

A 1 Scattering

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1 Introduction

Our present understanding of the properties and phenomena of condensed matter science is based on atomic theories. The first question we pose when studying any condensed matter system is the question concerning the internal structure: what are the building blocks (atoms, colloidal particles, ...) and how are they arranged? The second question concerns the microscopic dynamics: how do these building blocks move and what are their internal degrees of freedom? Once these fundamental questions are answered, the macroscopic properties are in principle determined by quantum theory and statistical physics. The macroscopic response and transport properties such as thermal conductivity, elasticity, viscosity, susceptibility etc. are the quantities of interest for applications. A deeper understanding of these properties has to be based on a microscopic picture.

For the development of modern condensed matter research, the availability of probes to study the structure and dynamics on a microscopic level is therefore essential. Modern scattering techniques can provide all the required information. Radiation, which has rather weak interaction with a sample under investigation provides a non-invasive, non-destructive probe for the microscopic structure and dynamics. This has been shown for the first time by W. Friedrich, P. Knipping and M. von Laue in 1912, when interference of x-ray radiation from a single crystal was observed. Max von Laue received the Nobel price for the interpretation of these observations. One cannot overestimate this discovery: it was the first proof that atoms are the elementary building blocks of condensed matter and that they are arranged in a periodic manner within a single crystal. The overwhelming part of our present-day knowledge of the atomic structure of condensed matter is based on x-ray structure investigations. Of course the method has developed rapidly since 1912. With the advent of modern synchrotron x-ray sources, the source brilliance has since then increased by 18 orders of magnitude. Currently x-ray Free Electron Lasers, e. g. the TESLA project (tesla.desy.de), are proposed which will increase this brilliance by another 10 orders of magnitude. Nowadays the structure of highly complex biological macromolecules can be determined with atomic resolution such as the crystal structure of the ribosome. Extremely weak phenomena such as magnetic x-ray scattering can be exploited successfully at modern synchrotron radiation sources. Besides x-ray scattering, light scattering is an important tool in soft condensed matter research. Light scattering is of particular interest for investigations on larger lengths scales, such as of colloidal particles in solution. Finally, intense neutron beams have properties, which make them an excellent probe for soft condensed matter investigations. In particular, contrast variation techniques are possible by selective deuteration of molecules or molecular subunits. Neutrons give access to practically all lengths scales relevant in soft condensed matter investigations from the atomic level up to about 1000 nm and are particularly well suited for the investigations of the movement of atoms and molecules. As with x-rays the experimental techniques are in rapid evolution and the proposed new spallation sources such as the European Spallation Source ESS (www.ess-europe.de) will increase the capabilities of neutron investigations in condensed matter science drastically in the years to come.

In the following we give an elementary introduction into scattering theory in general and show some applications in soft condensed matter investigations. More details can be found in [1-5].

This lecture is organised as follows: first we give a very basic introduction into elementary scattering theory for elastic scattering. Then we will discuss which probes are relevant for condensed matter investigations (light, x-rays, neutrons), list the properties of the various types of radiation and mention the modern radiation sources. Then we will drop the restriction of a static arrangement of scatterers assumed in the chapter on elastic scattering and discuss time fluctuations and how scattering processes can give information on internal dynamics. Examples will be given for high resolution neutron and light scattering experiments.

I have to emphasise that a lecture on scattering for all the different probes and for the static and dynamic cases is a subject for a full semester university course. With the limited space available it is impossible to deduce the results cited in a strict manner. I will use simple hand waving arguments to motivate the form of the equations presented and refer to the literature [1-5] for the detailed derivation.

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

2 Elementary Scattering Theory: Elastic Scattering

2.1 Scattering geometry and scattering cross section

In this chapter we assume that the building blocks within our sample are rigidly fixed on equilibrium positions in space. Therefore we only look at those processes, in which the recoil is being transferred to the sample as a whole so that the energy change for the radiation is negligible and the scattering process appears to be elastic. In chapter 4, we will drop this restriction and discuss so-called inelastic scattering processes due to internal fluctuations in the sample which give rise to an energy change of the radiation during the scattering process.

A sketch of the scattering experiment is shown in figure 1.

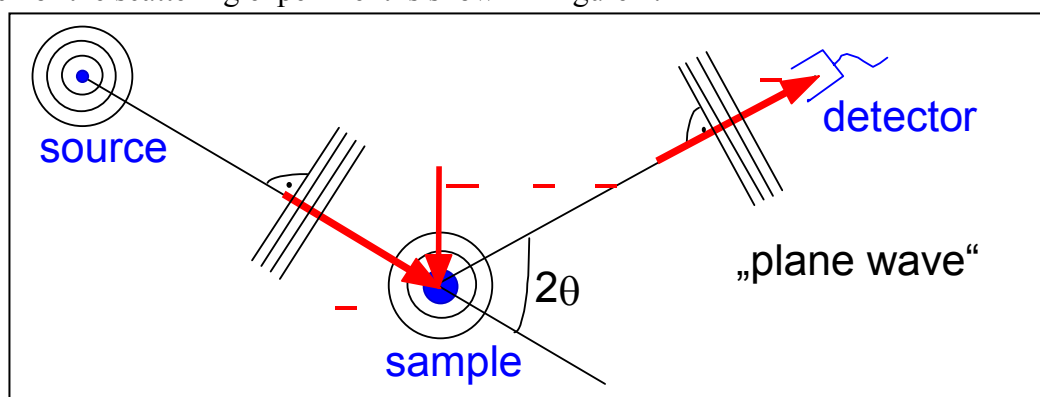


Fig. 1: A sketch of the scattering process in the Fraunhofer approximation in which it is assumed that plane waves are incident on sample and detector due to the fact that the distance source-sample and sample-detector, respectively, is significantly larger than the size of the sample.

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

$$k = |\underline{k}| = |\underline{k}'| = k' = \frac{2\pi}{\lambda} \quad (1)$$

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

$$\underline{Q} = \underline{k} - \underline{k}'. \quad (2)$$

The magnitude of the scattering vector can be calculated from wavelength λ and scattering angle 2θ as follows

$$Q = |\underline{Q}| = \sqrt{k^2 + k'^2 - 2kk'\cos 2\theta} \Rightarrow Q = \frac{4\pi}{\lambda} \sin \theta. \quad (3)$$

A scattering experiment comprises the measurement of the intensity distribution as a function of the scattering vector. The scattered intensity is proportional to the so-called *cross section*, where the proportionality factors arise from the detailed geometry of the experiment. For a definition of the scattering cross section, we refer to figure 2.

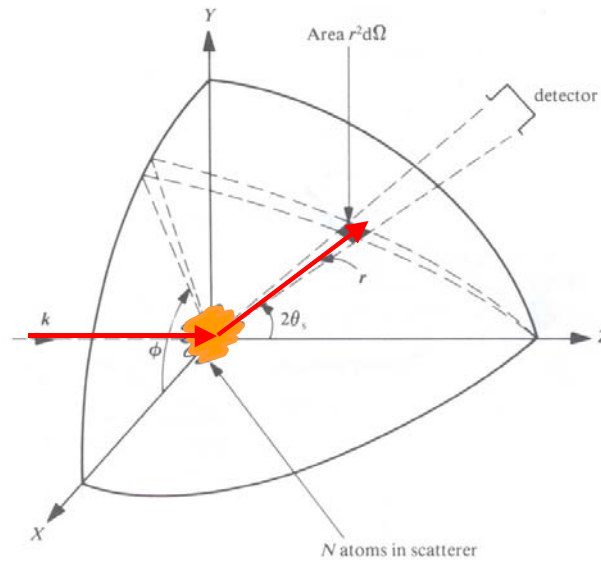


Fig. 2: Geometry used for the definition of the scattering cross section.

If n' particles are scattered per second into the solid angle $d\Omega$ seen by the detector under the scattering angle 2θ and into the energy interval between E' and $E' + dE'$, then we can define the so-called *double differential cross section* by:

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{n'}{j d\Omega dE'}. \quad (4)$$

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

$$\frac{d\sigma}{d\Omega} = \int_0^\infty \frac{d^2\sigma}{d\Omega dE'} dE'. \quad (5)$$

Finally the so-called *total scattering cross section* gives us a measure for the total scattering probability independent of changes in energy and scattering angle:

$$\sigma = \int_0^{4\pi} \frac{d\sigma}{d\Omega} d\Omega. \quad (6)$$

Our task therefore is to determine the arrangement of the atoms in the sample from the knowledge of the scattering cross section $d\sigma/d\Omega$. The relationship between scattered intensity and the structure of the sample is particularly simple in the so-called *Born approximation*, which is often also referred to as *kinematic scattering approximation*. In this case, refraction of the beam entering and leaving the sample, multiple scattering events and the extinction of the primary beam due to scattering within the sample are being neglected. Following figure 3 the phase difference between a wave scattered at the origin of the coordinate system and at position $\underline{r}$ is given by

$$\Delta\Phi = 2\pi \cdot \frac{(\overline{AB} - \overline{CD})}{\lambda} = \underline{k}' \cdot \underline{r} - \underline{k} \cdot \underline{r} = \underline{Q} \cdot \underline{r}. \quad (7)$$

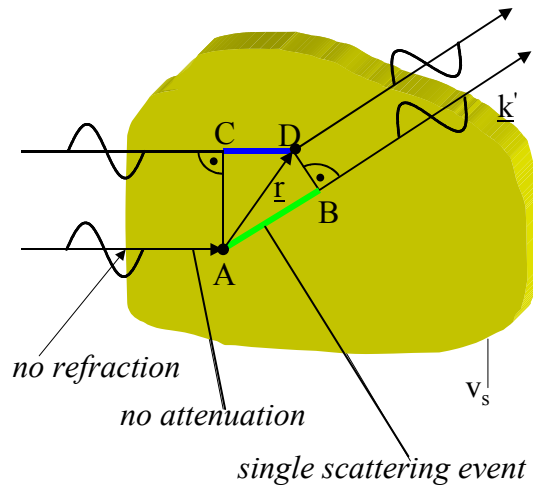


Fig. 3: A sketch illustrating the phase difference between a beam scattered at the origin of the coordinate system and a beam scattered at the position $\underline{r}$.

The scattered amplitude at the position $\underline{r}$ is proportional to what I will refer to as the scattering power density $\rho_s(\underline{r})$. ρ_s depends on the type of radiation used. Its meaning will be given in chapter 3. Assuming a laterally coherent beam, the total scattering amplitude is given by a coherent superposition of the scattering from all points within the sample, i. e. by the integral

$$A = A_0 \cdot \int_{V_s} \rho_s(\underline{r}) \cdot e^{i\underline{Q} \cdot \underline{r}} d^3r. \quad (8)$$

Here A_0 denotes the amplitude of the incident wave field. (8) demonstrates that the scattered amplitude is connected with the scattering power density $\rho_s(\underline{r})$ by a simple Fourier transform. A knowledge of the scattering amplitude for all scattering vectors $\underline{Q}$ allows us to determine via a Fourier transform the scattering power density uniquely. This is the complete information on the sample, which can be obtained by the scattering experiment. Unfortunately nature is not so simple. On one hand, there is the more technical problem that one is unable to determine the scattering cross section for all values of $\underline{Q}$. The more fundamental problem,

however, is given by the fact that normally the amplitude of the scattered wave is not measurable. Instead only the scattered intensity

$$I \sim |A|^2 \quad (9)$$

can be determined. Therefore the phase information is lost and the simple reconstruction of the scattering power density via a Fourier transform is no longer possible. This is the so-called *phase problem* of scattering.

Before we address the question, which information we can obtain from a scattering experiment, let us ask ourselves, which wavelength we have to choose to obtain the required real space resolution. For information on a length scale L , a phase difference of about $Q \cdot L \approx 2\pi$ has to be achieved. Otherwise according to (7) $\underline{k}'$ and $\underline{k}$ will not differ significantly. According to (3) $Q \approx 2\pi/\lambda$ for typical scattering angles ($2\theta \sim 60^\circ$). Combining these two estimates, we end up with the requirement that the wavelength λ has to be in the order of the real space length scale L under investigation. To give an example: with the wavelength in the order of 0.1 nm, atomic resolution can be achieved in a scattering experiment.

2.2 The Patterson or pair correlation function

From (9) we see that the phase information is lost during the measurement of the intensity. For this reason the Fourier transform of the scattering power density is not directly accessible in most scattering experiments (note however that phase information can be obtained in certain cases). In this section, we will discuss which information can be obtained from the intensity distribution of a scattering experiment.

Substituting (8) into (9), we obtain for the magnitude square of the scattering amplitude, a quantity directly accessible in a scattering experiment:

$$\begin{aligned} I \sim |A(\underline{Q})|^2 &\sim \int d^3r' \rho_S(\underline{r}') e^{i\underline{Q} \cdot \underline{r}'} \int d^3r \rho_S^*(\underline{r}) e^{-i\underline{Q} \cdot \underline{r}} \\ &= \iint d^3r' d^3r \rho_S(\underline{r}') \rho_S^*(\underline{r}) e^{i\underline{Q} \cdot (\underline{r}' - \underline{r})} = \iint d^3R d^3r \rho_S(\underline{R} + \underline{r}) \rho_S^*(\underline{r}) e^{i\underline{Q} \cdot \underline{R}}. \end{aligned} \quad (10)$$

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

$$I(\underline{Q}) \sim \int d^3R P(\underline{R}) e^{i\underline{Q} \cdot \underline{R}} \quad (11)$$

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

$$P(\underline{R}) = \int d^3r \rho_S^*(\underline{r}) \rho_S(\underline{r} + \underline{R}). \quad (12)$$

$P(\underline{R})$ correlates the value of the scattering power density at position $\underline{r}$ with the value at the position $\underline{r} + \underline{R}$, integrated over the entire sample volume. If, averaged over the sample, no correlation exists between the values of the scattering power densities at position $\underline{r}$ and $\underline{r} + \underline{R}$, then the Patterson function $P(\underline{R})$ vanishes. If, however, a periodic arrangement of a pair of atoms exists in the sample with a difference vector $\underline{R}$ between the positions, then the Patterson function will have an extremum for this vector $\underline{R}$. Thus the Patterson function reproduces all the vectors connecting one atom with another atom in a periodic arrangement.

2.3 Form-factor

So far we have not specified the nature of our sample. Now we assume an assembly of N scatterers of finite size, see figure 4.

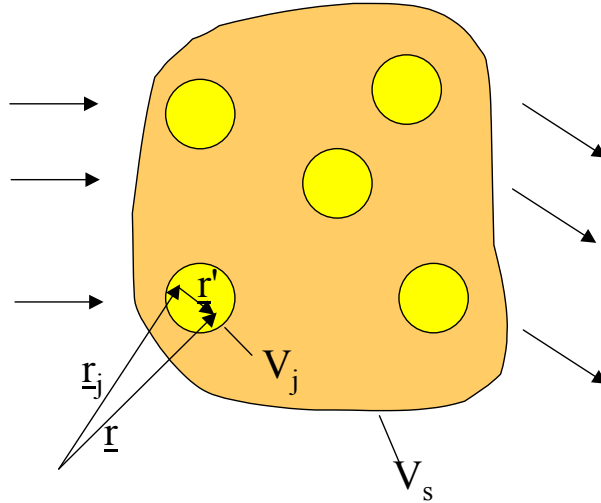


Fig. 4: Sketch showing the assembly of N scatterers of finite size and defining the quantities needed for the introduction of the form factor.

These could be atoms in a solid or colloidal particles in a homogeneous solution. In what follows, we will separate the interference effects from the scattering within one such particle from the interference effects arising from scattering from different particles. With the decomposition of the vector $\underline{r}$ into the center-of-gravity-vector $\underline{r}_j$ and a vector $\underline{r}'$ within the particle, the scattering amplitude can be written as:

$$\begin{aligned}
 A \propto \int_{V_S} d^3r \rho_S(\underline{r}) e^{i\mathbf{Q} \cdot \underline{r}} &= \sum_{j=1}^N \int_{V_j} d^3r \rho_S(\underline{r}) e^{i\mathbf{Q} \cdot \underline{r}} = \sum_{j=1}^N e^{i\mathbf{Q} \cdot \underline{r}_j} \int_{V_j^0} d^3r' \rho_S(\underline{r}') e^{i\mathbf{Q} \cdot \underline{r}'} \\
 \Rightarrow A &\sim \sum_{j=1}^N A_j(0) \cdot f_j(\underline{Q}) e^{i\mathbf{Q} \cdot \underline{r}_j}.
 \end{aligned} \tag{13}$$

The *form-factor* is defined as the normalised amplitude of scattering from within one particle:

$$f(\underline{Q}) \equiv \frac{\int_{V_j^0} d^3r' \rho_s(\underline{r}') e^{i\mathbf{Q} \cdot \underline{r}'}}{\int_{V_j^0} d^3r' \rho_s(\underline{r}')}. \tag{14}$$

For a homogeneous sphere

$$\rho_s(\underline{r}) = \begin{cases} 0 & |\underline{r}| > R \\ 1 & |\underline{r}| \leq R \end{cases}, \quad (15)$$

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

$$\Rightarrow f(Q) = 3 \cdot \frac{\sin QR - QR \cdot \cos QR}{(QR)^3}. \quad (16)$$

The function (16) is plotted in figure 5. In forward direction, there is no phase difference between waves scattered from different volume elements within the sample (note: we assume the Fraunhofer approximation and work in a far field limit). The form-factor takes its maximum value of one. For finite scattering angles 2θ , the form-factor drops due to destructive interference from various parts within one particle and finally for large values of the momentum transfer shows damped oscillations around 0 as a function of QR .

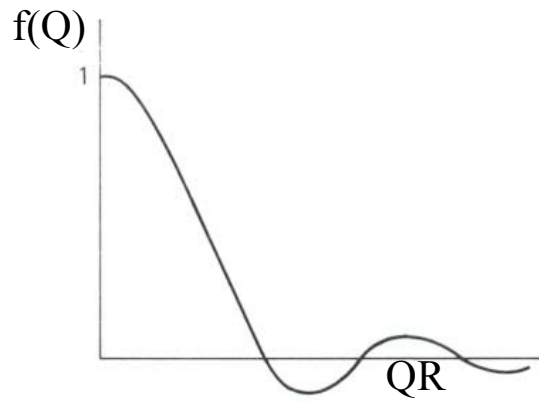


Fig. 5: Form-factor for a homogeneous sphere according to (16).

2.4 Scattering from a periodic lattice in three dimensions

As an example for the application of (8) and (9), we will now discuss the scattering from a three dimensional lattice of point-like scatterers. As we will see later, this situation corresponds to the scattering of thermal neutrons from a single crystal. More precisely, we will restrict ourselves to the case of a Bravais lattice with one atom at the origin of the unit cell. To each atom we attribute a scattering power α . The single crystal is finite with N , M and P periods along the basis vectors $\underline{a}$, $\underline{b}$ and $\underline{c}$. The scattering power density, which we have to use in (8) is a sum over δ -functions for all scattering centers:

$$\rho_s(\underline{r}) = \sum_{n=0}^{N-1} \sum_{m=0}^{M-1} \sum_{p=0}^{P-1} \alpha \cdot \delta(\underline{r} - (n \cdot \underline{a} + m \cdot \underline{b} + p \cdot \underline{c})). \quad (17)$$

The scattering amplitude is calculated as a Fourier transform:

$$A(\underline{Q}) \sim \alpha \sum_{n=0}^{N-1} e^{in\underline{Q} \cdot \underline{a}} \sum_{m=0}^{M-1} e^{im\underline{Q} \cdot \underline{b}} \sum_{p=0}^{P-1} e^{ip\underline{Q} \cdot \underline{c}}. \quad (18)$$

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

$$I(\underline{Q}) \sim |A(\underline{Q})|^2 = |\alpha|^2 \cdot \frac{\sin^2 \frac{1}{2} N \underline{Q} \cdot \underline{a}}{\sin^2 \frac{1}{2} \underline{Q} \cdot \underline{a}} \cdot \frac{\sin^2 \frac{1}{2} M \underline{Q} \cdot \underline{b}}{\sin^2 \frac{1}{2} \underline{Q} \cdot \underline{b}} \cdot \frac{\sin^2 \frac{1}{2} P \underline{Q} \cdot \underline{c}}{\sin^2 \frac{1}{2} \underline{Q} \cdot \underline{c}}. \quad (19)$$

The dependence on the scattering vector $\underline{Q}$ is given by the so-called *Laue function*, which separates according to the three directions in space. One factor along one lattice direction $\underline{a}$ is plotted in figure 6.

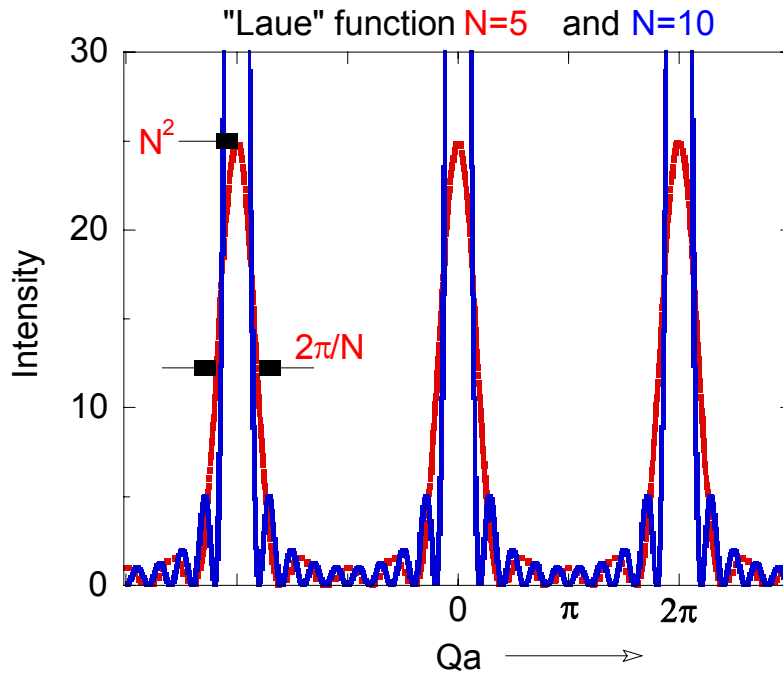


Fig. 6: *Laue function along the lattice direction $\underline{a}$ for a lattice with five and ten periods, respectively.*

The main maxima occur at the positions $Q = n \cdot 2\pi/a$. The maximum intensity scales with the square of the number of periods N^2 , the half width is given approximately by $\Delta Q = 2\pi/(N \cdot a)$. The more periods contribute to coherent scattering, the sharper and higher are the main peaks. Between the main peaks, there are $N-2$ site maxima. With increasing number of periods N , their intensity becomes rapidly negligible compared to the intensity of the main peaks. The main peaks are of course the well known *Bragg reflections*, which we obtain when scattering from a crystal lattice. From the position of these Bragg peaks in momentum space, the metric of the unit cell can be deduced (lattice constants a, b, c and unit cell angles α, β, γ). The width of the Bragg peaks is determined by the size of the coherently scattering volume (parameters N, M , and P) - and some other factors for real experiments (resolution, mosaic distribution, internal strains, ...).

3 Probes for Scattering Experiments in Condensed Matter Science

In this chapter, we will discuss which type of radiation is suitable for condensed matter investigations. For each radiation, we will then discuss the relevant interaction processes with matter separately. Finally, we will mention the radiation sources.

3.1 Suitable types of radiation

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

1. The achievable spatial resolution should be in the order of the inter-particle distances, which implies (see section 2.1) that the wavelength λ is in the order of the inter-particle distance L .
2. If we want to study volume effects, the scattering has to originate from the bulk of the sample, which implies that the radiation should be at most weakly absorbed within matter.
3. For a simple interpretation of the scattering data within the Born approximation (see chapter 2), multiple scattering effects should be negligible, i. e. the interaction of the radiation with matter should be weak.
4. For the sake of simplicity, the probe should have no inner degrees of freedom, which could be excited during the scattering process (i. e. avoid beams of molecules, which have internal vibrational or rotational degrees of freedom).
5. If, in addition to structural studies, we want to investigate elementary excitations, we would like the energy of the probe to be in the order of the excitation energies, so that the energy change during the scattering process is easily measurable.

This list of requirements leads us to some standard probes in condensed matter research. First of all, electromagnetic radiation governed by the Maxwell equations can be used. Depending on the resolution requirements, we will use x-rays with wavelength λ about 0.1 nm to achieve atomic resolution or visible light ($\lambda \sim 350 - 700$ nm) to investigate e. g. colloidal particles in solution. Besides electromagnetic radiation, particle waves can be used. It turns out that thermal neutrons with a wavelength $\lambda \sim 0.1$ nm are particularly well adapted to the above list of requirements. The neutron beams are governed by the Schrödinger equation of quantum mechanics. An alternative is to use electrons, which for energies of around 100 keV have wavelengths in the order of 0.005 nm. As relativistic particles, they are governed by the Dirac equation of quantum mechanics. The big drawback of electrons as a condensed matter probe is the strong Coulomb interaction with the electrons in the sample. Therefore neither the absorption, nor the multiple scattering effects can be neglected. However the abundance of electrons and the relative ease to produce optical elements predestinates them to imaging purposes (electron microscopy). Scattering experiments with electrons will not be further discussed here.

3.2 X-rays: Thomson scattering

X-rays are electromagnetic waves with wavelengths typically shorter than 1 nm. For electromagnetic waves, the relation between energy and wavelength is given by

$$E = h\nu = \frac{h \cdot c}{\lambda} \quad (20)$$

or in practical units

$$E[\text{keV}] = \frac{1.24}{\lambda[\text{nm}]} \quad (21)$$

i. e. x-rays with a wavelength of 0.1 nm have an energy of 12.4 keV. The corresponding elementary particle - the photon - is massless, has no charge, but spin 1. For a massless particle of spin 1, two polarisation states can be distinguished, corresponding to left or right circular polarised light. According to de Broglie, the relation between momentum p and wavelength λ is given by

$$\underline{p} = \hbar \underline{k}; p = h / \lambda. \quad (22)$$

Electromagnetic radiation has a very complex interaction with matter, as discussed in many quantummechanics, electrodynamics or atomic physics textbooks. Here we consider only the simplest interaction mechanism, which is also the one most relevant for x-ray scattering: the interaction of the electromagnetic wave via the Coulomb force with a free electron without spin. This interaction gives rise to the so-called classical *Thomson scattering*. The process is sketched in figure 7. The incident electromagnetic wave gives rise to an oscillating electric field at the position of the electron. Due to the Coulomb force, the electron will start an oscillatory movement. The accelerated charge gives rise to the re-radiation of electric dipole radiation.

It is straightforward to calculate the scattering cross section, starting from the classical equation of motion

$$-e \cdot \underline{E} = m \cdot \ddot{\underline{x}} \quad (23)$$

and inserting the correct time dependence for the electric field vector $\underline{E} = \underline{E}_0 \cdot e^{i(\omega t - \underline{k} \cdot \underline{r})}$.

The cross section can be written in the form

$$\frac{d\sigma}{d\Omega} = r_0^2 \cdot P(\theta) \quad (24)$$

where r_0 denotes the classical electron radius, $r_0 = e/m_e c^2 = 2.82 \text{ fm}$ and $P(\theta)$ is a polarisation dependent factor, corresponding to the typical Hertz dipole characteristic. For an unpolarised x-ray beam $P(\theta) = 1 + \cos^2 2\theta$.

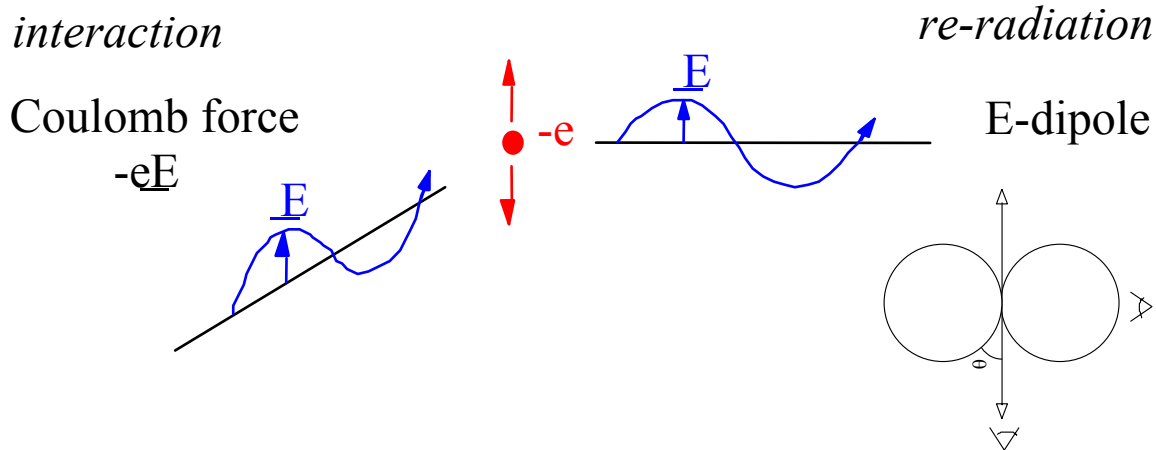


Fig. 7: Sketch showing the interaction of a free electron without spin with the incident electromagnetic wave via the Coulomb force. The insert explains the origin of the polarisation factor $P(\theta)$: an observer which looks precisely into the direction of movement of the electron cannot see the accelerated motion of the electron and does not observe any re-radiation. An observer in a plane perpendicular to the motion of the electron sees the full acceleration and thus observes the maximum intensity of re-radiation.

3.3 Light scattering

Light is electromagnetic radiation with a wavelength in the range 350 - 750 nm and (20) - (22) hold correspondingly. Quite in contrast to x-rays, the wavelength of light is about three orders of magnitude larger than a typical diameter of an atom. Therefore we can neglect the atomic structure and work in a continuum description. The propagation of light in matter is governed by the Maxwell equations and for a scattering process, we assume that there are no vacuum sources:

$$\begin{aligned}\underline{\nabla} \times \underline{H}(\underline{r}, t) &= \frac{\partial}{\partial t} \underline{D}(\underline{r}, t) \quad ; \quad \underline{\nabla} \cdot \underline{D} = 0 \\ \underline{\nabla} \times \underline{E}(\underline{r}, t) &= -\frac{\partial}{\partial t} \underline{B}(\underline{r}, t) \quad ; \quad \underline{\nabla} \cdot \underline{B} = 0.\end{aligned}\tag{25}$$

In our case of soft matter investigations, we can usually neglect the magnetic response

$$\begin{aligned}\underline{D}(\underline{r}, t) &= \underline{\epsilon}(\underline{r}) \cdot \underline{E}(\underline{r}, t) \\ \underline{B}(\underline{r}, t) &= \mu_0 \cdot \underline{H}(\underline{r}, t)\end{aligned}\tag{26}$$

and thus describe the properties of matter by the tensor of the dielectric constant $\underline{\epsilon}(\underline{r})$. Inhomogeneities are described by the spatial variation of the dielectric constant. Anisotropies lead to the fact, that the dielectric displacement vector $\underline{D}$ may not be parallel to the electric field strength $\underline{E}$. Our task is now to solve the Maxwell equations for the incident plane wave $\underline{E} = \underline{E}_0 \cdot \exp[i(\omega t - \underline{k} \cdot \underline{r})]$. Here we will just quote the solution for the case of light scattering from colloidal particles in a homogeneous solvent. For a detailed derivation we refer to [5]. The scattered amplitude is given by:

$$\underline{E}_s(\underline{r}, \underline{Q}) = \frac{k^2}{4\pi} \frac{e^{ikr}}{r} \underline{P}(\underline{k}') \cdot \sum_{j=1}^N \underline{B}_j(\underline{Q}) \cdot e^{i\underline{Q} \cdot \underline{r}_j} \cdot \underline{E}_0. \quad (27)$$

$\underline{E}_0$ is the amplitude of the incident wave. The scattering amplitude of a given particle j is denoted by $\underline{B}_j(\underline{Q})$. $e^{i\underline{Q} \cdot \underline{r}_j}$ is the phase factor for particle number j . $\underline{P}(\underline{k}')$ is a polarisation factor and e^{ikr}/r corresponds to the decrease of intensity with distance from the sample in the far field spherical wave limit.

If we refer to our simple scattering theory explained in chapter 2, we recognise all the factors appearing in (27). The main difference to our simple scalar scattering theory is the vector nature of the electromagnetic wave giving rise to polarisation effects. The polarisation can be changed during the scattering from each single particle and therefore, the scattering amplitude of the j^{th} particle, as well as the polarisation factor have to be tensors. Their explicit form is given by

$$\underline{P}(\underline{k}') = \underline{1} - \frac{\underline{k}' \underline{k}'}{k^2} \quad (28)$$

$$\underline{B}_j(\underline{Q}) = \int_{V_j} d^3r \frac{\underline{\epsilon}(\underline{r}) - \underline{1}\epsilon_f}{\epsilon_f} e^{i\underline{Q} \cdot \underline{r}}. \quad (29)$$

The quantity that we have called in chapter 2 "scattering strength density" corresponds to the expression $\rho_s(\underline{r}) \sim (\underline{\epsilon}(\underline{r}) - \underline{1}\epsilon_f)/\epsilon_f$, where ϵ_f is the dielectric constant of the solvent.

The scattering theory for light under the Born approximation is referred as the *Rayleigh-Gans-Debye-scattering theory* and in what follows, we will refer to the process as *Rayleigh light scattering*. (Note: the factor k^2 gives rise to a dependence of the emitted power on the fourth power of the frequency, which provides the explanation for the blue sky).

3.4 Neutron scattering

We mentioned in the introduction that neutron beams provide a particularly useful probe for condensed matter investigations. The neutron is an elementary particle, a nucleon, consisting of three valance quarks, which are hold together by gluons. It thus has an internal structure, which, however, is irrelevant for condensed matter physics. Keeping in mind the difference in lengths scales (diameter of an atom: about $0.1 \text{ nm} = 10^{-10} \text{ m}$; diameter of a neutron: about $1 \text{ fm} = 10^{-15} \text{ m}$), we can safely consider the neutron as point-like particles without internal structure for our purposes. Due to the weak interaction, the neutron is not a stable particle. A free neutron undergoes a β -decay after an average lifetime of about 15 minutes:



This leaves ample time for scattering investigations. In contrast to the massless photon, the neutron has a mass m of about one atomic mass units $\sim 1.675 \cdot 10^{-27} \text{ kg}$. The finite neutron mass is comparable to the mass of a nucleus and thus an appreciable amount of energy can be transferred during the scattering process. The neutron is a chargeless particle and thus does not show the strong Coulomb interaction with matter which results in large penetration depths. The neutron has a nuclear spin $1/2$ giving rise to a magnetic dipolar moment of

$$\mu_n = \gamma \mu_N; \quad \gamma = 1.91; \quad \mu_N = 5.05 \cdot 10^{-27} \text{ J/T} . \quad (31)$$

Due to this magnetic moment, the neutron can interact with the magnetic field of unpaired electrons in a sample leading to strong magnetic scattering. Thus magnetic structures and excitations can be studied by neutron scattering, a very important application outside of soft condensed matter research. To calculate the interference effects during the scattering process, a neutron has to be described as a matter wave with momentum

$$\underline{p} = m \cdot \underline{v} = \hbar \underline{k} = h / \lambda \quad (32a)$$

and energy

$$E = \frac{1}{2} m v^2 = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2} \equiv k_B T_{eq} \quad (32b)$$

where $\underline{v}$ is the velocity of the neutron and T_{eq} defines the temperature equivalent of the kinetic energy of the neutron. In practical units, (32) leads to:

$$\begin{aligned} \lambda[\text{nm}] &= \frac{400}{v[\text{m/s}]} \\ E[\text{meV}] &= \frac{0.818}{\lambda^2[\text{nm}]} \end{aligned} \quad (33)$$

Let us consider the example of so-called *thermal neutrons*, which are defined by $T_{eq} \sim 300 \text{ K}$. According to (33), their wavelength is 0.18 nm, matching perfectly the distance between atoms. The energy of thermal neutrons is around 25 meV, which matches well the energy of elementary excitations, such as spin waves (magnons) or lattice vibrations (phonons). Together with the usually large penetration depths (charge = 0) and the magnetic interaction, these properties make neutrons so extremely useful for condensed matter investigations.

We will now look at the neutron scattering cross section in some more detail. The dominant interactions of the neutron with matter are the magnetic dipole interaction of the neutron with the magnetic field of unpaired electrons, which we will no longer discuss in this lecture, and the strong interaction of the neutron with the nuclei. To calculate the cross section for neutron scattering, we are looking for a perturbative solution of the Schrödinger equation for the system "sample plus neutron beam". Here we cannot reproduce the full derivation of the form of the cross section and have to refer to [1, 2, 4] or to textbooks of quantum mechanics, e. g. [6]. An elegant way is the expansion into a *Born series*, which separates single, double, triple etc. scattering events. For a sufficient weak interaction, we can neglect all multiple scattering events and write the cross section in the *first Born approximation*:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = \frac{k'}{k} \left(\frac{m}{2\pi \hbar^2} \right)^2 \sum_a P_a \sum_{a'} \left| \langle \underline{k}', a' | V | \underline{k}, a \rangle \right|^2 \delta(\hbar\omega + E_a - E_{a'}) . \quad (34)$$

The various terms in this cross section can be understood as follows. The δ -function ensures energy conservation: the energy transfer onto the neutron $\hbar\omega$ has to be equal to the energy change within the sample $E_{a'} - E_a$. The term in front of the δ -function can be interpreted in terms of *Fermis' Golden Rule*. It's the magnitude square of the transition matrix element of the interaction potential V (nucleus $\leftrightarrow$ neutron) between the initial state of the system (neutron with wave vector $\underline{k}$, sample in the quantum state a) and the final state (neutron with wave vector $\underline{k}'$, sample in the state a'). In general, neither the initial nor the final state of the sample are pure states. Therefore we have to sum over all processes leading to different final states, but also to sum over the initial states with a weight P_a corresponding to the thermodynamical

occupation of state a of the sample. Finally the prefactor k'/k results from the density-of-state consideration in Fermis' Golden Rule.

To evaluate the cross section (34), we have to specify the interaction potential with the nucleus. To derive this interaction potential is one of the fundamental problems of nuclear physics. Fermi has proposed a phenomenological potential based on the argument that the wave length of thermal neutrons is much larger than the nuclear radius. This means that the nuclei are pointlike scatterers and lead to isotropic, Q -independent, (so-called s -wave) scattering. The same argument holds for classical Thomson scattering, where the only angular dependence came from a polarisation factor. We will therefore use the so-called *Fermi-pseudo-potential*:

$$V(\underline{r}) = \frac{2\pi\hbar^2}{m} b\delta(\underline{r} - \underline{R}) \quad (35)$$

to evaluate the cross section (34).

Note, that despite the fact that the strong interaction of high energy physics is responsible for the scattering of the neutron with the nucleus, the scattering probability is small due to the small nuclear radius. Therefore, we can apply the first Born approximation. The quantity b introduced in (35) is a phenomenological quantity describing the strength of the interaction potential and is referred to as the scattering length. The total cross section of a given nucleus is $\sigma = 4\pi|b|^2$, corresponding to the surface area of a sphere with radius b . Since the interaction potential obviously depends on the details of the nuclear structure, b is different for different isotopes of the given element and also for different nuclear spin states. This fact gives rise to the appearance of so-called *coherent* and *incoherent scattering*.

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

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= \left\langle \sum_i b_i e^{i\mathbf{Q}\cdot\mathbf{r}_i} \sum_j b_j^* e^{-i\mathbf{Q}\cdot\mathbf{r}_j} \right\rangle = \sum_i \sum_j \left\langle b_i b_j^* \right\rangle e^{i\mathbf{Q}\cdot(\mathbf{r}_i - \mathbf{r}_j)} \\ &= \langle b \rangle^2 \left| \sum_i e^{i\mathbf{Q}\cdot\mathbf{r}_i} \right|^2 + N \left\langle (b - \langle b \rangle)^2 \right\rangle \end{aligned} \quad (36)$$

The scattering cross section is the sum of two terms. Only the first term contains the phase factors $e^{i\mathbf{Q}\cdot\mathbf{r}}$, which result from the coherent superposition of the scattering from pairs of scatterers. This term takes into account interference effects and is therefore named *coherent scattering*. Only the scattering length averaged over the isotope and nuclear spin distribution enters this term. The second term in (36) does not contain any phase information and is proportional to the number N of atoms (and not to N^2 !). This term is not due to the interference of scattering from different atoms. It corresponds to the scattering from single atoms, which subsequently super impose in an incoherent manner (adding intensities, not amplitudes!). For this reason, the intensity is proportional to the number N of atoms. Therefore, the second term is called *incoherent scattering*. This situation is illustrated graphically in figure 8.

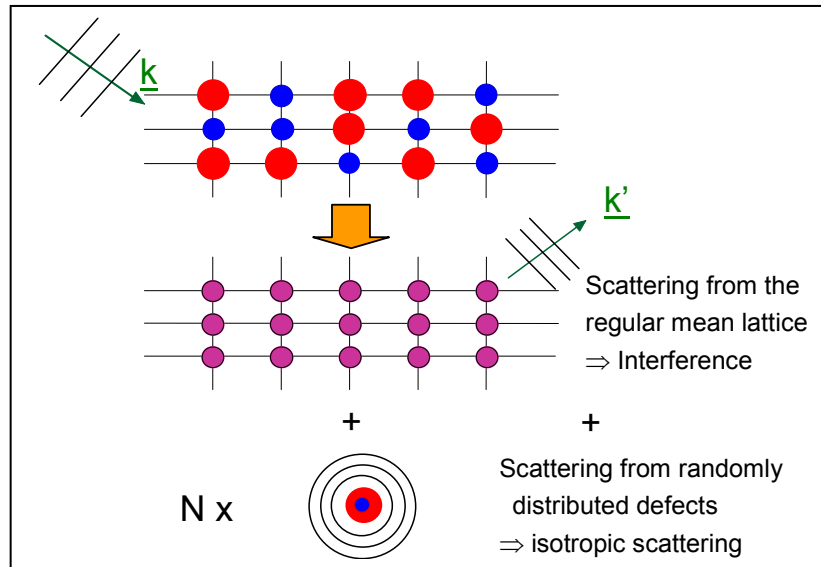


Fig. 8: Two dimensional illustration of the scattering process from a lattice of N atoms of a given chemical species, for which two isotopes (small blue circle and large red circle) exist. The area of the circle represents the scattering cross section of the single isotope. The incident wave, top part of the figure for a special arrangement of the isotopes, is scattered coherently only from the average lattice. This gives rise to Bragg peaks in certain directions. In the coherent scattering, only the average scattering length is visible. Besides these interference phenomena, an isotropic background is observed, which is proportional to the number N of atoms and to the mean quadratic deviation from the average scattering length. This incoherent part of the scattering is represented by the lower part of the figure.

In summary for each element we can define a coherent and an incoherent scattering cross section by the following equations:

$$\sigma_{\text{coh}} = 4\pi \langle b \rangle^2 \quad (37)$$

$$\sigma_{\text{inc}} = 4\pi \langle (b - \langle b \rangle)^2 \rangle. \quad (38)$$

The most prominent example for isotope incoherence is elementary nickel. The scattering lengths of the nickel isotopes are listed together with their natural abundance in table 1. The coherent and incoherent scattering cross sections can be calculated according (37) and (38) and are also given in table 1. The large incoherent cross section of nickel is mainly due to isotope incoherence.

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

$$\Rightarrow {}_{28}\text{Ni} : \sigma_{\text{coh}} = 13.3 \text{ barn} ; \sigma_{\text{inc}} = 5.2 \text{ barn}$$

Tab. 1: Scattering lengths for the nickel isotopes and resulting cross sections for natural Ni.

The most prominent example for nuclear spin incoherent scattering is elementary hydrogen. The nucleus of the hydrogen atom - the proton - has the nuclear spin $I = 1/2$. The total nuclear spin of the system $H + n$ can therefore adopt to values: $J = 0$ and $J = 1$. Each state has its own scattering length: $b_- = -47.5$ fm for the singlet state ($J = 0$) and $b_+ = 10.85$ fm for the triplet state ($J = 1$). With the relative weight $1/4$ and $3/4$ for the singlet and triplet state, respectively, the cross sections can be calculated according to (37) and (38) to be:

$$\Rightarrow {}_1\text{H}: \sigma_{\text{coh}} = 1.76 \text{ barn}; \sigma_{\text{inc}} = 80.26 \text{ barn}. \quad (39)$$

(39) shows that hydrogen scatters mainly incoherently. As a result, we observe a large background for all samples containing hydrogen.

3.5 Comparison of probes

Figure 9 shows a double logarithmic plot of the dispersion relation "wave length versus energy" for the three probes neutrons, electrons and photons (compare (20) and (32)). The plot demonstrates, how thermal neutrons of energy 25 meV are ideally suited to determine interatomic distances in the order of 0.1 nm, while the energy of x-rays or electrons for this wavelength is much higher. However with modern techniques at a synchrotron radiation source, energy resolutions in the meV-region become accessible even for photons of around 10 keV corresponding to a relative energy resolution $\Delta E/E \approx 10^{-7}$! The graph also shows that colloids with a typical size of 100 nm are well suited for the investigation with light of energy around 2 eV. These length scales can, however, also be reached with thermal neutron scattering in the small angle region. While figure 9 thus demonstrates for which energy-wave-length combination a certain probe is particularly useful, modern experimental techniques extend the range of application by several orders of magnitude.

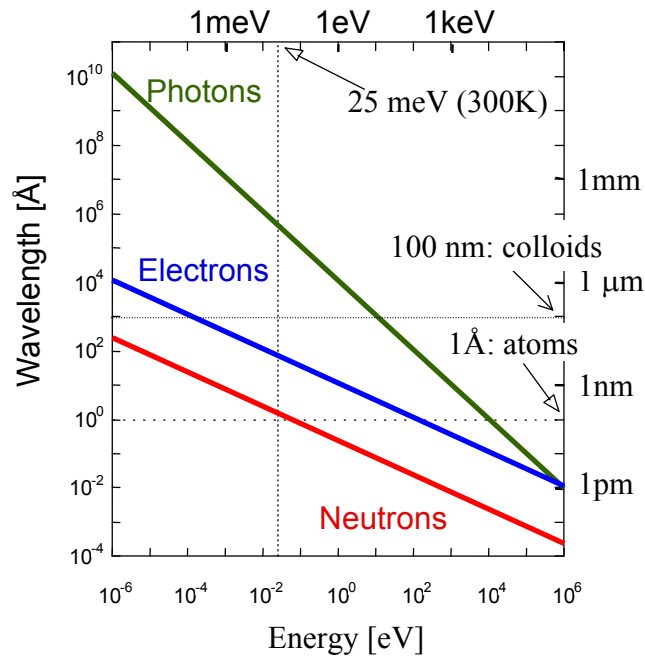


Fig. 9: Comparison of the three probes - neutrons, electrons and photons - in a double logarithmic energy-wave length diagram.

It is therefore useful to compare the scattering cross sections as it is done in figure 10 for x-rays and neutrons.

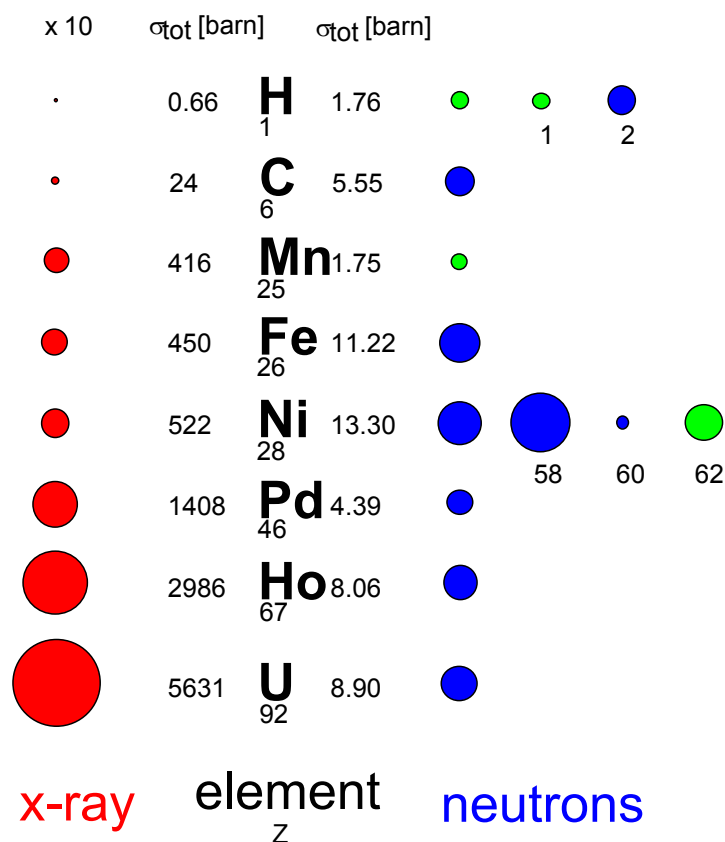


Fig. 10: Comparison of the scattering cross sections for x-rays and neutrons for a selection of elements throughout the periodic table. The area of the coloured circles represent the scattering cross section, where in the case of x-rays a scale factor 10 has to be applied. For neutrons, the green and blue coloured circles distinguish the cases where the scattering occurs with or without a phase shift of π .

Note that the x-ray scattering cross sections are in general a factor of 10 larger as compared to the neutron scattering cross sections. This means that the signal for x-ray scattering is stronger for the same incident flux and sample size, but that caution has to be applied that the conditions for kinematical scattering are fulfilled. For x-rays, the cross section depends on the number of electrons and thus varies in a monotonic fashion throughout the periodic table. Clearly it will be difficult to determine hydrogen positions with x-rays in the presence of heavy elements such as metal ions. Moreover, there is a very weak contrast between neighbouring elements as can be seen from the transition metals Mn, Fe and Ni in figure 10. For neutrons the cross sections depend on the details of the nuclear structure and thus varies in a non-systematic fashion throughout the periodic table. As an example, there is a very high contrast between Mn and Fe. The hydrogen atom is clearly visible even in the presence of such heavy elements as uranium. Moreover there is a strong contrast between the two hydrogen isotopes. This fact can be exploited for soft condensed matter investigations by selectively deuterating certain molecules or functional groups and thus varying the contrast within the sample.

3.6 Radiation sources

State of the art scattering studies require very well adapted radiation sources. Just like in a light scattering experiment lasers are used instead of simple light bulbs, modern x-ray scattering experiments are often performed at *high brilliance synchrotron radiation sources* instead of the conventional laboratory x-ray tube. Synchrotron radiation is produced in a circular accelerator. Highly relativistic electrons or positrons, which are stored in a storage ring, are being accelerated radially and as any accelerated charge emit electromagnetic radiation. Due to the Lorentz transformation, this radiation is highly collimated in the direction of the movement of the electron bunches. This leads to a number of excellent properties of synchrotron radiation depicted in figure 11. The synchrotron radiation beams have a broad wave length spectrum and thus allow to tune the wave length to the optimum conditions for the scattering experiment. The beams are highly collimated with divergencies in the order of 0.1 mrad and have a time structure in the 100 ps range. The synchrotron radiation beams are polarised (linearly in the orbital plane, elliptically above and below). Wigglers and undulators are magnet structures that force the electron beam into a sinusoidal movement and since synchrotron radiation is emitted at every magnet pole, the intensity is largely enhanced due to the number of poles.

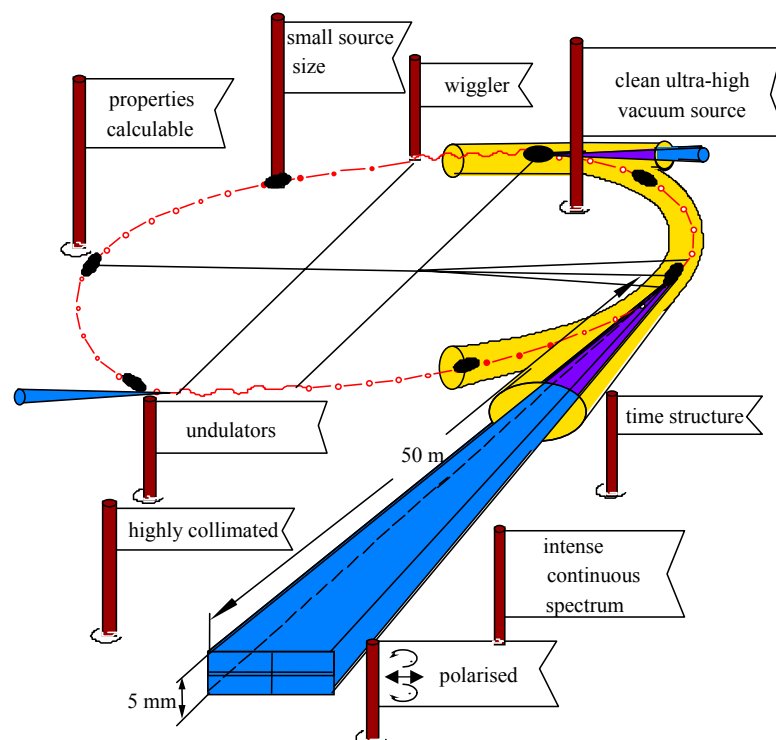


Fig. 11: Schematic sketch of a synchrotron radiation source.

Free neutrons are normally produced by fission processes in nuclear reactors. Through beam holes in the biological shieldings, neutrons are guided to the scattering experiments. Taking advantage of external total reflection, neutrons can be guided over long distances in so-called *neutron guides*, thus allowing a very efficient use of a neutron reactor by arranging further instruments in a neutron guide hall. The research center Jülich operates such a research reactor. The layout of the experimental facilities is depicted schematically in figure 12.

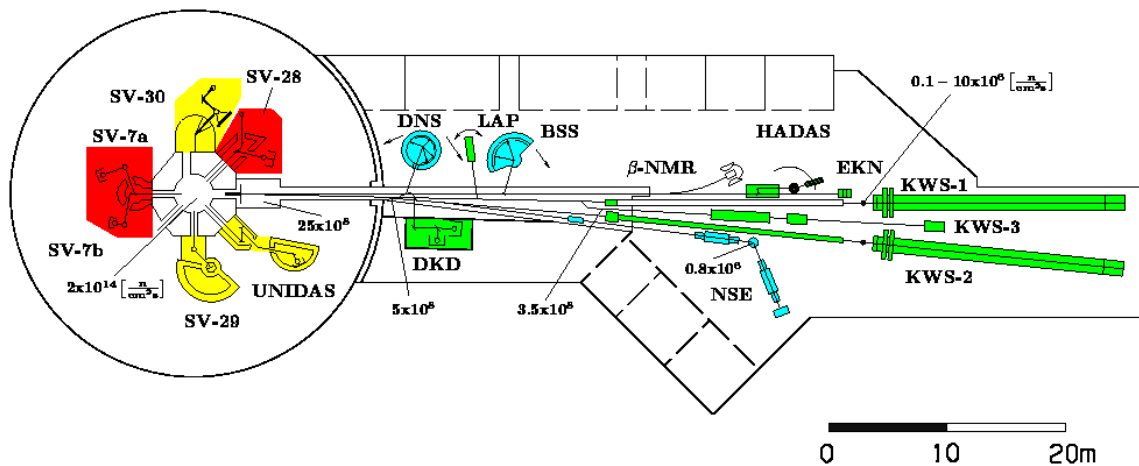


Fig. 12: Instrument arrangement for the research reactor FRJ-2 DIDO at the research center in Jülich. The neutron flux in the DIDO reactor operating at 20 MW is the order of $2 \cdot 10^{14} \text{ n/s cm}^2$. Elastic (red colour) and inelastic (yellow colour) neutron scattering experiments are arranged around the reactor core within the reactor hall. In a so-called cold source, the neutron spectrum is shifted to longer wave lengths and these neutrons are guided into an external guide hall, where they deserve again elastic (green) and inelastic (blue) neutron scattering experiments.

This facility is open to the use by guest groups from universities, industry and other research centers through a proposal system. Non-neutron-experts are supported by the instrument responsible during a neutron scattering experiment at such a service facility. Details for the access to neutron beams are described in the internet page "www.neutrons scattering.de", where one finds detailed instrument descriptions, a list of instrument responsible as contact persons, a description of the beamtime application procedure, conditions for travel reimbursement for EU-supported projects and a proposal form to download. The Forschungszentrum Jülich is also participating in an European project for a next generation neutron source, the so-called European Spallation Source (ESS). In such a source, neutrons are not produced in a nuclear chain reaction as fission products, but they are produced by the so-called *spallation process*, where a high energy proton beam hits a heavy metal target. When a proton of energy about 1 GeV is absorbed in a nucleus, the nucleus will evaporate about 10 - 20 neutrons per proton. Peak fluxes can be achieved, which are more than two orders of magnitude higher than at present day reactor sources. More information about the ESS-project can be found on the internet (www.ess-europe.de).

4 Fluctuations

So far, we have assumed a fixed static arrangement of scatterers. This gives rise to elastic scattering, where the intensity or cross section is directly proportional to the spatial pair correlation function or Patterson function of crystallography (compare (11) and (12)). In this chapter, we will generalise these results to the more realistic case, where density fluctuations in time are allowed. One example are colloidal particles in Brownian motion. Not surprisingly, we will have to deal with auto correlation functions in time and a general discussion of their properties is given in appendix A1.

4.1 Van Hove theory

In what follows, we will quote results of the so-called Van Hove theory for correlation functions in the case of neutron scattering. The derivation starts from the general form of the cross section (34). By rewriting the δ -function in an integral representation (Fourier transform) and introducing time-dependent Heisenberg operators, one can show [1, 2, 4] that the cross section for inelastic or quasielastic scattering takes the following form:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = \frac{k'}{k} N \left\{ \left(|\underline{b}|^2 - |\underline{b}|^2 \right) S_{\text{inc}}(\underline{Q}, \omega) + |\underline{b}|^2 S_{\text{coh}}(\underline{Q}, \omega) \right\}. \quad (40)$$

As discussed for the case of elastic scattering in section 3.4, the cross section separates into a coherent and incoherent part. In (40), we have introduced the so-called *coherent and incoherent scattering functions* $S_{\text{coh}}(\underline{Q}, \omega)$ and $S_{\text{inc}}(\underline{Q}, \omega)$. These functions depend solely on the system under investigation and not on the detailed interaction between its constituents and the probe. The strength of this interaction is represented by the coupling constants in front of the scattering functions. The scattering function is given by

$$S_{\text{coh}}(\underline{Q}, \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \int d^3r e^{i\underline{Q} \cdot \underline{r}} G(\underline{r}, t) \quad (41)$$

i. e. is a double Fourier transform of the spatial and temporal pair correlation function:

$$G(\underline{r}, t) = \frac{1}{N} \sum_{ij} \int d^3r' \left\langle \delta(\underline{r}' - \underline{r}_i(0)) \cdot \delta(\underline{r}' + \underline{r} - \underline{r}_j(t)) \right\rangle = \frac{1}{N} \int d^3r' \langle \rho(\underline{r}', 0) \rho(\underline{r}' + \underline{r}, t) \rangle. \quad (42)$$

Here, $\langle \dots \rangle$ denotes the thermal average. (42) shows that $G(\underline{r}, t)$ can be interpreted as the *correlator of the particle density*. Thus (40) - (42) represent a natural generalisation of the concept of a Patterson function discussed in section 2.2. Besides the scattering functions, which depend on scattering vector and energy transfer, it is often useful to introduce the *intermediate scattering functions*

$$S_{\text{inc}}(\underline{Q}, t) \equiv \frac{1}{N} \sum_i \left\langle e^{-i\underline{Q} \cdot \underline{r}_i(0)} \cdot e^{i\underline{Q} \cdot \underline{r}_i(t)} \right\rangle; S_{\text{coh}}(\underline{Q}, t) \equiv \frac{1}{N} \sum_{i,j} \left\langle e^{-i\underline{Q} \cdot \underline{r}_i(0)} \cdot e^{i\underline{Q} \cdot \underline{r}_j(t)} \right\rangle \quad (43)$$

which are related to the scattering function by a Fourier transform:

$$S_{\text{inc}}(\underline{Q}, \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt e^{-i\omega t} S_{\text{inc}}(\underline{Q}, t). \quad (44)$$

The incoherent scattering function is given by a double Fourier transform

$$S_{\text{inc}}(\underline{Q}, \omega) = \frac{1}{2\pi\hbar} \int dt e^{-i\omega t} S_{\text{inc}}(\underline{Q}, t) = \frac{1}{2\pi\hbar} \int dt e^{-i\omega t} \int d^3r e^{i\underline{Q} \cdot \underline{r}} G_s(\underline{r}, t) \quad (45)$$

of the *self correlation function*

$$G_s(\underline{r}, t) = \frac{1}{N} \sum_i \int d^3r' \left\langle \delta(\underline{r}' - \underline{r}_i(0)) \cdot \delta(\underline{r}' + \underline{r} - \underline{r}_i(t)) \right\rangle. \quad (46)$$

In a natural generalisation of the situation for static scattering, the coherent scattering arises from the correlation of a pair of particles, while the incoherent scattering arises from scattering from single particles (see figure 13).

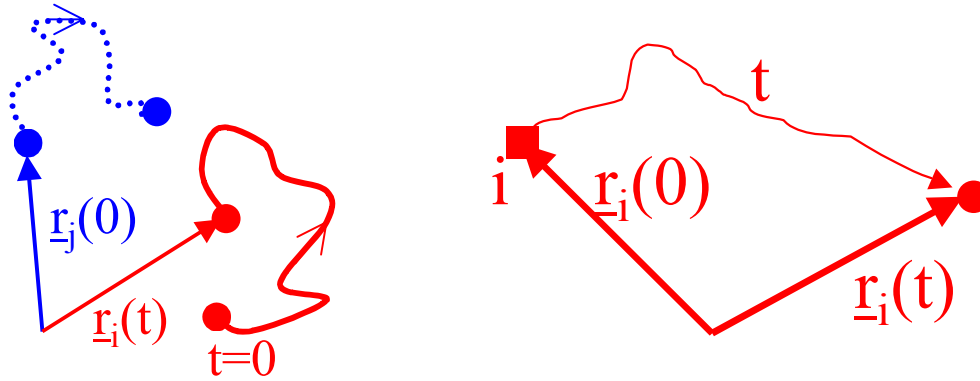


Fig. 13: Illustration of the correlations responsible for coherent scattering (left) and incoherent scattering (right). In the case of coherent scattering, the position of particle j at time 0 is correlated with the position of particle i at time t, while in incoherent scattering the movements of the individual particles are visible.

Let us finally discuss the case of so-called *integral scattering*, where the experimental conditions are such that the energy change during the scattering process is not resolved, but instead an integration over all energies is being performed. This scattering function for integral scattering $S(\underline{Q})$ is given by (here we drop the distinction between coherent and incoherent scattering for simplicity):

$$S(\underline{Q}) = \int_{-\infty}^{\infty} S(\underline{Q}, \omega) d\omega = \frac{1}{2\pi\hbar} \int dt \int d\omega e^{-i\omega t} \int d^3r e^{i\underline{Q} \cdot \underline{r}} G(\underline{r}, t) = \int d^3r e^{i\underline{Q} \cdot \underline{r}} G(\underline{r}, 0) \quad (47)$$

(47) shows that with integral scattering, the instantaneous correlations are being measured: a snap shot of the sample at time $t = 0$ is observed.

Correlation functions are rather abstract concepts and we want to illustrate them for the example of a simple liquid. The constituents of this liquid (atoms, molecules) are assumed to be spherical particles, which have a strong repulsive interaction potential for short distances and an attractive one for larger distances (see figure 14). The minimum in the interaction potential will give rise to a preferred nearest neighbour distance. Due to the hardcore potentials, the spheres cannot penetrate into each other and produce the excluded region in the pair correlation function for small distances r . This naturally explains the shape of the $t = 0$ correlation function, depicted in figure 14. The scattering function for integral scattering is obtained via a Fourier transform and is also depicted in figure 14.

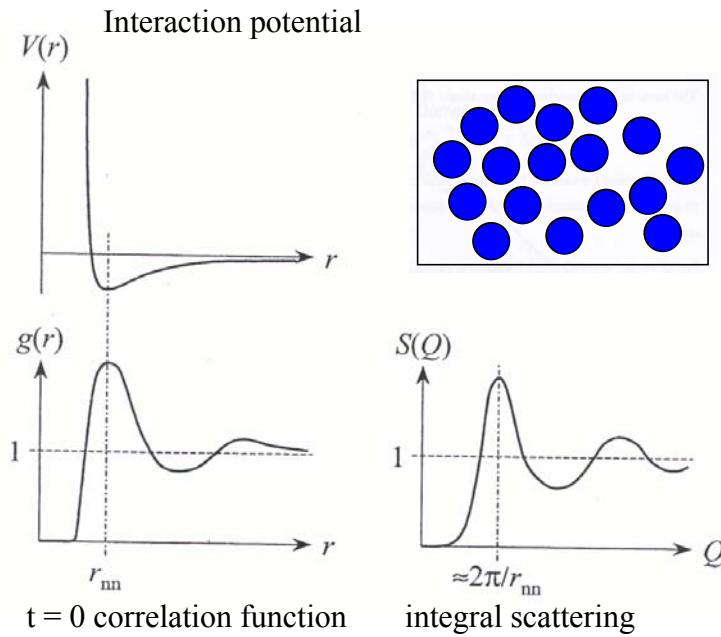


Fig. 14: Snap shot (top right), pair interaction potential (top left), $t = 0$ correlation function (bottom left) and the scattering function for integral scattering (bottom right) for a simple liquid.

Let us now look at the time dependence of the pair correlation and self correlation functions (see figure 15).

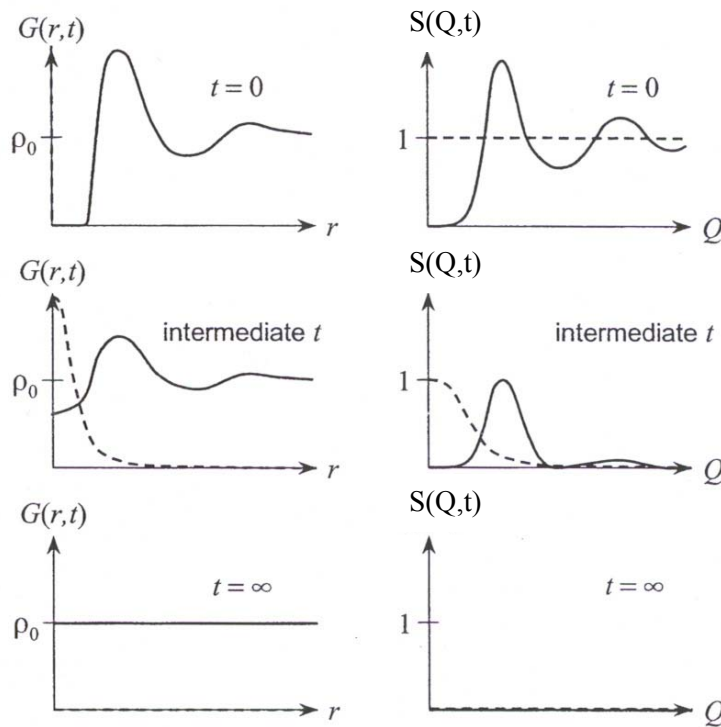


Fig. 15: Schematic plot of the pair correlation (solid line) and self correlation functions (dotted line) on the left and the resulting intermediate scattering functions on the right for a simple liquid at different times.

For $t = 0$ the self correlation function is given by a δ -function at $r = 0$. The pair correlation function follows the static correlation function. For intermediate times, the self correlation function broadens to a bell-shaped function due to the diffusion process, while the pair correlation function loses its structure. Finally in the long time limit, the self correlation simply vanishes for a liquid while the pair correlation function assumes a constant value. The incoherent intermediate scattering function as the Fourier transform of the self correlation function is Q -independent at $t = 0$, decays for intermediate t with respect to the $t = 0$ value, where the decay is faster for higher Q , and finally vanishes in the long time limit. The coherent scattering function is given by the static coherent scattering function for $t = 0$. It decays for intermediate times with respect to the $t = 0$ value, but the decay is less pronounced at the structure factor maximum. In the long time limit, the coherent scattering function decays to zero for any Q just as the incoherent scattering function.

Let us return to the case of integral scattering from a simple liquid. We make the simplification that the liquid consists of identical spherical and isotropic particles. Then it is easy to show [1, 4] that the intensity is given by

$$\Rightarrow I_{\text{static}} \sim |f(Q)|^2 \cdot \left\{ 1 + \bar{\rho} \int_{V_s} d^3R \, g(\underline{R}) e^{i\mathbf{Q} \cdot \underline{R}} \right\} \equiv |f(Q)|^2 \cdot S(Q) \quad (48)$$

i. e. the intensity for static scattering separates into a pre-factor depending on the experimental geometry and the type of radiation, the square of a form factor, which describes scattering from a single particle, and the scattering function (for the static case often referred to as *structure factor*), which contains information on the particle correlation and is independent of the type of radiation used. The structure factor gives an average snap shot picture $g(\underline{R})$ of the sample. As an example, figure 16 shows the structure factor of liquid ^{36}Ar at 85 K. The points are deduced from a neutron scattering experiment, the curve is generated by a molecular dynamics calculation using a Lennard-Jones potential. The insert shows the pair correlation function $g(R)$ of liquid Ar calculated by a Fourier transform of the data [7].

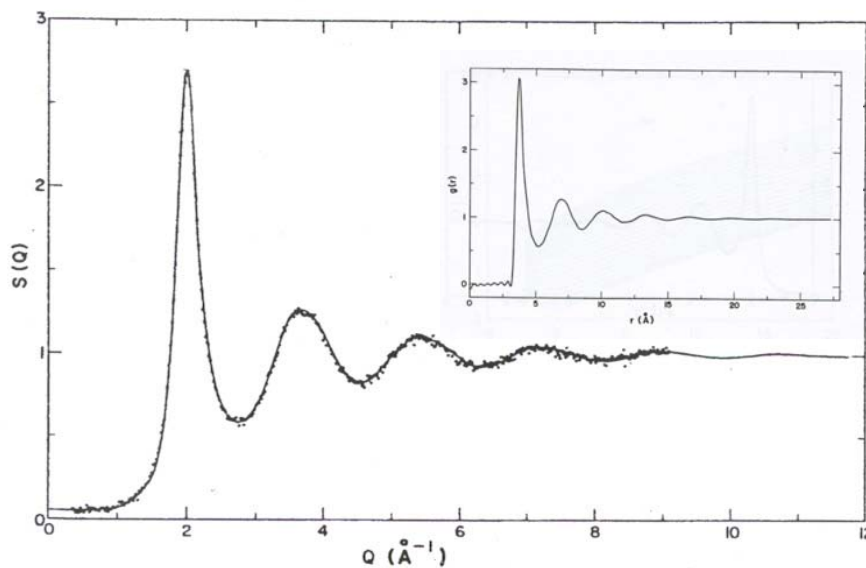


Fig. 16: Static scattering function for liquid ^{36}Ar at 85 K and resulting pair correlation function (insert) [7].

4.2 Inelastic light scattering

We have seen in section 4.1 that inelastic or quasielastic scattering is related to density fluctuations. An instructive example is given by a sound wave in a simple liquid. The sound wave will give rise to periodic density modulations travelling through the sample (see figure 17 for a static snap shot). For static density modulations, we expect with a hand waving argument "diffuse Bragg scattering" to occur under an angle giving by $Q = 4\pi / \lambda \cdot \sin \theta = 2\pi / \Lambda_{\text{soundwave}}$. The soundwave can be understood as a moving pattern of periodic density modulations. In a wave picture, this will give rise to a Doppler shift of the emitted wave. In a particle picture, the scattered particles will receive the recoil energy from the sound wave particles. We can determine the dispersion relation by considering momentum- and energy conservation for this collective excitation:

$$\begin{aligned}\hbar \underline{k}' &= \hbar \underline{k} - \hbar \underline{Q} \\ \hbar \omega' &= \hbar \omega - \hbar \omega_{\text{CE}}\end{aligned}\tag{49}$$

Such elementary excitations can be measured with different probes. Here, we will discuss the case of inelastic light scattering. Visible light has a characteristic frequency of $10^{14} - 10^{15}$ Hz. The frequency shift in the scattered light can be analysed either by an optical grating monochromator, if the frequency shifts are rather large ($> 10^{11}$ Hz) or a Fabry-Perot-interferometer for rather small frequency shifts ($10^7 - 10^{12}$ Hz). The technique using optical gratings is referred to as *Raman spectroscopy*, while the technique employing an interferometer is referred to as *Brillouin spectroscopy*. A typical energy spectrum for an elementary excitation such as a sound wave would then for a given momentum transfer consist in a central elastic *Rayleigh line* accompanied by two inelastic lines for energy loss and energy gain, referred to as the *Stokes and Anti-Stokes* line, respectively.

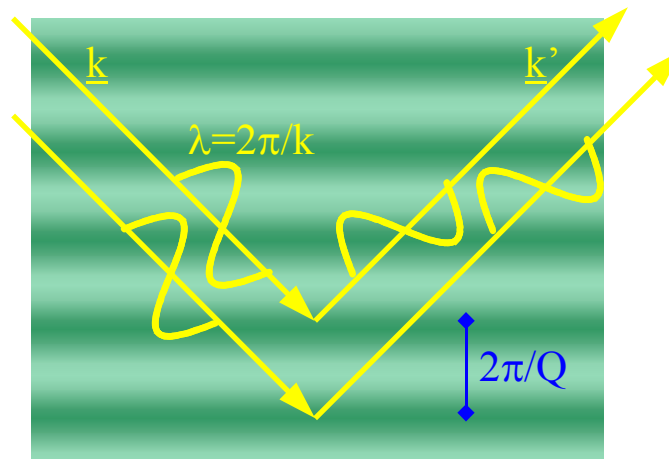


Fig. 17: The scattering from density fluctuations can be visualised as "diffuse Bragg scattering".

4.3 Inelastic neutron scattering

There are many techniques, which allow to measure the double differential cross section by means of neutron scattering. For a more detailed discussion, we refer to [1]. Here we just

want to give two examples most relevant for soft condensed matter research: *time-of-flight* (TOF) and *neutron spin echo* (NSE) spectroscopy.

A neutron time-of-flight spectrometer is depicted schematically in figure 18.

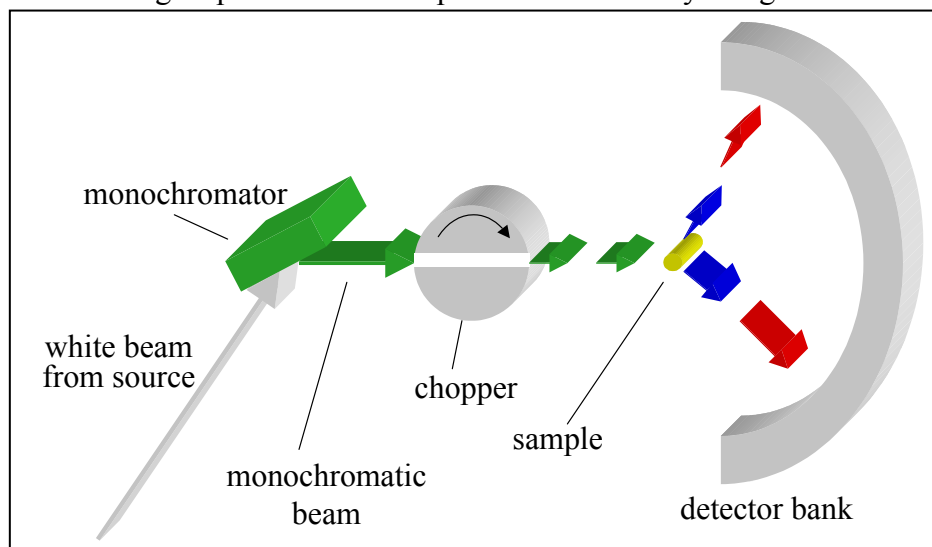


Fig. 18: A schematic sketch of a neutron time-of-flight spectrometer.

The white continuous neutron beam from a reactor source is monochromatised by Bragg reflection from a single crystal. By means of a rotating neutron absorbing drum with one slit opening, the beam is chopped into small portions in time. Such a device, which opens the beam pass periodically for a short moment, is called a *neutron chopper*. These neutron pulses travel to the sample, are scattered from the sample and are detected in a detector bank, covering as large solid angle around the sample as possible. From the travelling time of the neutron from the chopper to the detector, the average speed of the neutron and from (32), the energy change of the neutron during the scattering process can be determined. Finally from the positions in the detector and the energy transfer, the momentum transfer for each given neutron can be calculated. The histogram "neutron countrate versus energy and momentum transfer" finally gives us a measure for the double differential neutron scattering cross section.

The limitation of the time-of-flight method arises from the finite energy resolution determined by the uncertainties in the distances and the monochromaticity of the beam. Slow movements of large molecules evidently give rise to relatively small energy transfers. To measure small energy transfers, we have to increase the energy resolution by increasing the monochromaticity and reducing the sample size. Evidently, we will reduce the neutron countrate, which poses a natural limit to the energy resolution of a time-of-flight machine. Typically the energy resolution $\Delta E/E$ of a time-of-flight spectrometer amounts to some 1 %.

How can we improve the energy resolution without reducing the neutron flux? The solution is to use the property that the neutrons carry a magnetic dipole moment and thus undergo a neutron spin precession in a magnetic field. If we can conceive a time-of-flight method, where we use the neutron spin precession as an individual clock for each individual neutron, we can, in principle, use a broad wave length band (about 10 %) and still obtain an energy resolution

up to the neV range. This principle is realised in the so-called *neutron spin echo (NSE) spectrometer*. A sketch of the experimental set up is shown in figure 19.

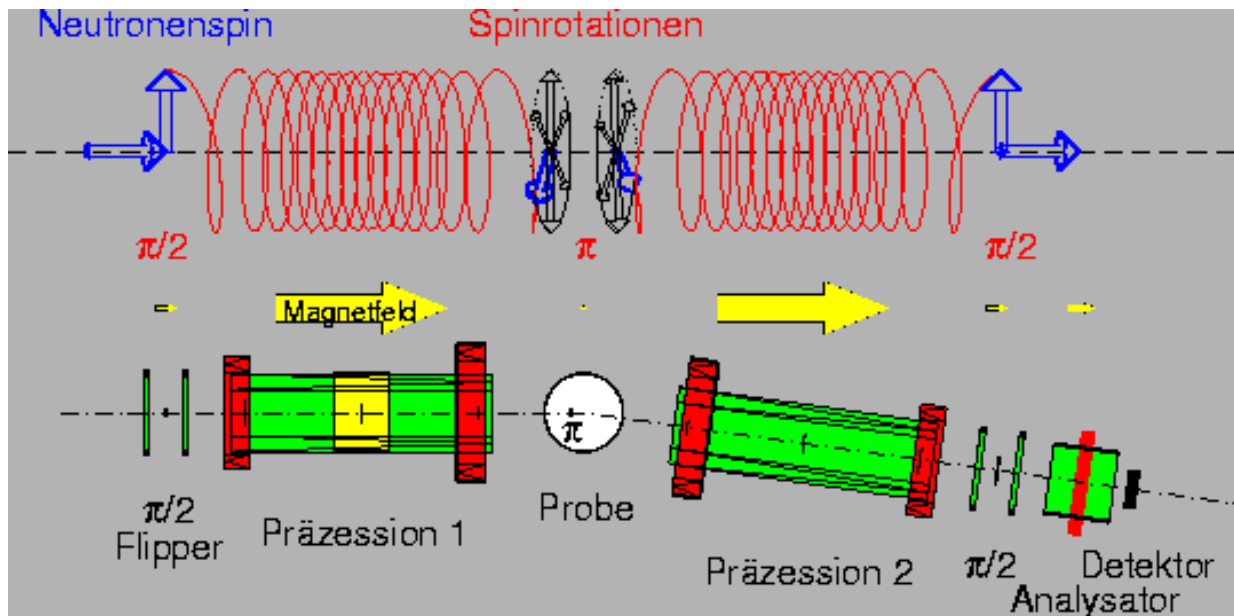


Fig. 19: Spin rotations and set up of a NSE spectrometer (from Monkenbusch in [2]). In the upper part, the spin precession in the magnetic field shown in the middle part is depicted schematically. The lower part shows a schematic set up of the neutron spin echo spectrometer realised at Forschungszentrum Jülich.

A "pink" neutron beam with a wavelength spread of $\Delta\lambda/\lambda \approx 10\%$ is being polarised, i. e. all the neutron spins point in the same direction, eventually perpendicular to the longitudinal magnetic field. The neutrons traverse a region of homogeneous magnetic field, where they undergo a number of spin precessions (typically 10^4 rotations) in one precession coil of about 3 m length. Neutrons with different velocities spent different times in this field region and thus undergo a different number of spin rotations. Therefore the neutron beam arriving at the sample positions is depolarised. To illustrate the principle, we first assume elastic scattering at the sample. After the scattering events, the spins are flipped by an angle of 180° around a vertical axis by the so-called π flipper. Then they traverse a field region of exactly the same field strength and length as in the primary arm of the spectrometer. The neutrons now undergo the same spin precessions as in the primary arm just in the opposite sense. Therefore all neutrons with different velocities have the same spin orientation after the precession field: the polarisation is fully restored. By means of a polarisation analyser and detector unit, the polarisation of the scattered beam can now be measured. If inelastic scattering occurs at the sample, the polarisation will not be recovered for a completely symmetric arrangement of primary and secondary arm. Only if the field strength in the secondary coil is varied, the resonance condition can be restored. An oscillatory behaviour of the count rate as a function of the current in the secondary coil is observed (see figure 20).

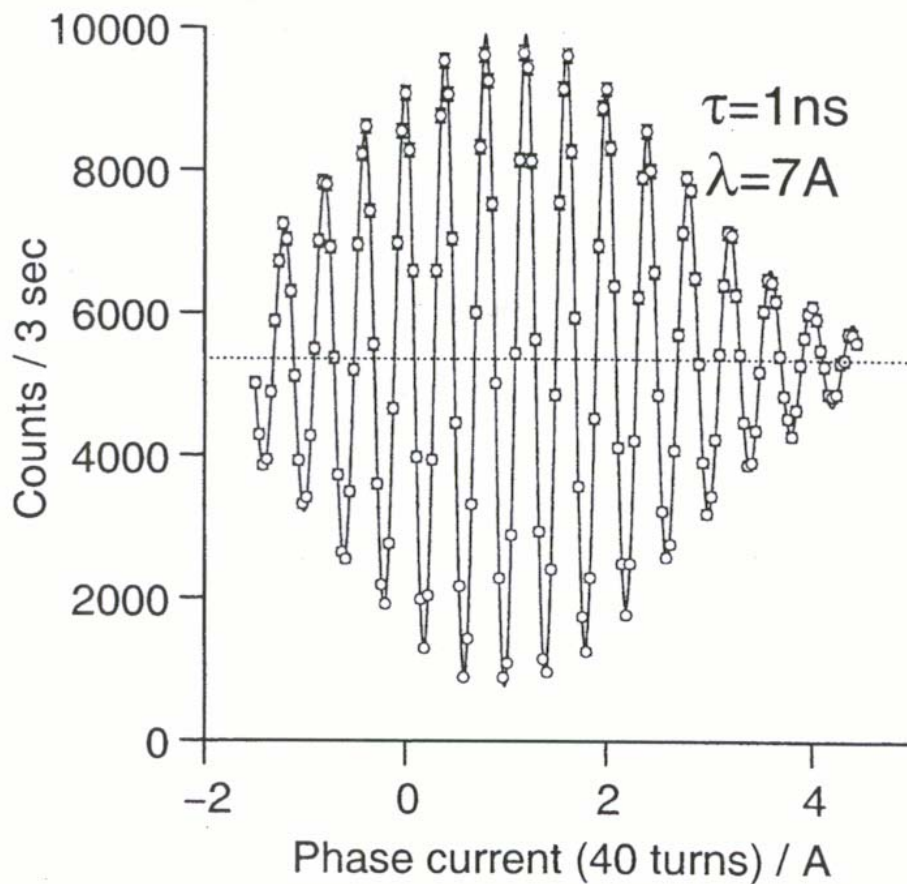


Fig. 20: Example for a typical echo line shape (Monkenbusch, [2]): countrate as function of the magnetic symmetry proportional to the phase current.

In fact, a neutron spin echo spectrometer measures the intermediate scattering function with the time being proportional to the field integral

$$\frac{I(\underline{Q}, t)}{I(\underline{Q}, 0)} = \frac{S(\underline{Q}, t)}{S(\underline{Q})} \quad \text{with} \quad t = \gamma \cdot \int B dl \cdot \frac{m_n^2}{2\pi\hbar^2} \cdot \lambda^3. \quad (50)$$

A typical example of the NSE technique comes from the field of polymer dynamics. In the simplest model for the movement of a polymer chain in a melt, one assumes that the different chains are not hindering each others movements. Entropic forces determine the movement of a single polymer chain. This is the so-called *Rouse model*. However, for longer times, a given chain will feel the restrictions imposed by the other chains encircling it. The motion of a chain in a melt is heavily impeded in directions lateral to its own profile. Therefore the dominant diffusive motion proceeds along the chain profile. The chain will move through the melt like a snake, which gave the name to this *reptation model* of de Gennes. With neutron spin echo techniques, the Rouse dynamic for short times and the cross-over to the reptation model by de Gennes for longer times could be observed (see contribution C2 by D. Richter in this lecture course and figure 21).

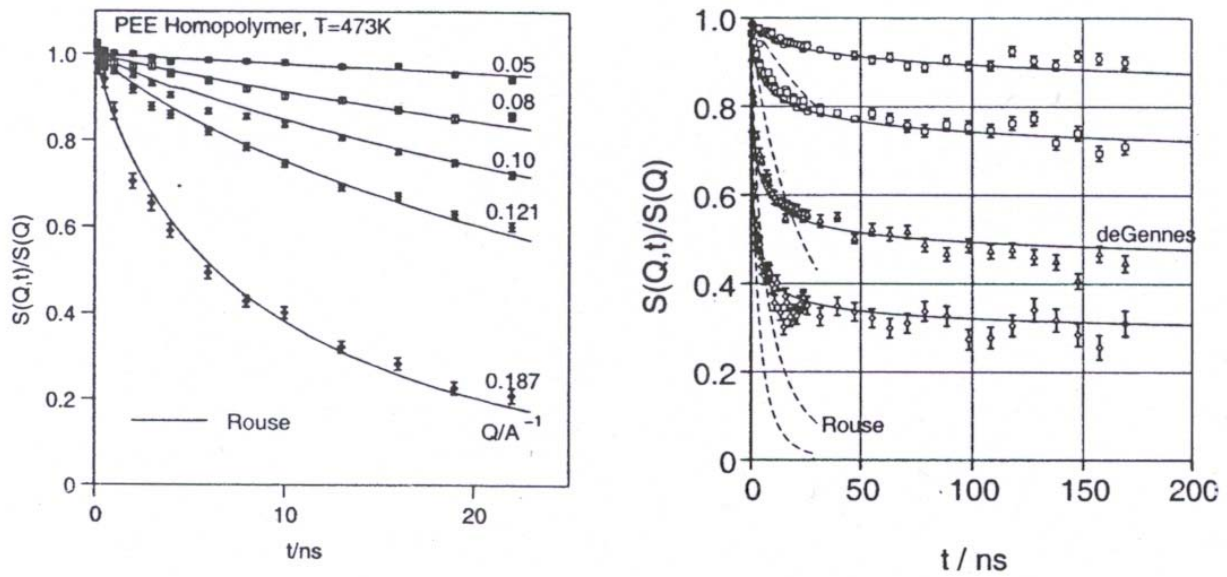


Fig. 21: NSE observation of Rouse dynamics for short times (left figure; points are experimental, the lines represent the theory for the rouse model) and the cross-over to the reptation model for longer times (right hand side; solid line: reptation model; dashed line: Rouse model).

4.4 Dynamic light scattering

In section 4.2 we have seen that with inelastic light scattering, where we measure with spectroscopic methods the frequency power spectrum of the auto correlation function, we can observe dynamics from optical frequencies (10^{14} Hz) down to some $10^6 - 10^7$ Hz. With neutron spin echo spectroscopy, this frequency range can be extended by about one order of magnitude. In this section we want to ask the question how we can observe even slower dynamics.

The answer is to measure the time evolution of the instantaneous correlation function, i. e. by measuring an integral spectrum at a given time all fast processes have relaxed and we are left with the slow dynamics. In dynamic light scattering, one measures the normalised intensity auto correlation function (IACF):

$$\hat{g}_I(\underline{Q}, t) := \langle I(\underline{Q}, 0) \cdot I(\underline{Q}, t) \rangle / I^2. \quad (51)$$

In practise the detector is positioned at a given scattering angle corresponding to a momentum transfer $\underline{Q}$. The intensity fluctuations in the detector are determined and an auto correlation function is calculated according to appendix A1. This auto correlation function is normalised to the square of the average intensity I in the detector. However, in section 3.3 and 4.1, we have learnt that the quantity of interest is actually the auto correlation function of the electric field (EACF). The normalised EACF is given by

$$\hat{g}_E(\underline{Q}, t) := \frac{1}{2} \sqrt{\frac{\epsilon_F}{\mu_0}} \langle E_S(\underline{Q}, 0) \cdot E_S^*(\underline{Q}, t) \rangle / I. \quad (52)$$

Since the electric field $E_S^*(\underline{Q}, t)$ is related to the scattering power density via the Fourier transform, the EACF is related to the intermediate scattering function. It can be shown that the intensity auto correlation function and the electric field auto correlation function are connected by the so-called *Siegert relation*:

$$\hat{g}_I(\underline{Q}, t) = 1 + |\hat{g}_E(\underline{Q}, t)|. \quad (53)$$

Thus by an experimental determination of the intensity auto correlation function, we get access to the Fourier transform of the density auto correlation function, which is the quantity of interest.

Let us discuss an example for photon correlation spectroscopy. We have chosen the scattering of coherent 8.2 keV x-rays from a synchrotron radiation source by porous silica gel. When the sample is illuminated by the coherent x-ray beam, we observe on the area detector a so-called speckle pattern (figure 22), which is due to the instantaneous density modulations within this sample.

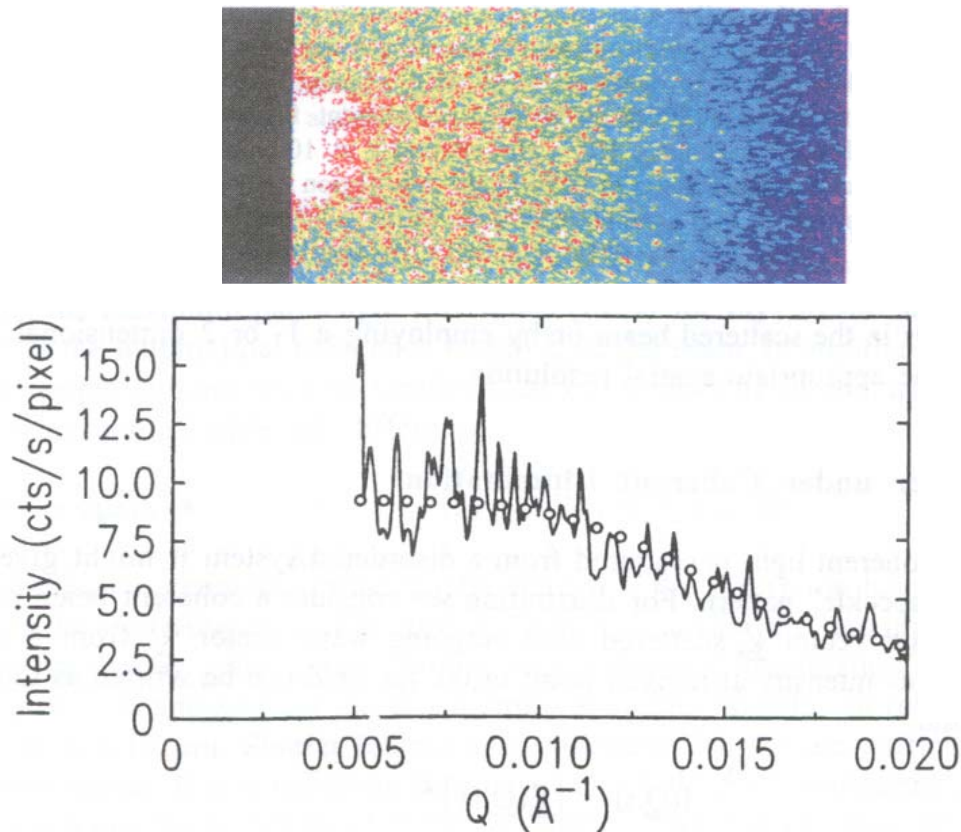


Fig. 22: Speckle pattern from an aerogel recorded with a CCD detector using coherent x-rays [8]. The speckle structure becomes better visible, if one pixel row in the horizontal direction is plotted (continuum line in the bottom picture).

For an inhomogeneous sample with a density distribution constant in time, we will observe a static speckle pattern. However for a sample, which has internal slow dynamics, the speckle

pattern will change with time and we can observe the intensity in a given direction with a small pinhole or within one pixel of an area detector. From the Siegert relation, we can deduce the time dependence of the intermediate scattering function. This function is depicted for colloidal silica, suspended in a solvent (water glycerol mixture) in figure 23.

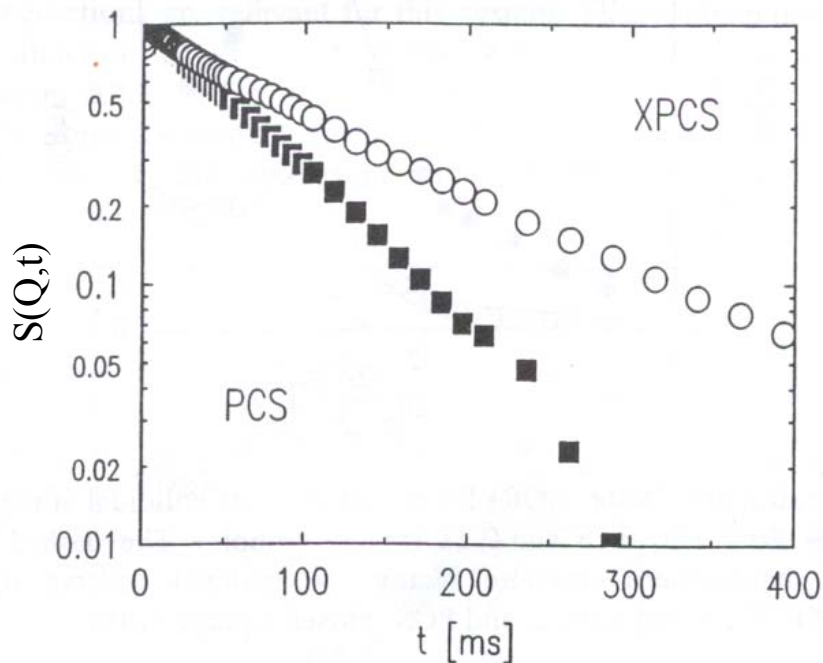


Fig. 23: Intermediate scattering function measured by x-ray photon correlation spectroscopy XPS (open circles) and optical photon correlation spectroscopy (closed squares) for the same momentum transfer $Q = 9 \cdot 10^{-4} \text{ \AA}^{-1}$ in an optically opaque sample of colloidal silica [8].

An exponential decay can be fitted to the XPCS measurement and the translational diffusion coefficient can be determined. Figure 22 shows that the PCS intermediate scattering function relaxes faster as compared to the XPCS data. The authors attribute this effect to multiple scattering events, which are present in the optical experiment.

5 Summary

An introduction into the investigation of soft condensed matter systems by scattering methods has been given. We have seen that neutrons, light and x-rays are particularly useful for such studies. However independent of the probe, coherent scattering always measures pair correlation functions and the scattering cross section is proportional to the spatial and temporal Fourier transform of these correlation functions.

Condensed matter investigations face the problem that relevant lengths and time scales cover many orders of magnitude. Figure 24 gives an overview over the characteristic time scales found in condensed matter investigations. These time scales range from the fs regime for fast electronic excitations up to macroscopic time scales for relaxation processes in glasses or spin glasses.

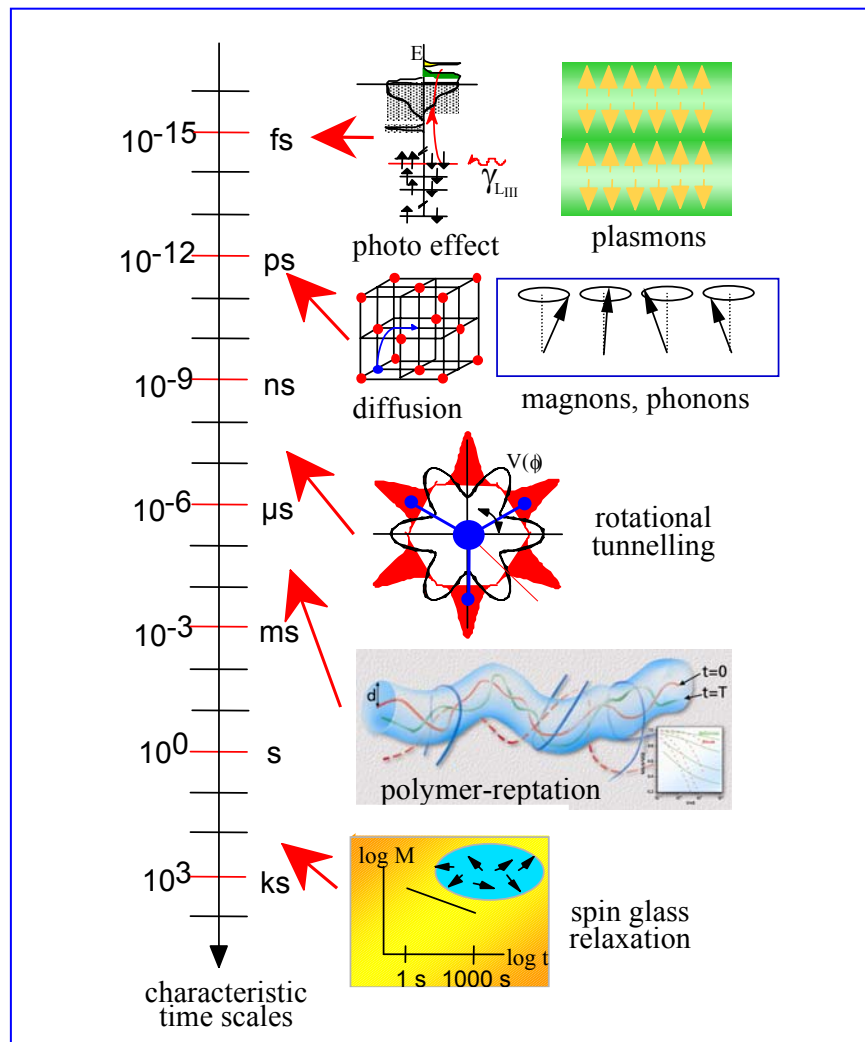


Fig. 24: Characteristic time scales found in condensed matter research.

With appropriate scattering methods, all these processes on different time scales can be investigated. Which scattering method is appropriate for which region within the "scattering vector Q - energy E plane" is plotted schematically in figure 25. A scattering vector Q corresponds to a certain length scale, an energy to a certain frequency, so that the characteristic lengths and times scales for the various methods can be directly determined from figure 25.

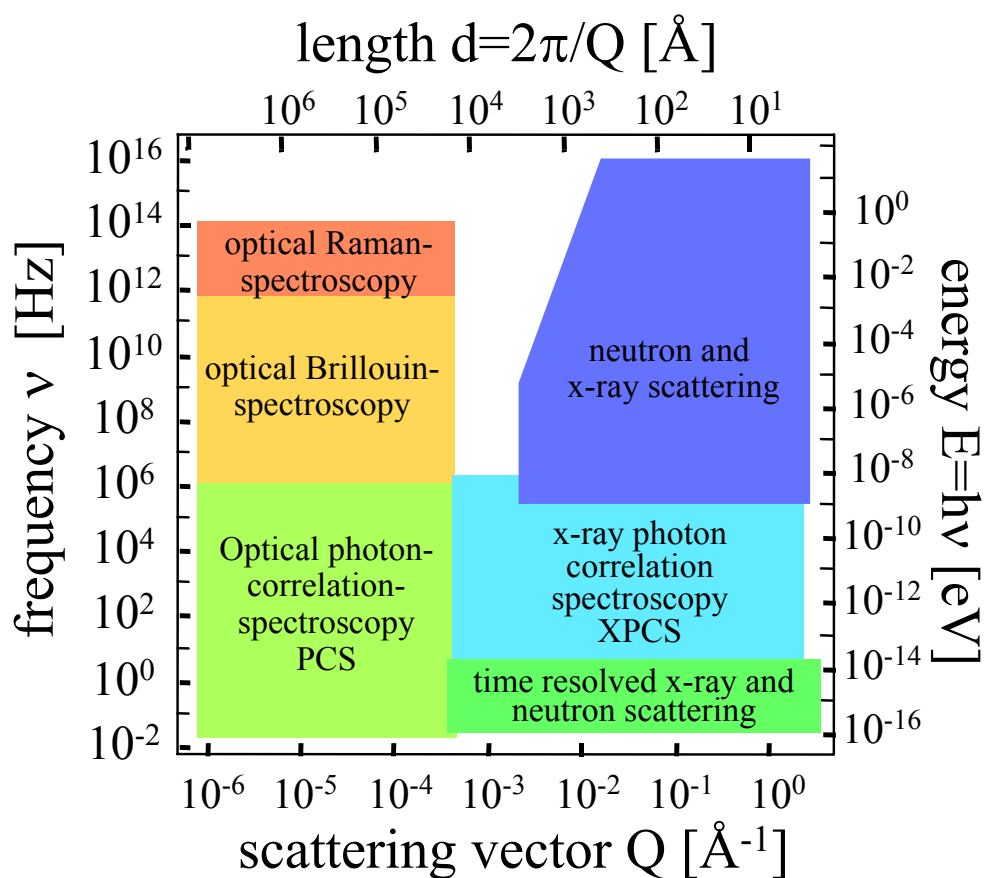


Fig. 25: Regions in frequency ν and scattering vector Q or energy E and length d plane, which can be covered by various scattering methods.

Appendices

A Autocorrelation Functions

Let us assume a quantity A that fluctuates in time as depicted in the insert of figure A1.

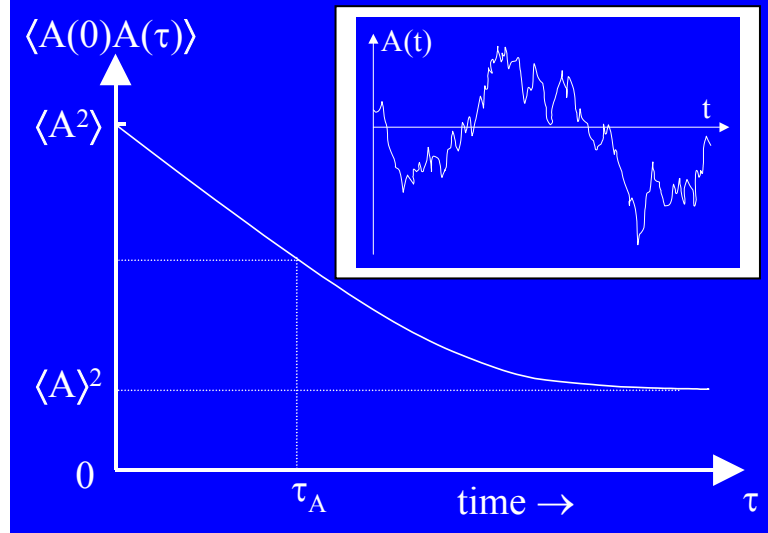


Fig. A1: The insert gives an example of a quantity $A(t)$ that fluctuates in time. The main figure shows the general behaviour of the autocorrelation function. It has a maximum of $\langle A^2 \rangle$ for $\tau = 0$. From this maximum, it decays with a time constant τ_A towards the asymptotic value of $\langle A \rangle^2$ for infinite times.

For this quantity, we can define the average value

$$\langle A \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt A(t). \quad (\text{A1})$$

Around this average value, fluctuations $\delta A(t) = A(t) - \langle A \rangle$ are being observed. If the function $A(t)$ varies monotonically, $A(t+\tau)$ approaches the values of $A(t)$ for small values of τ , which means that both are correlated in time. Similar correlations can occur at larger times, e. g. for quasi-periodic fluctuations. As a measure of this correlation, the autocorrelation function is introduced:

$$\left. \begin{aligned} \langle A(0)A(\tau) \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt A(t)A(t+\tau) \end{aligned} \right\} \begin{aligned} &\tau \rightarrow 0: \langle A^2 \rangle \\ &\tau \rightarrow \infty: \langle A \rangle^2 \end{aligned} \quad (\text{A2})$$

This autocorrelation function has a very general property depicted in figure A1: it decays from a maximum value of $\langle A^2 \rangle$ for $\tau = 0$ to the asymptotic value of $\langle A \rangle^2$ for infinite times with a characteristic time constant of τ_A . Often times, this decay follows a simple exponential law $\exp(-\tau/\tau_A)$.

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