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Water penetration and intercalation in synthetic clay: a neutron and x-ray study on fluorohectorite

Master's thesis for Stud. Ariel Fischer

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Preface

This master thesis has been performed at the Department of Physics at the Norwegian University of Science and Technology (NTNU) and Institute for Energy Technology (IFE) in the autumn semester of year 2007. The work was in the division of Complex Materials and my diploma work has been supervised by Prof. Dr. Ing. Jon Otto Fossum at NTNU and Prof. Kenneth Dahl Knudsen, Principal Research Scientist at IFE, Kjeller.

I acknowledge Prof. Jon Otto Fossum for introducing me to the exciting field of structural studies on nano-silicates. I also would like to present a huge gratitude to my external advisor, Kenneth Dahl Knudsen, for showing me how to operate the SANS-instrument, helping me initiating experiments, and for all the enlightening talks. A huge thanks go to my boss Kristian Semmen and colleagues Halvor Hulberg and Yngve Jordal at Orkla for giving me the support and time needed.

A special thanks goes to Sabrina for being the most beautiful motivation and inspiration.

Ariel Fischer, *Oslo, November 30th, 2007.*

Summary

Small angle scattering (SAS) is the collective name given to the techniques of Small-Angle Neutron Scattering (SANS), X-ray Scattering (SAXS) and Light Scattering (SALS). In each of these techniques radiation is elastically scattered by a sample and the resulting scattering pattern is analyzed to provide information about surface, size, orientation and shape of some component in a sample.

Nickel-Fluorohectorite (*NiFH*) and Sodium-fluorohectorite (*NaFH*) are synthetic smectite clays consisting of silicates, or platelets, with a lateral dimension as high as 200 times the particle thickness. The layer charge is sufficiently high for the platelets to stack in a robust face-to-face orientation, but still moderate enough to allow intercalation of water and other polar molecules into the interlayer space - a feature that places this substance in the group of swelling clays. The crystallites in *NiFH* have the ability to expand up to several times its dehydrated size while still maintaining a two-dimensional crystallographic integrity [1].

In this thesis the analysis of the power-law behavior of Small-Angle Neutron Scattering (SANS) has been used to obtain information on surface roughness, size and order in different samples consisting of *NiFH* and *NaFH*. We have observed structural changes and effects that occur in a sample when varying parameters such as temperature and humidity. The effect of adding dry powder samples into a fluid making a suspension is also investigated. Compared to x-rays, neutrons have the advantage that SANS-data may reflect more accurately the dimensionality of matrix-pore interfaces [2].

Fluorohectorites are polydisperse, with a platelet diameter ranging from several *nm* all the way up to about 1 μm . When the sample is in the dissolved state, the polydispersity causes a macroscopic gravity-induced phase separation, where as many as four different phases have been observed to exist simultaneously in the same sample [2]. A four-phase suspension has been observed and analyzed in this thesis.

Wide-Angle X-ray Scattering (WAXS) have been used observe water transportation in *NiFH*. This has been done by lowering/rising the temperature and imposing a humidity gradient over a quasi one dimensional powder sample inside a glass capillary. The (001) Bragg peak, which is a direct measure of the hydration state of the sample, is investigated. The unstable 2WL state in *NiFH* previously observed [3] is investigated in more detail.

The neutron experiments have been performed using the SANS-instrument at the *JEEP-II* reactor at IFE, Kjeller. For the WAXS-experiments a *Bruker AXS NanoSTAR* x-ray instrument located at NTNU, Trondheim, was used.

Before the experiments are described and analyzed, a theory section will cover clays, neutron and x-ray scattering to make the foundation for understanding the performed experiments.

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Chapter 1

Theory

1.1 The clay mineral group

Clays is a term used to describe a subgroup of the phyllosilicates¹, or layered silicates, that are of grain size less than $2\mu m$ in diameter and with a thickness substantially smaller. Clays are traditional materials with a vast number of applications including ceramics, building material and barriers for radioactive waste and they have been widely studied from a phenomenological point of view - especially in geo-science [2].

The majority of naturally occurring clays are strongly heterogeneous mineral mixtures which can cause difficulties both experimentally and theoretically. Modern chemistry science now allows us to synthesize clays in which we can achieve well-controlled structures and enable detailed experimental investigation. This in turn has led to an increasing interest in finding answers to the many open questions regarding the nano-structural organization of its constituents and the complex microscopical dynamics in solid to liquid phase transitions.

Many clays have the ability to absorb, retain, release, and incorporate a great variety of ions or molecules into its structure. Clays are made up of particles that may form stable suspensions in water [4].

Clays may be considered *physical colloids* in the form of *aqueous suspensions* made up of silicate platelets as primary particles. On the other hand, dehydrated clays are described in terms of *intercalation compounds* within the general context of nano-sandwiches [2].

¹Origin from modern Greek **phullon**, meaning "leaf"

1.1.1 Elementary structure of clays

The microscopic structure of clay consists of layers of minerals with spaces in between [5]. As with minerals in general, it is normal habit to characterize *phyllosilicates* by a unit cell². Let us now consider the unit cell at the scale of a single layer in three dimensions. One may define the xy -plane as where the largest faces are oriented and the a - and b -dimensions are in this plane. The c -dimension along the z -axis corresponds to the thickness of the layer (see figure 1.1).

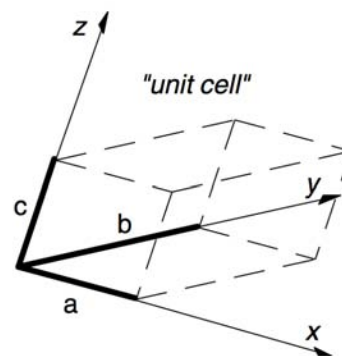


Figure 1.1: The a , b and c dimensions of a unit cell. Taken from [4].

A lamellar clay layer³ is made up of two (or more) basic *sheets*; that is a *tetrahedral*⁴ and *octahedral*⁵ sheet. A tetrahedral sheet is composed of individual tetrahedrons where generally a silicon atom is bound tetrahedrally to four oxygen atoms, whereas a octahedral sheet is composed of individual octahedrons where generally an aluminum or magnesium atom is octahedrally bound to six oxygen atoms or a hydroxyl group⁶. (For illustration see figure 1.2).

The substitutions in the octahedral and or tetrahedral sheets by less charged cations induce a net negative layer charge on the platelet. To balance this structural layer charge, individual platelets tend to stack in a crystallite by sharing intercalated cations. The term *platelet*, or a silicate, is a term used for different associations of the two layer types, and a stack of such identical platelets is called a *crystallite*.

²the smallest group of atoms in a substance that has the overall symmetry of a crystal of that substance, and from which the entire lattice can be built up by repetition in i.e. three dimensions [6]

³often referred to as platelet

⁴tetrahedron: a polyhedron with four triangular faces. In a regular tetrahedron all four triangles are congruent equilateral triangles. It constitutes a regular triangular pyramid.

⁵octahedron: a polyhedron with eight triangular faces. In a regular octahedron all eight triangles are congruent equilateral triangles.

⁶to form a sheet, the tetrahedras are linked together by sharing three of four vertices (three basal oxygens, the fourth being the apical oxygen), and the octahedrons are linked together by sharing their six vertices. [7]

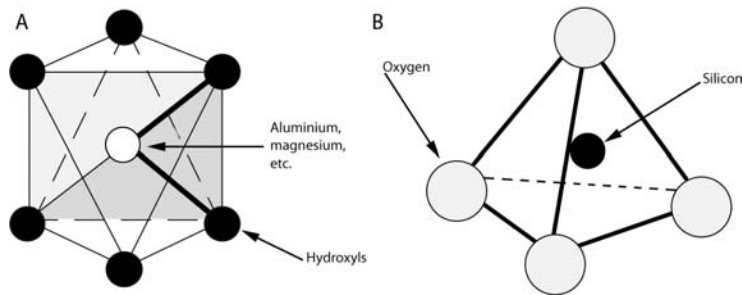


Figure 1.2: An octahedral structure (A) and a tetrahedral structure (B)

1.1.2 Classification of layer structure

Clay minerals can be placed in subgroups according to the underlying layer structure, layer charge and type of octahedral sheet⁷. One have 1:1 layered, 2:1 layered and 2:1:1 layered clay minerals and each has its own characteristic tetrahedral-octahedral sheet combination. (see figure 1.4 for a graphical representation of the different kinds). In this project report Ni-Fluorohectorite⁸ is analyzed, and this is a 2:1 layered clay and hence the main focus will be on this structure. For a complete description of all the layerings, the interested reader is referenced to literature such as [8] and [9].

In a 2:1 layering there is one octahedral sheet sandwiched between two tetrahedral sheets (see figure 1.3). One can further subdivide this group according to layer charge; either *neutral* or *charged*. In some 2:1 clays the structure may have a cation interlayer sheet located in the ditrigonal cavities outlined by two opposite tetrahedral sheets [4]. The magnitude of the interlayer charge tells how strong the layers are bond together. If there is a high negative charge the layers tend to stick together preventing expansion of the interlayer sheet - this is referred to as *high-charge* structures⁹. In this structure a typical charge per unit cell is between 0.9 and $1.0e^{10}$ [8].

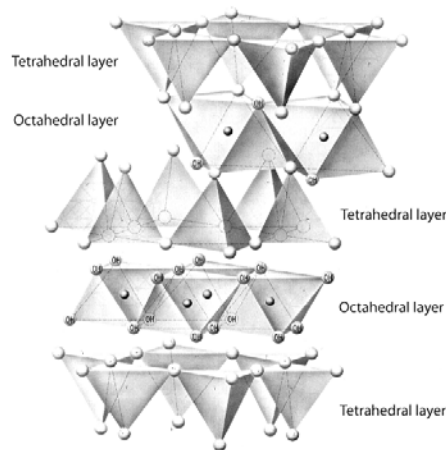


Figure 1.3: An Octahedral sheet sandwiched between two tetrahedral sheets. Taken from [10].

⁷one differ between di- and trioctahedral sheets.

⁸belonging to the smectite group (see section 1.1.4).

⁹examples are micas and chlorites

¹⁰ e being the elementary electron charge

One also have *low-charge* structures where the unit cell charge lies between 0.2 to $0.9e$. These structures may expand by interlayer influx of polar molecules, as water, and hence increasing the layer-spacing. The structure is still considered a crystal even though the basal distance changes upon intercalation. In 1:1 and 2:1:1 layerings hydrogen bondings between the oxygen and

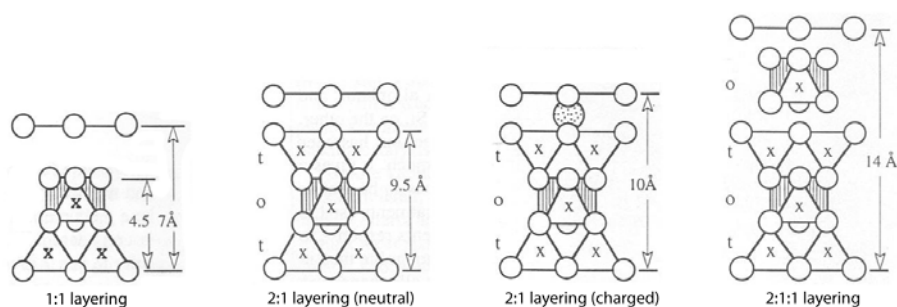


Figure 1.4: The different layering structures. 1:1) one tetrahedral sheet is bonded to one octahedral sheet (usually low layer charge). Neutral 2:1) one octahedral sheet is sandwiched between two tetrahedral sheets (zero layer charge). Charged 2:1) one octahedral sheet is sandwiched between two tetrahedral sheets with interlayer cation. 2:1:1) combination of a 2:1 layer with a charged octahedral sheet. Modified from [11]

the associated tetrahedrally arranged cation and hydroxyl group makes the the crystallite stable. In a 2:1 layering it is electrostatic forces between the platelets keeping the sheets together [1].

Crystallite organization How crystallites are organized within a sample may vary. In figure reffig:lamellarhouse you can see some possible structures a clay sample may have.

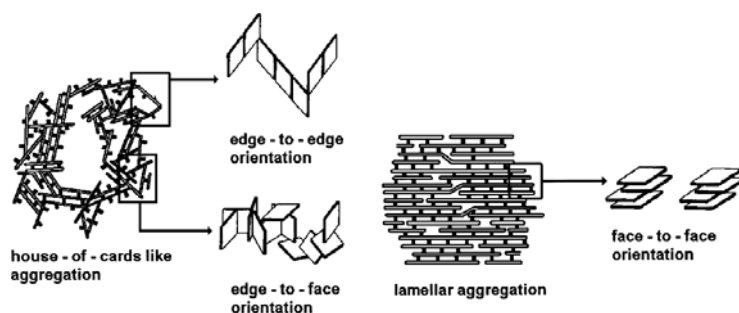


Figure 1.5: Schematic representation of (left) a lamellar and (right) a "house of cards" like aggregation. Taken from [12].

1.1.3 Intercalation and swelling properties

Low-charge structures exhibit a special and important property that *zero-charge*¹¹ and *high-charge* structures do not have. This feature is called interlayer swelling. Though all clays have the ability to *adsorb* water onto its external crystal surfaces¹², *absorption* is a feature supported only by *low-charge* structures as *smectites* and *vermiculites*. Such materials have the capacity to change their volume by absorbing water molecules or other polar liquids into the interlayer spacings. The number of water layers a clay is capable to absorb can be as high as four layers. Factors determining the number of water layers intercalated is mainly temperature and relative humidity. Ni-Fluorohectorite and Na-fluorohectorite investigated in this project report is a strong-swelling 2:1 clay.

In a 1 water layer (1WL) state the cation is normally surrounded by two water molecules, while in a 2WL hydration state the cation is surrounded by four. One see an increase in the basal distance of $\sim 2.5\text{\AA}$ from the dehydrated situation to the 1WL case, and the double of this ($\sim 5\text{\AA}$) in the 2WL situation.

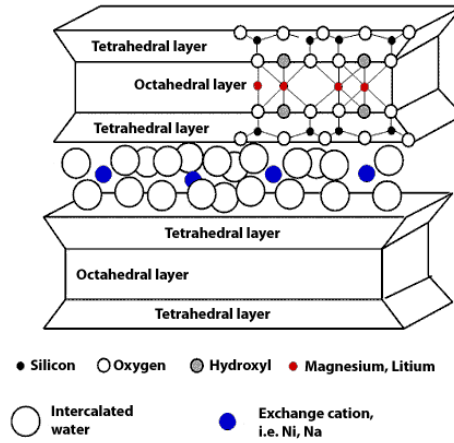


Figure 1.6: Graphical presentation of the swelling property. Modified from [13].

The swelling property is a very important characteristic, and hence it is usual to classify clays as either *swelling* and *non-swelling* [8]. Water can enter a clay in two ways - the first one being crystalline water where the water is bound in the structure as hydroxyls, and the second being what we refer to as absorption where water enters the interlayer spacing in its ordinary form, H_2O (see figure 1.6). Water intercalated in the interlayer space is lost at temperatures $\sim 120^\circ C$, and crystalline water is lost at temperatures substantially higher ($\sim 500^\circ C$).

¹¹examples are kaolinite and pyrophyllite

¹²d-spacings remain constant

Pores

Water can be intercalated into a clay in pores. A is a minute opening in a surface through which i.e. liquids and molecules may pass or build up. One usually differ between three types of pores according to their size range. The *porosity* of a material is a measure of the volume of the pores relative to the volume of the dried out state of the material in question. This is due to the fact that the pores expand if the material has swollen.

Micropores The height of the interlayer space between two platelets is an example of a micropore (nanopore). The order of magnitude of this spacing is $\sim 1nm$, and in a layered silicate this is where water and guest ions may form layers that can be controlled to a certain extent by varying parameters as temperature, relative humidity and pressure [14].

Mesopores Intermediate in size, $\sim 1nm - 50\mu m$, these pores form in the space between crystallites.

Macropores Macropores occurs mostly as a packing effect, and i.e. by applying pressure to a material the size of the macropores decrease.

1.1.4 The Smectite Group

Smectites, having two tetrahedral sheets around the central octahedral sheet, are 2:1 phyllosilicates with total layer charge between 0.2 to 0.6 e per half unit cell layer and they are typically hydrated. Differences in layer charge and interlayer cations results in different physical and chemical properties, such as, thermal stability and swelling behavior [12]. The cations are generally available to participate in cation exchange reactions unless they are large polyanions of aluminum or iron. Smectites have the widest range of interlayer swelling observed in phyllosilicates, an they have the ability to expand up to several times its dehydrated size while still maintaining a two-dimensional crystallographic integrity [1]. Under soil conditions, interlayer swelling is generally limited to the range from 0 to about 10 Å, giving rise to a 100% increase in the volume of the smectite crystals. Polar molecules and water are highly absorbed by smectites.

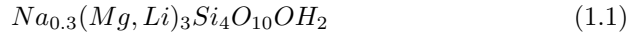
The layer charge is sufficiently high for the individual platelets to be able to stack by sharing cations, and at the same time moderate enough to allow further intercalation of water molecules into the interlayer space between the platelets. A smectite can be either dioctahedral if two thirds of the octahedral sites are occupied by trivalent cations, or trioctahedral if all octahedral sites are filled with bivalent cations [12].

Typically a smectite crystallite is $\sim 0.1\mu m$ high in stacking direction and consists of $\sim nm$ -sized platelets. This results in a total of ~ 100 platelets in one stack.

Interlayer cation exchange The interlayer cations are not tightly bound, and they may be exchanged in an aqueous solution which have a high concentration of another ion. This property is very handy when one wants to study clays with different cation composition.

1.1.5 Hectorite

Hectorite is a trioctahedral smectite clay found widespread in nature, and is formed by the alteration of oceanic and continental basalts and other basic volcanic rocks at low temperature and pressure [12]. It consists of SiO_4 -tetrahedrals, hydroxyls, magnesium- and lithium ions. The chemical formula per half unit cell for unaltered hectorite is:



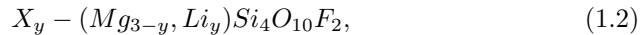
Of the seven crystal system groups, hectorite is categorized as a (normal) monoclinic crystal. Its natural color is white (see figure 1.7) and molecular weight is 383.25gm.



Figure 1.7: A sample of hectorite. Taken from [15].

1.1.6 Ni- and Na-Fluorhectorite

Fluorhectorite is a synthetic 2:1 clay that has one of the largest values for the particle diameter for its kind and a layer charge of 1.2 e per unit cell, which is very large compared to other synthetic 2:1 clays. The high surface charge leads to a high degree of stacking of the platelets, resulting in crystallites effectively consisting of ~ 100 stacked platelets. The particles are of order $0.1 \mu m$ ($\sim 1 nm$ per platelet) thick and they remain quasi-two-dimensional geometry, as the lateral dimensions may be as much as 200 times the particle thickness. $NiFH$ and $NaFH$ are on the other hand polydisperse with a wide distribution in lateral sizes, so that this ratio is not fixed. The chemical formula is:



where X is the exchangable cation - in this context Ni^{2+} and Na^+ . We note that an F^- ion has been replaced with the hydroxyl group in hectorite in eq. 1.1.

1.2 Neutron Scattering

Among the principal and most powerful experimental methods for studying structure and dynamics of materials on nanometer scale one find neutron scattering. Neutron scattering is used by an increasing numbers of scientists around the world and the scope of the method is continuously broadening.

Looking back to the early start (around forty years ago) neutron scattering was a tool for solid state physics and crystallographers, but today it serves purposes in all scientific fields that deal with condensed matter - nano science, biology, earth sciences, planetary science and engineering, to mention a few.

In the following section the theory of neutron scattering is explained. A quantum mechanical description is used to arrive at the scattering equation. The reader may skip the first few sections until subsection 1.2.8, where small angle neutron scattering is explained.

1.2.1 General properties of the neutron

The neutron was first discovered by J. Chadwick in 1932 and constitutes, together with the proton, the building blocks for all nuclei. Neutrons are, as the name suggests, non-charged particles that have the ability to penetrate deeply into matter. The neutron does not exist naturally in free form, but decays by the weak interaction into a proton, p , an electron, e and an anti-neutrino, $\bar{\nu}$, in the following reaction:

$$n \rightarrow p + e + \bar{\nu} \quad (1.3)$$

Furthermore the neutron is a fermion and its rest mass is $m_n = 1.675 \cdot 10^{-27} kg \equiv 939.8 MeV$, which is slightly higher than the sum of the decay products in (1.3). The lifetime of a free neutron is $\tau \approx 886s$ which is indeed much longer than the time of a neutron within a scattering experiment, where it spends merely a fraction of a second.

Though the neutron is a zero-charge particle it possesses a magnetic moment:

$$\mu_n = \gamma \mu_N \quad (1.4)$$

where $\gamma = -1.913$ is the neutron magnetogyric ratio and $\mu_N = \frac{e\hbar}{m_p}$ is the nuclear magneton. The neutrons magnetic moment is coupled anti-parallel to its spin, which has the value $s = \frac{1}{2}$. The neutron interacts with nuclei via the strong nuclear force and with magnetic moments via the electromagnetic force.

1.2.2 The wave-particle duality of neutrons

One of the consequences of quantum mechanics is that matter can have both a particle and a wave nature. The neutron is no exception from this. In neutron scattering experiments, neutrons behave as particles when they are created, as waves when they scatter, and again as particles when they are detected[16].

A neutron moving with constant velocity, v , have a corresponding *de-Broglie wavelength*, given by:

$$\lambda = \frac{2\pi\hbar}{m_n v}, \quad (1.5)$$

where $\hbar$ is the Planck constant¹³ In neutron scattering, the wave nature is often referred to in terms of the neutron *wave number*, $k = \frac{2\pi}{\lambda}$, or the *wave vector* of value k and with same direction as the velocity:

$$\vec{k} = \frac{m_n \vec{v}}{\hbar} \quad (1.6)$$

Usually wavelengths are measured in $\text{\AA}$, wave numbers in $\text{\AA}^{-1}$, while the neutron velocity is measured according to SI-units. For the purpose of this text the neutrons are considered non-relativistic, and the neutron kinetic energy is given by:

$$E = \frac{\hbar^2 k^2}{2m_n}, \quad (1.7)$$

which is measured in eV , where $1eV = 1.602 \cdot 10^{-19} Js$.

1.2.3 The neutron cross section

The flux of the neutron beam is defined as:

$$\Psi = \frac{\text{\# of neutrons impinging on a surface per second}}{\text{surface area perpendicular to the neutron beam direction}} \quad (1.8)$$

Furthermore the *neutron scattering cross section*, σ , of a system is defined by its ability to scatter neutrons:

$$\sigma = \frac{\text{\# of neutrons scattered per second}}{\Psi}, \quad (1.9)$$

which has the units of area. This scattering cross section is the total cross section, which depends on the sample size. For most samples, this can be described by the volume specific cross section, Σ , through:

$$\sigma = V_{\text{sample}} \cdot \Sigma \quad (1.10)$$

The angular dependence of the scattered neutrons is the most important aspect of all neutron scattering. To describe this, we employ the *differential scattering cross section*:

$$\frac{d\sigma}{d\Omega} = \frac{\text{\# of neutrons scattered into solid angle } d\Omega \text{ per second}}{d\Omega} \quad (1.11)$$

The total number of scattered neutrons is the sum of neutrons in all of the 4π solid angle:

$$\sigma = \int \frac{d\sigma}{d\Omega} d\Omega \quad (1.12)$$

¹³ $\hbar = 1.034 \cdot 10^{-34} Js$

1.2.4 Scattering and absorption of neutrons

The number of neutrons scattered is necessarily limited by the number of incoming neutrons. (1.10) is valid only when the total scattering cross section of a given sample is much smaller than its area perpendicular to the beam.

In the opposite case, one must consider successive thin slices of thickness dz , each attenuating the incident beam which one here take to travel in the positive z -direction. The number of neutrons scattered from dz per second, N_{dz} , is:

$$N_{dz} = \Psi(z) \Sigma A(z) dz, \quad (1.13)$$

where $A(z)$ is the area of a sample slice perpendicular to the beam. One assume that the scattering cross section is uniform within the sample and the flux of the incident beam in the neutron beam direction is attenuated according to:

$$\Psi(z) = \Psi(0) e^{-\mu_{sc} z}, \quad (1.14)$$

where μ_{sc} is the scattering part of the attenuation coefficient.

Neutron absorption takes place as a result of neutron-induced nuclear processes, which destroys the neutrons and emits secondary radiation as a result. In most cases, the absorption cross section of thermal neutrons is inversely proportional to the neutron velocity; i.e. proportional to the corresponding wavelength, λ .

Traditionally, the absorption cross sections are given per nucleus in units of *barns* ($1 \text{ barn} = 10^{-28} \text{ m}^2$) and is listed at the typical thermal velocity $v_{th} = 2200 \frac{\text{m}}{\text{s}}$ (corresponding to $\lambda_{th} = 1.798 \text{ \AA}$). The absorption cross section is given by:

$$\sigma_a = \sigma_{a,th} \frac{v_{th}}{v} = \sigma_{a,th} \frac{\lambda}{\lambda_{th}} \quad (1.15)$$

As in (1.14), the resulting attenuation due to absorption is exponential and described by the attenuation coefficient:

$$\mu_a = \sum_i \frac{N_i \sigma_{a,i}}{V} = \sum_i n_i \sigma_{a,i} \quad (1.16)$$

Here N is the number of nuclei of the given isotope (labeled i) in the volume V , and $n_i = \frac{N_i}{V}$ is their atomic density. The attenuation coefficients for scattering and absorption are additive resulting in $\mu_{tot} = \mu_{sc} + \mu_a$ and thus (1.14) can be rewritten as:

$$\Psi(z) = \Psi(0) e^{-\mu_{tot} z}, \quad (1.17)$$

1.2.5 Quantum mechanics of scattering

The initial and final states

One define the state of the incoming wave as:

$$|\psi_i\rangle = \frac{1}{\sqrt{Y}} e^{i\vec{k}_i \cdot \vec{r}}, \quad (1.18)$$

where $Y = L^3$ can now be identified as the normalization volume for the state which is assumed enclosed in a cubic box with a side length L . The final state, which is a superposition of plane waves, is expressed as:

$$|\psi_f\rangle = \frac{1}{\sqrt{Y}} e^{i\vec{k}_f \cdot \vec{r}}, \quad (1.19)$$

The *number density*, $\frac{dn}{dV_k}$, in $\vec{k}$ -space is defined as:

$$\frac{dn}{dV_k} = \left(\frac{2\pi}{L}\right)^{-3} = \frac{Y}{(2\pi)^3} \quad (1.20)$$

We now consider a spherical shell in $\vec{k}$ -space to calculate the *energy density of states*:

$$\frac{dn}{dE} = \frac{dn}{dV_k} \frac{dV_k}{df_k} \left(\frac{dE}{dk_f}\right)^{-1} = \frac{Y}{(2\pi)^3} 4\pi k_f^2 \frac{m_n}{k_f \hbar^2} = \frac{Y k_f m_n}{2\pi^2 \hbar^2}. \quad (1.21)$$

1.2.6 The scattering equation

The interaction responsible for the scattering is described by the operator $\hat{V}$. The scattering process is described by the *Fermi Golden Rule*. This gives the rate of change between the neutron in the single incoming state, $|\psi_i\rangle$, and a continuum of final states, $|\psi_f\rangle$:

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} \frac{dn}{dE_f} \left| \langle \psi_i | \hat{V} | \psi_f \rangle \right|^2 \quad (1.22)$$

where $\frac{dn}{dE_f}$ is the energy density of final states. To account for only the neutrons scattered into the solid angle $d\Omega$ one use (1.21), (1.22) and the fraction of the unit sphere, $\frac{d\Omega}{4\pi}$, one get the expression:

$$W_{i \rightarrow f, d\Omega} = \frac{Y k_f m_n}{(2\pi)^3 \hbar^2} d\Omega \left| \langle \psi_i | \hat{V} | \psi_f \rangle \right|^2 \quad (1.23)$$

$W_{i \rightarrow f, d\Omega}$ is the number of neutrons scattered into $d\Omega$ per second. The incoming flux is given by (using (1.6)):

$$\Psi = \frac{v}{Y} = \frac{\hbar k_i}{Y m_n}. \quad (1.24)$$

The expression for the *differential scattering cross section* (1.11) is now:

$$\frac{d\sigma}{d\Omega} = \frac{1}{\Psi} \frac{W_{i \rightarrow f, \Omega}}{d\Omega} = Y^2 \frac{k_f}{k_i} \left(\frac{m_n}{2\pi \hbar^2}\right)^2 \left| \langle \psi_i | \hat{V} | \psi_f \rangle \right|^2 \quad (1.25)$$

Here the normalization volume, Y , will eventually vanish due to the factor $\frac{1}{\sqrt{Y}}$ in the states $|k_i\rangle$ and $|k_f\rangle$. This is due to the fact that the interactions, $\hat{V}$, are always independent of Y . The Y -dependence will be omitted in the following.

Comment One note that the pre-factor $\frac{k_f}{k_i}$ equals unity when one have elastic scattering ($k_f = k_i$).

1.2.7 Elastic nuclear scattering

The interaction between the neutron and a single nucleus is expressed by the *Fermi pseudo-potential*:

$$\hat{V}(\vec{r}) = \frac{2\pi\hbar^2}{m_n} b_j \delta(\vec{r} - \vec{r}_j). \quad (1.26)$$

Here, the spatial δ -function represents the short range of the strong nuclear force and is a sufficient description for the scattering of thermal neutrons[16]. One can now calculate the scattering cross section. The matrix element is:

$$\langle \psi_i | \hat{V} | \psi_f \rangle = \frac{2\pi\hbar^2}{m_n} b_j \int e^{i\vec{k}_i \cdot \vec{r}} \delta(\vec{r} - \vec{r}_j) e^{-i\vec{k}_f \cdot \vec{r}} d^3\vec{r} \quad (1.27)$$

$$= \frac{2\pi\hbar^2}{m_n} b_j e^{i\vec{q} \cdot \vec{r}_j} \quad (1.28)$$

Inserting this into (1.25) one get:

$$\frac{d\sigma}{d\Omega} = b_j^2, \quad (1.29)$$

where the Y -dependence is canceled and elastic scattering is assumed.

For a system of two nuclei, we can write the scattering potential as a sum; $\hat{V} = \hat{V}_j + \hat{V}_{j'}$. Now we get for the matrix element:

$$\langle \psi_i | \hat{V} | \psi_f \rangle = \frac{2\pi\hbar^2}{m_n} (b_j e^{i\vec{q} \cdot \vec{r}_j} + b_{j'} e^{i\vec{q} \cdot \vec{r}_{j'}}) \quad (1.30)$$

1.2.8 Small-angle neutron scattering

In this section the theory of small-angle neutron scattering (SANS) is described. This is a technique that can provide information on surface and size of nanometer-sized objects. The SANS technique is particularly useful within biological and other organic systems, where the difference in scattering length between hydrogen and deuterium can be utilized to enhance domains of specific interest in the sample.

Lets review the result in (1.25) with cancelled Y -dependence and elastic scattering assumed:

$$\frac{d\sigma}{d\Omega} = \left(\frac{m_n}{2\pi\hbar^2} \right)^2 \left| \langle \psi_i | \hat{V} | \psi_f \rangle \right|^2 \quad (1.31)$$

We now consider the scattering from a system of nuclei. From (1.30), the scattering potential can be considered as the sum of the single nuclear potentials:

$$\hat{V} = \frac{2\pi\hbar^2}{m_n} \sum_j b_j \delta(\vec{r} - \vec{r}_j) \quad (1.32)$$

By insertion into (1.31) the *scattering cross section* becomes:

$$\frac{d\sigma}{d\Omega} = \left| \sum_j b_j e^{i\vec{q} \cdot \vec{r}_j} \right|^2 \quad (1.33)$$

We here consider the nuclei as being fixed in position, i.e. we take r_j as constants. This is for small-angle scattering a very good approximation [16].

1.2.9 The SANS cross section

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

$$q \cdot a \ll 1, \quad (1.34)$$

where a is on order interatomic distance. For larger values of q , we are in a regime where the crystalline structure of the material is responsible for the scattering. Since such Bragg-scattering is not analyzed using neutrons as a probe theory of scattering from a lattice will be given in the chapter on X-ray scattering.

In a typical SANS experiment $q_{max} \leq 0.5 \text{\AA}^{-1}$ and only structures larger than $\frac{2\pi}{q_{max}} \approx 12 \text{\AA}$ are resolved. This implies that the scattering from the single atoms can not be distinguished and that it becomes valid to transform the sum in (1.33) into an integral:

$$\sum_j b_j e^{i\vec{q} \cdot \vec{r}_j} \rightarrow \int_V \rho_b e^{i\vec{q} \cdot \vec{r}} dV, \quad (1.35)$$

1.2.10 SANS from particles in solution

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

$$\frac{d\sigma}{d\Omega} = \left| \int_{obj} \rho_b(\vec{r}) e^{i\vec{q} \cdot \vec{r}} dV + \rho_{sol} \int_{sol} e^{i\vec{q} \cdot \vec{r}} dV \right|^2 \quad (1.36)$$

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

$$\frac{d\sigma}{d\Omega} = \left| \int_{obj} \rho_b(\vec{r}) e^{i\vec{q} \cdot \vec{r}} dV + \rho_{sol} \int_V e^{i\vec{q} \cdot \vec{r}} dV \right|^2 \quad (1.37)$$

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

$$\frac{d\sigma}{d\Omega} = \left| \int_{obj} \rho_b(\vec{r}) e^{i\vec{q} \cdot \vec{r}} dV \right|^2 \quad (1.38)$$

One note the that the cross section depends on the square of the contrast in scattering length density. Hence, the scattered intensity can be changed strongly by i.e. varying the scattering length density of the solvent. This is typically done by deuteration.

In a sample with a particle density of $n = \frac{N}{V}$ and assuming no interaction between the particles the cross section is given as:

$$\frac{d\sigma}{d\Omega} = n \cdot \left| \int_{obj} \rho_b(\vec{r}) e^{i\vec{q} \cdot \vec{r}} dV \right|^2 \quad (1.39)$$

In an actual sample the interference between particles must also be accounted for. This results in a multiplicative term on the right side of (1.39), the *inter-particle structure factor*. In the dilute limit $S(\vec{q})$ approaches unity.

The inter-particle structure factor

As mentioned, (1.39) is valid for scattering from N uncorrelated particles, and the multiplicative structure factor, $(\vec{q})$, modify the intensity when one have spatial correlation between the particles.

The spatial correlations, or structure, in a concentrated system are usefully described in terms of the *radial distribution function*, $g(\vec{r})$, related to the probability of finding the centre of any particle at a distance r from the center of a given particle. Specifically, for a system of N particles in a volume V , the number of particles in a volume element dV at a distance r from a given particle is:

$$\frac{N}{V} g(\vec{r}) dV \quad (1.40)$$

It is not shown here, but the structure factor is related to $g(\vec{r})$ by:

$$S(\vec{q}) = 1 + \frac{4\pi N}{V} \int_0^\infty [g(\vec{r}) - 1] \vec{r}^2 \frac{\sin(\vec{q} \cdot \vec{r})}{\vec{q} \cdot \vec{r}} d\vec{r}. \quad (1.41)$$

1.2.11 The particle form factor

For *mono-disperse, homogeneous* particles, the cross section (1.39) simplifies to:

$$\frac{d\sigma}{d\Omega} = n \cdot \left| \int_{obj} \rho_b(\vec{r}) e^{i\vec{q} \cdot \vec{r}} dV \right|^2 \quad (1.42)$$

$$= n \Delta \rho_b^2 V^2 P(\vec{q}) S(\vec{q}), \quad (1.43)$$

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

$$P(\vec{q}) = \left| \frac{1}{V} \int_{obj} \rho_b(\vec{r}) e^{i\vec{q} \cdot \vec{r}} dV \right|^2. \quad (1.44)$$

1.2.12 In the limits of small and large q

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

The Guinier approximation The Guinier approximation is a helpful expression for calculating size of particles at low values of q . In the case of an arbitrary particle it may be shown that the form factor may be given by the *Guinier-expression*:

$$P(q) = 1 - \frac{1}{3}q^2 R_g^2 + \mathcal{O}(q^4 R_g^4) \quad (1.45)$$

$$\approx e^{-\frac{1}{3}R^2 q^2} \text{ for } qR_g \ll 1, \quad (1.46)$$

where R_g is the *radius of gyration* and is expressed as:

$$R_g^2 \equiv \frac{1}{N} \sum_{m=1}^N |\vec{R}_m - \vec{R}_{CM}|^2 \quad (1.47)$$

$$= \frac{1}{2N^2} \sum_{m=1}^N \sum_{n=1}^N |\vec{R}_m - \vec{R}_n|^2 \quad (1.48)$$

(1.47) describes the distribution of particles (or infinitesimal elements) in a D -dimensional space by relating it to an equivalent distribution in a D -dimensional sphere.

Hence, for a dilute solution where $I(q) \propto \text{const} \cdot P(q)$, by plotting $\ln[P(q)]$ as a function of q^2 we expect to obtain a linear function with a gradient of $-\frac{1}{3}R_g^2$. This is valid regardless of particle shape. The gyration radius $R_g < R$ always, but not substantial. For a sphere the exact relation is:

$$R_g^2 = \frac{3}{5}R^2 \quad (1.49)$$

Porod's law If the boundary between the scattering objects and the matrix is sharp (smooth surfaces) one has for large values of q :

$$I(q) = \frac{2\pi\Delta\rho^2}{q^4} \frac{S}{V} \propto q^4, \quad (1.50)$$

where S is the total interface area. At large values of q , measurements are sensitive to small real-space structures. However, the only real-space structure visible at this scale is a sharp surfaces: The boundary between two different scattering length densities.

Scattering law for fractal systems When one has scattering from fractal systems:

$$I(q) \approx q^{-\alpha} \quad (1.51)$$

For mass fractals $\alpha = D_m$ where $1 \leq D_m \leq 3$. For surface fractals $\alpha = 6 - D_s$ where $3 \leq \alpha \leq 4$. For irregular, or non smooth boundaries, the apparent surface area increases as the measurement scale r decreases.

1.3 X-ray scattering

The x-ray scattering theory needed to understand why we detect diffraction patterns and what we can achieve from it is described in this section. If the reader is familiar with the basic theory he or her could jump to the chapter about scattering from a layered clay in section 1.5.

X-rays are electromagnetic waves described by Maxwells equations (see figure 1.8). As we will learn in the following sections, it is the electric field that is the important in the description of x-ray diffraction, and for the purpose of this text an x-ray beam may be thought of as an electric wave with electric field vector varying sinusoidally with time and directed perpendicular to the direction of propagation of the beam.

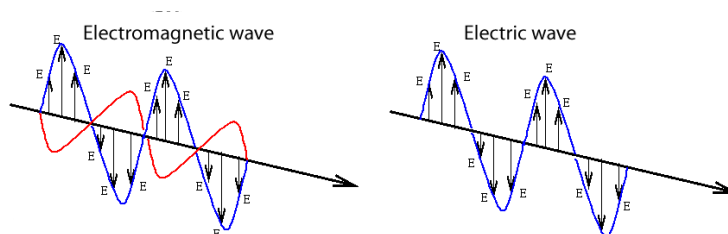


Figure 1.8: An electromagnetic wave. The blue graph represents the electric field, and the red the magnetic. In this text we only deal with the electric field.

Due to the particle-wave duality, electromagnetic radiation may also be described as consisting of particle-like photons traveling with the speed of light, c , and having a frequency ω . Diffraction is a wave phenomenon, and hence it is more conveniently described wave-property of the radiation.

1.3.1 X-rays as a probe

X-ray Diffraction (XRD) is a powerful technique used to identify crystalline phases present in materials and to measure structural properties like strain, crystallite size, orientation and defects of such phases. XRD is also used to determine multilayer thickness and atomic arrangements in amorphous materials. XRD offers very precise measurements of atomic spacings, and intensities measured with XRD can provide quantitative information on the atomic arrangements in i.e. multilayers. X-rays have the ability to penetrate many microns deep in matter, and hence is a bulk probe method, but there are ways to make XRD more surface sensitive.

The electric field of an x-ray interact with electrons surrounding the nucleus of atoms, and the interaction for high Z -elements is larger than low Z -elements. This property makes lighter elements, like oxygen ($Z = 8$), less "visible" to x-rays compared to i.e. heavy mercury atoms ($Z = 80$). A consequence of this is that x-rays can penetrate straight through light materials without being greatly attenuated or deflected [17].

Some alternatives to XRD include transmission electron microscopy (TEM), low-energy and reflection high-energy electron diffraction (LEED and RHEED respectively) and neutron diffraction. LEED and RHEED are limited to surfaces and do not probe the bulk. The elemental sensitivity in neutron diffraction¹⁴ is very different from XRD. Neutron sources are much weaker than x-ray sources, but if adequately large specimens are available, neutron diffraction is a good alternative for low Z -elements and for materials where the magnetic structure is of interest. TEM and electron diffraction tend to be more destructive techniques and also require a high level of vacuum.

1.3.2 Absorption and scattering of x-rays

When x-rays *interact* with matter, radiation can either be *absorbed* or *scattered* by the medium. In absorption the photon energy is taken up by another entity, for example, by an atom whose valence electrons make transitions between two electronic energy levels. The absorbed energy may be re-emitted as radiant energy or transformed into heat energy. When it comes to scattering, one differs between two types of scattering: *elastic* (Thomson scattering) and *inelastic* (Compton scattering).

Absorption of x-rays

When x-rays pass through matter, radiation energy is dissipated by scattering and the ejection of orbital electrons. If I_0 is the intensity (energy passing through a unit area per unit time) of the incident monochromatic x-ray, the x-ray intensity I after passage through a thickness z of a substance having density ρ is given by:

$$I = I_0 e^{-\mu_m \rho z} = I_0 e^{-\mu z} \quad (1.52)$$

where $\mu_m = \frac{\mu}{\rho}$ and is the mass absorption coefficient. This quantity is characteristic of the medium and varies with the probe wavelength. Literature often give tabulated values for μ rather than μ_m . The variation of absorption with increasing atomic number is not monotonic for a given wavelength, but shows sudden changes, and that discontinuous variations is also to be expected for a given element with varying wavelengths [4].

Scattering of x-rays

Thomson scattering

When the electromagnetic x-ray wave traverse through matter they induce vibrations in the shell electrons of the atom due to the oscillating $\vec{E}$ -field. When electrons are accelerated they radiate - this secondary radiated wave is stimulated by the oscillating electric field of the incident x-rays, it is synchronous with it (having the same period), consisting therefore of x-rays having the same frequency and wavelength as the incident x-rays. This is the classical description of a scattering process and one assume that the electron absorb only a negligible amount of energy. This scattering without change in wavelength is known as Thomson scattering and is the main type of scattering involved in x-ray diffraction. This is referred to as elastic and coherent scattering. [18]

¹⁴neutrons interact with the nuclear potential in an atom

Compton scattering

X-rays may also interact inelastically with electrons, and the re-radiated photon has lower energy (longer wavelength). The energy change varies with the collision conditions, and the scattered x-rays have a continuous spectrum at wavelengths greater than that of the incident wave. This scattering is known as Compton scattering and is historically important as an evidence for the particle-wave duality [11].

Comment In Thomson scattering the incident radiation induces numerous secondary waves. Since these waves are all produced by the same incident wave there is a clear relationship between their phases and consequently mutual interference giving rise to diffraction effects. Compton scattering, on the other hand, is due to independent collisions between x-ray photons and electrons, with no phase relationship between the scattered waves, and therefore no diffraction occurs (incoherent scattering) [17]. Although Compton-scattering do not contribute to the diffraction, it is observed as a weak background scattering over the whole angular range, and its effect must be taken into account for precise measurements.

X-rays interact with the electrons surrounding the nucleus, and this interaction is modified in three ways. The electron configuration, the atomic arrangements within the unit cell and the thermal vibrations that induce a blurring effect on the scattering center. These effects will be discussed in detail in the following sections.

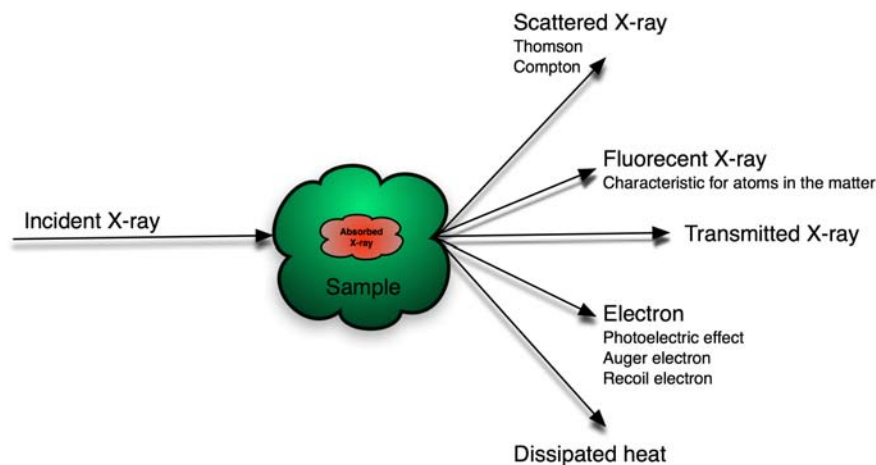


Figure 1.9: The interaction of x-rays with matter. Made with inspiration from [4].

1.3.3 Two perspectives - Classical and quantum mechanical

X-rays are electromagnetic waves, and since the scatterers (electrons) interfere with the electric field of the incoming wave, the magnetic field may be left

out for simplicity and from classical electrodynamics a monochromatic linearly polarized electric wave is described as:

$$\vec{E}(\vec{r}, t) = \vec{E}_0 e^{i(\vec{k}\vec{r} - \omega t)} \quad (1.53)$$

where $\vec{E}_0$ is the polarization vector with length, $|\vec{E}_0|$, being maximum amplitude, $\vec{k}$ is the incoming wave vector in the direction of the propagation, $\vec{r}$ is the positional vector, ω is the angular frequency and t is the time.

Through a quantum mechanical perspective one has that the wave is quantized in photons with energy $\hbar\omega$ and momentum $\hbar\vec{k}$ and the intensity. Intensity is here the number of photons passing through a given area per unit time and is proportional to the square of the electric field¹⁵. This imply that the the magnitude of the electric field is also quantized.

The non-relativistic¹⁶ relation between wavelength, λ , and photon energy, ϵ (in *keV*), is:

$$\lambda = \frac{hc}{\epsilon} \quad (1.54)$$

1.3.4 Scattering

In section 1.3.2 two types of scattering were mentioned, *Thomson*- and *Compton*-scattering. Thomson-scattering is the classical perspective where the scattering is assumed elastic, but this is not the general case. According to quantum mechanics the incoming photon carries a momentum $\hbar\vec{k}$ and energy $\omega\hbar$, and energy may be transferred to the electron making the scattered wave less energetic and one have *inelastic* scattering. It was also mentioned that this form of scattering do not give rise to diffraction, and hence Thomson-scattering is the process revealing the structure of materials, and a classical approach is sufficient in most cases.

Of course this does not prevent momentum to be transferred, and we define the scattering vector (or momentum transfer vector) $\vec{Q}$ which is the difference between the propagation vectors of the incident and scattered wave [19]. See figure 1.10.:

$$\vec{Q} = \vec{k}_i - \vec{k}_s \quad (1.55)$$

Other literature may define this quantity the other way around, as the difference between k_s and k_i - the physics is of course the same. The scattering vector is the variable of choice when describing elastic scattering.

1.3.5 Scattering from one electron

A single electron is the scattering unit of x-rays, and upon radiation it becomes an oscillating dipole and emits a wave with amplitude, E_0 falling of as $\frac{1}{R}$, where

¹⁵this relation is found by using $\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$ and Poyntings vector (intensity is the temporal average of this quantity) $\vec{S} = \vec{E} \times \frac{\vec{B}}{\mu}$, where $\vec{B}$ is the magnetic field and μ here being the magnetic permeability.

¹⁶adequate for the purpose of this text

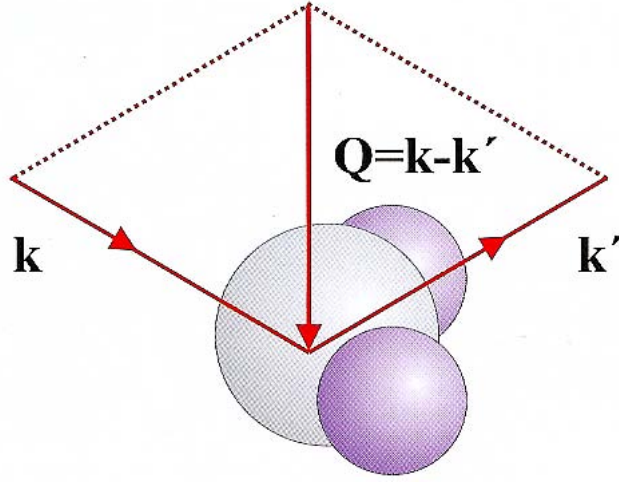


Figure 1.10: The momentum transfer vector. On the figure $Q = \vec{Q}$, $k = k_i$ and $k' = k_s$. Taken from [20].

R is the distance from the scatterer. The electron belongs to the lepton family and does not interact with the strong nuclear force. It is a fermion particle and is structureless, and hence the simplest structure one can probe with x-rays is a system consisting of two electrons.

There is a quantity associated with the electron that gives the ability of an electron to scatter an incoming wave. This is referred to as the *scattering length*, r_0 and expressed as:

$$r_0 = \frac{e^2}{4\pi\epsilon_0 mc^2} = 2.8179 \cdot 10^{-15} m \quad (1.56)$$

and this is also the classical electron radius.

Let us now define the cross-section which is an important quantity and the meeting point between experiment and theory [20]. First, let us differ between two scattering events; the first one being the case where the beam radius as a whole is intercepted by the sample, and the second where the beam is only partly intercepted.

What one typically measure in a scattering experiment is the number of photons arriving at a finite detector, $I_{scattered}$, that subtends a solid angle $\Delta\Omega$. In a sample there is a number, N , scatterers per unit area seen along the beam. If the whole beam is intercepted it is natural that the scattered intensity will be proportional to the incoming intensity, I_0 , and N in addition to $\Delta\Omega$.

The effectiveness of the scattering by one particle, is just as important. We call this quantity *the differential cross-section* and is denoted $\frac{d\sigma(\theta, \phi)}{d\Omega}$ ¹⁷, where $\sigma(\theta, \phi)$

¹⁷ $\frac{d\sigma(\theta, \phi)}{d\Omega} = \frac{\text{Number of photons scattered per second into } \Delta\Omega}{\text{Incident flux} \times \Delta\Omega}$

is the cross section dependent on the polar angles. These proportionalities let us write down the expression for the intensity:

$$I_{scattered} = I_0 N \Delta\Omega \frac{d\sigma(\theta, \phi)}{d\Omega} \quad (1.57)$$

In the scattering event where one only have a partly intercepted beam it is clear that one need to consider the *flux*, Φ_0 , of the incoming intensity, which is the number of photons per second per unit area. In this situation eq. 1.57 is given by:

$$I_{scattered} = \Phi_0 A N \Delta\Omega \frac{d\sigma(\theta, \phi)}{d\Omega} \quad (1.58)$$

where $\frac{d\sigma(\theta, \phi)}{d\Omega}$ now refers to the whole sample.

Polarization

When calculating the differential cross-section for a scattering geometry it is vital to incorporate how the detector is placed in relation to the polarization of the incoming field. If one assume a monochromatic linearly polarized wave it makes difference if the detector is placed in the same plane as the polarization, or in a plane perpendicular to it. For the latter the electron acceleration is the same for all angles, and having the detector in the same plane, the electron acceleration has to be multiplied by $\cos\psi$. For an unpolarized source the amplitude may point in all directions with equal probability and here it can be shown that it is $\frac{1}{2}(1 + \cos^2\psi)$. Hence, the source dependent polarization factor, $P(\theta)$, is:

$$P(\theta) = \begin{cases} 1 & \text{vertical scattering plane} \\ \cos^2\theta & \text{horizontal scattering plane} \\ \frac{1}{2}(1 + \cos^2\theta) & \text{unpolarized source} \end{cases} \quad (1.59)$$

The differential cross-section for Thomson scattering is:

$$\frac{d\sigma(\theta, \phi)}{d\Omega} = r_0^2 P(\theta) \quad (1.60)$$

where r_0 is the electron scattering length as defined in eq. 1.56.

1.3.6 Interference

Before developing the theory for scattering from an atom and finally a crystal lattice, the phenomenon of interference will be described. Interference can be defined as a superposition of two or more waves resulting in a new wave pattern. When a beam of light shines onto an ensemble of scatterers a phase difference occurs between the scattered waves as a result of difference in optical path length traveled. The waves may reinforce each other, either fully or partial, or cancel out. When two or more waves with no phase difference (coherent waves) are superimposed we observe constructive interference, whereas destructive interference occurs if they are out of phase.

1.3.7 Scattering from an atom

An atom consists of one or more electrons, and now we proceed to calculate the scattering from one atom. First, now one must take into account the phase difference that arises when the x-ray interacts with electrons at different positions. In addition one assume elastic scattering so that $|k_i| = |k_s| = \frac{2\pi}{\lambda}$.

Letting the origin be placed at the center of the atom the phase difference between an electron in d^3r around origin and at a volume element d^3r at position $\vec{r}$ is (using eq. 1.55):

$$\Delta\phi(\vec{r}) = (\vec{k}_i - \vec{k}_s) \cdot \vec{r} = \vec{Q} \cdot \vec{r} \quad (1.61)$$

The contribution to the scattered field from the particle at $\vec{r}$ is $-r_0\rho(\vec{r})d^3r$ with a phase factor $e^{i(\vec{Q}\cdot\vec{r})}$, where $\rho(\vec{r})$ is *electron number density*, a continuous function of the classical charge cloud surrounding the nucleus. Integrating this quantity give us the total scattering length of the atom:

$$-r_0 \int_V \rho(\vec{r}) e^{i(\vec{Q}\cdot\vec{r})} d^3r = -r_0 f^0(\vec{Q}) \quad (1.62)$$

where $f^0(\vec{Q})$ is named the *atomic form factor*¹⁸. The scattered intensity from an atom is this quantity multiplied with its complex conjugate. The phase differences lead to partial interference and a net decrease in the scattered amplitude for an atom, so that the scattering efficiency is a function of the angle, θ , (Bragg angle, see section 1.3.10) and falls off with $\frac{\sin\theta}{\lambda}$.

The atomic form factor (also known as the scattering factor) express the efficiency of cooperation among the scatterers for an atom and may be defined as the ratio of the scattered amplitude from an atom at rest to that scattered by a single electron [21].

We see immediately from eq. 1.62 that when $\vec{Q}$ approaches 0 all the volume elements scatter in phase so that $f^0 = Z$, the total number of electrons. In the other extreme where $\vec{Q} \rightarrow \infty$, we must consider how the phases of the scattered waves combine when the wavelength of the incoming beam becomes much smaller than the atom. From the complex notation any electron may be represented as a point on the unit circle in the complex plane. When the momentum transfer vector is large, the phase will be much larger than 2π , and the phase factors from the different scatterers will fluctuate rapidly around the unit circle [20]. Hence, when integrating $f^0 \rightarrow 0$.

Recognizing the left hand side of eq. 1.62 as a *Fourier* integral one may also write:

$$-r_0 \int_V f^0(\vec{Q})(\vec{r}) e^{-i(\vec{Q}\cdot\vec{r})} d^3Q = -r_0 \rho(\vec{r}) \quad (1.63)$$

The physical significance of this is that the scattering length of a substance can be calculated from eq. 1.62 if the electron density distribution is known, and the $\rho(r)$ of a substance can be calculated from eq. 1.63 if the scattering length

¹⁸for x-rays this quantity is strongly angle dependent, but for neutron i.e. the scattering is isotropic

is known for all $\vec{Q}$. The structure of a substance and the X-ray scattering length are therefore always related. One can go back and forth between real and reciprocal space (Q has the dimensions of $\frac{1}{[L]}$).

Dispersion corrections

The atomic scattering factor $f^0(\vec{Q})$ derived here is independent of the wavelength of the incident x-rays only under the assumption that the bound electrons of the atom scatter as free electrons. However, if the wavelength is very close to an absorption edge the scattering power of a bound electron may be either greater or less than that of a free electron, and the phase of the scattered electron may be different, and should be taken into account [4]. Thus the atomic scattering factor must be represented as a complex quantity:

$$f(\vec{Q}, \hbar\omega) = f^0(\vec{Q}) + f'(\hbar\omega) + if''(\hbar\omega), \quad (1.64)$$

where f' and f'' are known as dispersion corrections to f^0 , and arise from the excitation of electrons from the inner electron shell (K) [4]. f'' and f' represents the imaginary and real dispersion corrections respectively. They may be considered Fourier-transforms of highly localized scattering distributions and so will decrease with scattering angle much more slowly than the Fourier transform of the total distribution of electrons of the atom, f^0 [18, 22].

1.3.8 Scattering from one molecule

Now we consider scattering from a single molecule formed by N atoms held closely together by chemical bonds. One first combine the scattered waves from its individual atoms with respect to the position occupied by the molecule as a whole. Let the scattering factors of the atoms in the molecule be $f_1, f_2, \dots, f_N$ and let the position vectors of these atoms be $\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N$ so that the path differences of the scattered waves from the various atoms with respect to this origin are $\vec{Q} \cdot \vec{r}_1, \vec{Q} \cdot \vec{r}_2, \dots, \vec{Q} \cdot \vec{r}_N$. The molecular scattering length $F^{molecule}$ which results from the combination of waves is found by summation of eq. 1.62:

$$F^{molecule}(\vec{Q}) = \sum_{j=1}^N f_j(\vec{Q}) e^{i(\vec{Q} \cdot \vec{r}_j)} \quad (1.65)$$

For the intensity to be given in absolute units the multiplication of the electron scattering length, $-r_0$, is needed.

Physically this means that if one collects the intensity $|F^{molecule}(\vec{Q})|^2$ for a large interval of $\vec{Q}$ -values one may determine the positions $\vec{r}_j$, and hence hence get structural information. A single molecule have a scattering length too small to give a measurable signal - for that one need a lattice of molecules.

1.3.9 Diffraction

A diffracted wave is a resulting wave from a series of constructively interfering waves. Such a wave can only occur at a certain angles from the incident wave, and later in this text you can read how these angles can be determined through

Bragg's law or equivalently the *Laue-condition*. Interference and diffraction (see figure 1.11) is common to all types of waves, including sound-, water- and electromagnetic waves. An important criteria for diffraction to occur is that the magnitude of the probe wavelength is of the same order as the separation distance between the scatterers.

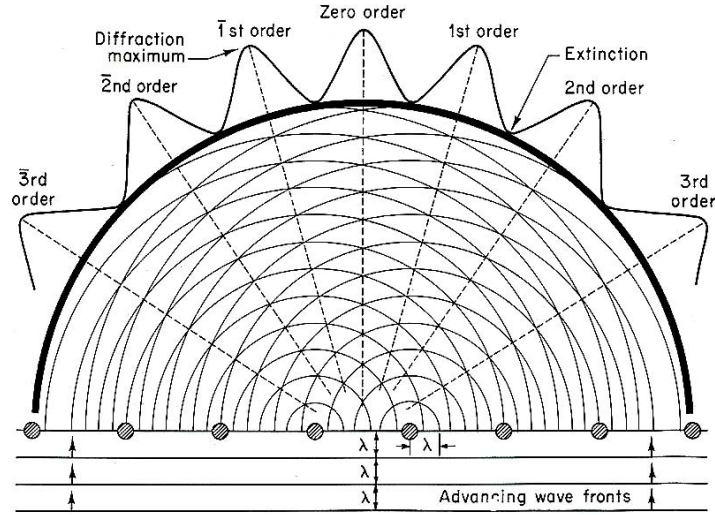


Figure 1.11: Interference and diffraction. Taken from [21]

The kinematical approximation

The kinematical approximation is a term used when scattering can be considered to be weak. The scattering from each volume element in a crystal is considered to be independent of that from other volume elements, and the scattered wave is assumed to leave the crystal without further scattering. In quantum mechanics this corresponds to a perturbation in the incident beam, and the first *Born-approximation* is valid. By neglecting such multiple scattering effects the theory is considerably simplified, and such treatment give the direction of the diffracted beams, and often their intensities, with good accuracy for many purposes [21].

When this assumption no longer holds one need to use the theory of dynamical scattering. However, in this text the kinematical approximation is considered valid.

1.3.10 Bragg's law of diffraction

The Bragg formulation of x-ray diffraction was proposed by William Lawrence Bragg and William Henry Bragg in year 1912. They discovered that upon x-ray radiation crystalline solids produced patterns of diffracted waves. They found that in such crystals, for certain specific wavelengths and incident angles, intense peaks of scattered radiation was observed.

Figure 1.12 shows two parallel crystal lattice planes at which both incident and diffracted (reflected) x-ray beams subtend angle θ . The path difference between waves reflected by the first plane and the second plane is $2d \sin \theta$. If the path differences between successive waves are equal to one wavelength of the beam, or some integer multiple of it, there is constructive interference, i.e. waves are in phase, and the reflected beam is intense in the direction indicated. The intensity decrease abruptly with any deviation from the critical value of θ . One observe that the phase of the scattered wave changes only if it moves along $\vec{Q}$ since there is no path difference between points in the same plane [23]. Bragg's law is from these simple geometrical consideration:

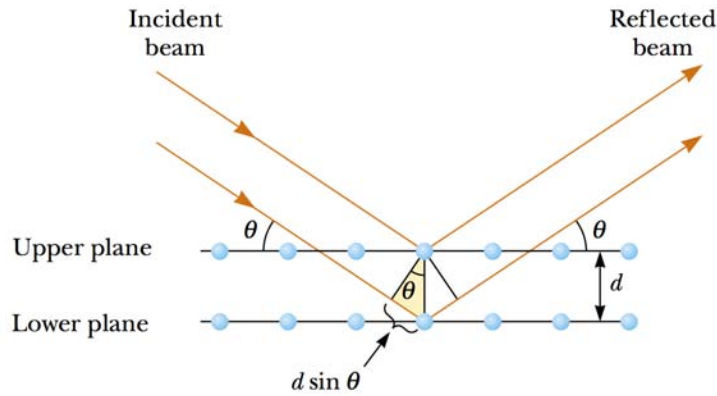


Figure 1.12: A two-dimensional description of the reflection of an x-ray beam from two parallel crystalline planes separated by a distance d . The beam reflected from the lower plane travels farther than the one reflected from the upper plane by a distance $2d \sin \theta$. Taken from [24]

$$2d \sin \theta = m\lambda, \quad (1.66)$$

where $m \in \{1, 2, 3, \dots\}$.

While eq. 1.66 is very useful, it has its limitations. One can i.e. not calculate the intensity at Bragg-peaks. The Laue function, is of more general significance than the Bragg condition in that it yields information on the angular distribution of the diffracted beam about the average direction.

1.3.11 Scattering from a crystal lattice

A crystal is a regular periodic arrangement of atoms, ions, or molecules that constitute the material. Even if the periodically arranged assembly of atoms consists of complicated molecules, each molecule or group of molecules can be replaced by some fixed representative point, and these points will then form a regular arrangement having the characteristic period of the particular crystal.

For x-rays to be diffracted in a certain direction by a crystal, the Laue conditions must be satisfied (derived later in this chapter). This occurs whenever

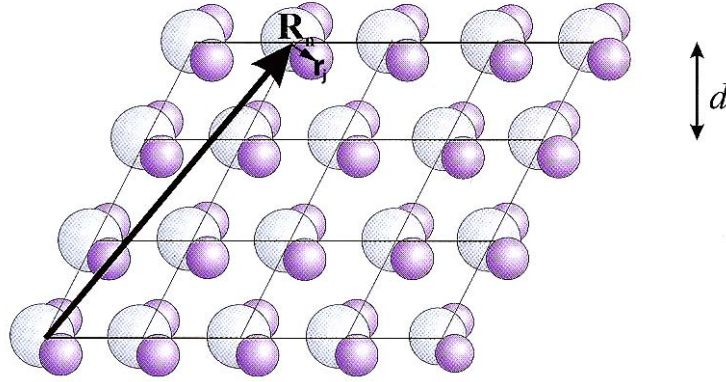


Figure 1.13: $\vec{R}_n + \vec{r}_j$ can give us the position at every atom in a lattice. Modified from [20]

the orientation of the crystal with respect to the direction of the incident x-rays is such that a particular lattice plane (hkl) is normal to $\vec{Q}$, and $d = \frac{2\pi}{|\vec{Q}|}$.

The condition that $\vec{Q}$ should be perpendicular to a lattice plane is equivalent to the condition that both the incident and diffracted beams subtend the same angle with respect to the plane. Before diffraction can occur, however, the second condition must also be satisfied. Thus if θ , the angle that the incident beam makes with the lattice plane, is gradually altered, diffraction occurs only at those angles for which $d = \frac{2\pi}{Q}$. These values of θ are necessarily those which satisfy the Laue condition given in eq. 1.78 later in this chapter.

In order to find the scattering amplitude of the crystal one need to build on what we have done until now. A lattice reflects the symmetry of a crystal, and each lattice point has a unit cell associated with it. If $\vec{R}_n$ are the lattice vectors and $\vec{r}_j$ is the position of the atoms from the lattice site, the the vector $\vec{R}_n + \vec{r}_j$ may give the position of any crystal site in the lattice (see figure 1.13). Then the scattering amplitude yields:

$$F^{crystal}(\vec{Q}) = \sum_{n,j}^{N,J} f_j(\vec{Q}) e^{i(\vec{Q} \cdot (\vec{R}_n + \vec{r}_j))} \quad (1.67)$$

$$= \underbrace{\sum_n^N e^{i(\vec{Q} \cdot \vec{R}_n)}}_{\text{Lattice sum}} \cdot \underbrace{\sum_j^J f_j(\vec{Q}) e^{i(\vec{Q} \cdot \vec{r}_j)}}_{\text{Structure factor}} \quad (1.68)$$

$$(1.69)$$

The first term is a sum over all lattice sites, whereas we recognize the second term as the unit cell structure factor. The multiplicative factor $-r_0$ is again omitted. We see that the lattice sum is over phase factors distributed around the unit circle in the complex plane. Performing the summation we see that it

will be of order unity unless the condition:

$$\vec{Q} \cdot \vec{r}_n = 2\pi \cdot n, \quad (1.70)$$

where n is an integer is met. Then the lattice sum becomes of order N . The lattice vectors $\vec{R}_n$ is on the form:

$$\vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3, \quad (1.71)$$

where $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$ is the basis vectors of the lattice and (n_1, n_2, n_3) are integers. Now one introduce the reciprocal lattice vector that turns out to be a solution to the condition in eq. 1.70. The new reciprocal basis vectors are derived from the real-space vectors in the following way:

$$\vec{a}_1^* = \frac{2\pi(\vec{a}_2 \times \vec{a}_3)}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \quad (1.72)$$

$$\vec{a}_2^* = \frac{2\pi(\vec{a}_3 \times \vec{a}_1)}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \quad (1.73)$$

$$\vec{a}_3^* = \frac{2\pi(\vec{a}_1 \times \vec{a}_2)}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \quad (1.74)$$

$$(1.75)$$

resulting in a reciprocal lattice vector given by:

$$\vec{G} = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*, \quad (1.76)$$

where (h, k, l) are called the Miller indecies and are all integers. Taking the product of $\vec{G}$ and $\vec{R}_n$ we get:

$$\vec{G} \cdot \vec{R}_n = 2\pi(hn_1 + kn_2 + ln_3) = 2\pi \cdot n, \quad (1.77)$$

and a solution to eq. 1.70. This is a proof of the fact that $F^{crystal}(\vec{Q})$ is non-vanishing if and only if $\vec{Q}$ coincides with a reciprocal lattice vector:

$$\vec{Q} = \vec{G} \quad (1.78)$$

This means that only certain points in reciprocal space give rise to scattering. We know that the intensity is modulated by the square of eq. 1.67, and by measuring a huge number of intensity sets from a crystal one are able to deduce the positions of the atoms and molecules in a unit cell. It may be shown that eq. 1.78, namely the Laue condition, is equivalent to Bragg's Law described earlier in this text (this is also demonstrated in 1.14).

Calculation of the lattice sum

The lattice points in a three dimensional lattice are specified by the lattice vector $\vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$ (See eq. 1.71). In the case of a finite lattice with $N = (N_1, N_2, N_3)$ unit cells, the lattice sum in eq. 1.67 can be written:

$$S_N(\vec{Q}) = \prod_{j=1}^3 \sum_{n_j=0}^{N_j-1} e^{iQ_j n_j |\vec{a}_j|} \quad (1.79)$$

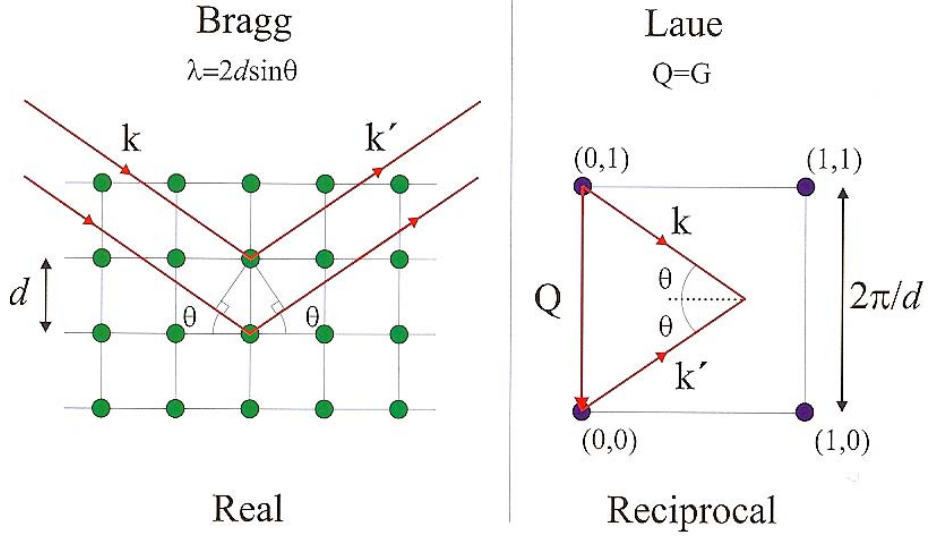


Figure 1.14: The equivalence between Bragg's law (eq. 1.66) and the Laue condition (eq. 1.78). Taken from [20].

We will now proceed to calculate the lattice sum when the Laue condition is almost fulfilled. A small displacement parameter $\vec{\xi} = \xi_1 + \xi_2 + \xi_3$ from the Miller indices is introduced, and this gives:

$$\vec{Q} = \vec{G}_{hkl} + \vec{\xi} = (h + \xi_1)\vec{a}_1^* + (k + \xi_2)\vec{a}_2^* + (l + \xi_3)\vec{a}_3^* \quad (1.80)$$

where $\vec{a}_j^*$ ($j = 1, 2, 3$) is the lattice basis vectors in reciprocal space, $\vec{Q}$ is as before the momentum transfer vector and h, k, l is the Miller indices.

Recognizing the sum in Equation (1.79) as a geometrical series, rewriting Equation (1.79) gives:

$$S_N(\vec{\xi}) = \prod_{j=1}^3 e^{i\pi\xi_j(N_j-1)} \frac{\sin(N_j\pi\xi_j)}{\sin(\pi\xi_j)} \quad (1.81)$$

Thus the absolute value in one dimension is:

$$|S_{N_j}(\xi_j)| = \frac{\sin(N_j\pi\xi_j)}{\sin(\pi\xi_j)} \quad (1.82)$$

When N is large:

$$\lim_{\xi_j \rightarrow 0} \frac{\sin(N_j\pi\xi_j)}{\sin(\pi\xi_j)} = N_j \quad (1.83)$$

Setting $\xi = \frac{1}{2N_j}$ give us a measure for the peak width:

$$\left| S_{N_j}(\xi_j = \frac{1}{2N_j}) \right| \approx \left(\frac{2}{\pi} \right) N_j \approx \frac{1}{2} (\text{Peak Height}) \quad (1.84)$$

Eq. 1.83 gives a peak height of N_j and that the full width at half maximum (FWHM) is approximately $2 \cdot \frac{1}{2N_j} = \frac{1}{N_j}$.

It can be shown, since both FWHM and the amplitude is dependent on N_j that the area and hence the integrated intensity stays constant (in fact equals unity) even though N_j becomes large and the width narrows. The lattice sum may be written in terms of a Dirac delta function:

$$\left| S_{N_j}(\vec{\xi}) \right| \longrightarrow \delta(\vec{\xi}) \quad (1.85)$$

The lattice sum may be equivalently written:

$$\left| S_N(\vec{Q}) \right| \longrightarrow |\vec{a}_1^*| |\vec{a}_2^*| |\vec{a}_3^*| \delta(\vec{Q} - \vec{G}) \quad (1.86)$$

It is the squared lattice sum that is of interest in a diffraction experiment and if the number of unit cells in all dimensions is large, then for any crystal shape we have:

$$\left| S_N(\vec{Q}) \right|^2 \longrightarrow N v_c^* \delta(\vec{Q} - \vec{G}) \quad (1.87)$$

where $N = N_1 N_2 N_3$ is the number of unit cells and v_c^* is the volume of a unit cell in reciprocal space.

1.3.12 Phonons - thermal lattice vibrations

In the formalism used until now one have assumed every lattice point to be fixed (perfectly rigid lattice). In equation 1.62 the scattering length of an atom was given by the Fourier transform of its electron density, $\rho(\vec{r})$. This is a severe simplification that must be dealt with for real systems since the atoms in a crystal are not at rest, but undergo thermal vibrations about their respective "rest" positions.

From quantum mechanics we have learned about the unavoidable temperature *independent* zero-point fluctuations originating from the uncertainty principle. In addition, one also have temperature *dependent* lattice vibrations that is due to thermally excited phonons in the structure. The displacements of the various atoms from their "rest" (mean) positions at a given instant must therefore be taken into account in calculating the structure factor.

The scattering amplitude for a type of atom located at each lattice point is:

$$\sum_n^N f(\vec{Q}) e^{i(\vec{Q} \cdot \vec{R}_n)} \quad (1.88)$$

If we now let the instantaneous position of the lattice point be $\vec{R}_n + \vec{u}_n$, where $\vec{R}_n$ is the temporal average mean position and $\vec{u}_n$ ($\langle \vec{u}_n \rangle = 0$) being the displacement. We know from before that the intensity is the temporal average of the absolute square of the scattering amplitude. Thus:

$$I = \left\langle \sum_m^M f(\vec{Q}) e^{i(\vec{Q} \cdot \vec{R}_m + \vec{u}_m)} \cdot \sum_n^N f^*(\vec{Q}) e^{-i(\vec{Q} \cdot \vec{R}_n + \vec{u}_n)} \right\rangle \quad (1.89)$$

$$= \sum_m^M \sum_n^N f(\vec{Q}) f^*(\vec{Q}) e^{i\vec{Q} \cdot (\vec{R}_m - \vec{R}_n)} \left\langle e^{i\vec{Q} \cdot (\vec{u}_m - \vec{u}_n)} \right\rangle, \quad (1.90)$$

$$(1.91)$$

where u_{Qm} and u_{Qn} is the component of the displacement parallel to $\vec{Q}$ for the m 'th and the n 'th atom respectively. Since $Q \cdot (u_{Qm} - u_{Qn})$ in the exponent in the temporal average is described by a Gaussian distribution we can use the Baker-Hausdorff¹⁹ theorem to simplify further to get the result:

$$\left\langle e^{iQ \cdot (u_{Qm} - u_{Qn})} \right\rangle = e^{-\frac{1}{2}Q^2 \langle u_{Qm}^2 \rangle} \cdot e^{-\frac{1}{2}Q^2 \langle u_{Qn}^2 \rangle} \cdot e^{Q^2 \langle u_{Qm} u_{Qn} \rangle} \quad (1.92)$$

Writing the last term on the form:

$$e^{Q^2 \langle u_{Qm} u_{Qn} \rangle} = 1 + \left[e^{Q^2 \langle u_{Qm} u_{Qn} \rangle} - 1 \right], \quad (1.93)$$

allow us to separate the intensity in two terms:

$$I = \sum_m \sum_n f(\vec{Q}) e^{-\frac{1}{2}Q^2 \langle u_{Qm}^2 \rangle} e^{i\vec{Q} \cdot \vec{R}_m} f^*(\vec{Q}) e^{-\frac{1}{2}Q^2 \langle u_{Qn}^2 \rangle} e^{-i\vec{Q} \cdot \vec{R}_n} \quad (1.94)$$

$$+ \sum_m \sum_n f(\vec{Q}) e^{i\vec{Q} \cdot \vec{R}_m} f^*(\vec{Q}) e^{-i\vec{Q} \cdot \vec{R}_n} \left[e^{Q^2 \langle u_{Qm} u_{Qn} \rangle} - 1 \right] \quad (1.95)$$

$$(1.96)$$

We immediately recognize the first term being the scattering amplitude for a lattice, except that the atomic form factor, f^{atom} , has been replaced by $f(\vec{Q}) e^{-\frac{1}{2}Q^2 \langle u_{Qm}^2 \rangle} = f(\vec{Q}) e^{-W(\vec{Q})}$, where $W(\vec{Q})$ is the *Debye-Waller-factor*. This term influence the intensity in the way that it gets reduced, but the width of the diffraction peaks is not influenced. The second term, however, is increasing as the as the mean square displacement is increasing, but the width is modulated by the correlation between u_{Qm} and u_{Qn} , which is only contributing over a short distance. This makes lattice sum extend over only a few lattice sites, and gives rise to a width much greater than the Bragg contribution [20].

For a unit cell with different types of atoms this generalizes to:

$$F^{unitcell} = \sum_{\vec{r}_j} f_j(\vec{Q}) e^{-W_j(\vec{Q})} \cdot e^{i\vec{Q} \cdot \vec{r}_j} \quad (1.97)$$

We know that in thermal equilibrium lighter atoms vibrate more than heavier ones, and therefore there are different Debye-Waller factors for each atom. The Debye-Waller factor has a dramatic effect when the momentum transfer vector, $\vec{Q}$, is increased in length [20].

1.3.13 The total cross section

In eq. 1.60 we defined the Thomson cross-section, which we saw were dependent on the polarization of the x-ray beam. Then in section 1.3.11 we derived the scattering amplitude in the case of a crystal (eq. 1.67), and then calculated the lattice sum with the result given in eq. 1.87. We now combine these results, to yield:

$$\frac{d\sigma(\theta, \phi)}{d\Omega} = r_0 P \left| F(\vec{Q}) \right|^2 N v_c^* \delta(\vec{Q} - \vec{G}), \quad (1.98)$$

¹⁹The theorem states that if x is described by a Gaussian distribution, then: $\langle e^{ix} \rangle = e^{-\frac{1}{2}\langle x^2 \rangle}$

where r_0 is the Thomson scattering length (see eq. 1.56), $P(\theta)$ is the polarization factor (see page 21 and eq. 1.59), $F(\vec{Q})$ is the unit cell scattering length (see eq. 1.97), N is the number of unit cells, v_c^* is the unit cell volume in reciprocal space.

Throughout our calculations we have made simplifying assumptions to arrive at the Bragg criteria for intensity peaks. We have assumed a perfectly monochromatic and perfectly parallel (no divergence) beam, and also that the crystal must be perfectly oriented for diffraction to occur. This is the idealized situation and under real circumstances the beam may have some divergence. We saw on page 27 when calculating the lattice sum that the Laue condition needed not to be exactly fulfilled to get scattered intensity, and the Bragg peaks had a measurable width.

The Lorentz factor

What we have derived in eq. 1.98 applies to one single setting of the instrument, whereas the intensity that we readily measure in an experiment is an integrated intensity. We must allow for both integration over the scattered wave vector $\vec{k}_s$ and over the scattering angle, θ to resemble an experimental intensity measurement. The result of this is an additional term, known as the Lorentz factor. This factor is dependent on exactly how the intensity is integrated and hence details of the experiment [20]. What we need to do is to integrate the delta function in eq. 1.98 over an infinitesimal solid angle element, $d\hat{k}_s$:

$$\int \delta(\vec{Q} - \vec{G}) d\hat{k}_s = \int \delta(\vec{k}_i - \vec{k}_s - \vec{G}) d\hat{k}_s, \quad (1.99)$$

by using the identity in eq. 1.55. The calculation of this integral is done properly in i.e. [20], but here simply the result is given:

$$\int \delta(\vec{k}_i - \vec{k}_s - \vec{G}) d\hat{k}_s = \frac{2}{|\vec{k}_i|} \delta(|\vec{G}|^2 - 2|\vec{k}_i||\vec{G}|\sin\theta) \quad (1.100)$$

Now we proceed to integrate over the angle, θ , and the result is:

$$\int \frac{2}{|\vec{k}_i|} \delta(|\vec{G}|^2 - 2|\vec{k}_i||\vec{G}|\sin\theta) d\theta = \frac{2}{|\vec{k}_i|} \cdot \frac{1}{20|\vec{k}_i|^2 \sin 2\theta} = \frac{1}{|\vec{k}_i|^3 \sin 2\theta} \quad (1.101)$$

Now, with these modifications, the differential cross-section can be expressed:

$$\frac{d\sigma(\theta, \phi)}{d\Omega} = r_0 P \left| F(\vec{Q}) \right|^2 N \frac{\lambda^3}{v_c} \frac{1}{\sin 2\theta}, \quad (1.102)$$

where we have used $\lambda = \frac{2\pi}{|\vec{k}_i|}$, and the reciprocal unit cell volume in eq. 1.98 is replaced with its real space volume, v_c . The term, $\frac{1}{\sin 2\theta}$, in eq. 1.102 is named the *Lorentz*-correction. Eq. 1.102 holds for a single, small, but otherwise perfect crystal. Macroscopic crystals however are often imperfect, and may be

thought of as being composed of small²⁰ crystallites with small orientational defects ($0.01 - 0.1^\circ$). Such multiple scattering is known as a *primary extinction* effect, and lowers the measured intensity from eq. 1.102.

One also have *secondary extinction*, which is a term used to describe the dissipation of radiation energy as it penetrates into the sample due to diffracted intensities from higher lying crystallites. In the situations where one can neglect these intensity moderating effects, the crystal is said to be *ideally imperfect*. [20]. Making high-grade powder samples is one way to make this assumption hold.

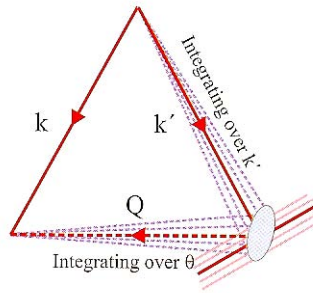


Figure 1.15: The grey ellipse resembles a small crystallite which reflects the Fourier-transform of the crystal. For a given orientation of the crystal the finite detector accepts all of the scattered $\vec{k}_s$'s (on the figure $k' = \vec{k}_s$) that fall on the red line. Taken from [20].

Comment As mentioned we must allow for integration both in $\vec{k}$ and θ , as the beam is not perfectly parallel and monochromatic. The Lorentz factor is essentially a reflection-time factor, due to the geometrical fact that planes that make an angle with the rotational axis are in reflecting position a longer time than those parallel to the axis. Due to this fact the intensities will be higher for the planes inclined at an angle relative to the rotational axis [25].

The Lorentz factor from a perfect powder

The Lorentz factor derived in section 1.3.13 describes a single crystal, where one get the diffraction pattern by rotating the sample relative to the beam. For a random powder the situation is different. A high-grade crystalline powder consists of thousands of tiny crystallites randomly oriented and the reciprocal lattice vectors are isotropically distributed over a sphere in reciprocal space.

Upon x-ray radiation, many crystallites are favorably oriented for Bragg diffraction. This results in a modification in the Lorentz polarization factor.

²⁰So that the kinematical approximation still holds, and multiple scattering effects can be neglected

The calculations of this factor is not included in this text (see [20]), but the result for a perfect powder is:

$$L_p(\theta) = \frac{m_{hkl}}{\sin \theta \sin 2\theta} \quad (1.103)$$

Where θ is, as before, the scattering angle. The factor m_{hkl} is the multiplicity which is a measure of the fact that permutation of the hkl -indices make different orientation Bragg reflect into the same angle [20]. It is natural that the measured intensity is proportional to this factor since several planes superpose to give a single spot or line in the intensity plot, and hence imply a greater intensity than from just one reflection.

Comment The difference in L_p^{powder} and $L_p^{crystal}$ are very different for low scattering angles. Often one have a situation where the sample is neither one of the two cases, as is the situation for a layered clay (see section 1.5. One then proceed to find some intermediate $L_p(\theta)$ between the two poles.

1.4 Diffraction line broadening

If one have a perfect crystal with infinitely many unit cells and a perfectly collimated monochromatic beam, any deviation from the diffraction condition will result in $I(Q) = 0$, and the diffraction pattern will consist of delta function (perfectly sharp scattering). However, such criteria are not realistic - finite crystal size, strains, defects and instrumental effects results in line broadening. By analyzing this broadening it is possible to extract information about the structure of a material. In the following different contributions to the broadening effect will be described.

1.4.1 Sample specific broadening

The maybe simplest case of crystal imperfection is the effect of crystallite size [18]. Crystallite size is a measure of the size of a coherently diffracting domain. If one have polycrystalline aggregates it is important to know that the crystallite size is not generally the same as particle size [26]. Equation 1.67 is the quantity that modulates the intensity, and we, on page 27, saw how we could derive an expression for the peak width (FWHM) by calculating the effect of a small displacement, $\vec{\xi}$ from the exact Laue condition. In equation 1.85 it was also demonstrated how this resulted in a delta function for large N_j .

For small crystals where N_1, N_2 and N_3 are small the expression in (1.79) broadens and the width can be expressed in terms of the crystallite size, and in this way a measurement of the peak width can give us valuable information on crystallite size in the range up to $\sim 1000\text{\AA}$ (see figure 1.16). After correcting our x-ray scan for background and instrumental contribution, the diffraction pattern can give us structural parameters like crystallite size and strain.

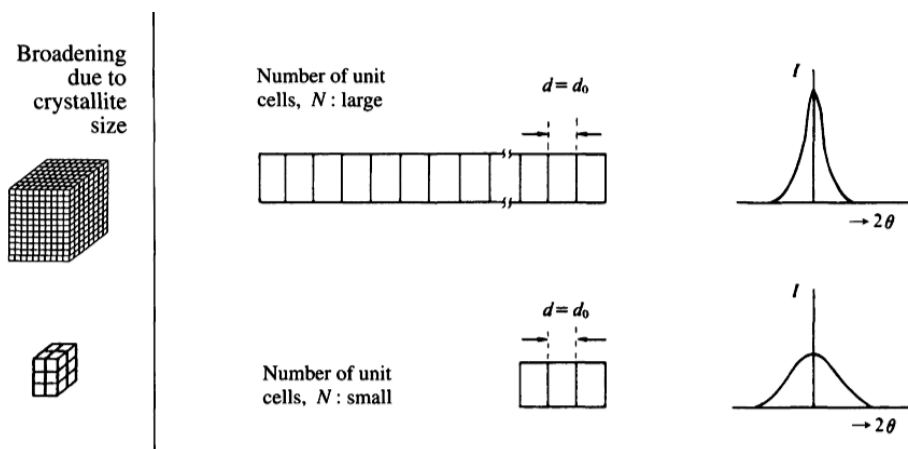


Figure 1.16: Broadening as a result of crystal size. Taken from [4].

Lattice strain distortion

Strain is defined as the ratio between the deformation of a unit cell by its ideal length, $\frac{\Delta d}{d}$. One differ between two main types of strain; *uniform* and *non-uniform*. The first kind causes the unit cells to expand (or contract) in an isotropic way. This leads to a change in the unit cell parameters, and hence causes a peak shift from the original size. There is no broadening associated with this type of strain. Non-uniform strain leads to a shift of atoms from their ideal positions and contributes to line broadening (for illustration review figure 1.17).

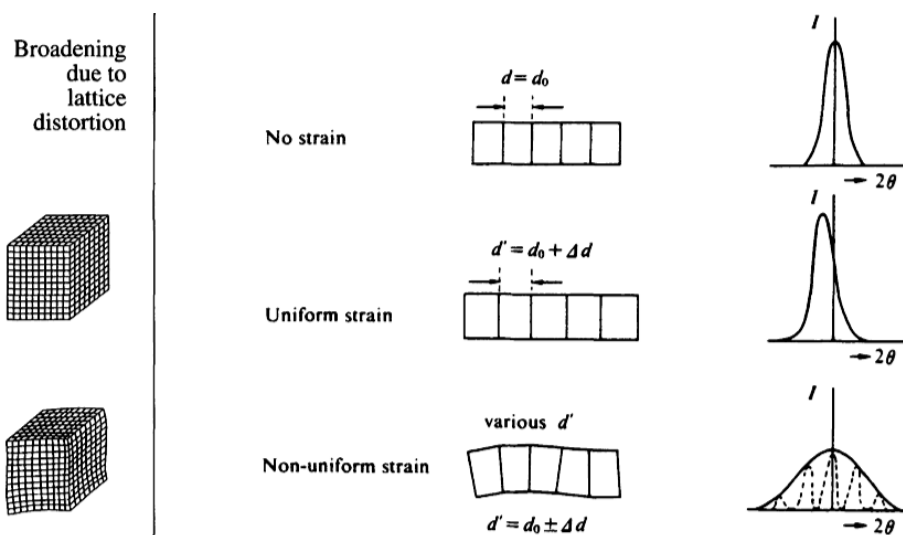


Figure 1.17: Peak broadening and displacement as a result of lattice strain. Taken from [4].

Thermal vibration The lattice itself may constitute an ideal crystal, but thermal vibration about the lattice points (phonons) that tends to blur out the the scattering centers with increasing temperature. See section 1.3.12 on page 29.

Frozen structure The lattice points may be somewhat displaced from their theoretical positions. The motivation for the term frozen is because one can think of this imperfection as as a thermally vibrating crystal frozen at a certain instant [4].

Defect lattice Some of the lattice atoms are missing, or some extra atoms may be placed irregularly throughout the lattice.

Impurities Impurities within the sample also contributes to line broadening, but the degree of impurity in a synthetic clay used in this experiment is very low. Still the quality of the cation exchange may have impact on the diffraction width.

1.4.2 Instrumental broadening

As mentioned in the introduction of this section, additional broadening is due to instrumental effects such as a not perfectly collimated and monochromatic beam. There are also other instrumental broadening due to i.e. slit widths, sample size, penetration depth in the sample and imperfect beam focusing [18].

Comment To get appreciable results from a line broadening analysis (crystallite size, strain, etc.) it is of course necessary that the broadening is dominated by the sample specific broadening and not the instrumental contribution. If this criteria is fulfilled one can calculate the size range over which this analysis is accurate, and also the upper limit for reasonable accuracy by looking at the crystallite size that would lead to broadening equal to the instrumental broadening [26].

1.5 Scattering from a layered clay

This section describes the factors that builds up the expression for the measured intensity from a layered clay. If this is familiar theory the reader may skip this section and move to the experimental part.

X-ray diffraction is the by far most powerful method for clay mineral identification [8]. We have learned that the intensity peaks get broader as the sample consist of small (thin) crystals, as is the case for clay minerals²¹ [11]. We have also seen that we get measured intensity adjacent to the hkl planes. This peak broadening peak give us valuable information in addition to more traditional measurements like the peak intensity and peak position.

²¹for large crystals with higher order the shape of the diffraction peaks carries little information

Characteristics of diffraction peak shapes that results from this extra scattering, and their correlation with the nature of the crystalline aggregates of unit cells, can be separated from the structure of the unit cell described in equation 1.97 [11]. The resulting diffraction pattern due to the additional scattering, is described by the interference function, Φ , which is angle dependent. This function will be examined more thoroughly in the following.

The Lorentz polarization factor, $L_p(\theta)$

As mentioned this factor is the combination of the instrument specific polarization factor, $P(\theta)$ given in eq. 1.59, and the sample specific Lorentz factor described in section 1.3.13. For structures that are neither single crystals or powder one have achieved good results from modifying $L_p(\theta)$ with a parameter, β , in the following way:

$$L_p(\theta) = \frac{P(\theta)m_{hkl}}{\sin 2\theta \sin^\beta \theta} \quad (1.104)$$

We see that letting $\beta = 1$ we get the Lorentz polarization factor for a powder, whereas using $\beta = 0$ resembles the expression for $L_p(\theta)$ for single crystal. For other structures the β -parameter is unknown, but lies between 0 and 1 and may be determined by fitting a model intensity to the experimental diffraction data as we shall see in a later section.

The layer structure factor, $G(\theta)$

The structure factor of a unit cell we have from eq. 1.97:

$$F^{unitcell} = \sum_{\vec{r}_j} f_j(\vec{Q}) e^{-W_j(\vec{Q})} \cdot e^{i\vec{Q} \cdot \vec{r}_j} \quad (1.105)$$

This expression is not continuous in θ , as it gives us values for single scattering angles. The layer structure factor, $G(\theta)$ is identical to eq. 1.105 in directions that coincide with the allowed lattice reflections[1]. $|G(\theta)|^2$ give us the square of the scattered amplitude from a single unit cell oriented such that its ab-plane (review figure 1.1) makes the angle θ with respect to the incident beam.

Our starting point in the transformation into a continuous function of θ is Braggs law (see eq. 1.66). We proceed with the calculations in one dimension. Since operating in one dimension, n is readily replaced with l , and we write the following relation directly from eq. 1.66:

$$l = \frac{2d(00l) \sin \theta}{\lambda} \quad (1.106)$$

When having a monoclinic or triclinic symmetry, d must not be confused with the unit cell dimension c . By using the Laue condition in eq. 1.78, $k = \frac{2\pi}{\lambda}$ and substituting with eq. 1.106 one may show that:

$$G(\theta) = \sum_j^J n_j f_j^{TC}(\theta) \cos(4\pi z_j \frac{\sin \theta}{\lambda}) \quad (1.107)$$

where n_j is the number of atoms of type j , f_j^{TC} is the thermally corrected value of the form factor (see eq. 1.105), z_j is the distance from the center of the

structure and λ is the wavelength of the incoming beam. We have that the temperature corrected form factor, f^{TC} :

$$f^{TC} = f_0 e^{-B_T \left(\frac{\sin \theta}{\lambda}\right)^2}, \quad (1.108)$$

with B_T being a measure of the magnitude of mean square displacement from the rest position. Now we may write eq. 1.107 as:

$$G(\theta) = \sum_j^J n_j f_0 e^{-B_T^j \left(\frac{\sin \theta}{\lambda}\right)^2} \cos(4\pi z_j \frac{\sin \theta}{\lambda}) \quad (1.109)$$

The Laue interference function, $\Phi(\theta)$

A layered clay is not a perfect crystal, and we get scattered intensity around and between the diffraction angles calculated from Braggs law. If this was not the case, the values of the structure factor $F(\vec{Q})$ would be an adequate description of the diffraction pattern. The continuous intensity function, $\phi(\theta)$, describes these phenomenons [11].

Our first step is to consider diffraction from a one-dimensional system consisting of N equally spaced unit cells. This is a relevant description to many clays which have regularly spaced layers of the same kind. The resulting scattered amplitude observed from N scattering units is:

$$E(\theta) = \sum_n^N E_j(\theta) = A \sum_n^N e^{i(n-1)\Delta\phi}, \quad (1.110)$$

where A is the scattered amplitude from each scattering unit, $\Delta\phi$ is the phase difference between waves scattered from successive unit cells. This is recognized as a geometrical series with N terms and can be written:

$$E(\theta) = A \frac{1 - e^{iN\Delta\phi}}{1 - e^{i\Delta\phi}} \quad (1.111)$$

The intensity is obtained as before by multiplying the amplitude, $E(\theta)$, with its complex conjugated:

$$I(\theta) = |E(\theta)|^2 = A \frac{1 - e^{iN\Delta\phi}}{1 - e^{i\Delta\phi}} \times A^* \frac{1 - e^{-iN\Delta\phi}}{1 - e^{-i\Delta\phi}} = I_0 \left[\frac{\sin^2(\pi d \frac{\sin \theta}{\lambda} N)}{\sin^2(2\pi d \frac{\sin \theta}{\lambda})} \right], \quad (1.112)$$

where we have substituted $4\pi d \frac{\sin \theta}{\lambda}$ with the phase difference, $\Delta\phi$, as a result of the optical path difference between successive beams being $2d \sin \theta$.

This modeling imply that the layered clay consist of crystallites with exactly N platelets, which is not the case nor what we expect. It is much more physically realistic if we let N vary in some interval, and the diffraction pattern from $\Phi(\theta)$ reflect the situation where we have different values for N . If we let $q(N)$ represent the proportion of crystallites of thickness N normalized so that:

$$\sum q(N) = 1, \quad (1.113)$$

we may modify eq. 1.112 to get:

$$\Phi(\theta) = \sum_{N=n_1}^{N=n_2} \frac{q(N)}{N} \frac{\sin^2(\pi d \frac{\sin \theta}{\lambda} N)}{\sin^2(2\pi d \frac{\sin \theta}{\lambda})}, \quad (1.114)$$

which is much more similar to an experimental measure of the diffraction pattern. The intensity calculated in eq. 1.112 is shown in figure 1.18 where one observe ripples. This is not a realistic pattern, and one can see the change by assuming different N in figure 1.19. Effects of multiplications of these terms, cancellation

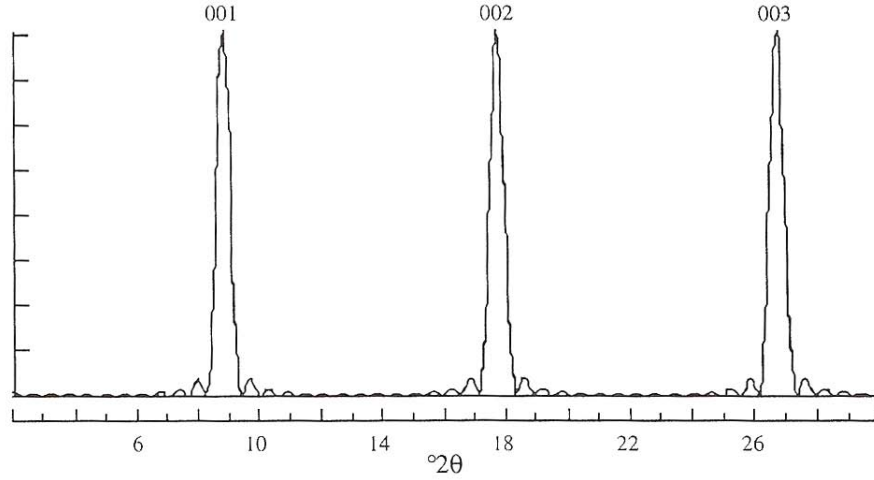


Figure 1.18: The interference function, $\Phi(\theta)$, plotted with $N = 15$ and $d(00l) = 10\text{\AA}$. Taken from [11].

1.5.1 Modeling intensity

In this section three factors which all modulate the intensity are treated. The intensity can now be modeled as:

$$I_{modeled} \propto L_p(\theta) |G(\theta)|^2 \Phi(\theta), \quad (1.115)$$

where $L_p(\theta)$, $|G(\theta)|^2$ and $\Phi(\theta)$ is the Lorentz polarization factor, the square of the layer structure factor and the interference function respectively.

Lets review some of the features and limit effects of this modeled intensity. We see that having $N = 1$ makes the interference function in eq. 1.112 equal to unity, and no intensity peaks is observed - this is natural since Bragg peaks only occur with more than one scattering center[11]. We also note that the width of the peaks narrows as N gets larger. The interference function has its maxima (with equal intensities) when $\sin \theta = \frac{n\pi}{2d}$, which is the Bragg angles. The FWHM of the peaks, β , formed by this function is found by the Scherrer-equation:

$$\beta = \frac{\lambda k}{L \cos \theta}, \quad (1.116)$$

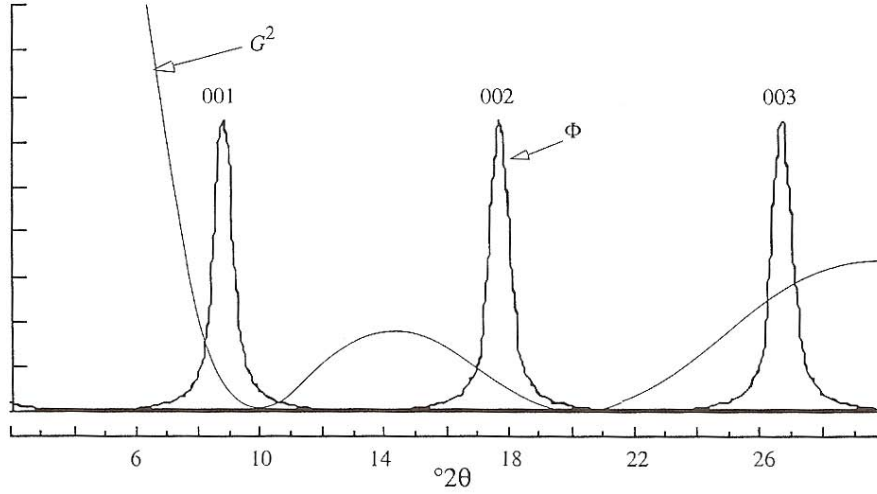


Figure 1.19: The interference function, $\Phi(\theta)$, plotted together with a layer structure factor, $G(\theta)$, with $N = 2 - 15$ and $d(00l) = 10\text{\AA}$. Taken from [11].

where λ is the wavelength, k is a near-unity constant and L is the mean crystallite size.

The full shape of the modeled diffraction pattern is given by eq. 1.115. In eq. 1.115, $\Phi(\theta)$ is the principal factor which determines the width of the diffraction peaks [11]. However, if the width of $\Phi(\theta)$ is large (N is small) the peak may be shifted from its Bragg position if the product of $L_p(\theta)$ and $|G(\theta)|^2$ have a significant slope over the peak (and especially at small angles). The layer structure factor, $|G(\theta)|^2$, varies considerably from one Bragg peak to another, but over the interval of any one peak it is generally taken to be constant[11].

Relative humidity

Relative humidity is defined as the ratio of the partial pressure of water vapor in a gaseous mixture of air and water to the saturated vapor pressure of water at a given temperature. Relative humidity is expressed as a percentage and is expressed as:

$$RH = \frac{\rho_{H_2O}^p}{p_{H_2O}^s} \quad (1.117)$$

1.6 Line profile analysis

1.6.1 Cauchy-Lorentz distribution

The Lorentz distribution is a continuous probability distribution with probability density function:

$$f_L(x; x_0, \omega) = \frac{1}{\pi\omega \left[1 + \left(\frac{x-x_0}{\omega}\right)^2\right]} = \frac{1}{\pi} \left[\frac{\omega}{(x-x_0)^2 + \omega^2} \right] \quad (1.118)$$

where where x_0 is the parameter specifying the location of the peak, and ω is the scale parameter which specifies the half-width at half-maximum (HWHM). The importance of this distribution in spectroscopy is the description of the line shape of spectral lines which are broadened by many mechanisms including resonance broadening.

1.6.2 Gauss-distribution

The probability density function of the normal distribution with mean μ and variance σ^2 is on the form [27]:

$$f_G(x; \mu, \sigma) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} = \frac{1}{\sigma} \varphi\left(\frac{x-\mu}{\sigma}\right) \quad (1.119)$$

where,

$$\varphi(x) = \frac{1}{\sqrt{2\pi}} e^{-\frac{x^2}{2}} \quad (1.120)$$

is the density function of the standard normal distribution - the normal distribution with $\mu = 0$ and $\sigma = 1$. For a demonstration of the line profile of this function review figure 1.20.

1.6.3 Pseudo-Voigtian approximation

Sample-related X-ray diffraction profiles, in particular for size-strain analysis, is well described by a Voigt-distribution. The Voigt distribution does not have an analytical form, so one use a practical approximation to the distribution called *pseudo*-Voigtian approximation, which is a linear combination of a Lorentz and a Gaussian function [28]. The peak-width bear information about crystallite size, mean-square strain and other micro-structural properties, but as mentioned instrumental effects also lead to broadening.

The Voigt-function is a convolution of of a Gaussian and a Lorentzian line shape:

$$V(x; \mu, \sigma, x_0, \omega) = f_L(x; x_0, \omega) \otimes f_G(x; \mu, \sigma) = L \otimes G \quad (1.121)$$

This is a normalized distribution as it is a convolution of two normalized functions. The analytical form of the *pseudo*-Voigt is written as:

$$f_{pV}(x; x_c, \eta, \omega_G, \omega) = \eta L(x) + (1 - \eta)G(x), \quad (1.122)$$

where we have introduced the shape parameter, η . We readily see that setting $\eta = 1$ give us the pure Lorentzian line, while setting $\eta = 0$ give us the pure Gaussian line profile. The η -parameter and the width, ω , are both dependent on the width of the Lorentzian profile, ω_L , and the Gaussian profile width, ω_G , and is given by [7]:

$$\omega = (\omega_G^5 + 2.6927\omega_G^4\omega_L + 2.4284\omega_G^3\omega_L^2 + 4.471\omega_G^2\omega_L^3 + 0.0784\omega_G\omega_L^4 + \omega_L^5)^{\frac{1}{5}} \quad (1.123)$$

and

$$\eta = 1.36603\frac{\omega_L}{\omega} - 0.47719\frac{\omega_L^2}{\omega^2} + 0.1116\frac{\omega_L^3}{\omega^3} \quad (1.124)$$

In figure 1.20 is a comparison of the Gaussian, Lorentzian and pseudo-Voigtian distribution. One see that the Lorentzian spreads out from the center position much more than the Gaussian. One also notice the symmetry of these functions. There exist two versions of the pseudo-Voigt function. In Type I the width, ω ,

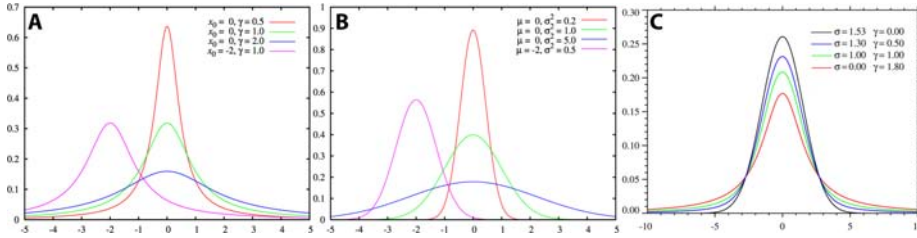


Figure 1.20: Demonstration of all profiles. A) Lorentzian, B) Gaussian and C) pseudo-Voigtian. Taken from [29]

is the same for both profiles, and in Type II the width may be different. Type I is given as:

$$f_{PV1} = y_0 + A \left[\eta \frac{2}{\pi} \frac{\omega}{4(x - x_c)^2 + \omega^2} + (1 - \eta) \frac{\sqrt{4 \ln 2}}{\sqrt{\pi} \omega} e^{-\frac{4 \ln 2}{\omega^2} (x - x_c)^2} \right], \quad (1.125)$$

where y_0 is a constant, A is the area, η the shape parameter, x_c the symmetry center and ω the FWHM. Type II is only slightly modified from eq. 1.125:

$$f_{PV1} = y_0 + A \left[\eta \frac{2}{\pi} \frac{\omega_L}{4(x - x_c)^2 + \omega_L^2} + (1 - \eta) \frac{\sqrt{4 \ln 2}}{\sqrt{\pi} \omega_G} e^{-\frac{4 \ln 2}{\omega_G^2} (x - x_c)^2} \right], \quad (1.126)$$

where ω_L is the Lorentzian width and ω_G being the Gauss width.

Chapter 2

Experimental setup

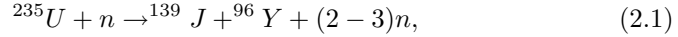
2.1 SANS-experiments

2.1.1 Experimental setup

The experiments were performed at the SANS beam line at Jeep-II, a research neutron reactor at Institute for Energy Technology at Kjeller, Norway.

The Jeep-II reactor

The neutron source is a $2MW$ D_2O -moderated reactor working on enriched fuel, 3.5% ^{235}U . The exothermic fission reaction is:



where $(2 - 3)$ indicates that between two and three neutrons are released in the reaction. The reactor has a total of nine beam channels; two radial out from the core and one tangential. See Fig. 2.1.

The SANS instrument is supplied with neutrons from the tangential channel because of the reduced amount of fast neutrons and gamma radiation when the reactor core is not in direct sight. Furthermore the channel is equipped with a cold moderator source based on liquid H_2 at $20.4K$. This element is chosen due to the hydrogen atoms high scattering cross section combined with its low weight providing a huge momentum transfer.

Ideally, the cold source moderates all the impinging neutrons to low energy before they escape in a favorable direction. If they reach thermal equilibrium their velocities are distributed according to the familiar Maxwellian distribution:

$$f(v)dv = \left(\frac{m_n}{2\pi k_B T} \right)^{\frac{3}{2}} e^{\frac{-m_n v^2}{2k_B T}} 4\pi v^2 dv \quad (2.2)$$

where k_B is the Boltzmann constant, T is the temperature of the moderator. However, neutron absorption in H_2 constraints the size of the cold source. The cold source is formed as a rotational ellipsoid with a $105mm$ major axis pointing towards the core and a slightly less minor axis parallel to the tangential channel. This is to ensure the best possible moderation in the radial direction combined with a shorter escape distance for neutrons traveling along the neutron channel.

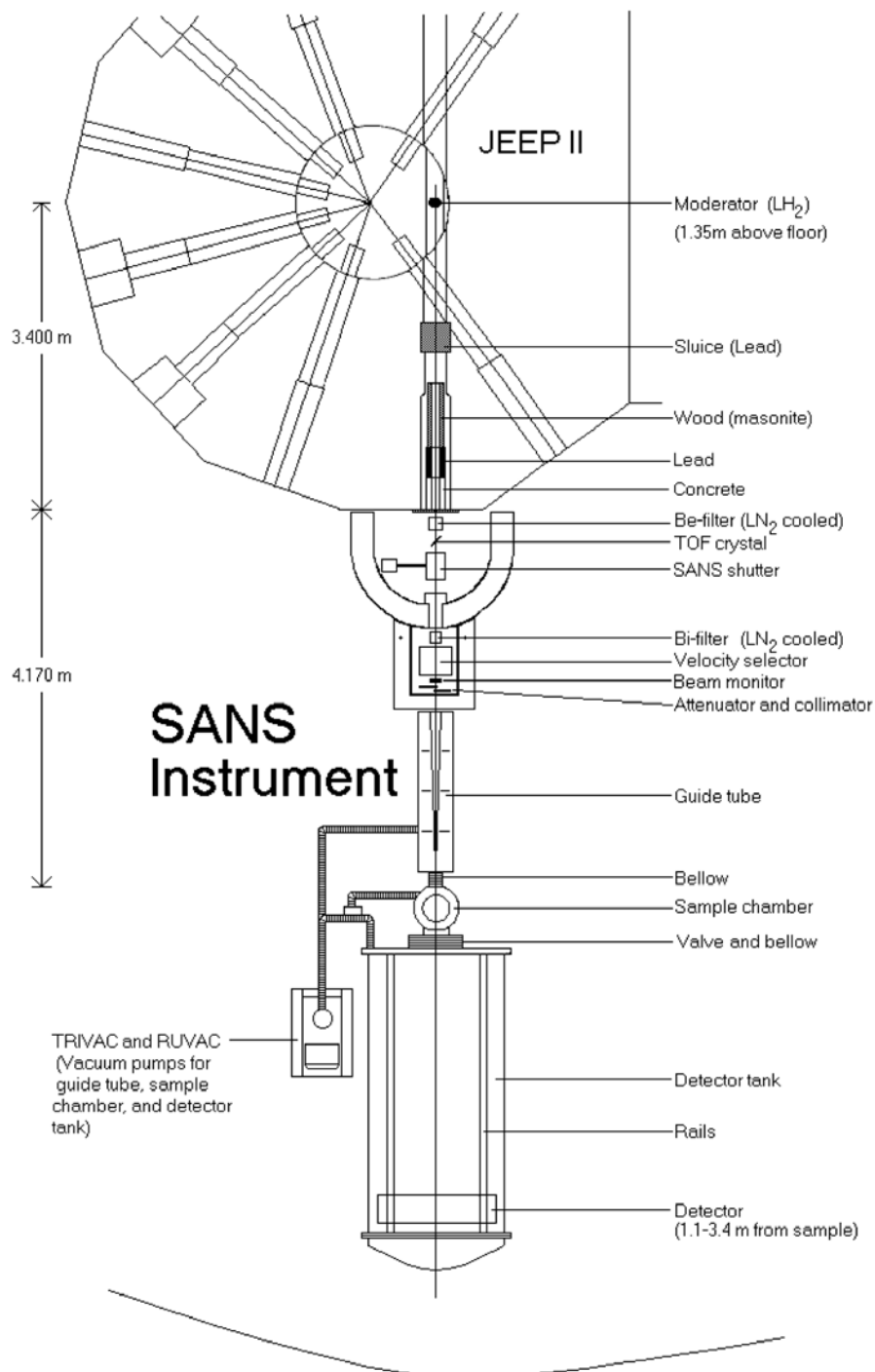


Figure 2.1: Schematical overview of the SANS instrument.

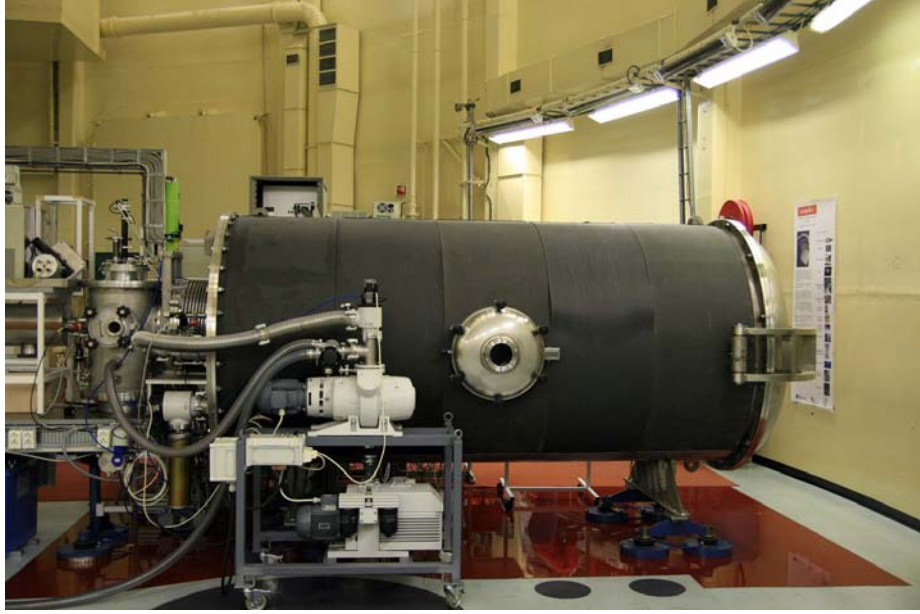


Figure 2.2: A picture of the evacuated detector tank of the SANS-instrument at *JEEP-II*

Shutters and filters In Fig. 2.2 one see the 30cm thick lead shutter positioned approximately 1.5m meters from the moderator. A liquid nitrogen cooled *Be*-filter is used to stop fast neutrons with $\lambda < 4.1\text{\AA}$. Because of the linear setup of the SANS-instrument and the sensitivity to gamma radiation in the ^3He -detector, a cooled 15cm ^{83}Bi -filter is situated in front of the velocity selector. There is a thin graphite filter in the beam channel to pick out appropriate neutrons for the time-of-flight instrument, but is not expected to substantially reduce the flux of neutrons for the SANS-instrument.

Velocity selector The velocity selector is a high speed mechanical selector made by *Dornier* and is based upon helically twisted lamellae made of carbon fibre epoxy. It runs under vacuum conditions. The transmission and the wavelength resolution depend on the beam divergence, the beam height and the tilt angle. There is a resolution of $\frac{\Delta\lambda}{\lambda} \sim 20\%$ and the transmission is a triangular function of the wavelength λ .

Collimator The collimator is an evacuated tube with circular pin holes at the entrance and exit. It is shielded to protect the outside from gamma radiation and to avoid stray neutrons. The beam divergence was set by an input collimator (18.4 or 12.2 mm in diameter) located 2.2m from the sample, together with a sample collimator which was fixed to 4.9mm.

Sample chamber and holder The sample chamber supports vacuum and has its own heating/cooling (water) system. The sample holder is a remotely

controlled rotating wheel with seven slots for sample cells. There are kits available for mounting kuvettes capillaries and other sample types.

Detector and beam stop The detector is located inside an evacuated tank (see Fig. 2.2). It is a two dimensional (59cm active diameter) ^3He -filled *RISØ-type* detector and general features for this detector is good linearity, good gamma discrimination and position determination. Gas detectors have a high efficiency, η , for thermal neutrons:

$$\eta \propto 1 - e^{-\rho\sigma_a d}, \quad (2.3)$$

where ρ is the number density of ^3He atoms and d is the detector thickness. Although a near unity efficiency can be reached, η is typically chosen to be about 80% in order to reduce the sensitivity to fast neutrons. The detector consists of a large circular disk with parallel thin metal strings. In front of the detector there is a layer of ^3He . When scattered neutrons hits a ^3He -molecule an electron is emitted and detected by the metal strings. The position of the scattered neutron (XY -coordinate) is found by calculating the time-difference between the instances where the signal reaches one end and the other.

The detector can be moved back and forth on the beam axis inside a 3.5m long evacuated metal container. The detector is placed close to the sample chamber if one wants to measure scattering at relatively large angles and vice versa.

In front of the detector a remotely controlled beam stop is installed to avoid saturation of the detector by un-scattered neutrons. The beam stop is made of B_4C and has a diameter of 40mm. The beam stop must be sufficiently big to cover any interference region between the scattered and the un-scattered beam, but not too big as this will reduce the available q -range.

2.1.2 Design of a sample holder

A collaboration project was initiated with Lars Ramstad Alme (NTNU, Trondheim). With XRD Alme has investigated water diffusion through a powder sample of a nano porous layered synthetic smectite clay, Na-Fluorohectorite.

To achieve supplementary data to the observed x-ray diffraction an attempt using small-angle neutron scattering on the same sample was planned. The objective was to use the same sample holder and sample positioning system used at the *SAXS NanoSTAR* at NTNU in Trondheim, but unfortunately limited space in the SANS sample chamber of JEEP-II reactor made this impossible without doing serious adjustments to the sample chamber.

Instead a process of designing an alternative sample holder was started. The demands for the design was:

- The holder must fit the geometry in the sample chamber
- The holder must be able to hold a 5cm capillary (seen by the beam) in a horizontal orientation as previously

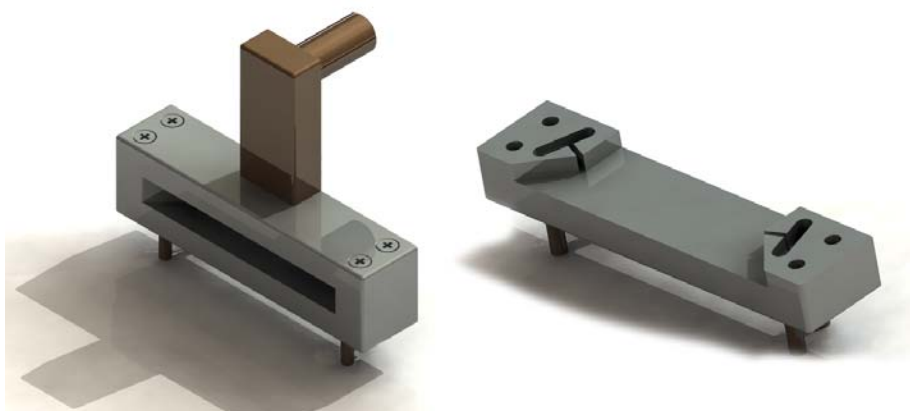


Figure 2.3: A 3D-demonstration of the sample holder and a cross section of the humidity chambers.

- There must be allowed for horizontal translation of the sample/holder
- The holder must be compatible with a typical humidity control setup so that a humidity gradient can be induced over the capillary.

In the chamber the sample changer is a circular rotating disk with multiple sample slots. The sample changer is remote controlled with the same computer controlling the SANS-instrument. The user initiates scans by making Unix shell scripts where one set the basic properties: wavelength, sample detector distance, collimator, monitorcounts and sample slot.

There are also commands that allows the sample changer to rotate at much smaller increments than whole sample slots. This fact allowed for an alternative design where a sample holder was made compatible with the SANS sample changer. A result of this design was that to preserve the same scattering volume one needed a curved capillary with the same curvature as the sample changer wheel. This turned out to be possible by using moderate heat and gentle force and the design process started.

To make the drawings *SolidWorks 2007* was used. This is an industry standard 3D-design program for technical drawing. As there was limited space inside the chamber precise measurement were done to assure the design will fit.

In Fig. 2.3 and Fig. 2.4 the results are shown and in the appendix technical drawings for the different parts are included.

Comments An initial experiment was done, but the transmission varied too much across the capillary and it was concluded that a 1mm capillary is too thin (gives a too small scattering volume) to provide appreciable scattered intensity. A two millimeter capillary could give better results, but the sample holder was made for the smaller capillary and we had no time to modify the sample holder.

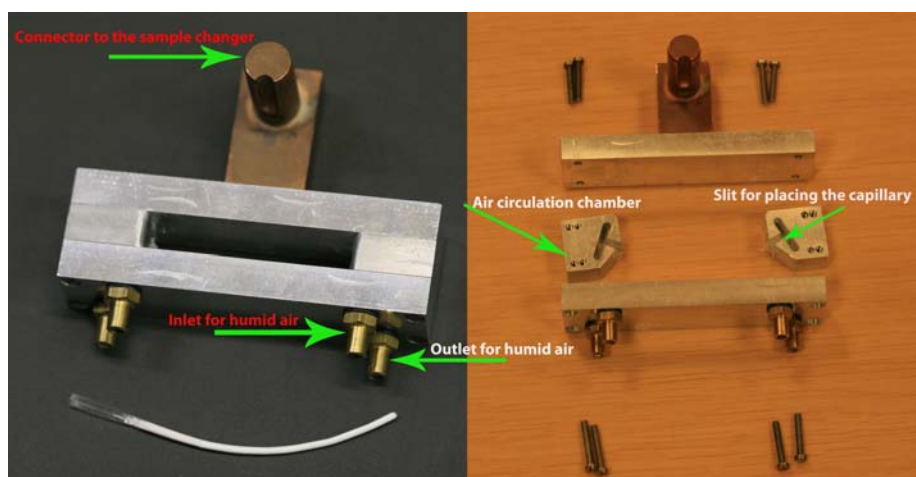


Figure 2.4: The finished model

2.2 SAXS-experiments

2.2.1 Experimental setup

The X-ray diffraction experiments were performed on a *Bruker AXS NanoSTAR* at Norwegian University of Science and Technology (NTNU). This apparatus is a small-angle X-ray scattering (SAXS) system which uses a 2D-detector and has the possibility of several different sample to detector distances. It can be used for the examination of structures which have dimensions in the range between a few nanometers to several hundreds of nanometers. Combining these ranges in experiments can reveal information on crystallite size and distribution, shape, surface and orientation in liquid, powder and bulk samples.

The Bruker AXS NanoSTAR, with its intense, collimated primary beam and 2D-detector, has a similar design to a synchrotron SAXS beamline. With a 2D-detector the misinterpretation of data due to a 0D or 1D data collection method is avoided, eliminating the need for restrictive initial assumptions about the sample. In fact, the NanoSTAR analyzes pure sample properties, even if the sample particles are asymmetric or show preferred orientation. Additionally, a real space image with μm SAXS resolution of the sample can be taken by performing Nanography.

The NanoSTAR features a brilliant x-ray source, combined with innovative multi-layer optics, which provides an intense, point-like incident beam upon the sample. Also included is the HiSTAR detector, a virtually noise-free, real-time 2D-detector with photon counting ability [30].

2.2.2 The main components of the SAXS-instrument

The rotating anode

The generating source is a water cooled rotating copper anode. A high voltage power source is connected across the cathodic filament and the rotating anode, and electrons are subsequently emitted from the cathode and collected by the anode. These electrons focused on the anode collide with and accelerate other electrons, ions and nuclei within the anode material, and part of the generated energy is emitted/radiated perpendicular to the path of the electron current as X-ray photons.

A crossed coupled multi layer monochromator, the *Göbel mirrors*, selects the characteristic K_α radiation from the continuous white Bremsstrahlung-spectrum and conditions the original two dimensional divergent beam to a two dimensional parallel beam.

The collimator system

The pinhole collimation system assures a small X-ray beam with a well defined cross section. The combination of three pinholes limits the divergence and shadows the edge scattering of the system. The outcome of the NanoSTAR is a well defined and conditioned parallel and monochromatic X-ray beam of diameter $400\mu\text{m}$ and wavelength, $\lambda = 1.541838\text{\AA}$.

The sample chamber

The sample chamber has a software operated goniometer drive allowing for precise positioning of the sample in an xy -plane perpendicular to the incoming beam. This automatic sample changer allows sample positioning over distances of 100mm in the y - and 80mm in the x -direction with an accuracy of better than $10\mu\text{m}$ each.

The detector

The HiStar detector is a two dimensional multi wire grid detector with pressurized xenon gas which enables the determination of the x - and y -positions of X-rays in its imaging area. Noble gas atoms are ionized by incident X-rays. These charged particles are attracted to and interact with an electrode assembly to produce electrical signals indicative of the x - and y -positions of the original X-ray.

In Fig. 2.5 the four main components of the NanoSTAR is highlighted. Below these four parts and their functionality is described.

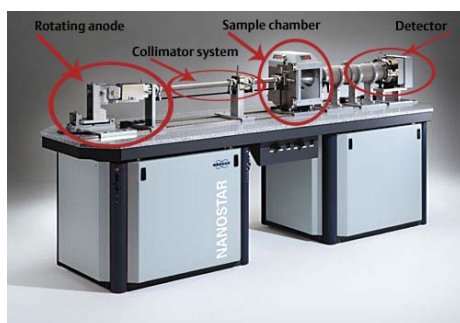


Figure 2.5: A picture of the *Bruker AXS NanoSTAR*

The temperature controller

The temperature controller system consists of a *LakeShore Model 321*. The setup for temperature control applies a *Peltier cooling device* for effective cooling of the sample holder. Water circulating in channels below the Peltier element removes excess heat from the *Peltier element*.

The humidity controller

A humidity gradient was imposed across the sample by exposing the two open ends of the capillary tube to closed chambers with different humidities. This was obtained by circulating air with controlled humidity through channels drilled through these chambers. One end was kept at high humidity by circulating air through a saturated K_2SO_4 solution, whereas the opposite end was kept dry by circulating air through a silica gel desiccant column.

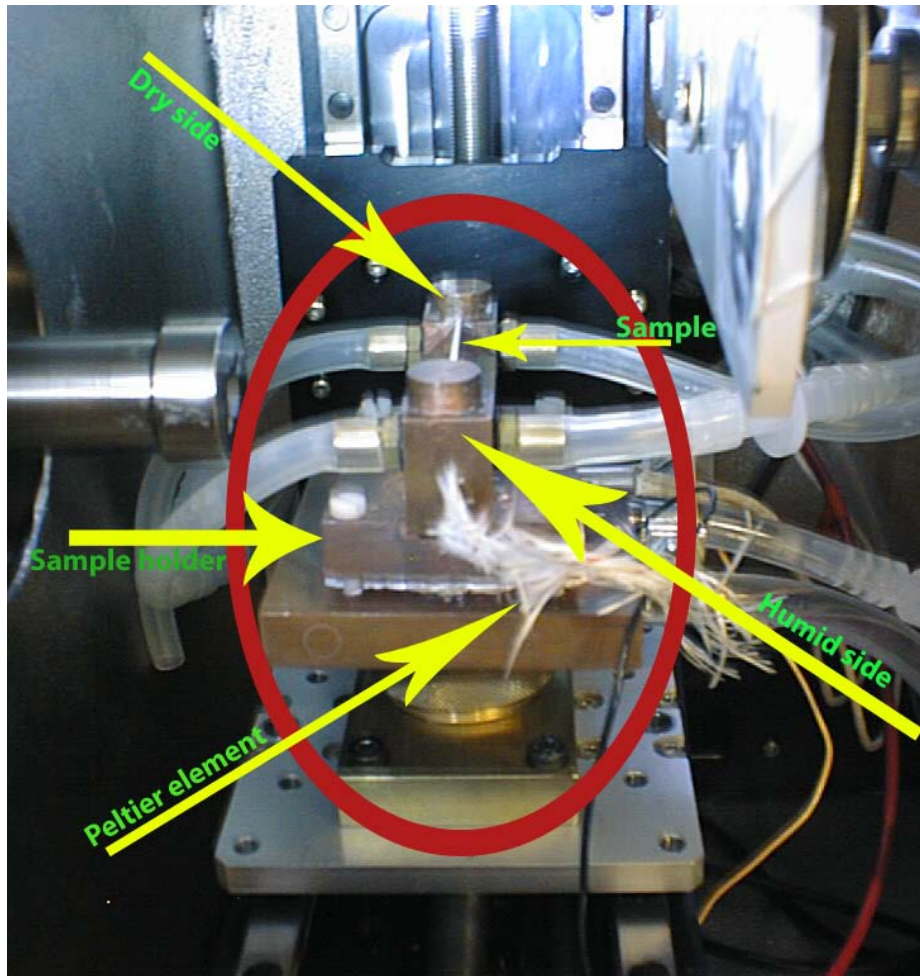


Figure 2.6: The mounted sample cell inside the sample chamber with humidity and temperature control connected.

The sample holder

A humidity- and temperature controlled sample holder was utilized in the experiment. A glass capillary containing the sample was mounted with thermal paste on the sharp top edge of a copper block for good thermal connection. In Fig. 2.6 the mounted sample cell is shown.

Chapter 3

Data processing, analysis and results

3.1 SANS data processing, analysis and results

In this section four separate experiments using SANS will be described and analyzed. Unless otherwise noted the temperature during the experiments was 22°C. First, a brief look on the data acquisition and processing will be given.

3.1.1 Data acquisition and processing

The SANS-instrument at the *JEEP-II*-reactor determines the position of an incident neutron by a position-sensitive detector. The instrument stores each scan as a two-dimensional matrix consisting of 128×128 pixels. To the left in Fig. 3.1 a recorded SANS-pattern is shown, while to the right the same pattern is sector integrated in the horizontal direction.

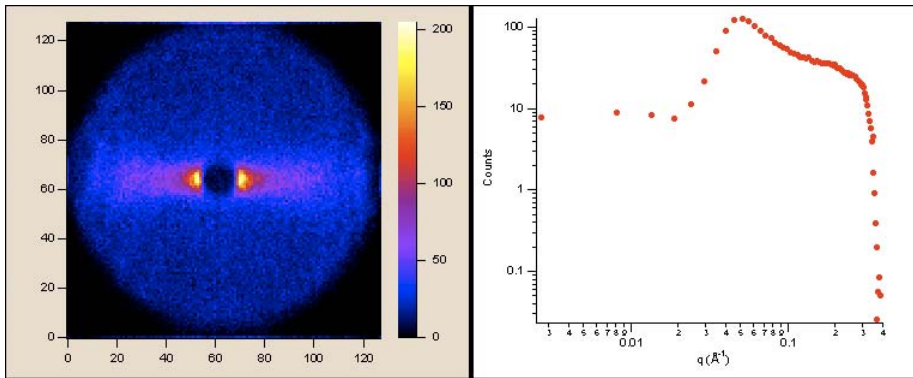


Figure 3.1: Left: A recorded two-dimensional SANS pattern. The accompanying color gradient is a measure of detector counts per pixel. Right: The same pattern sector integrated in the horizontal direction.

3.1.2 Data reduction

Not only sample specific scattering contributes to detector counts in the recorded data. There are several other factors that must be corrected for. These are in general:

- Scattering from the empty cell, collimator slits and air scattering.
- Stray neutrons (these neutrons do not pass through the sample. An example is high-energy neutron background present in the reactor hall) and electric noise, detector dark current and cosmic radiation.

As one is interested in the sample scattering, and in particular the coherent scattering that contains the structural information of the sample (incoherent scattering is flat background), we need additional measurements in order to subtract the background and normalize the data. The background subtraction and the normalization of the raw data are done pixel by pixel for each of the 128×128 detector pixels according to the following formula:

$$I_s^{reduced} = \left[\frac{I_s}{M_s} - \frac{I_{BG}}{M_{BG}} \right] - \frac{T_s}{T_{EC}} \left[\frac{I_{EC}}{M_{EC}} - \frac{I_{BG}}{M_{BG}} \right], \quad (3.1)$$

where M is the monitor counts (in order to make the intensities comparable) and T is the transmission. I is the number of detector counts for the sample, S , background, BG and empty sample holder (cell), EC . In the second parenthesis the contribution from an empty cell is subtracted, whereas in the first parenthesis other background is subtracted. The data reduction program, *IGOR Pro 6* used here, also adjusts for the absolute intensity of the beam and the sample thickness.

The wanted q -interval is obtained by stitching together three separate scans, low- q , mid- q and high- q . What defines these regions is a combination of sample-detector distance and wavelength.

3.1.3 Absorption of D_2O in $NaFH$ -powder

For the characterization of surface irregularity in porous materials, the concept of fractal geometry is a useful tool. The SANS method probes spatial differences in scattering length in the bulk of a material. Thus internal boundaries between empty pores (with scattering length density equal to zero) and a substance with a neutron scattering length different from zero will show up as a scattered intensity with a certain q -dependence.[2]

As mentioned in the theory section the Porod region of small-angle scattering, i.e. in the region of small length scales (high q), the scattering reflects the structure of the surface between the pores and the matrix (surrounding material).

The objective of the experiment described in this section was to track changes in the SANS over time as heavy water penetrates $NaFH$ -powder. Heavy water, D_2O , is preferred instead of H_2O due to the much smaller incoherent cross section, σ_{inc} ¹.

Sample

Pure sodium fluorohectorite ($NaFH$) powder filled inside a 2mm quartz cuvette.

The aged powder was made from synthetic fluorohectorite (*Corning Inc., New York*). A brief description of this process (though not performed) is given here: $NaFH$ is processed from raw material by dissolving clay powder in deionized water with subsequent stirring for several days. In order to make pure sodium fluorohectorite samples, an ion exchange method is then utilized. Na^+ in the form of $NaCl$ is added to the clay suspension in an amount of approximately 10 times the interlayer charge[2].

Due to the added salt, flocculation will occur, and after stirring for some weeks the supernatant can be removed. The flocculated clay is then placed in dialysis membranes and excess ions is removed by dialysis. The sediment is then heated to release its water content.

Scan series

Seven runs were performed in sequence on the aged sample. The first run was done on a dry sample, then D_2O was added on top of the powder and six consecutive runs were recorded.

Macro A macro were made to run seven times. The three distance/wave-length combinations were $\{d_1, \lambda_1\} = 1000mm, 5.1\text{\AA}$ (high- q), $\{d_2, \lambda_2\} = 3400mm, 5.1\text{\AA}$ (medium- q) and $\{d_3, \lambda_3\} = 3400mm, 10.2\text{\AA}$ (low- q), which should cover the most essential q -range from about $0.008 - 0.3\text{\AA}^{-1}$, with a corresponding range in particle size that can be studied of $d \sim 21\text{\AA} - 785\text{\AA}$ applying the relation $d = \frac{2\pi}{q}$.

¹makes less background noise

Results

In Fig. 3.2 a typical SANS-pattern (after data reduction) for *NaFH* is shown. One notices that *counts per pixel* fall one order of magnitude from the low/mid-range (20-80) to the high- q range (0.5-2) - this is normal behavior due to the power-law behavior of the intensity. Further one sees the isotropic scattering which is expected for a powder sample with no preferred orientation for the crystallites.

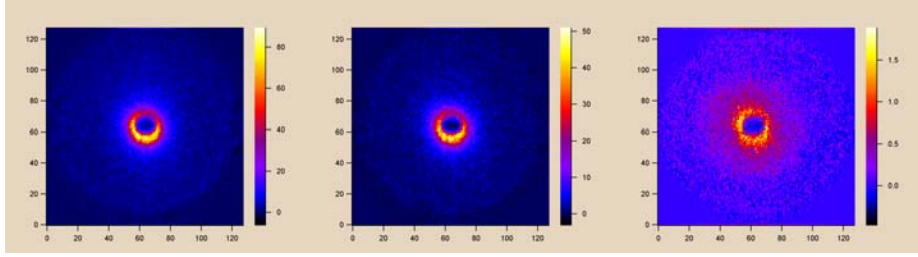


Figure 3.2: The three q -ranges side by side; left: low- q , middle: medium- q , right: high- q . One notices the isotropic scattering and intensity fall from low/mid to high q -range. This scan is from the last run on the fifth day of the experiment.

Given isotropic scattering we integrate the reduced 2-dimensional SANS-data over the full ϕ -angle. This transforms the 2D scattering pattern into a 1-dimensional scattering pattern. On Fig. 3.3 the logarithm of the intensity, $\log(I)$, is plotted against the momentum transfer, q for all the seven runs (after ϕ -integration and stitching the q -ranges together).

Due to the power law behavior of the scattering at low angles:

$$I(q) \propto q^{-\alpha} \quad (3.2)$$

plotting I vs. q in a *log-log*-plot we are able, by a linear fit, to estimate the α -parameter that provides us with information about particle surface. On the left side of Fig. 3.4 a *log-log-fit* for run 6 is presented as an example. The different slope parameters, α , for all the performed runs are plotted to the right in Fig. 3.4.

The results show that after adding water on top of the sample, the slope parameter goes gradually from representing smooth surfaces with $\alpha \approx 4$ ($D_s = 2$) to a mass fractal with $D_m \equiv \alpha \approx 2.5$.

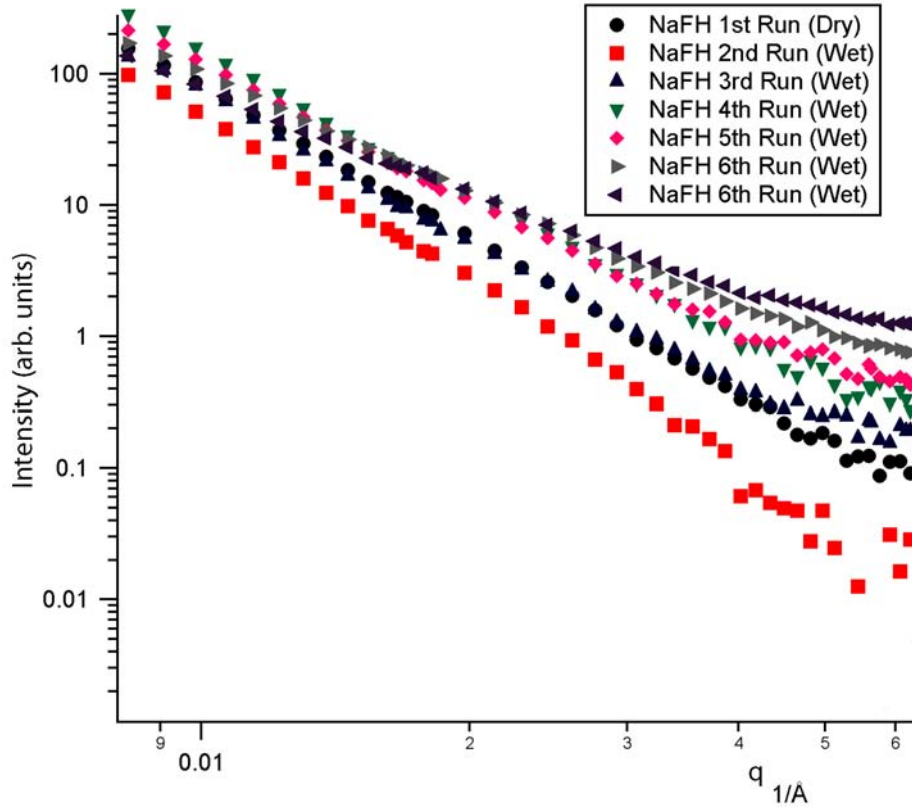


Figure 3.3: All seven runs plotted together after ϕ -integration and connecting the q -ranges.

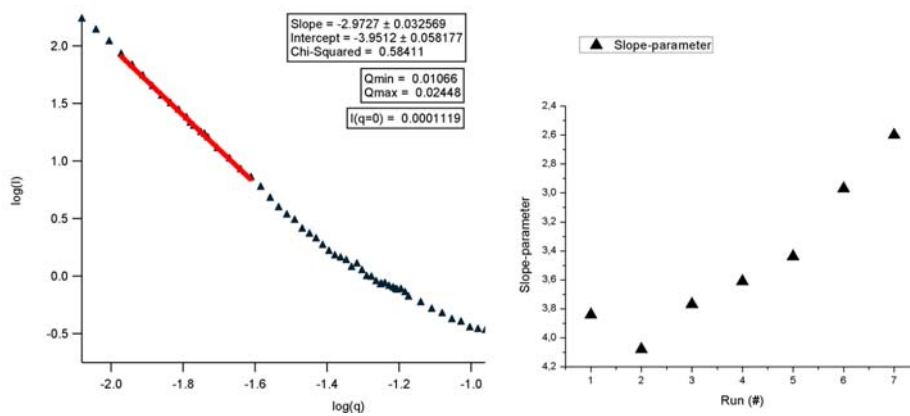


Figure 3.4: Left: a linear fit of I versus q in a $\log\text{-}\log$ -plot. Right: The slope parameter for all runs plotted together

3.1.4 Analysis of four phases in $NaFH$ -suspension

In this experiment the objective was to investigate an occurred phase separation in a $1.5wt\%$ $NaFH$ -suspension with a $NaCl$ -concentration of $10^{-3}mM$. Four phases could easily be detected visually (see A in Fig. 3.5). This behavior differs from that observed for a $3.0wt\%$ and a $4.5wt\%$ which were both very gel-like (see C in Fig. 3.5). The experiment was run over six days and measurements were done at $T = 22^{\circ}C$ and at $60^{\circ}C$.

Samples The samples analyzed were (see Fig. 3.5):

Phase 1, topmost A clear transparent phase

Phase 2 Slightly opaque phase

Phase 3 Gel phase

Phase 4 Thick sediment phase

Extract from $3wt\%$ -suspension Gel phase

$1ml$ sample from each phase was pulled out carefully with a syringe and put in four quartz cuvettes. See B in Fig. 3.5 for illustrations (the cuvette with the sediment is not shown).

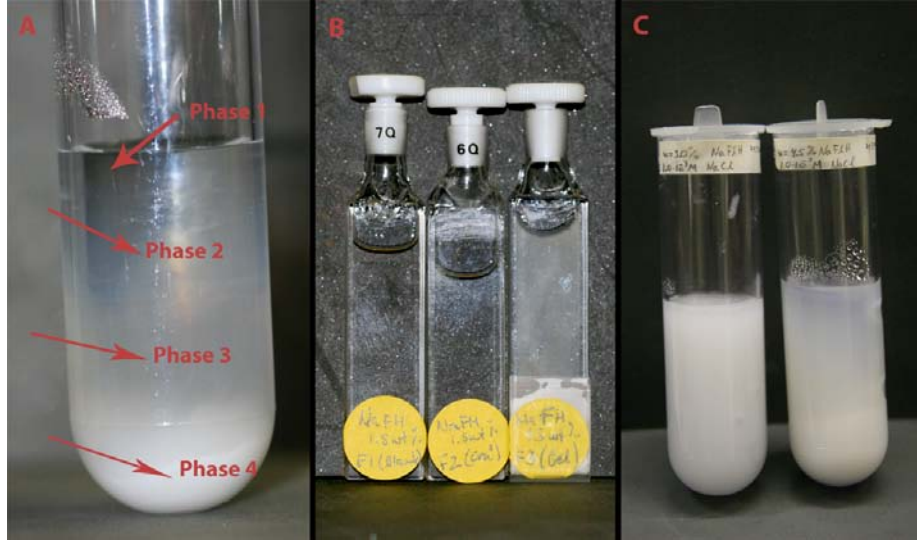


Figure 3.5: A: The $1.5wt\%$ suspension. B: Phase 1, 2 and 3 inside cuvettes. C: The gel-like $3.0wt\%$ and $4.5wt\%$ samples

Scan series Three runs were performed on each phase:

- Right after putting the sample inside the cuvette.
- Two days after putting the sample inside the cuvette (to see if we could observe a more nematic structure).

- After two more days and using $T = 60^\circ\text{C}$ (to see if there is an effect of temperature, i.e. a less nematic structure).

Results

The low concentration in phase 1 and 2 caused very low scattering and hence is not analyzed.

Phase 3 SANS-patterns from the third phase (gel-like) at room temperature ($T = 22^\circ\text{C}$) (A) and 60°C (B) are shown in Fig. 3.6. We observe that phase

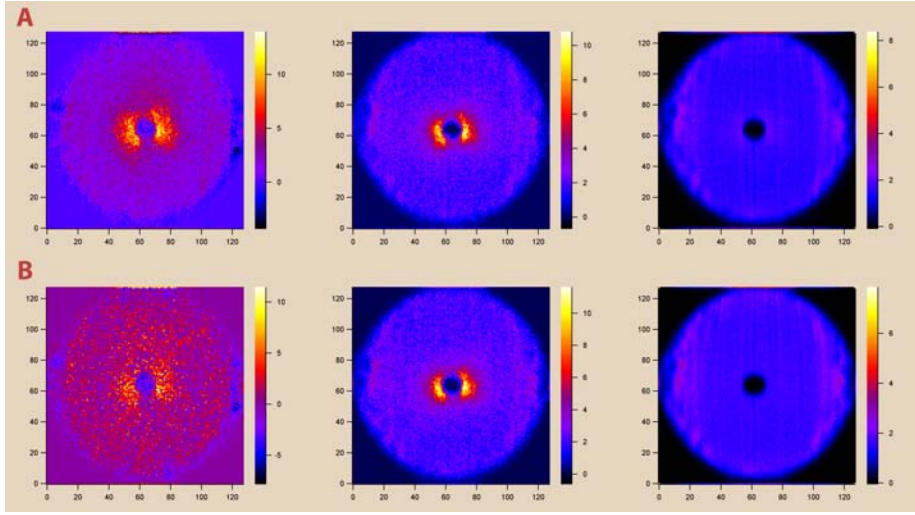


Figure 3.6: Two recorded SANS patterns. A: 3rd gel-like phase of a $1.5\text{wt}\%$ suspension at room temperature ($T = 22^\circ\text{C}$). B: The same sample at 60°C .

three clearly shows a preferred ordering. The clay platelets are oriented vertically (tilted $\approx +7^\circ$) since the scattering pattern is the Fourier transform of the structure (inverse space). Comparing scan series A (room temperature) and B (60°C) a visible change in the scattering is observed for low- q . This is most likely caused by an increase of brownian motion inside the sample which breaks up ordering on the largest probed length scale.

In Fig. 3.7 three runs performed on phase 3 are plotted together. Since this sample shows a clear anisotropic pattern a sector integration is done with a ϕ -angle offset of $+7^\circ$ and $\Delta\phi = 45^\circ$. The 1st run is right after sample is taken out with a syringe, 2nd run is recorded after two days of relaxation and the third run is recorded after four days and at a temperature of 60°C .

Again a linear fit is done in a $\log$ - $\log$ -plot and slope parameters are extracted. A demonstration of the linear fit for run 1 is given in Fig. 3.8 and the slope values calculated for the three runs are listed in table 3.1.

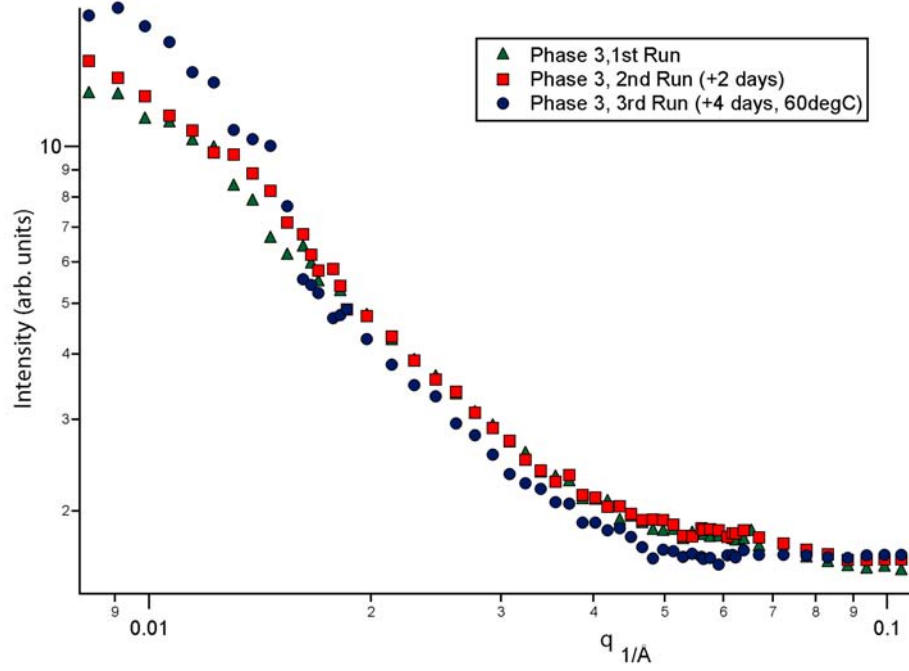


Figure 3.7: All three runs plotted together for phase three.

Run #	1	2 (after two days)	3 (after 4 days and 60°C)
α	1.27	1.45	1.36

Table 3.1: Slope parameters for three runs on phase three.

Phase four Phase four is the sediment sample. In figure Fig. 3.9 a SANS-pattern recorded on the sediment after two days of relaxation is shown. The results for the three runs, after the angle dependency is integrated out, are shown in Fig. 3.10. Performing the linear fitting procedure in a *log-log*-plot for the three runs on phase four gives the slope-parameters listed in table 3.2 In Fig. 3.11 a linear fit in a log-log-plot is demonstrated for phase four.

As is obvious from Fig. 3.10 a threshold is visible in the intensity around $q = 0.02$. This is usually related to a characteristic length of the system. A *Guinier-plot* over the region results in a radius of gyration, $R_g \approx 52\text{\AA}$. This characteristic length could be related to an average crystallite size or pore space, but no additional experiments have been performed to check this assertion. The eccentricity of the iso-intensity lines in the ordered samples shows $e = 0.84$ and this was invariant through the whole experiment.

Run #	1	2 (after two days)	3 (after 4 days and 60°C)
α	1.25	1.29	1.25

Table 3.2: Slope parameters for three runs on phase four.

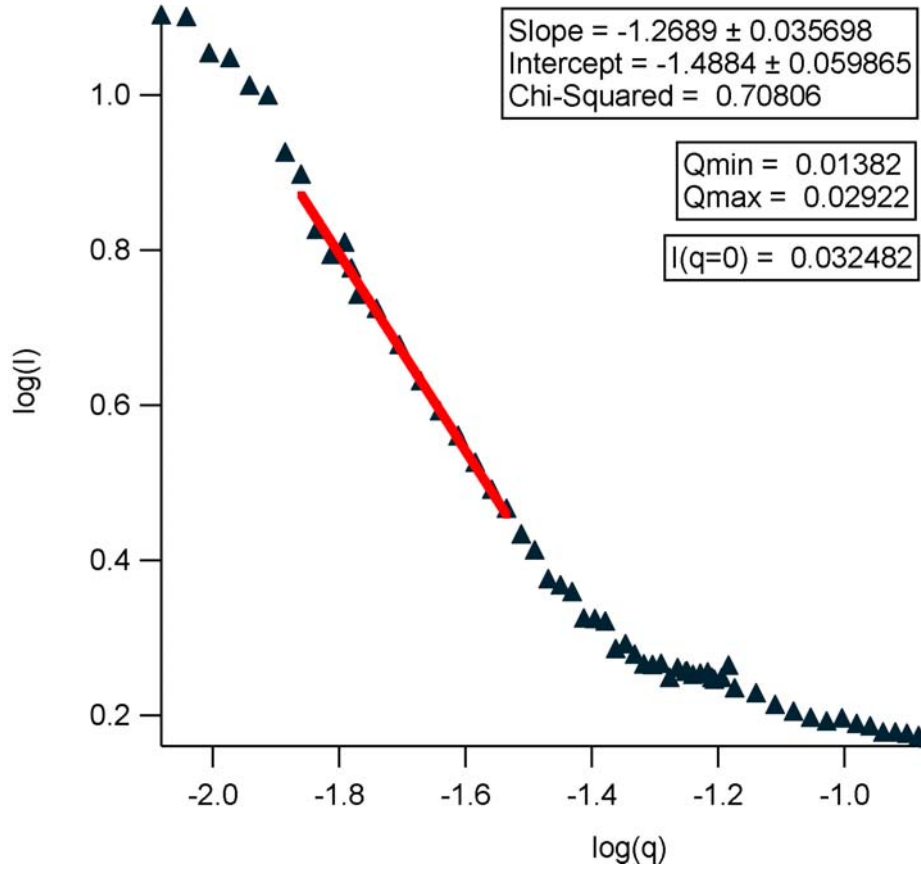


Figure 3.8: Linear fit in a log-log-plot for phase three

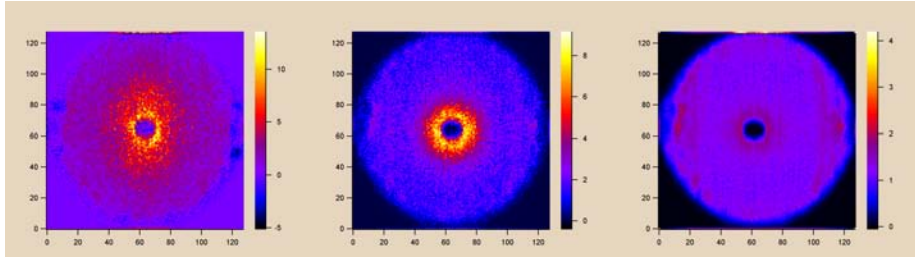


Figure 3.9: SANS pattern from phase four after two days of relaxation.

Extract from 3wt%-suspension In Fig. 3.12 we observe the anisotropy of the gel phase and that the absolute value of the tilt in ϕ -angle is indeed comparable to the angle for phase three in the 1.5wt%-suspension. Fig. 3.13 shows the result after sector integration with a ϕ -angle offset of -7° and $\Delta\phi = 45^\circ$ on all runs. α -parameters are given in table 3.3 and the fit for run 2 is shown in Fig. 3.14.

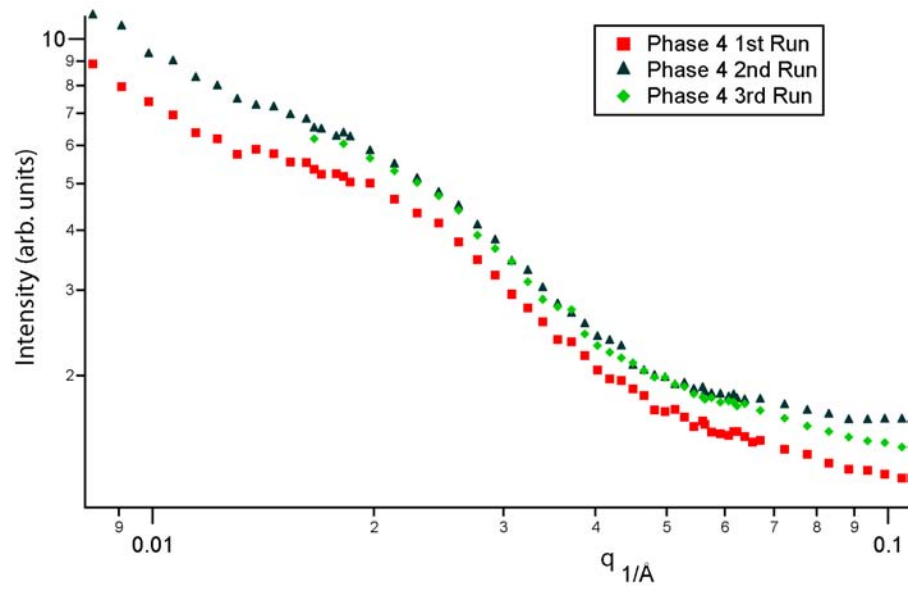


Figure 3.10: Three runs plotted together for phase four.

Run #	1	2 (after two days)	3 (after 4 days and 60°C
α	1.12	1.27	1.15

Table 3.3: Slope parameters for three runs on the gel phase from the 3.0wt%-sample.

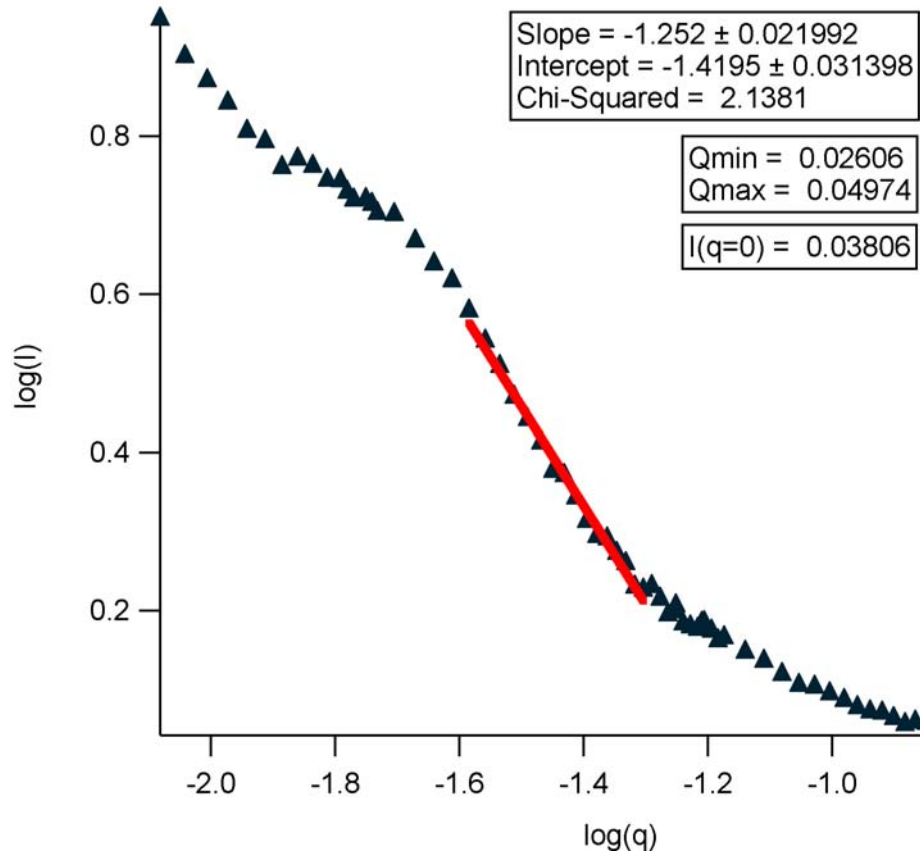


Figure 3.11: Linear fit in a log-log-plot for phase four

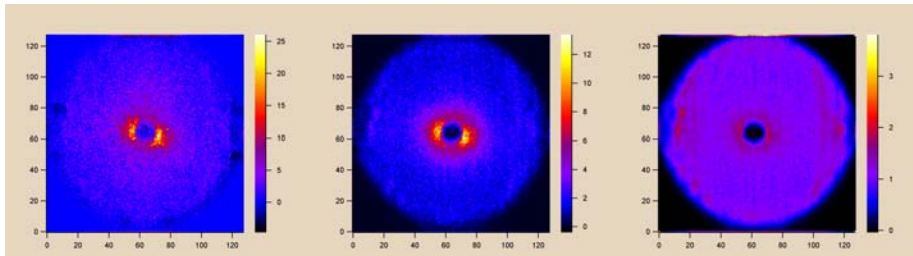


Figure 3.12: SANS-pattern for the 3.0wt% gel phase.

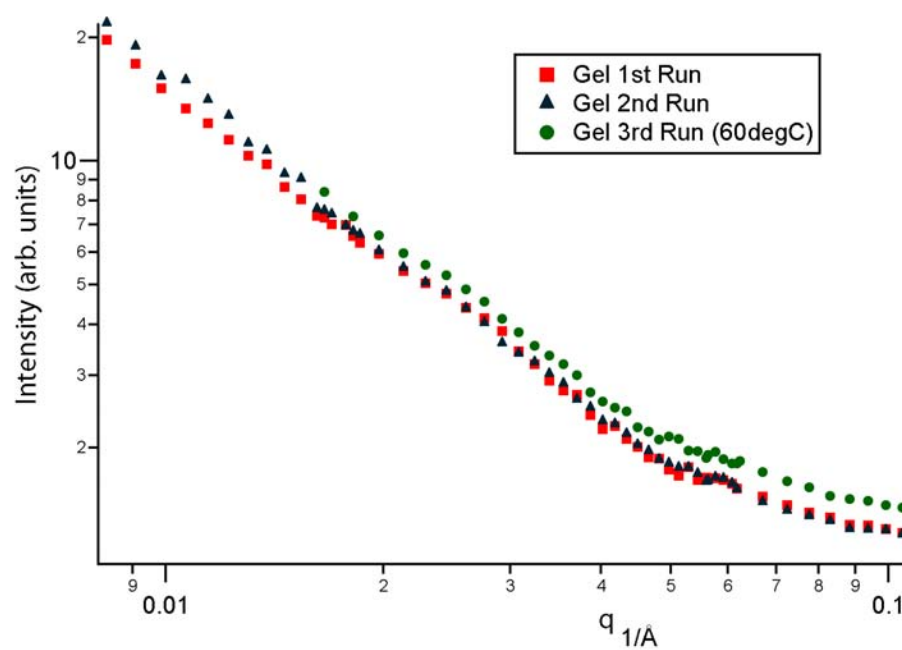


Figure 3.13: The three runs from the gel-sample (3.0wt%) plotted together

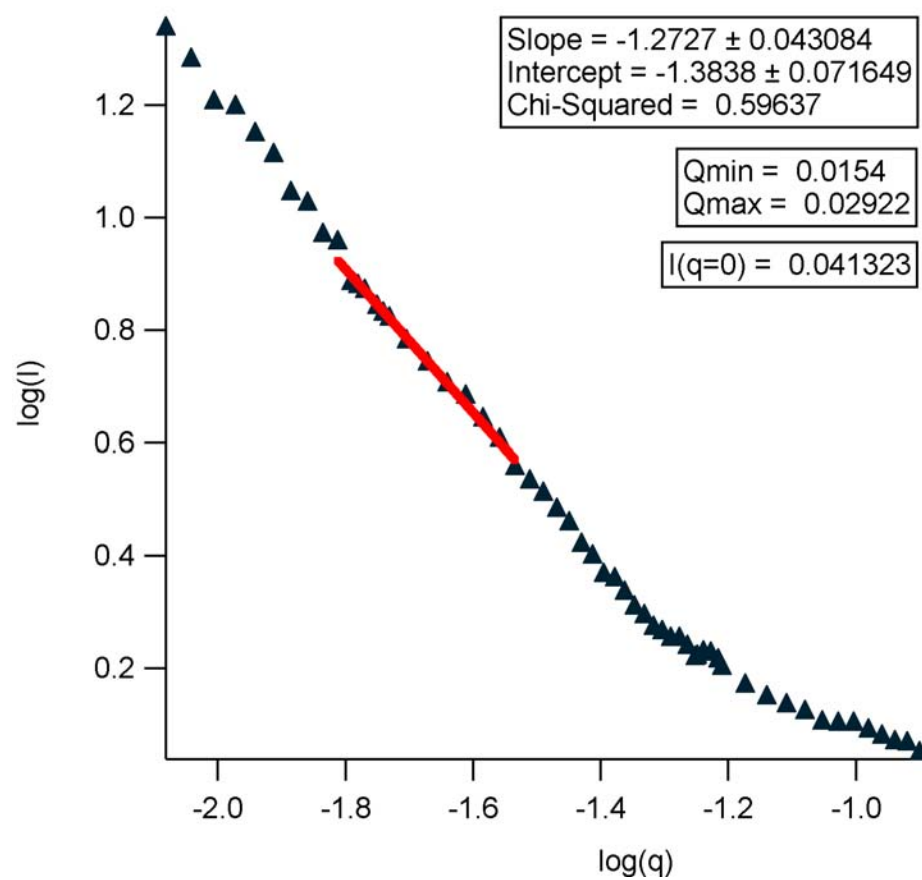


Figure 3.14: A linear fit in a log-log-plot for the 3.0wt% gel phase

3.1.5 Oriented *NiFH*-samples in D_2O

The objective of this experiment was to observe a possible change in signal with time, both for a sample oriented perpendicular to the beam and parallel.

Samples Pressed (under 10t pressure) dry layers of *NiFH*.

Sample with perpendicular orientation One piece with dimensions $(20 \times 8 \times 1)mm$ placed inside a $2mm$ cuvette and oriented in the normal direction. Covered with D_2O right before data recording.

Sample with parallel orientation $1mm$ thin slices side by side in parallel orientation inside a $2mm$ cuvette. One run was recorded on dry layers before D_2O was added.

Scan series Seven runs (full q -range) were recorded on *NiFH* in perpendicular orientation (with D_2O). One full q -range for dry *NiFH* in parallel orientation. 15 runs on high- q for *NiFH* in parallel orientation in D_2O .

Results In Fig. 3.15 one sees the pattern recorded when having thin layers of Nickel Fluorohectorite oriented perpendicular (A) and parallel (B) with the beam. We clearly observe the anisotropy for the sample oriented in parallel with the beam. Having the sample oriented perpendicular to the beam shows an isotropic pattern. Fitting the iso-intensity lines from the anisotropic scattering shows an eccentricity, $e = 0.88$. In Fig. 3.16 one sees the scattering in

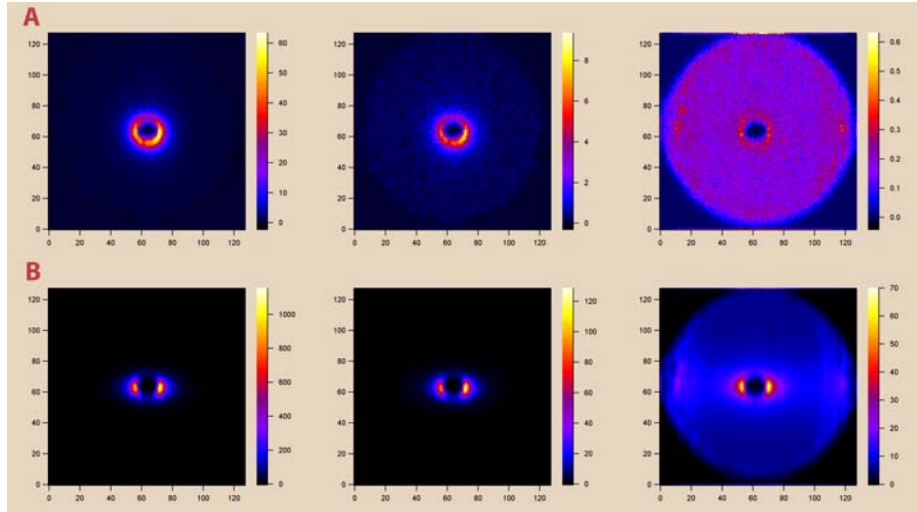


Figure 3.15: A: SANS-pattern for the *NiFH*-layers in perpendicular orientation. B: SANS-pattern for the *NiFH*-layers in parallel orientation.

one dimension after integrating out the angle dependency and connecting the different q -ranges for parallel orientation. Fig. 3.17 shows a fit for finding the α -parameter in parallel orientation which was found to be $\alpha = 3.86$.

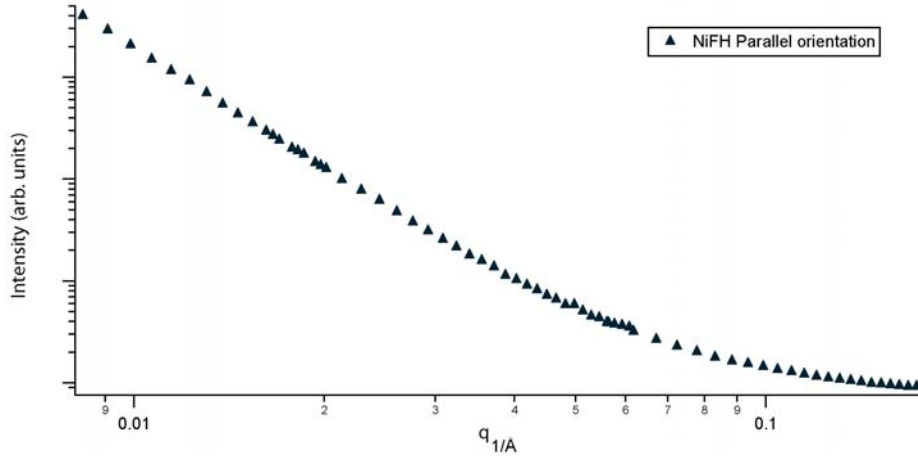


Figure 3.16: SANS-pattern with the angular dependence integrated out for dry *NiFH*-sample in parallel orientation.

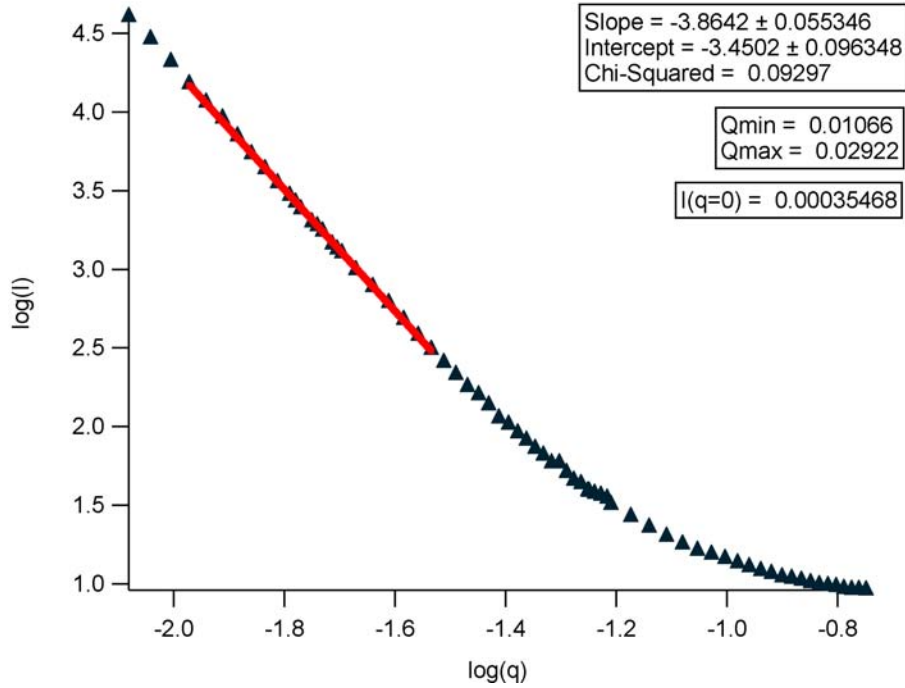


Figure 3.17: Linear fit in a log-log-plot to extract the α -parameter for the parallel orientation.

In Fig. 3.18 one sees the scattering in one dimension after integrating out the angle dependency and connecting the different q -ranges for perpendicular orientation. In Fig. 3.19 a fit for finding the α -parameter in perpendicular orientation is shown. Slope parameter for the run for parallel orientation was

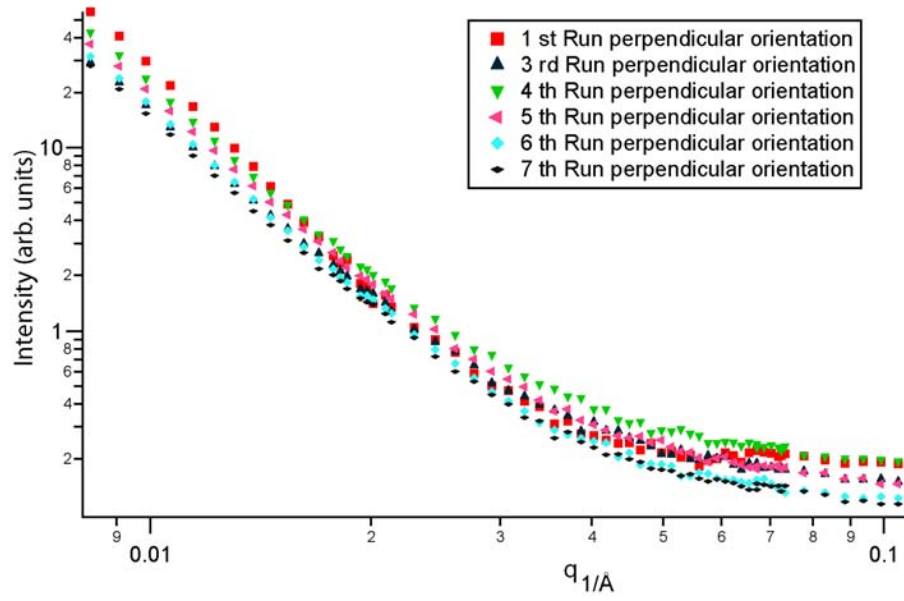


Figure 3.18: SANS-pattern with the angular dependence integrated out for *NiFH*-sample in perpendicular orientation

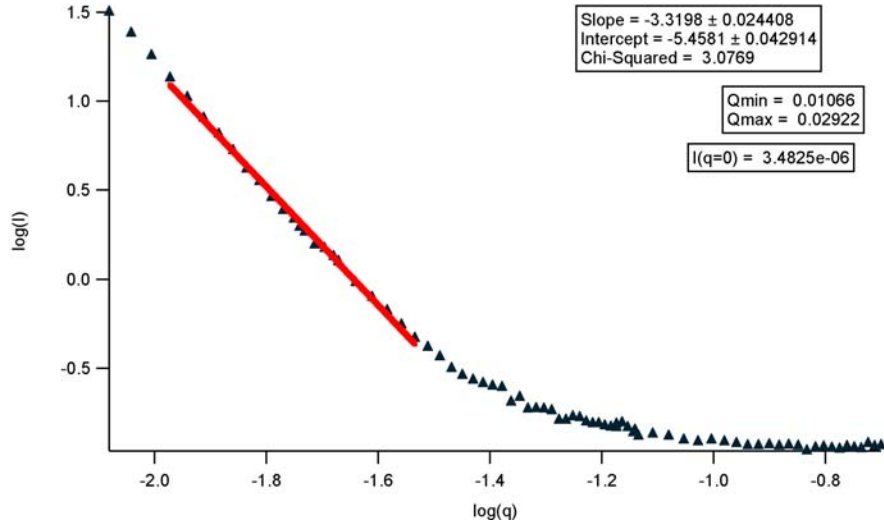


Figure 3.19: Linear fit in a log-log-plot to extract the α -parameter for perpendicular orientation.

found to be $\alpha = 3.86$ (Only one full range q -interval was recorded for the parallel orientation (dry state) and similar parameters for perpendicular orientation are listed in table 3.4.

Run #	1	2	3	4	5	6	7
α	3.88		3.13	3.19	3.27	3.32	3.22

Table 3.4: Slope parameters for six runs on the *NaFH*-layers in perpendicular direction.

3.1.6 New *NaFH*-suspensions

The objectives of these experiments were to compare the results on new freshly prepared *NaFH*-suspensions to the three year old sedimented *NaFH*-suspension described before and also look for differences between two different *NaFH*-concentrations, 1.5wt% and 3.0wt%. A possible self-orientation as a function of time is also investigated.

Samples Two new samples were prepared: one 1.5wt% *NaFH* in D_2O and one 3.0wt%. Since heavy water was used as a solvent no salt was added because a large amount of D_2O is needed to be able to weight the correct amount of *NaCl* - only a few *ml* of sample is needed.

After weighing the *NaFH* powder for the two samples and mixing with heavy water, both samples were left in a magnetic stirrer for three days.

A total of six samples was measured:

- 1.5wt% *NaFH*-suspension right after the sample was inserted into a 2mm cuvette.
- 3.0wt% *NaFH*-suspension right after the sample was inserted into a 2mm cuvette.
- Upper (clear) phase of 1.5wt% *NaFH*-suspension after four months.
- Upper (clear) phase of 3.0wt% *NaFH*-suspension after four months.
- Lower (sediment) phase of 1.5wt% *NaFH*-suspension after four months.
- Lower (sediment) phase of 3.0wt% *NaFH*-suspension after four months.

Scan series One full q -range scan for all six samples.

Results SANS-measurements performed on *NaFH*-suspensions right after the sample was inserted into a 2mm cuvette can be seen in Fig. 3.20 for 1.5wt% (A) and 3.0wt% (B). We can not clearly differ between the scattering of the two suspensions. In Fig. 3.21 the two scattering curves after integration are shown for both the 1.5wt%- and the 3.0wt%-suspension right after stirring. In Fig. 3.22 the four scattering curves, relatively to the upper phase and the lower phases, are shown after integration for both the 1.5wt%- and the 3.0wt%-suspension after a time period of four months. 3.23 shows both samples after phase separation. The α -parameters found for the samples can be found in table 3.5.

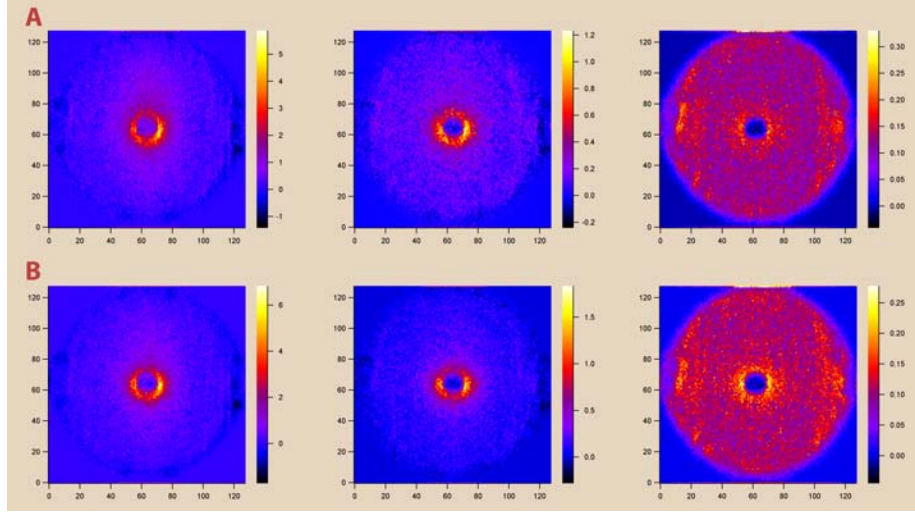


Figure 3.20: SANS-patterns for new *NaFH*-suspensions. A: 1.5wt% and B: 3.0wt%

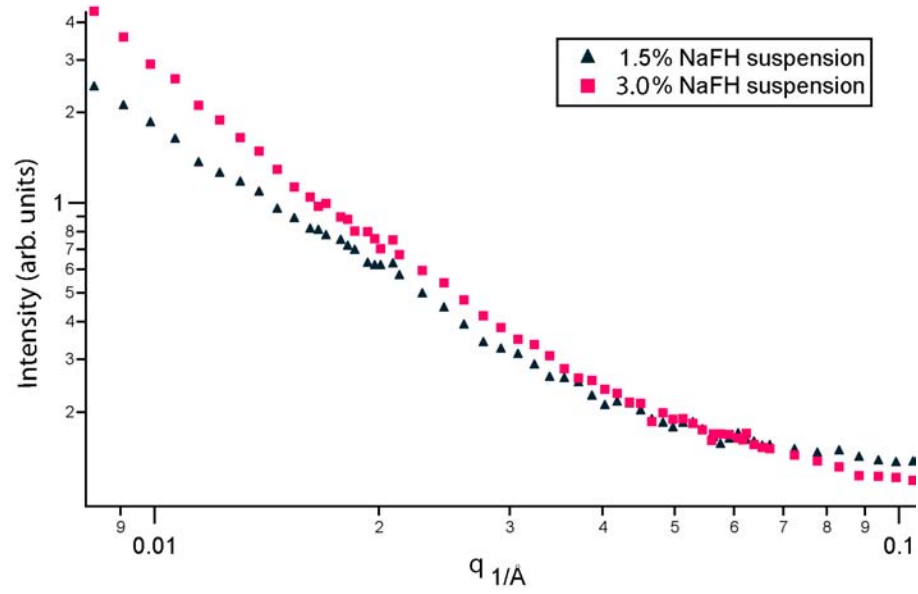


Figure 3.21: Two runs that show the scattering measured for both the 1.5wt% and 3.0wt% right after stirring

Run #	1.5wt%	3.0wt%	1.5wt% (P1)	3.0wt% (P1)	1.5wt% (P2)	3.0wt% (P2)
α	1.46	1.78	1.51	1.55	1.78	1.45

Table 3.5: α -values for the evolution of the 1.5wt%- and 3.0wt%-samples. P1 is the clear first phase and P2 is the sediment.

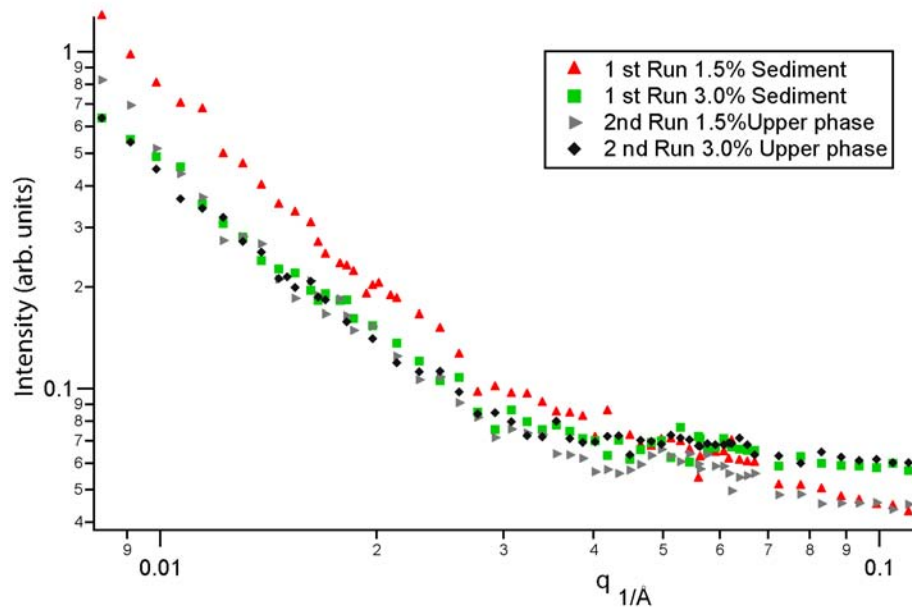


Figure 3.22: Four runs plotted together that shows upper and lower phases for both the 1.5wt% and 3.0wt% after a relaxation of approximately four months.



Figure 3.23: The new $NaFH$ -solutions after four months of relaxation. One sees clearly that the lower concentrated phase is higher in the 3.0wt% (cuvette to the right) sample than in the 1.5wt% suspension (cuvette to the left).

3.2 WAXS data processing, analysis and results

Experiments described in this chapter were performed at the *Bruker AXS NanoSTAR* at *The Norwegian University for Science and Technology* (NTNU).

Wide Angle X-ray Scattering (WAXS) measurements of the water intercalation front have previously been performed on a powder sample of the synthetic clay mineral *Sodium-Fluorohectorite*, *NaFH*, inside a capillary [29]. Lowering the temperature and imposing a humidity gradient over the sample the dynamics of the interlayer spacing was monitored through the dynamics of the (001)-peak as water intercalated through the sample. At the prevailing conditions, $T \sim 15^\circ\text{C}$, $RH_{\text{humid}} \sim 99.9\%$ and $RH_{\text{dry}} \sim 0.03\%$, the position intercalation front, $x(t)$, for *NaFH* was shown to yield a good fit with a stretched exponential:

$$x(t) = x_0 \left(1 - e^{-\left(\frac{t}{\tau}\right)^\beta} \right) \quad (3.3)$$

with fitted parameters $x_0 = (9.1087 \pm 0.0305)\text{mm}$, $t = (25.1912 \pm 0.3461)\text{s}^{-1}$ and $\beta = (0.7271 \pm 0.0118)$. The constant x_0 indicates the penetration depth of the intercalation front, whereas the characteristic time constant, τ , gives information about the rate at which the intercalation front advances through the sample. The β -parameter is believed to say something about the possible anomaly of the diffusive character.

Looking at (3.3) when $t \rightarrow \infty$, the second term approaches zero and we are left with the position x_0 , which could therefore be interpreted as the maximum water penetration length.

Using the same approach as *Alme* [29] we wanted to perform a similar experiment, but on *Nickel fluorohectorite*, *NiFH*. Previous experiments on this sample [3] show an unstable 2WL-state near 15°C temperature and we expected to see this hydration state also in this experiment.

First a brief look on data acquisition and processing will be given, then the experiment will be described and analyzed.

3.2.1 Data acquisition and processing

The *Bruker AXS NanoSTAR* have a position-sensitive detector that provides a 2D-image of the diffraction pattern. Every scan is stored as a *pixel frame* with raw data as well as information on spatial and time coordinates in the frame header. Fig. 3.24 (A) illustrates the detector image for a single scan.

From the header in the *pixel frames* *xy*-coordinates, time and date of the scan are stored. $x = 1$ was defined as the first millimeter probed on the humid side of the capillary. The time for the individual scans was defined as the middle value between the starting time and the ending time. The pixel frames were radially integrated (this holds for isotropic scattering, but with present anisotropy a sector integration must be used to ensure correct normalization) with conic line segments utilizing the *SAXI-offline* software that is bundled with

the x-ray apparatus. See Fig. 3.24 (B) for a demonstration of the result after the integration process.

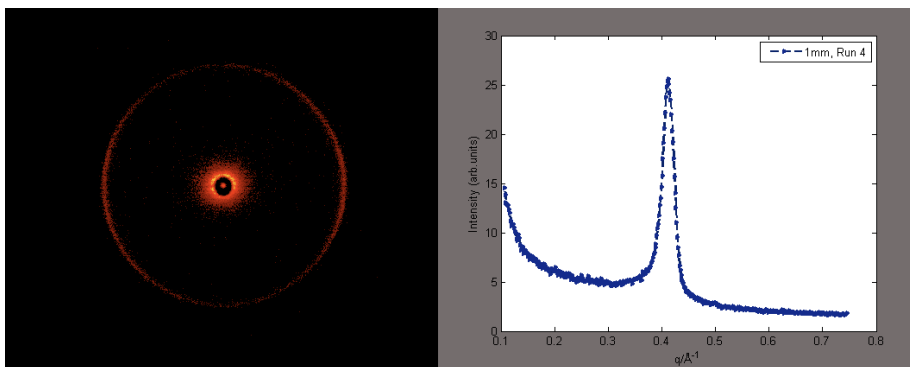


Figure 3.24: A: An example of a *Debye-Scherrer* scattering ring. B: A radially integrated scan.

3.2.2 H_2O -diffusion in NiFH

The aim was to use the same conditions as described previously for *NaFH* and also the same instrumental setup to investigate water transport in *Nickel-Fluorohectorite*.

Sample Pure aged *NiFH*-powder powder was filled inside a 1mm glass capillary with 0.01mm wall thickness. The closed end of the capillary was cut, and the now dual open ended capillary was attached to the sample holder.

Scan series Thirteen consecutive runs were performed. Each run was configured to move the sample with incremental steps of 1mm every 500s starting at the humid end of the capillary.

Run 1-8 Runs performed with $T = 15^\circ\text{C}$ and with an imposed humidity gradient.

Run 9-13 Runs performed with $T = 40^\circ\text{C}$ and with an imposed humidity gradient.

Run 1-3 were test runs and not used in the further analysis other than for a comparison to verify that no dynamics were lost. An uncertainty of about five millimeter in the sample-detector distance gave an uncertainty in measured q -values of $\sim 0.01\text{\AA}^{-1}$.

The data recording started three days after the humidity gradient and temperature had been set up. For this reason it is not possible to discuss the first days of dynamics.

3.2.3 Evolution of the (001)-peak

Looking at the collected data, a different approach than the one used for same measurements on NaFH was needed. The reason for this is that we observe the anticipated unstable state from the very beginning of the capillary at the humid side. This is shown in Fig. 3.25 where the peaks from the 1mm of the capillary on the humid side is shown for run 4-8. Doing a pseudo-Voigtian curve fit to the peak at lowest q , run 4, and the highest, run 6, we get peak center positions, x_c , in the range $(0.403 - 0.408)\text{\AA}^{-1}$.

An analysis of peak-positions further towards the dry side of the capillary shows that the spread around an average value, q_{avg} , for all runs decreases with the distance from the humid side. Further information and examples of this phenomenon are given in the end on this section.

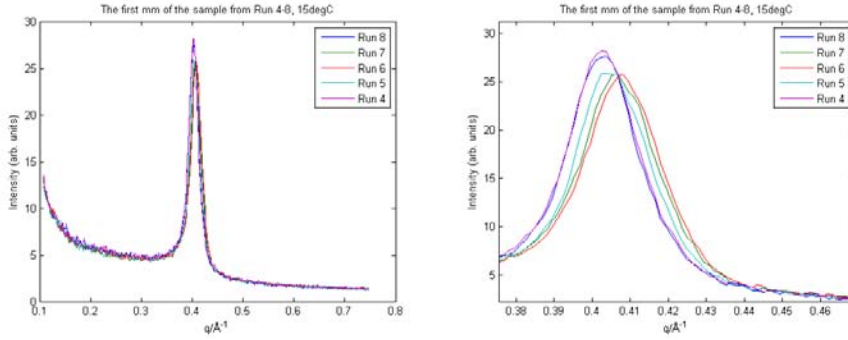


Figure 3.25: A demonstration of the instability at the very beginning of the capillary at 15°C . The right picture is an enlargement of the region of interest.

The peak position translates towards higher q -values as the scattering volume approaches the dry side. This is in itself an interesting observation and will be demonstrated in more detail in the following sections.

Measurements at 15°C

In figure Fig. 3.26 two runs are shown with 21h time difference. Scan 1 is the first mm scanned on the humid side and scan 5 is the fifth ($5 \times 500\text{s}$ later) etc. The horizontal translation of the peak (change in d -spacing) is clearly visible across the capillary and prevents us from tracking the intercalation front as done by *Alme* in previous studies [29]. For comparison a plot showing the transition from the 1WL state to the 2WL state as a function of time is shown in Fig. 3.27. In this case it is possible to track the intercalation front by investigating when a stable state transforms into a new state.

The horizontally translating peak make it difficult to track the intercalation front. Instead, the *water distribution profile* is investigated and in Fig. 3.28 the results are given for six consecutive runs. It is observed that the profiles vary very little between the runs, meaning that the d -spacing values are stable as a function of position (or more correctly, relative humidity) across the capillary

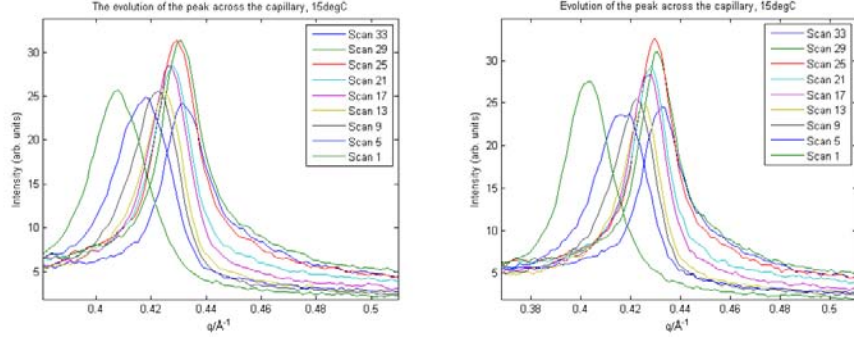


Figure 3.26: Two runs at 15°C separated by 21h. Scan 1 resembles the first probed millimeter of the capillary at the humid side and scan 2 the second millimeter etc. We notice a horizontal translation of the peak position as we go along the capillary indicating an unstable hydration state.

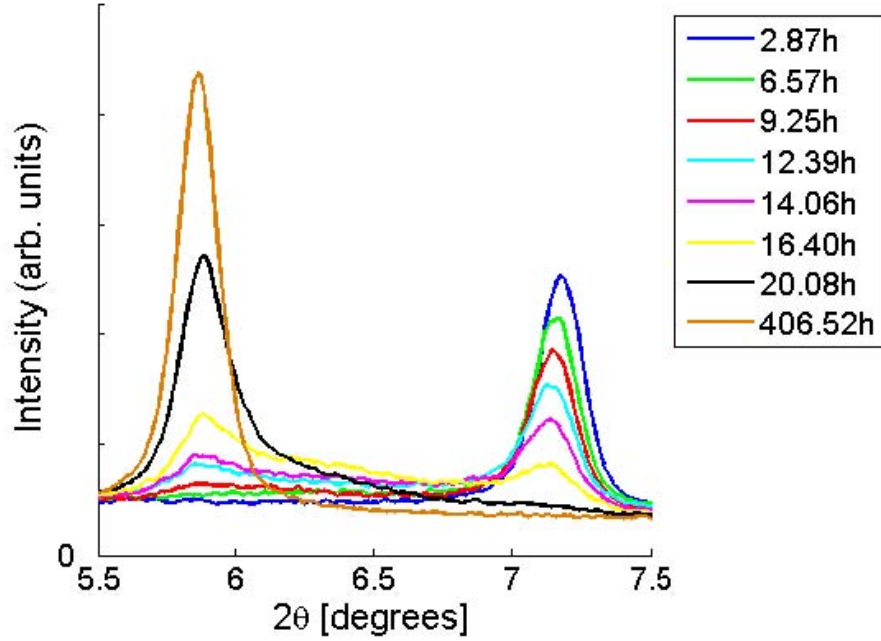


Figure 3.27: Demonstration of how one can track the hydration state (intercalation front) with stable hydration states. Here the units of the abscissae is 2θ , but this is easily converted to q through $q = \frac{4\pi}{\lambda} \sin \theta$. Here we clearly see the transition from the 1WL state to the 2WL state occurring after $\approx 20h$. Taken from [29].

indicating a reached equilibrium and absence of dynamics. The uncertainty in the measure peak center position is of order ± 0.001 .

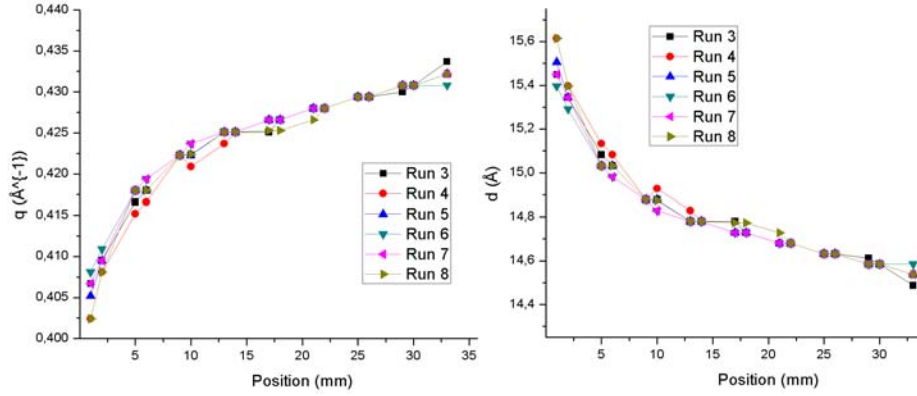


Figure 3.28: Left: q -values as a function of the position on the capillary. B: d -spacings as a function of the position on the capillary

From Fig. 3.28 one sees an intersection between all runs at $x \approx 25\text{mm}$. The corresponding d -spacing value is $d = 14.6\text{\AA}$. From previous experiments done on *NiFH* [3] a meta-stable (1.5WL) state is found at $d \approx 14.5\text{\AA}$. Taking into account the uncertainty of measured q -values² $\Delta q \sim 0.01$ this is an indication that at this position of the capillary the conditions are favorable for the meta-stable 1.5WL state. In figure Fig. 3.29 all peaks from $x = 25\text{mm}$ are plotted together.

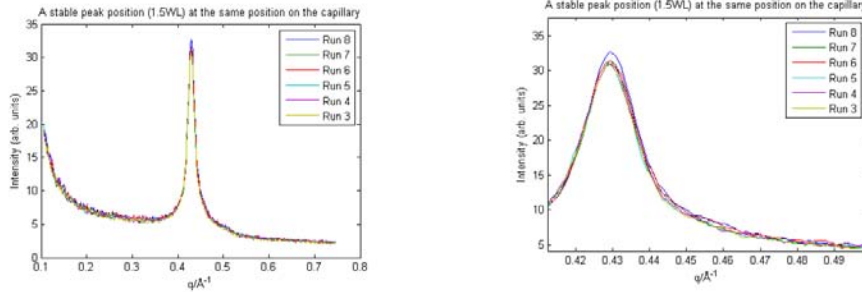


Figure 3.29: The possible meta-stable 1.5WL state at $x = 25\text{mm}$. The plot on the right is an enlargement of a q -range in the plot to the left.

Peak displacement around a q_{avg} for measurements with $T = 15^\circ\text{C}$

As mentioned before and shown in Fig. 3.25 there is a displacement of the peak around a q_{avg} at each position of order ± 0.0025 . After a thorough analysis of this displacement for every position across the capillary one sees less and less deviation from the q_{avg} between the runs when going further towards the dry side - this can also be seen in Fig. 3.28. Why the last point deviates from this trend (see also Fig. 3.30) is not clear at the present time.

²due to the uncertainty in sample-detector distance mentioned earlier

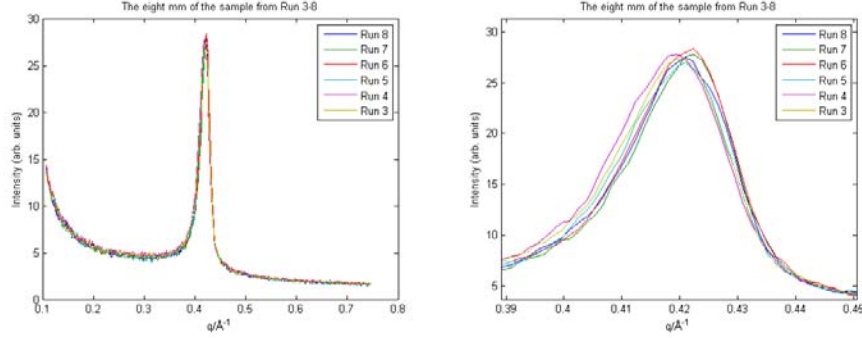


Figure 3.30: The displacement of the peaks from run 3-8 at position $x = 8mm$. The plot on the right is an enlargement of a q -range in the plot to the left.

Measurements at 40°C

After completing eight runs at 15°C, same measurements were performed after a considerable temperature step up to 40°C to track the impact this have on the system. The results are shown in Fig. 3.31. We still observe a horizontally translating Bragg-peak and the water distribution profile is investigated in Fig. 3.32. Comparing Fig. 3.28 and Fig. 3.32 we observe a completely different behavior between the sample at 15°C and at 40°C. At 40°C (Fig. 3.32) we no longer get an overlap of the water distribution profiles and we clearly see a sign of dynamics in our sample as the d -spacing is now a function of both time and relative humidity.

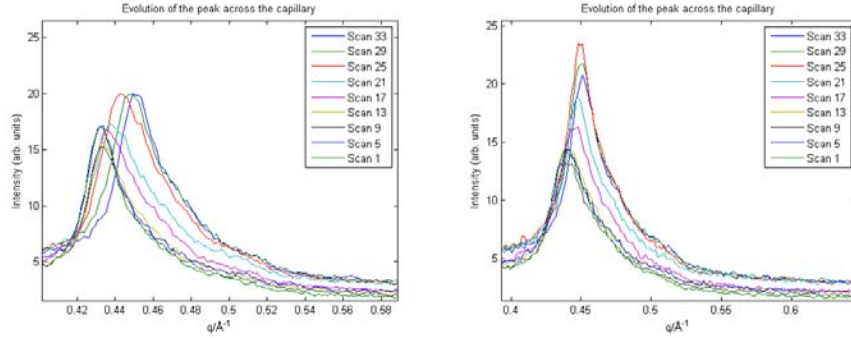


Figure 3.31: Two runs at 40°C separated by 21h. We notice still a horizontal translation of the peak position as we go along the capillary.

The curves seem to have the same trend in their shape (Fig. 3.32) and one notices the interesting intersection of the last point of run 10-13 indicating a possible end value for the d -spacing at the dry side of the capillary under the prevailing conditions, $d \approx 13.9\text{\AA}$. In [3] the d -value for the stable 1WL state in $NiFH$ has been found to be $d_{1WL} \approx 13.7\text{\AA}$, and with the uncertainty in sample-detector distance this is an indication that the stable 1WL state is reached at the dry side of the capillary. In Fig. 3.33 this is demonstrated.

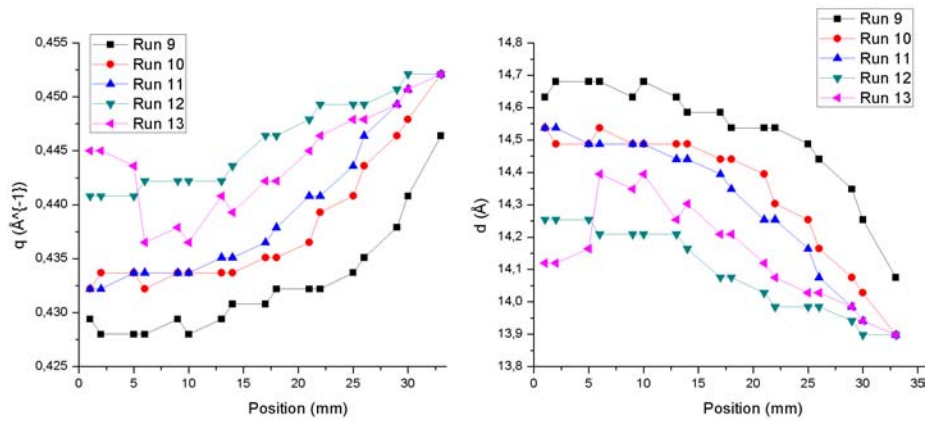


Figure 3.32: Left: q -values as a function of the position on the capillary. B: d -spacings as a function of the position on the capillary.

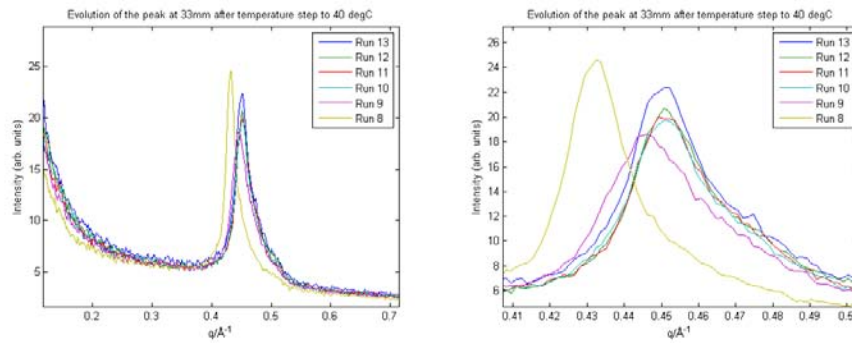


Figure 3.33: Peaks from run 8-13 demonstrates the transition into what could be the stable 1WL state. Run 8 from the $T = 15^\circ\text{C}$ -measurement is also displayed for comparison.

Recalling the possible meta-stable 1.5WL state of Fig. 3.29 at 15°C , we observe in Fig. 3.34 that the meta-stable state at $x = 25\text{mm}$ is no longer there after the increase in temperature to 40°C .

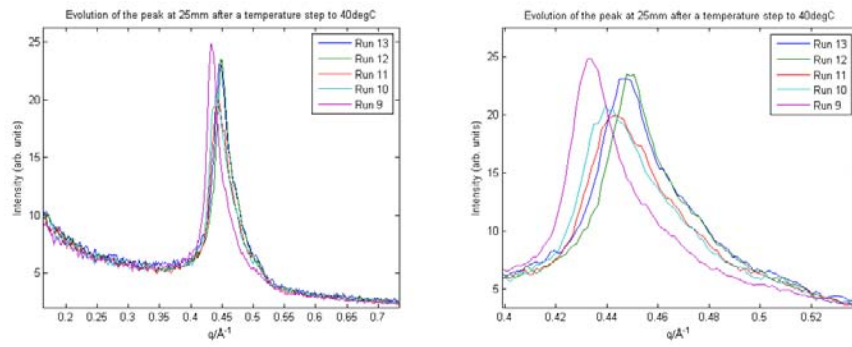


Figure 3.34: After heating up to 40°C we no longer see any meta-stable 1.5WL at $x = 25mm$

Chapter 4

Conclusion

In this thesis small-angle neutron scattering (SANS) experiments have been performed on two different synthetic smectite clays, *Ni-fluorohectorite* and *Na-fluorohectorite*. In addition, wide-angle x-ray experiments have been performed on *NaFH*. The main objective has been to investigate structural changes upon water intercalation and absorption into the clay.

Using the SANS-technique, analysis of the power-law behavior and the distribution of scattered intensity have provided information about surface roughness, ordering and size.

Absorption of D_2O in *NaFH*-powder We have observed that letting water (in form of D_2O) penetrate a dry sample of *NaFH*-powder the α -parameter describing the surface goes from representing smooth surfaces to a more rough surface and eventually turn into the mass fractal region. This is in agreement with literature as [31, 32].

Analysis of two nematic phases and sediment A nematic gel-phase have been identified in an aged phase separated suspension of 1.5wt% *NaFH*-powder by looking at the anisotropy of the scattering. The clay platelets in the nematic phase are observed to have a preferred orientation tilted $\approx 7^\circ$ away from the vertical. This is also true for the 3.0wt% gel phase. Neither a change in surface properties or orientation in the nematic phase was observed after putting the sample in a cuvette. Either the process of taking out extract from the phase did not perturb the sample in any way or the time to reach back to its previous state was shorter than $\sim$ one hour.

Heating up the nematic 1.5wt% *NaFH*-phase to $60^\circ C$ made the phase scatter isotropically most likely due to an increase in *Brownian motion* moving the platelets towards disorder.

A characteristic length of the isotropic sediment phase from the 1.5wt%-suspension was found to be $\sim 52\text{\AA}$ and additional experiments are needed in order to investigate what it represents. Possible explanations could be an average crystallite size or size of pore space.

Oriented NiFH-samples in D_2O The scattering from the sample oriented perpendicularly to the beam shows that in the dry state we have smooth surfaces on the probed length scale and that the addition of water causes a slightly more rough surface. For parallel orientation only the dry state was used for surface analysis since after wetting only measurements on high- q were performed - for the dry state we observed smooth surfaces as for the sample in perpendicular orientation.

New NaFH-suspensions A difference in scattering between the 1.5wt%- and 3.0wt%-suspension was not observed. This may be due to the fact that no salt was added making the electrostatic repulsion dominant (the salt function as a shield between the particles making them less interacting).

WAXS measurements on water diffusion in $NiFH$ The aim was to use the same conditions and instrumental setup as similar measurements performed on $NaFH$ [29]. Nevertheless, a different approach was chosen since these conditions induce the unstable 2WL state previously described in [3]. Very interesting results were observed - even if we did not have a good way to track the intercalation front nor have dynamics in our system at 15°C. The peak position of the unstable two water layer state seems to be an accurate and reproducible function of relative humidity (see Fig. 4.1). This means that if one maps the d -spacing value corresponding to a specific relative humidity (using an experimental setup where one can pinpoint the humidity inside the sample) it could be possible to use the d -spacing value as a *conversion key* for estimating the prevailing relative humidity.

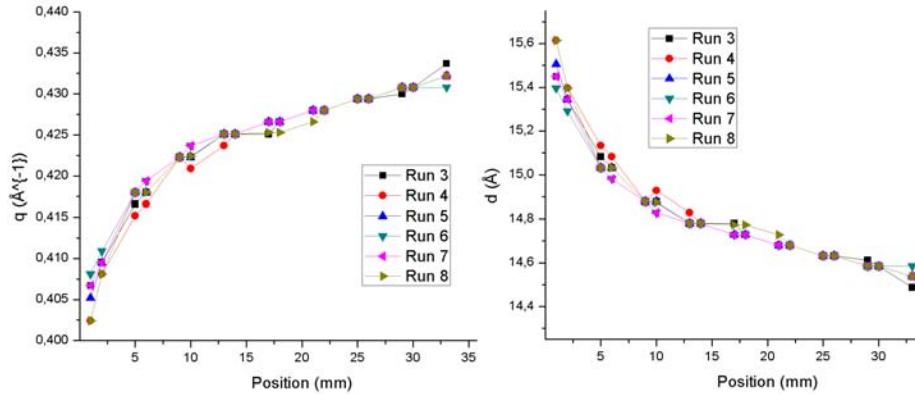


Figure 4.1: Left: q -values as a function of the position on the capillary. B: d -spacings as a function of the position on the capillary.

When making a temperature step up to 40°C we clearly see dynamics in our system, and they are according to expectations. As the temperature is raised more water evaporates reducing the d -spacings across the capillary (see Fig. 4.2). It is also observed that the increment in d -spacing changes is opposite from the experiment performed at 15°C. In Fig. 4.1 we see that the largest increments in d -spacing happen towards the humid side whereas after the temperature step

they are towards the dry side. A possible explanation of this trend could be that the water on the dry side is more free to evaporate than the water on the humid side.

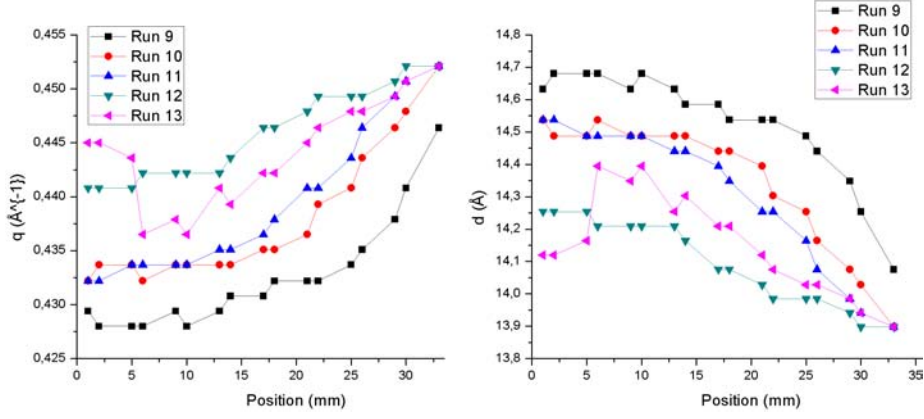


Figure 4.2: Left: q -values as a function of the position on the capillary. B: d -spacings as a function of the position on the capillary.

It is observed an interesting intersection of the last point of run 10-13 indicating a possible end value for the d -spacing at the dry side of the capillary under the prevailing conditions, $d \approx 13.9\text{\AA}$ (see Fig. 4.2 for illustration). In comparison with previous measurements of d -spacings in $NiFH$, this intersection value corresponds well to be the stable 1WL state.

Future experiments should be initiated right after the humidity gradient is imposed, so that one observes the dynamics. It could be interesting to see if there is any clear difference in the intercalation speed between a stable state (for example in $NaFH$) and the unstable state observed here for $NiFH$.

Appendix A

Technical drawings of the SANS sample holder

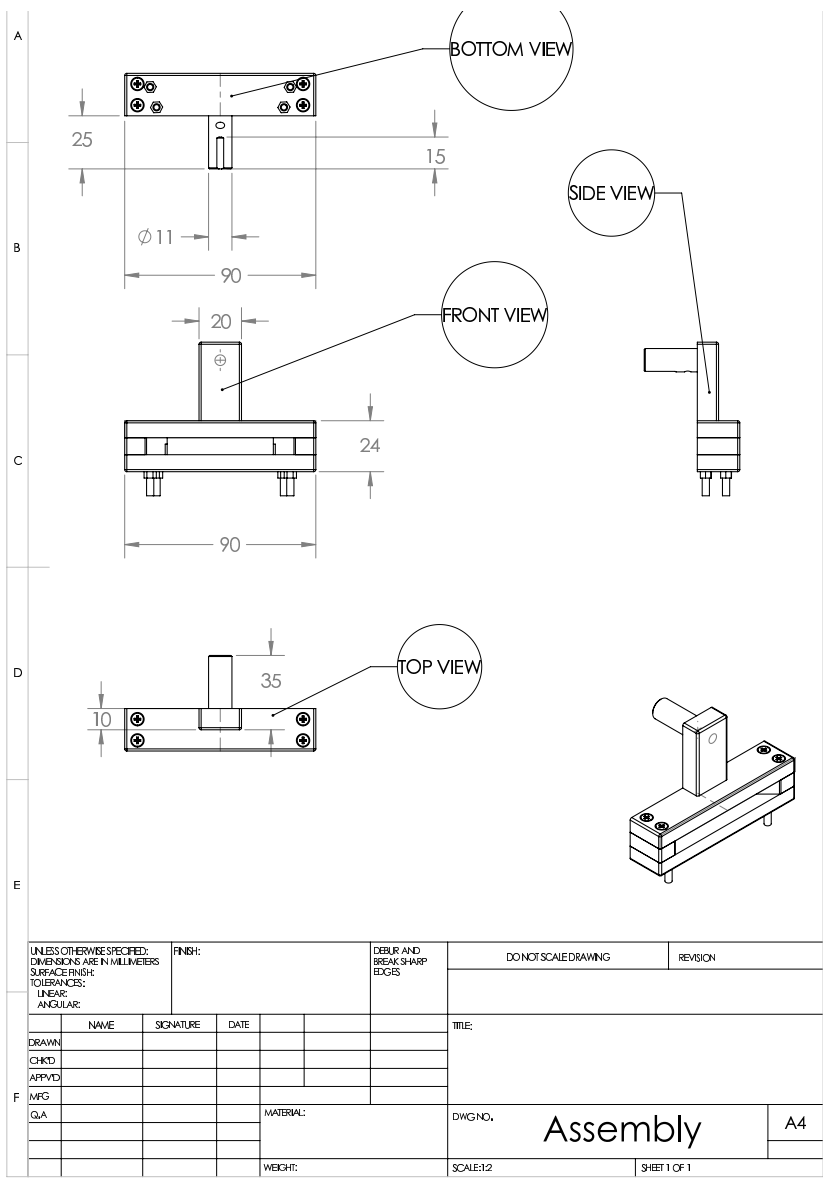


Figure A.1: Assembly drawing of the sample holder.

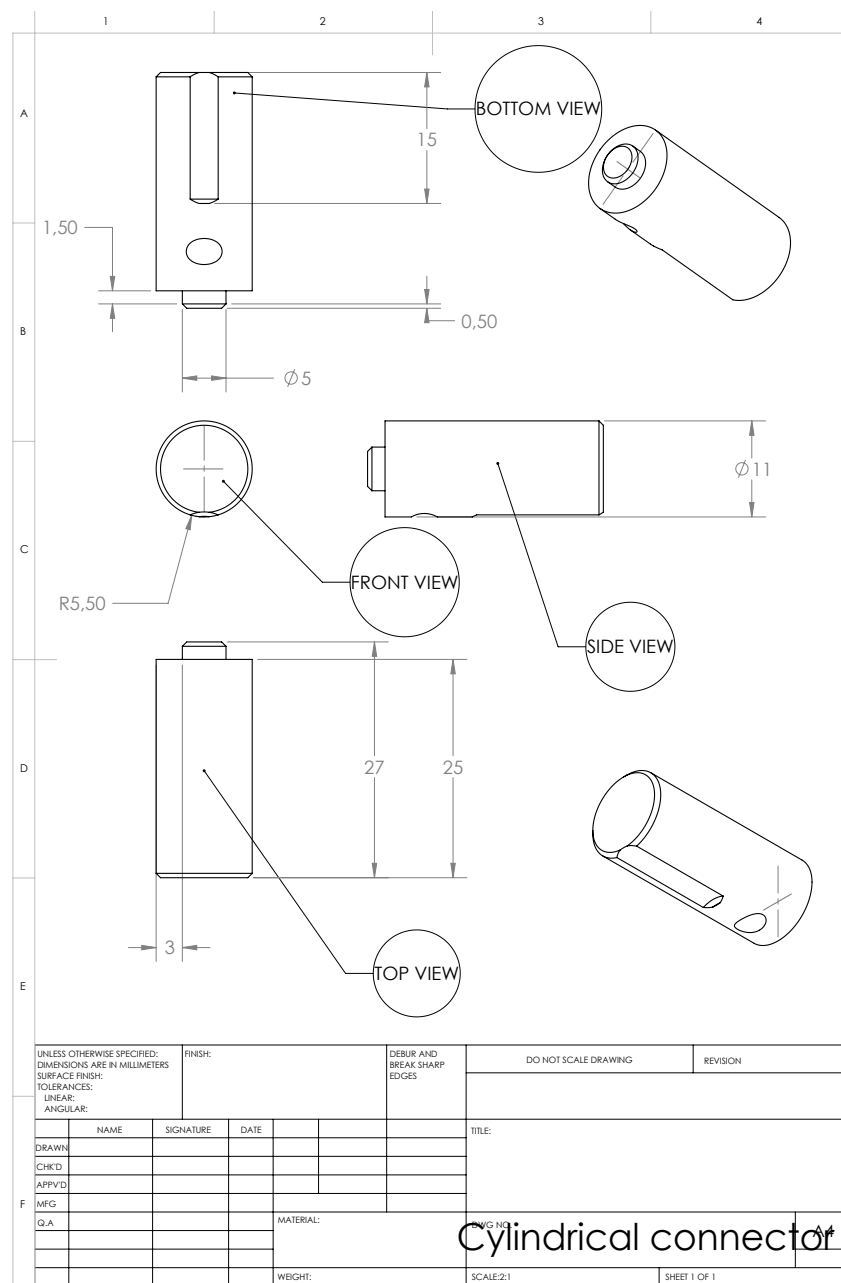


Figure A.2: Technical drawing of the cylindrical connector that is compatible with the sample changer used at the SANS-instrument at JEEP-II.

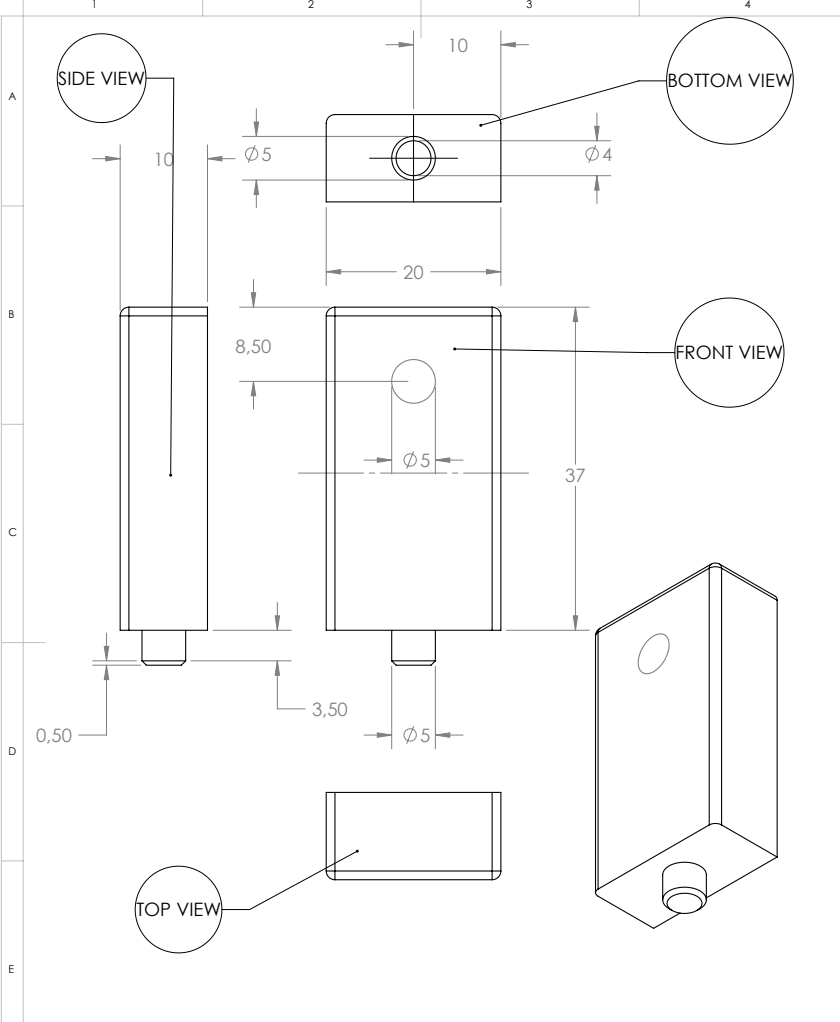


Figure A.3: Technical drawing of the holder.

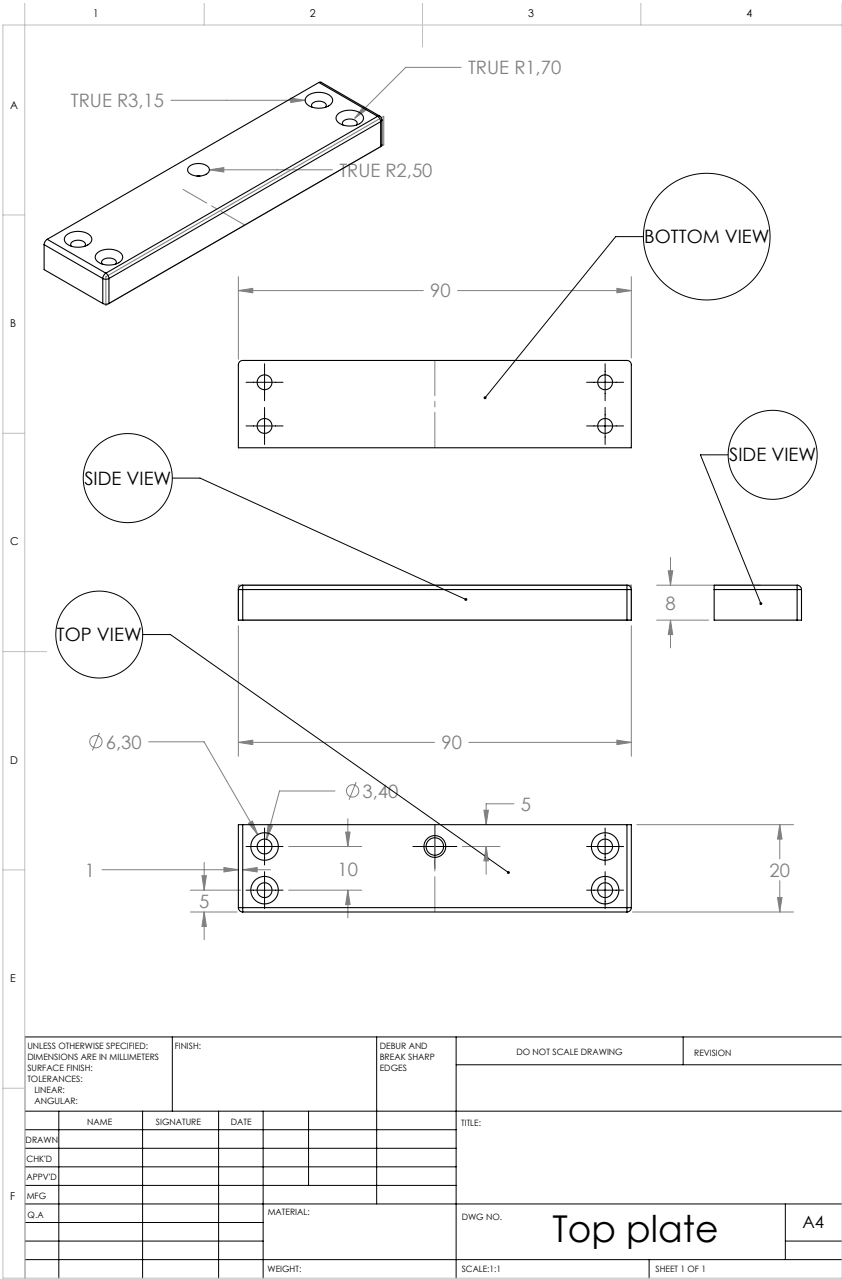


Figure A.4: Technical drawing of the top plate.

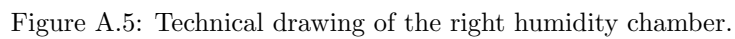


Figure A.5: Technical drawing of the right humidity chamber.

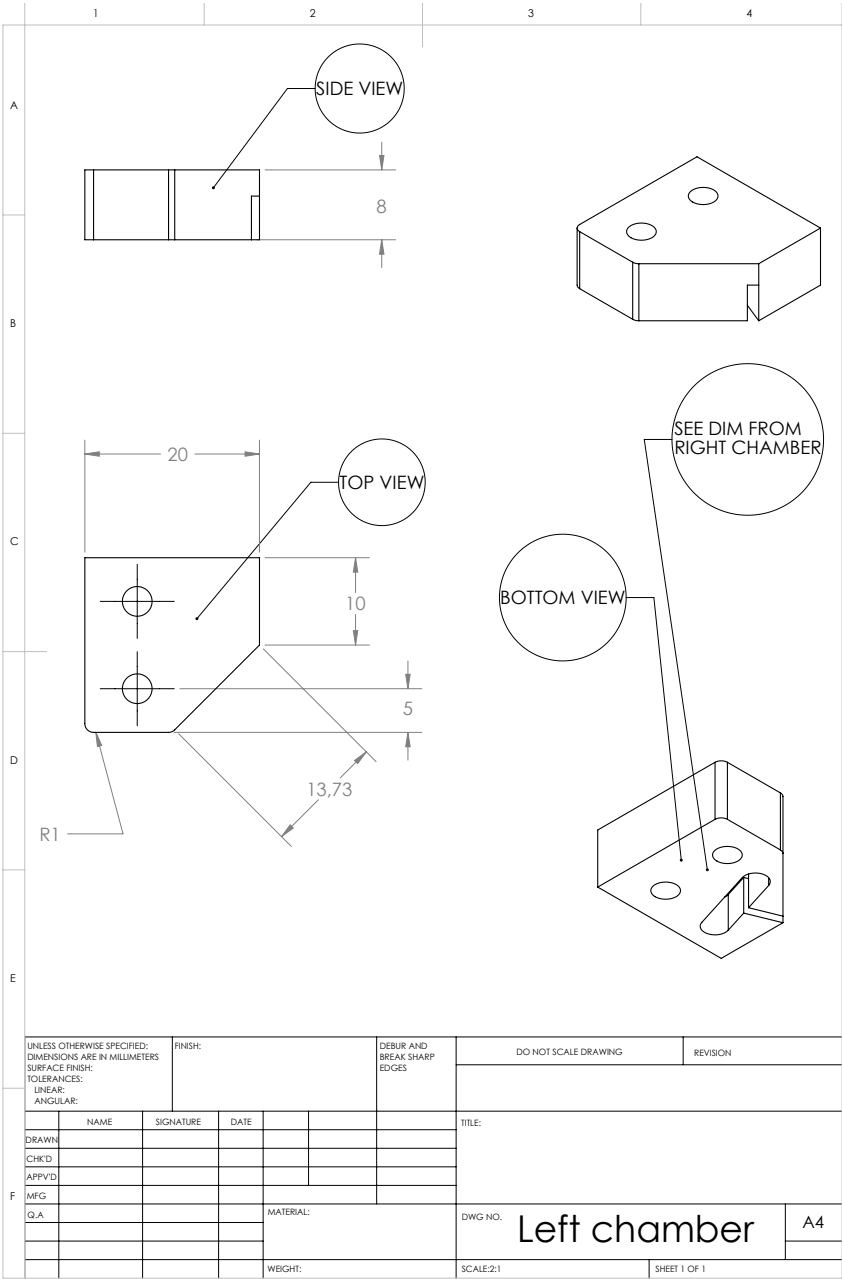


Figure A.6: Technical drawing of the left humidity chamber.

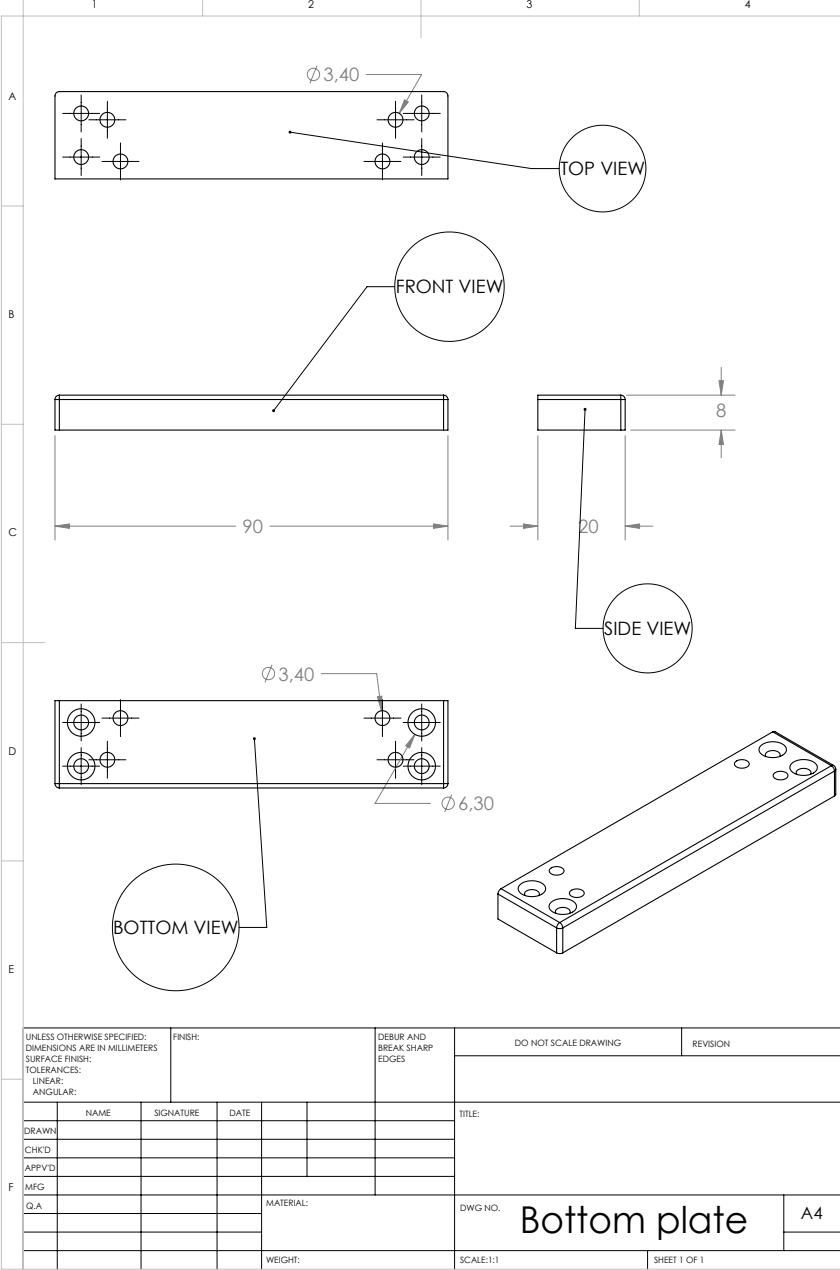


Figure A.7: Technical drawing of the bottom plate.

Appendix B

MATLAB peak-fitting script

pv1bgpower.m

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```

function [parameters,error_bars,squaredS,residual] = ...
    pv1bgpower(matrix,xpos,xlower,xupper,sensitivity,first,second,third,fourth,display_graph)

% Pseudo-voigtian fit (type 1) to input data (matrix form) with power law
% background approximation
% [PARAMETERS,ERROR_BARS] =
% PV1BGPOWER(MATRIX,XPOS,XLOWER,XUPPER,SENSITIVITY,DISPLAY_GRAPH)
%
% MATRIX:          normalized data input as a matrix (q-values,intensity)
% XPOS:            approximate peak position (q-value)
% XLOWER:          lower width of x-data on which to do the fit (q-value)
% XUPPER:          upper width of x-data on which to do the fit (q-value)
% SENSITIVITY:     criteria for aborting the least square fitting loop
% FIRST:           lower limit of left zone of interest for baseline approximation
% SECOND:          upper limit of left zone of interest for baseline approximation
% THIRD:           lower limit of right zone of interest for baseline approximation
% FOURTH:          upper limit of right zone of interest for baseline approximation
% DISPLAY_GRAPH:   graphical comparison of the input and fitting (type
%                  'y' for display, otherwise type 'n')
%
% Returns PARAMETERS - a matrix [mu,xc,w,A,wL,wG,amplitude,background at xc,
%                               max recorded intensity] with the parameters for the pseudo-Voigtian fit
%                               found by the method of least squares approximation, and the parameters for
%                               the background fit (power law:  $y(x) = a_3 \cdot x^{a_2 + a_1}$ );
% and ERROR_BARS - the errorbars of the fitted parameters
% and SQUARED_S - standard parameter on the degree of goodness of the fit
% and RESIDUAL - of the fit
%
% Made by:         Yves Meheust
% Modified by:     Lars Ramstad Alme      Trondheim 27/03/06
% Modified by:     Ariel Fischer
%
% Ex:              pv1bgpower(surface,2.74,0.02,0.03,0.001,2.58,2.62,2.88,2.92,'y')

%%%%% Interpretation of the function's arguments
if nargin<3
    fprintf('\nUsage:  fitwaxspeak(matrix,approximate position of the peak to fit,half-w
    fprintf('          matrix    => matrix with data\n');
    fprintf('          xpos      => approximate position of the peak maximum\n');
    fprintf('          xlower    => lower border of the zone on which to do the fit \n');
    fprintf('          xupper    => upper border of the zone on which to do the fit \n');
    return
end
fprintf('\n');

% Loading of the data and reduction to the correct domain
xdat=matrix(:,1);
ydat=matrix(:,2);

[xred,yred,imax]=Reduceddata(xdat,ydat,xpos,xlower,xupper);

% Determination of the baseline from normalized data
[backgroundparameters,maxerror,minerror] = powerbaseline2(matrix,first,second,...
    third,fourth,display_graph);
% Region of background fitting (for graphical representation)
leftcentre = 0.5*(first+second);
[xleft,yleft] = Reduceddata(xdat,ydat, leftcentre, leftcentre-first, second-leftcentre);
rightcentre = 0.5*(third+fourth);
[xright,yright] = Reduceddata(xdat,ydat, rightcentre, rightcentre-third, fourth-rightcentre);
xbg = [xleft,xright];
ybg = [yleft,yright];

```

```

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```

```

% Subtraction of baseline from normalized input data
ysub = ydat-BackgroundFunction(backgroundparameters,xdat);
xsub = xdat;
yredsub = yred-BackgroundFunction(backgroundparameters,xred);
xredsub = xred;

% Define set of lower and upper bounds on the design variables (mu,xc,w,A,y0)
LB = [0,0,0,0];
UB = [1,Inf,Inf,Inf];

% Initial values
mu=0.9;
xc=xredsub(imax);
% Extended interval for finding the width
factor = 2;
[xredwidth,yredwidth,imaxwidth]=Reducedata(xdat,ydat,xpos,factor*xlower,factor*xupper);
yredsubwidth = yredwidth-BackgroundFunction(backgroundparameters,xredwidth);
xredsubwidth = xredwidth;
w=Getwidth(imaxwidth,xredsubwidth,yredsubwidth);
A=0.5*yredsub(imax)/((2*mu/(pi*w)) + (2*(1-mu)*nthroot((log(2)/pi)/w,2)));

par0(1)=mu;
par0(2)=xc;
par0(3)=w;
par0(4)=A;

yfit_init=PseudoVoigt(par0,xredsub);

% Fitting of the data
par=lsqcurvefit(@PseudoVoigt,par0,xredsub,yredsub,LB,UB);
mu=par(1);
xc=par(2);
w=par(3);
A=par(4);

[parfit,squaredS,residual,exitflag,output,lambda,J]=lsqcurvefit(@PseudoVoigt,par,xredsub,
mu=parfit(1);
xc=parfit(2);
w=parfit(3);
A=parfit(4);

% Iteration of pseudo-voigtian fit
counter = 1;
abort = false;
while abs(1-parfit(1)/par(1))>sensitivity | abs(1-parfit(2)/par(2))>sensitivity | ...
abs(1-parfit(3)/par(3))>sensitivity | abs(1-parfit(4)/par(4))>sensitivity
par = parfit;
[parfit,squaredS,residual,exitflag,output,lambda,J] = ...
lsqcurvefit(@PseudoVoigt,par,xredsub,yredsub,LB,UB);
if counter==1000 %aborts function if no satisfying approximation is reached
parfit(:) = NaN;
abort = true;
break
end
counter = counter+1;
end
par = parfit;
fprintf(['Number of iterations = ',num2str(counter-1),'\n\n']);

% Estimation of the errors

```

```

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```

[dof,s,error_bars]=DetermineErrorBars(xredsub,par,squaredS,J);

% Visual comparison of the plot and data
if display_graph == 'y'
% Loaded data
    fig1 = figure;
    plot(xdat,ydat,'ob',xbg,ybg,'og',xred,yred,'or');
    legend('Loaded data','Region of background fitting','Region of peak fitting');
    title('Loaded raw data');

% Fitted data over reduced fitting interval
    fig2 = figure;
    [xrep,yrep,imax_rep]=Reducedata(xsub,ysub,xpos,xlower*2,xupper*2); %For graphical pu
    xi=xrep(1);
    xf=xrep(length(xrep));
    xstep=(xf-xi)/1000;
    xplot=xi:xstep:xf;
    yfit_init=PseudoVoigt(par0,xplot);
    yfit=PseudoVoigt(par,xplot);
    plot(xrep,yrep,'ob',xredsub,yredsub,'or',xplot,yfit_init,'-g',xplot,yfit,'-k');
    legend('Data','Region of peak fitting','Initial pseudo-voigtian estimate','Pseudo-voi
    title('Fitted pseudo-Voigt (type 1) over the reduced interval (after G2Lp subtracted

% Fitted data plotted over the entire data range
    fig3 = figure;
    xstep = (max(xsub)-min(xsub))/10000;
    xplot=min(xsub):xstep:max(xsub);
    yfit=PseudoVoigt(par,xplot);
    plot(xsub,ysub,'ob',xredsub,yredsub,'or',xplot,yfit,'-k');
    legend('Data','Region of peak fitting','Pseudo-voigtian fit');
    title('Fitted pseudo-Voigt (type 1) over the reduced interval (after G2Lp subtracted
end

% Deduce the natural width of the peak:
    global omega;
    global eta;
    omega=par(3);
    eta=par(1);

%Lorentzian
    wL_init=omega;
    wL = fsolve(@wL2eta,wL_init);
    global gammaL; % For later application
    gammaL=wL;

%Gaussian
    wG_init=omega/2;
    wG = fsolve(@wG2w,wG_init);

% Display results on screen
    fprintf('Fitted parameters:\n');
    fprintf('\t mu = %f',par(1)); fprintf('\t +- %f\n', error_bars(1));
    fprintf('\t xc = %f',par(2)); fprintf('\t +- %f\n', error_bars(2));
    fprintf('\t w = %f',par(3)); fprintf('\t +- %f\n', error_bars(3));
    fprintf('\t A = %f',par(4)); fprintf('\t +- %f\n', error_bars(4));
    fprintf('Natural width of the peak (lorentzian) - wL: %f\n',wL);
    fprintf('Instrumental resolution (gaussian) - wG: %f\n\n',wG);
    fprintf('Amplitude - Amp: %f\n',amplitude(par));
    fprintf('Background at Braggposition: %e\n',BackgroundFunction(backgroundparameters,par(2
    fprintf('Max recorded intensity: intensity = %e    x = %f \n\n',yred(imax),xred(imax));
    fprintf('sqrt(Chi^2/dof): %f\n',s);

```

```

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fprintf('Chi2 = %f\t dof = n - p = %d\t Chi2/(n-p) = %f\n', squaredS, dof, s*s);

parameters = [par, wL, wG, amplitude(par), BackgroundFunction(backgroundparameters, par(2)), yr

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%% Subroutines
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%%%%%%%% Subroutine wG2w
function y=wG2w(x)
global omega;
global gammal;
y= (x.^5 + 2.69269*gammal*x.^4 + 2.42843*gammal^2*x.^3 + ...
    4.47163*gammal^3*x.^2 + 0.07842*gammal^4*x + gammal^5 ).^(1/5) - ...
    omega* ones(1, length(x));
return

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%% Subroutine wL2eta
function y=wL2eta(x)
global omega;
global eta;
aux=x/omega;
y= 1.36603*aux-0.47719*aux.*aux+0.11116*aux.^3-eta*ones(1, length(aux));
return

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%% Subroutine Reducedata
function [x, y, imax]=Reducedata(xdat, ydat, xpos, x_width_lower, x_width_upper)
j=0;
for i=1:length(xdat)
    if ( xdat(i)<=xpos & (xpos-xdat(i)) <= x_width_lower ) |...
        ( xdat(i)>=xpos & (xdat(i)-xpos) <= x_width_upper )
        j=j+1;
        x(j)=xdat(i);
        y(j)=ydat(i);
        index(j)=i;
    end
end
[ypos, imax]=max(y);
return

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%% Subroutine Getwidth
function w=Getwidth(imax, xred, yred)
i=imax;
while yred(i)>yred(imax)/2
    i=i+1;
end
w=xred(i)-xred(imax);
return

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%% Subroutine 'PseudoVoigt'
function f=PseudoVoigt(par, xdata)
%%%%%%%% Parameters
mu=par(1);

```

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```

qc=par(2);
w=par(3);
A=par(4);

%%% Computation of the function at abscix value q
x=xdata-qc;
hw1=w/2;
fact1=sqrt(log(2)/pi)/hw1;
intens1=(1-mu)*fact1*exp(-log(2)*(x.*x)/(hw1*hw1));
hw2=w/2;
fact2=1/(hw2*pi);
intens2=(mu)*fact2./(1+(x.*x)/(hw2*hw2));
f=A*(intens1+intens2);
%%% Check of the function's integral
%integrale=trapz(q,intens)
return

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%% Subroutine BackgroundFunction
function f = BackgroundFunction(param,xdata)
    f = param(3).*xdata.^param(2)+param(1);
return

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%% Subroutine DetermineErrorBars()
function [dof,s,errorBars_vec]=DetermineErrorBars(xdata,par,squaredS,J)
    dof=length(xdata)-length(par); %degree of freedom
    s=sqrt(squaredS/dof);
    C=inv(transpose(J)*J);

    for i=1:length(par)
        errorBars_vec(i)=s*sqrt(C(i,i));
    end
return

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%% Subroutine Amplitude
function f = amplitude(parameters)
    mu=parameters(1);
    w=parameters(3);
    A=parameters(4);
    f = (2*A/w)*(mu/pi+(1-mu)*sqrt(log(2)/pi));
return

```

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```
function [backgroundparameters,maxerror,minerror] = powerbaseline2(data,first,second,third,fo

% Determine the baseline;          y = a3*x^a2+a1
% [BACKGROUNDPARAMETERS,MAXERROR,MINERROR] = POWERBASELINE(XPOS,START,FILENAME,FROM,TO)
%
% DATA:          integration matrix
% FIRST:          lower limit angle of left zone
% SECOND:         upper limit angle of left zone
% THIRD:          lower limit angle of right zone
% FOURTH:         upper limit angle of right zone
% DISPLAY_GRAPH:  graphical comparison of the input and background fitting
%                  (type 'y' for display, otherwise type 'n')
%
% Returns [BASELINEGRADIENT,MAXERROR,MINERROR]
% ORDER2:         second order of the gradient
% ORDER1:         first order of the gradient
% ORDER0:         the constant of the baseline
% MAXERROR:       max(datavalue-baselinevalue)
% MINERROR:       min(datavalue-baselinevalue)
%
% Made by:      Lars Ramstad Alme      Trondheim 03/04/06
% Last revision:
%

sensitivity = 0.001;

% Find y2,y1 and y0
[xleft,yleft] = Reducedata(data(:,1),data(:,2),first,second);
[xright,yright] = Reducedata(data(:,1),data(:,2),third,fourth);
xred = [xleft,xright];
yred = [yleft,yright];
%Datainterval of interest
[xinterval,yinterval] = Reducedata(data(:,1),data(:,2),first,fourth);
%Fitting of the data on power-law form:  y = a3*x^a2+a1
par0(1) = 0;
par0(2) = 0;
par0(3) = 0;

par = lsqcurvefit(@BackgroundFunction,par0,xred,yred);
parfit = lsqcurvefit(@BackgroundFunction,par,xred,yred);

counter = 1;
while abs(1-parfit(1)/par(1))>sensitivity | abs(1-parfit(2)/par(2))>sensitivity | ...
      abs(1-parfit(3)/par(3))>sensitivity
    par = parfit;
    [parfit,resnorm] = lsqcurvefit(@BackgroundFunction,par,xred,yred);
    if counter==1000      %aborts function if no satisfying approximation is reached
      parfit(:) = NaN;
      break
    end
    counter = counter+1;
end
par = parfit;

[maxerror,minerror]= ErrorEstimate(xred,yred,par);
backgroundparameters = [par(1),par(2),par(3)];

if display_graph == 'y'
% Plot the baseline approximation
backgroundfit = BackgroundFunction(par,xinterval);
```

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```

backgroundcomparison = figure;
hold on
    plot(xinterval,yinterval,'-k',xinterval,backgroundfit,':r','LineWidth',1.25);
    plot(xleft,yleft,'-b',xright,yright,'-b','LineWidth',2);
hold off
legend('Rawdata','Fitted background','Zone of background fitting','Location','Best');
title('Background approximation'); xlabel('2\theta'); ylabel('Intensity(arb. units)');
end

% For printing graphs to the report
display_subtracted = 'n';
if display_subtracted == 'y'
    % Plot the subtracted data
    backgroundfit = BackgroundFunction(par,data(:,1));
    yfit = data(:,2)-backgroundfit;
    xfit = data(:,1);
    backgroundsubtracted = figure;
    plot(xfit,yfit,'-k','LineWidth',1.25);
    legend('Background subtracted data','Location','Best');
    xlabel('2\theta'); ylabel('Intensity(arb. units)');
end

if display_subtracted == 'y'
    % Plot the subtracted data
    tth = data(:,1);
    [f1,f2] = G2Lp(tth,'y');

    backgroundfit = BackgroundFunction(par,data(:,1));

    yfit = data(:,2)-backgroundfit;
    xfit = data(:,1);
    backgroundsubtracted = figure;

    ydiv = yfit./f2;

    [max_div,index_div] = max(ydiv);
    [max_fit,index_fit] = max(yfit);
    factor = max_fit/max_div;

    plot(xfit(350:430),yfit(350:430),'-k',xfit(350:430),ydiv(350:430).*factor,'-b','LineW
    legend('Data (background subtracted)','Data divided by |G|^2Lp','Location','Best');
    xlabel('2\theta'); ylabel('Intensity(arb. units)');
end

return

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%% SUBFUNCTIONS
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Subroutine Reducedata
function [x,y]=Reducedata(xdat,ydat,left,right)
j=0;
for i=1:length(xdat)
    if left<=xdat(i) & xdat(i)<=right
        j=j+1;
        x(j)=xdat(i);

```

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```
        y(j)=ydat(i);
        index(j)=i;
    end
end
return;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Subroutine ErrorEstimate
function [maxerror,minerror] = ErrorEstimate(xdata,ydata,param);
    error = ydata-BackgroundFunction(param,xdata);
    [maxerror,indexmax] = max(error);
    [minerror,indexmin] = min(error);
return;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Subroutine BackgroundFunction
function f = BackgroundFunction(param,xdata)
    f = param(3).*xdata.^param(2)+param(1);
return
```

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