.2 Layered Structures

Layered objects, where the structure size in one dimension is much smaller than in the two other spatial dimensions, play an important role in many technical and biological processes. Typical examples are membranes in living cells or in batteries and fuel, where the permeability depends strongly on the structure. For catalysts, the structures of the surface naturally play a crucial role for their function. The electronic properties of 2 dimensional structures are explored in any transistor or diode. Neutrons come into play, when the layers have magnetic properties. Examples include exchange bias system, systems featuring the different magneto-resistance effects or correlated electron systems with emerging behavior at interfaces.

On a reflectometer, as sketched in Fig. 15.7 you record the specular reflectivity, i.e. the initial and the scattered neutron beam enclose the same angle with the sample surface

$$\alpha_i = \alpha_f \quad (15.11)$$

Accordingly, the scattering vector is parallel to the surface normal of the sample and the reflected intensity contains the information about the lateral average of the scattering length density (SLD). As you can see in Fig. 15.7, the beam is collimated only in one direction by two collimation slits. In the other direction we can accept a divergent beam to increase the intensity.

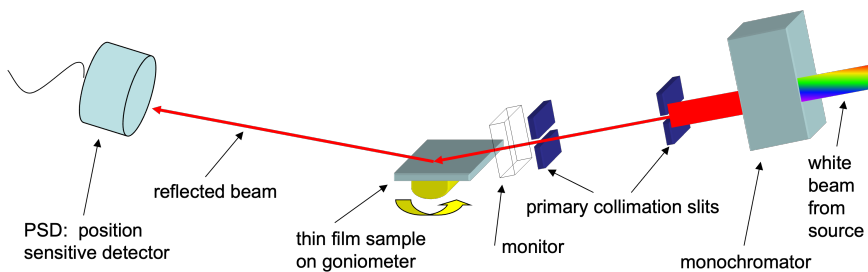


Fig. 15.7: Schematic of a reflectometer

The theoretical description of neutron reflectometry follows exactly along the lines of conventional optics, except that for neutrons in most cases the index of refraction is smaller than one and thus external total reflection occurs for neutrons coming from vacuum towards matter. The index of refraction n of neutrons of wavelength λ from a layer composed of elements with scattering length b_i and number density ρ_i and linear absorption coefficient μ_n

is given by:

$$n = 1 - \frac{\lambda^2}{2\pi} \sum_j b_j \rho_j - i \frac{\lambda}{4\pi} \mu_n := 1 - \delta - i\beta. \quad (15.12)$$

Using Snell's law to describe the refraction at the interface, we find that total reflection occurs for $\delta > 0$. This can be seen in Fig. 15.8. It shows the reflectivity curve from a Ni layer on a glass substrate. If the scattering vector $Q < 0.21 \text{ \AA}^{-1}$, all neutrons that impinge on the surface are reflected. This effect is used to guide collimated neutron beams over long distances to the instruments. For that, so-called neutron guides enclose a vacuum flight path, in which the neutrons travel from the source to the samples. In the practical part you will work mainly in neutron guide halls featuring neutron guides longer than 30 m. At the new long pulses spallation source ESS many of the instrument have a total length $> 150 \text{ m}$. These types of instruments are only possible, because so-called supermirrors have been developed, that increase the region of total reflection up to $Q = 0.14 \text{ \AA}^{-1}$, a seven fold increase compared to the elemental Ni neutron mirrors that have been used in the early days of neutrons sources.

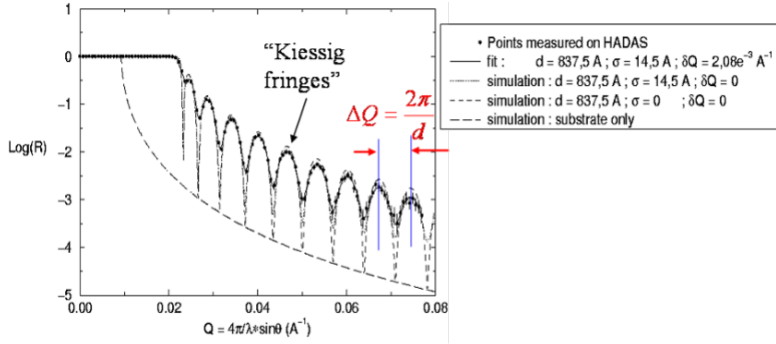


Fig. 15.8: Reflectivity of neutrons from a nickel layer on glass substrate on a logarithmic scale. Data points were measured on the HADAS reflectometer of the late FRJ-2 reactor. The solid line shows a fit, where the layer thickness was determined to be $837.5 \text{ \AA}$ with a root mean square roughness of $14.5 \text{ \AA}$ and where the resolution of the instrument $\delta Q = 2.08 \times 10^{-2} \text{ nm}^{-1}$ has been taken into account; the dotted line shows a simulation for the same structural parameters, but for an ideal instrument without resolution broadening; the short dashed line shows the simulation for the same layer thickness but without roughness; the long dashed line shows the simulation for the glass substrate only.

Besides the plateau of total reflection, the reflectivity curve in Fig. 15.8 contains more information about the layer. We observe the so-called Kiessig fringes, which are a result of interference of the wave reflected at the top and bottom of the layer. Based on the path length difference, we would expect

$$\Delta Q = \frac{2\pi}{d}. \quad (15.13)$$

But we see, that for smaller wave vector transfer, the periodicity in Q is smaller. This is an effect of the refraction at the interfaces leading to a longer path length difference from the

bottom surface.

We see also the effect of surface roughness, which smears out the sharp minima between the Kiessig fringes. It is strongly correlated with the Q -resolution of the instrument.

We conclude this section mentioning that variants of the a reflectivity measurement can be used to resolve also the lateral structure of a layer. Studying the off-specular scattering, we measure at angles $\alpha_i \neq \alpha_f$, but still collimate the beam only in one direction. In grazing incidence small angle scattering measurement (GISANS) the beam is collimated along both directions. The former can resolve inhomogeneities on the length scale > 100 nm, while the latter gives access to correlations on the nm length scale.

15.7 Following the time evolution

Neutrons do not only provide the information where atoms or spins are located, but also how they move. The diffraction of neutrons discussed so far depends basically on the time average position of the scatterers. The motion enters only in the so-called Debye-Waller factor, which takes into account how the intensity is reduced, when the atoms oscillate about this position. But with neutrons we can also probe, how the atoms actually move. Here we distinguish between oscillatory motions, which lead to inelastic scattering, where the initial and final neutron energy E, E' are distinct by a finite amount, or relaxational or diffusional motions, which lead to a broadening of the elastic signal and so-called quasi elastic scattering (QENS). With the former we can gain information about molecular and lattice vibrations, and spin excitations in ordered magnetic structures. The latter is used to study e.g. diffusion in batteries and fuel cells and biological membranes, relaxations of proteins or the spin relaxation in quantum magnets.

15.7.1 Inelastic neutron scattering

Typical examples of excitations in solid state physics are molecular vibrations, phonons or spin waves. The interactions between the atoms or the spins determine the energies needed to excite the corresponding motions. For crystalline materials, the motions are correlated across the crystal, giving rise to dispersive excitations such as phonons or spin waves, also called magnons. From the dispersion relation one can deduce, how the nuclei or spins are coupled and hence determine force constants or exchange parameters.

On the other hand, local excitations that are limited to a specific site, feature an inelastic signal, that shows no dispersion and varies weakly as a function of Q . So it can be recorded basically anywhere in Q -space. Typical examples are crystal field excitations of molecular vibrations.

These and other quasi-particles in the solid state have excitation energies $1\text{meV} < \hbar\omega < 1000\text{meV}$, matching the spectral range of cold and thermal neutrons. As neutrons interact both with the spins and the nuclei, they can create and annihilate their corresponding excitations. One determines the excitation energy at a specific wave vector transfer to deduce the dispersion relation, while the lifetime of the excitation determines the width of the signal

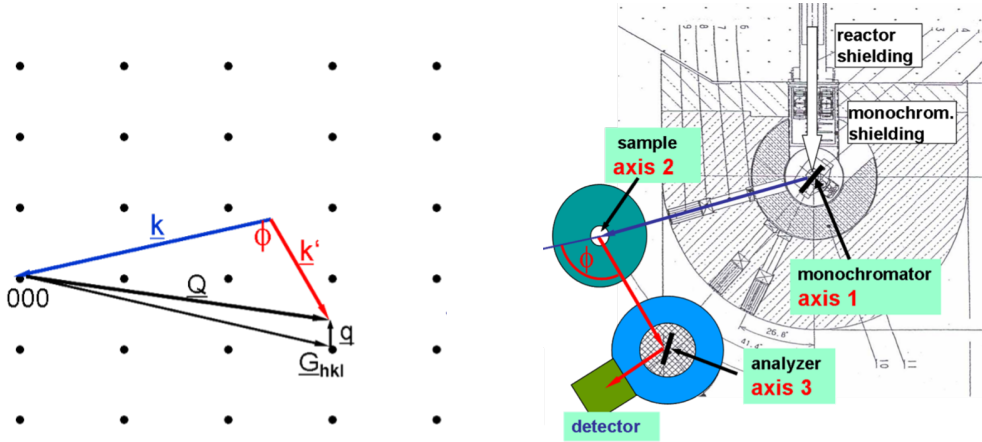


Fig. 15.9: Left: Scattering triangle for inelastic scattering from a single crystal. Right: Schematics of a three axis spectrometer. (Courtesy of Dr. H. Conrad)

giving additional information, how energy can be distributed within the crystal. This is an important information to understand phenomena such as thermal expansion, heat transport but also the Cooper pair coupling in superconductors.

The scattering triangle is now formed by $\mathbf{k}, \mathbf{k}'$ with different length. Of course, energy and momentum conservation must still be fulfilled. The lattice or spin excitations are characterized by the dispersion relation $\hbar\omega(\mathbf{q})$, where the wave vector lies within the first Brillouin zone. Energy and momentum conservation give then:

$$E - E' = \hbar\omega(\mathbf{q}) \quad (15.14)$$

$$\mathbf{k} - \mathbf{k}' = \boldsymbol{\tau} + \mathbf{q} \quad (15.15)$$

In the diffraction experiments discussed so far, we have assumed, that the scattering is dominantly elastic and hence $k = k'$. This is now not the case anymore and hence we need to determine also the final neutron wave vector $\mathbf{k}'$ after the interaction between neutron and sample.

15.7.1.1 Three axis spectrometer

To measure dispersive features, an instrument should be able to access the respective regions in reciprocal space and collect the scattered neutron effectively. In the early days of neutron scattering, Bertram Brookhouse developed for this task the so called three axis spectrometer, that is sketched in Fig. 15.9 on the right side. The first axis is the monochromator, that was already introduced in section 15.5. It sends neutrons with a well defined energy or wavelength towards the sample. This is the second axis. We place the analyzer, which is the third axis, to record neutrons that are sent into a specific direction. To determine the wavelength of the scattered neutrons, another monochromator crystal is placed at the position of axis 3. It Bragg diffracts then neutrons of a chosen wavelength towards the detector. So the Bragg angles of the monochromator and detector select, which initial and final energy is

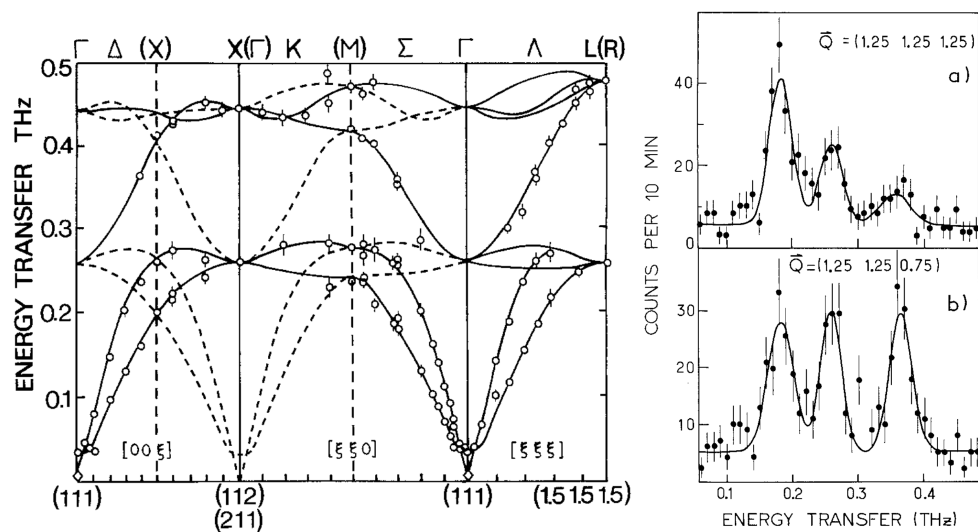


Fig. 15.10: Spin wave dispersion relations for the garnet $\text{Fe}_2\text{Ca}_3\text{Ge}_3\text{O}_{12}$ along main symmetry directions in reciprocal space. The data points are obtained from scans keeping the momentum transfer constant. The figure on the right shows examples of such “constant Q scans”. The solid lines are model calculations, from which the interaction (exchange) parameters between the spins in the unit cells can be determined; figure taken from [5]

recorded. Choosing the angle ϕ in Fig. 15.9, we can define the direction of $\mathbf{Q}$. So the TAS can scan any point in reciprocal space within the limits of the neutron spectrum.

As the inelastic scattering cross sections are much weaker than the elastic cross section measured in diffraction experiments, maximizing the sample flux is an important issue on these type of instruments. Typically one uses focusing monochromators to concentrate a high intensity into a small spot at the cost of angular resolution. The beam cross section at the position of the monochromator is typically $20 \text{ cm} \times 20 \text{ cm}$, which are focused into beamspot of $2 \text{ cm} \times 4 \text{ cm}$. This 10×5 fold beam compression results in 50 times wider divergence distribution. Choosing a proper geometry, the focusing affects only the Q resolution, but hardly the energy resolution [4].

The reciprocal space is typically explored by point scans in reciprocal space. The many degrees of freedom of the instrument allow arbitrary choices. Often constant- Q or constant- $\hbar\omega$ are chosen to follow the dispersion relation. Fig. 15.10 shows an example how to measure the dispersion of a spin wave. Different peak shapes are fitted to the scans shown in the right panels. From the position in $\mathbf{Q}$ and energy, the dispersion relation is derived. The width of the peak convoluted with the instrumental resolution is inversely proportional to the lifetime of the excitation.

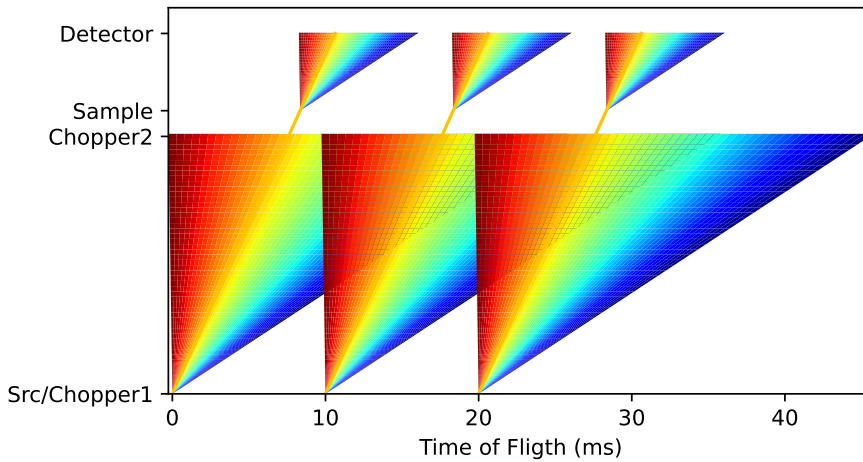


Fig. 15.11: Flight-path diagram of a chopper spectrometer: The source/chopper emits/transmits a white spectrum that disperses due to the different velocities. A second chopper selects the initial velocity and controls the sample illumination time. The sample emits again a spectrum of velocities. Recording the time-of-flight at the detector, the final velocity can be determined.

15.7.1.2 Time-of-flight spectrometer

As in the case of diffraction, we can also use the time-of-flight of the neutron to determine of initial and final neutron energy. As we need to introduce another monochromator, when we move from a monochromatic diffractometer to a TAS, we need in this case to add another chopper, see Fig. 15.11. This second chopper is placed just in front of the sample. Only neutrons of the right velocity will pass both choppers. So the pair of two choppers acts as a monochromator. The second chopper just in front of the sample limits also the illumination of the sample to a narrow neutron pulse. As we know the initial neutron velocity from the phases of the two choppers, we can calculate, when the neutrons arrive at the sample. Here they can change the velocity, but since we know, when the sample was illuminated and when the neutrons arrive at the detector, we can also determine the final neutron velocity and hence also the energy transfer.

As we do all the velocity analysis with time-of-flight, we can as in the case of time-of-flight diffraction place detectors everywhere around the sample. The detectors cover a large part of the solid angle and have an area of 15 to 30 m². Hence one collects the intensity distribution in reciprocal space over time, instead of scanning it as in the case of TAS. Dedicated software at the neutron facilities provide the 4 dimensional $S(\mathbf{Q}, \omega)$ for further treatment and analysis.

As we need to chop the beam, these instruments have a much lower sample flux at continuous neutron sources, leading to rather long integration times on the order of several hours. Still, when the signal from the sample is broadly distributed in reciprocal space, the time-of-flight method is very effective on a reactor. On the novel pulsed sources, either spallation or HiCANS, the pulsed beam comes for free, and hence here this is the only efficient way



Fig. 15.12: Large area detector of the TOPAS spectrometer under construction at FRM II. The height of the detector tubes is 2.2 m, it has an active area of 15 m² and covers a solid angle of approximately 2 sr.

to realize a spectrometer.

15.7.2 Quasi Elastic Neutron Scattering (QENS)

Diffusive or relaxational motions of atoms and spins result in a broadening of the elastic scattering, as they move with time away from their equilibrium position instead of oscillating around it. Examples of these motions are the diffusion of Hydrogen in fuel cell or storage materials, polymer dynamics in liquids or glasses or motions of functional biological molecules. In magnetism, the suppression of long range order leads to slow spin dynamics, which are important for the understanding of the corresponding quantum phenomena.

If this motions happen on the time scale from tens of ps to hundreds of ns, these processes can be explored by neutron spectroscopy. The corresponding energy resolution ranges from $100\mu\text{eV} > \delta\hbar\omega > 10\text{neV}$. The more relaxed part of this spectrum can be covered by variants of the instruments discussed so far. Chopper spectrometers can reach a resolution of $\approx 30\mu\text{eV}$ making use of long wavelength neutron with low velocities. The ultimate energy resolution for a TAS is reached, when the Bragg angle of the monochromator and the analyzer approach 90° . Then the energy resolution is dominated by the lattice spacing resolution in eq. 15.7. For perfect Si crystals, this allows an energy resolution $\delta\hbar\omega < 1\mu\text{eV}$.

At pulsed sources, a combination of time-of-flight and Bragg optics is used to reach an energy resolution $1\mu\text{eV} < \delta\hbar\omega < 20\mu\text{eV}$. Here, the primary wavelength is finely resolved by a very long flight path from the source to the sample and a short source or chopper pulse. The crystal analyzer array between sample and detector transmits only the high resolution λ' towards the detector. Accounting for the time-of-flight Bragg reflected neutrons need to travel from the sample to the detector, the initial wavelength λ can be calculated, see Fig.

15.13.

Complementary to the sub μeV resolution spectrometers at a reactor backscattering instrument, the spectrometers feature a very broad dynamic range up to a 1 meV. Hence one can identify different relaxation mechanisms or quasielastic and inelastic signal in parallel. An example is given in the right panel of Fig. 15.13. It shows the Q integrated scattering function $S(\omega)$ from an aqueous solution of a model protein, bovine serum albumin (BSA), measured at the near backscattering spectrometer BASIS at the SNS in the U.S. The measured spectrum can be modelled by a superposition of several Lorentzian peak shapes, each corresponding to a different relaxation.

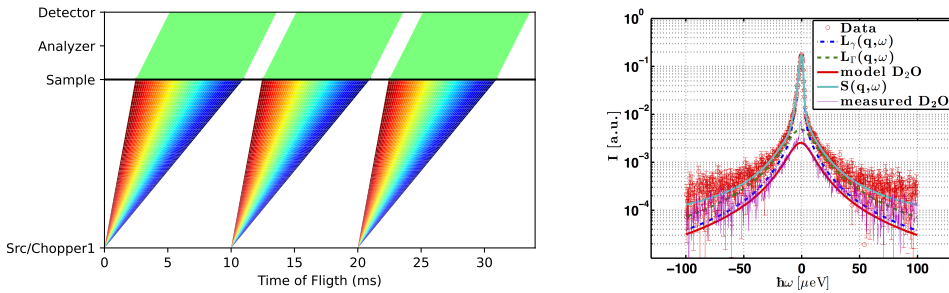


Fig. 15.13: Left: Flight-path diagram of a crystal analyzer spectrometer: The source/chopper emits/transmits a white spectrum that disperses due to the different velocities. The crystal analyzer transmits only a well defined λ' to the detector. Recording the time-of-flight at the detector, the final velocity can be determined. Right: Example of a wave vector integrated spectrum $S(\omega)$ (symbols) collected at BASIS, ORNL, including a fit and the various contributions to it (lines)

The high resolution instruments presented here allow analyzing motions on a time scale up to ns. For slower motions, the required energy resolution is prohibitive, as the transmission of the monochromating and analyzing optics becomes too low to acquire reasonable statistics in a decent time.

15.7.2.1 Spin Echo spectroscopy

So to perform measurements with a higher energy resolution or to study motions with characteristic times between ns and μs one needs to overcome the anti-correlation between intensity and resolution. Slow motions of macromolecules, e.g. polymers or proteins, slow spin dynamics in frustrated magnets or atomic diffusion fall into this time domain.

The spin of the neutron makes it possible to decouple the energy resolution of the scattering process from the monochromatization of the neutron beam. For that, we prepare a polarized neutron beam, i.e. nearly the spin of all neutrons point into the same direction, see Fig 15.14. The spin is then turned into the direction of the neutron beam and enters a homogeneous magnetic field parallel to this direction. As the spin is perpendicular to the field, the neutron performs a Larmor precession around the field direction. The field is designed in such a way

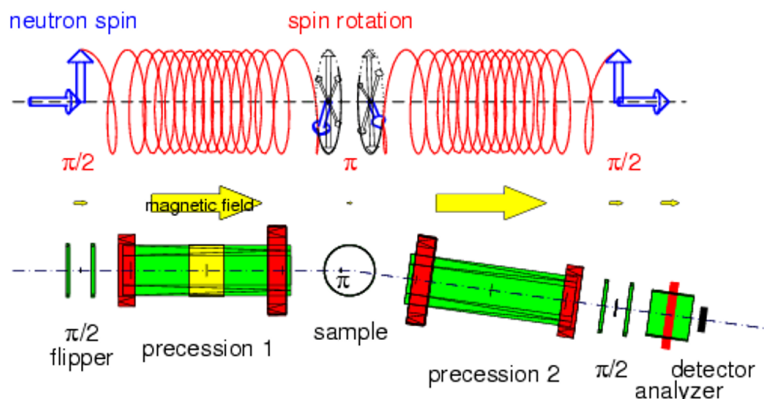


Fig. 15.14: Principle and schematic of a neutron spin echo spectrometer. Top: Evolution of the neutron spin along the flight path. Bottom: Schematic of the components of the spectrometer.

that the field integral $\int B(s)ds$ is identical for all neutrons passing through the field region to the sample. When arriving at the sample, the beam is depolarized and the spins are inverted by means of a π spin flipper. From the sample the neutrons pass through an identical field region. But as the polarization has been inverted, the neutron spin precesses in the opposite direction. If it travels at exactly the same speed, it will leave the field region with the spin polarization pointing into a direction that depends on the neutron velocity. A second $\pi/2$ flipper turns the polarization again. It is probed by a polarization analyzer that transmits neutrons with the spin in the original direction to the detector. The maximum intensity is only restored, if the speed in both arms of the spectrometer is equal. This situation is called spin echo. If the neutron has been slowed down by the interaction with sample, the spin echo is destroyed and the detector behind the polarization analyzer records a lower intensity. The echo signal can be measured by scanning the field of the second coil with respect to the field of the first coil. Since the echo signal depends by a cosine function on the time-of-flight which neutrons need to travel through the magnetic field region, the spin echo technique directly measures the intermediate scattering function $I(\mathbf{Q}, t)$ instead of $S(\mathbf{Q}, \omega)$, where t is the so-called Fourier time, which is directly related to the field integral.

The resolution depends on the field integrals that can be acquired and hence on the strength and the homogeneity of the magnetic field in the precession regions. Typical field integrals are in the range of 0.5 Tm, which allows to reach a Fourier time t of several hundreds of ns, which is equivalent to a energy resolution in the neV range. This time does not depend strongly on the monochromatization of the beam. A band width $\delta\lambda/\lambda = 0.2$ can be accepted. So the intensity is sufficient to realize a very high energy resolution. Still, this comes at a price: As it is necessary to scan the precession field, the measurements are time consuming and the typical duration of an experiment is rather a week than a day.

The neutron spin can also be used for very high resolution diffraction. These so-called Larmor labeling techniques enable extremely precise measurements of lattice spacing and strain and can be used to study very subtle structural changes.

15.8 Summary and conclusion

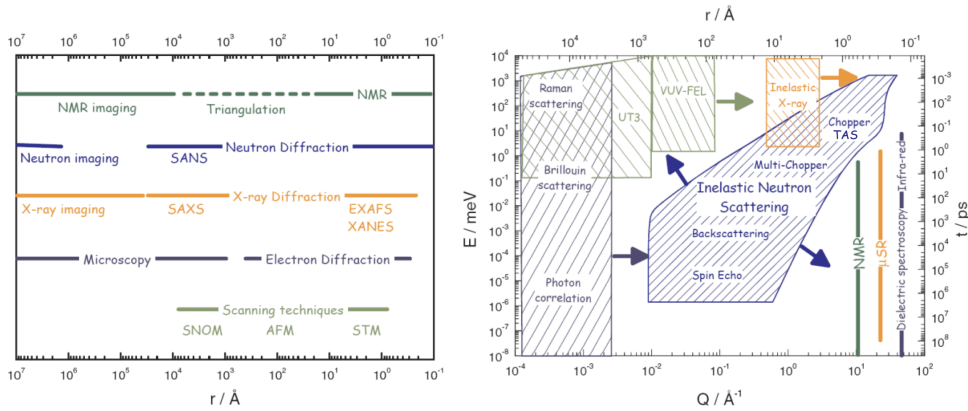


Fig. 15.15: Right: Comparison of experimental techniques with spatial resolution. Left: Accessible Q , E range for different experimental techniques.

In this chapter we have discussed the potential of the various neutron scattering methods and their experimental realizations. Neutron scattering probes pair correlations of nuclei and spins in space and time and hence provides information about the microscopic structure and motions in condensed matter. In Fig. 15.15 we compare the accessible length scales and the dynamic range that can be explored by neutron methods and other probes. This toolbox allows to understand the structures and motions of the materials which surround us and which we use. Neutrons have their place, whenever their unique properties are required, i.e. high penetration power, sensitivity to light elements and magnetism, non-destructive, weakly disturbing, etc. In particular the energy range below 1 meV of atomic and molecular motions and the resolution range from Å to hundreds of nm is well covered by the different neutron techniques. But still, neutron sources are scarce and even at neutron sources, free neutrons are scarce. Neutron scattering is complementary to other, more available methods. It comes into play when abundant probes like photons and electrons are not specific enough or too harsh to the sample. The well established theory of neutron scattering allows quantitative analysis of the data and hence is often used to validate new models in condensed matter research. Therefore neutron scattering is relevant in many areas of fundamental research. Applied research plays an increasing role, in particular due to the straightforward implementation of in-situ and in-operando methods. I am confident, that it will also be useful for your personal scientific career and wish you a good time exploiting the neutron scattering instruments.

References

- [1] H. M. Rietveld. A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography*, 2(2):65–71, Jun 1969.

- [2] A. Le Bail, H. Duroy, and J.L. Fourquet. Ab-initio structure determination of LiSbWO_6 by x-ray powder diffraction. *Materials Research Bulletin*, 23(3):447–452, 1988.
- [3] D. F. R. Mildner and J. M. Carpenter. Optimization of the experimental resolution for small-angle scattering. *Journal of Applied Crystallography*, 17(4):249–256, Aug 1984.
- [4] Reinhard H. Scherm and Eckhard Krüger. Bragg optics — focusing in real and k-space. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 338(1):1 – 8, 1994.
- [5] Th. Brueckel, B. Dorner, A. G. Gukasov, V. P. Plakhty, W. Prandl, E. F. Shender, and O. P. Smirnow. Dynamical interaction of antiferromagnetic subsystems: a neutron scattering study of the spinwave spectrum of the garnet $\text{Fe}_2\text{Ca}_3(\text{GeO}_4)_3$. *Zeitschrift für Physik B Condensed Matter*, 72(4):477–485, Dec 1988.

Multiple choice

1. Thermal neutrons have typical energies of
 - 0.2 meV ☐
 - 20 meV ☐
 - 2000 meV ☐
 - 20000 meV ☐
2. In 1 sec, cold neutrons cover a distance of
 - 10 m ☐
 - 100 m ☐
 - 1000 m ☐
 - 100000 m ☐
3. Neutron choppers rotate with frequencies up to
 - 5 Hz ☐
 - 600 Hz ☐
 - 60000 Hz ☐
4. Phonon- and Magnon-dispersions are usually measured at
 - ☐ small angle scattering instruments
 - ☐ triple axis spectrometers
 - ☐ backscattering spectrometers
 - ☐ neutron spin echo spectrometers
5. Interface structure in thin film systems is usually studied at
 - ☐ powder diffractometers
 - ☐ time-of-flight spectrometers
 - ☐ reflectometers
6. Polymer reptation has been extensively studied at
 - ☐ thermal time-of-flight spectrometers
 - ☐ triple axis spectrometers
 - ☐ spin-echo spectrometers
7. Incoherent scattering (e.g. of hydrogen) is very useful to
 - ☐ reduce the background
 - ☐ study magnetic properties
 - ☐ study diffusive motions
8. The scattering vector Q is directly related to
 - ☐ the momentum transfer of neutrons to the sample
 - ☐ the coherence of the neutron beam
 - ☐

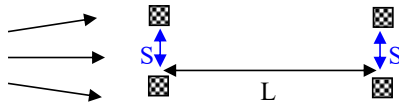
the phase shift during scattering

9. The resolution function of an instrument is directly related to
- ☐ the Fourier transform of the pair correlation function of the atoms in the sample
 - ☐ the coherence volume of the neutron beam
 - ☐ the collimation and monochromatization of the beam

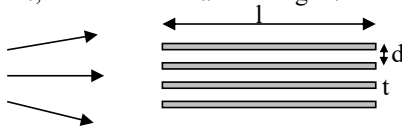
E15.1 Collimation

Assume you have to define the direction of a neutron beam by collimation. The incident beam has a flat angular distribution over an angular range much wider than needed. Employ the following three methods, plot the intensity distribution after your collimating device, comparing shape, width and transmission:

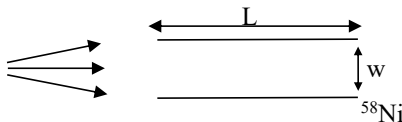
1. two slits with opening S in distance L



2. a “Soller Collimator” consisting of N neutron absorbing plane-parallel plates of thickness t , channel width d and length l :



3. a neutron guide of length $L \gg$ width w coated with ^{58}Ni ($b = 14.4 \text{ fm}$; fcc-structure; $a_0 = 3.520 \text{ \AA}$)



What is the principle difference between method 3 and methods 1 and 2?

E15.2 Monochromatization

You have now the task to monochromatize your ideally collimated neutron beam (neglect any angular divergence). Again, three methods are offered:

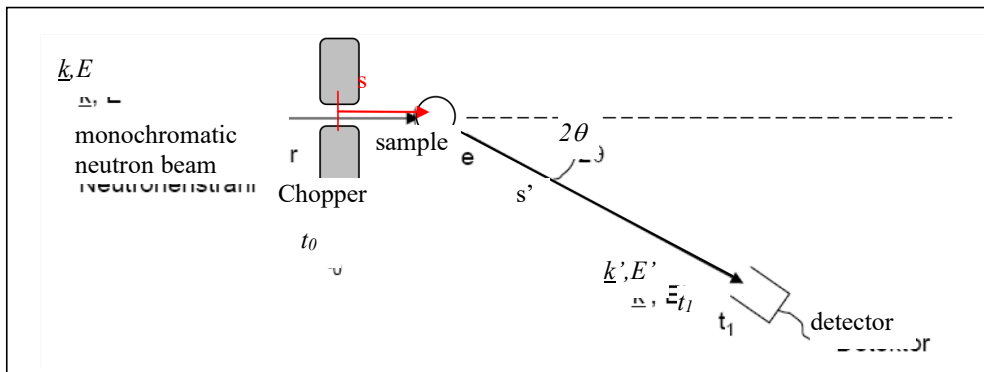
- a) A velocity selector, see figure 16.6. Take as parameters the thickness of the drums of 10 cm , an inner radius of the lamella of 6 cm , a distance between the lamella of 1 cm

and an inclination angle of 10° . How fast does this selector have to turn to monochromatize neutrons of wavelength $10 \text{ \AA}$? Estimate the wavelength spread in percent.

- b) A crystal monochromator made from pyrolytic graphite $PG(002)$ reflection with a lattice d -spacing of $3.343 \text{ \AA}$. PG is not an ideal crystal, but a mosaic crystal consisting of many small crystalline blocks slightly canted against each other within an angular width of say $40'$. Calculate the Bragg angle for a wavelength of $2.4 \text{ \AA}$ and $10 \text{ \AA}$, respectively, and estimate the wavelength spread in percent.
- c) A sequence of two disk choppers with radius R and opening d in a distance L . Take $L = 3 \text{ m}$, $R = 20 \text{ cm}$, $d = 1 \text{ cm}$. Which wavelength is selected, if the choppers rotate at 200 Hz with a phase shift of 100° ?

E15.3 TOF-Spectroscopy (optional!)

In a time-of-flight spectrometer, the energy change of the neutrons during scattering is being determined by the neutron time-of-flight:



- a) Calculate the time-of-flight between chopper and detector for a flight path length $s+s'=3\text{m}$ for neutrons of wavelength $1 \text{ \AA}$ for an elastic scattering process.
- b) Determine the relation between the delayed arrival time of neutrons at the detector and the energy loss during inelastic scattering at the sample.
- c) Determine the relation between energy transfer $\hbar\omega = E - E'$ and the magnitude of the momentum transfer $|\hbar\mathbf{Q}| = \hbar|\mathbf{k}' - \mathbf{k}|$ for a detector with fixed scattering angle 2θ .

Which factors determine the energy resolution of a TOF spectrometer? How does this affect the design of such an instrument?

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