



Spectrometers



The scattering of thermal neutrons by condensed matter is governed by conservation laws (momentum, energy, magnetic moment,...) applied to the whole system (scatterers and neutrons). The purpose of the spectrometer is to measure the variation of these different quantities for each scattered neutron.

The majority of spectrometers that are set up around a continuous source, such as Orphée reactor, are based on the same principles:

- to prepare, with the intention of «bombarding» the sample, a beam of neutrons that all have the same propagation direction \vec{k}_i , the same energy E_i and, in the case of a polarized beam, the same spin state $\vec{\sigma}_i$;
- to measure after scattering from the sample the proportion of neutrons that have the propagation direction \vec{k}_f , the energy E_f and, eventually, the spin state $\vec{\sigma}_f$.

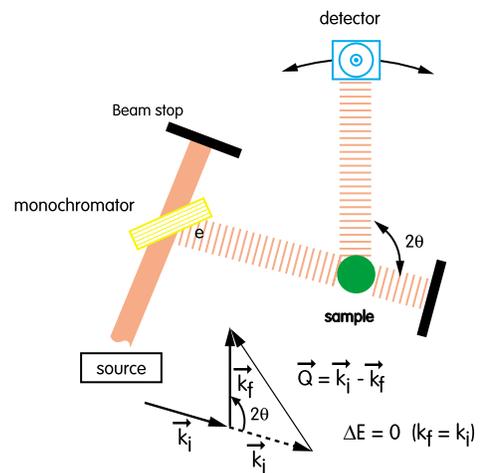
The different types of spectrometers that we are now going to briefly describe differ in the nature and number of final parameters that are measured, in the techniques used, or in the range of values (\vec{k}, E) for which they have been designed.

1 - The diffractometers

This class of instruments measures the number of neutrons having undergone a change $2\theta = (\vec{k}_f, \vec{k}_i)$ in their propagation direction due to the interaction with the scatterers in the sample. They allow to measure the average atomic and magnetic structure of a sample.

A parallel and monochromatic beam (wavelength λ_0) is sent onto the sample. The detector moves on a circle centred at the sample. Each position of the detector defines a propagation direction of the emerging neutrons (angle 2θ with the initial direction).

The recorded intensity measures the number of neutrons having undergone a momentum change $|\vec{Q}| = |\vec{k}_i - \vec{k}_f| = \frac{4\pi}{\lambda_0} \sin \theta$ (assuming a purely elastic scattering).

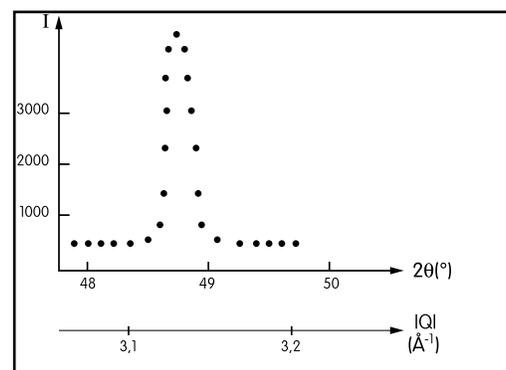


Schematic representation of a diffractometer

- The directions in which scattering is intense (Bragg peaks) correspond to the «long range order of the average structure»: a lattice of atomic planes separated by a distance (d) will induce a maximum of intensity in the direction $2\theta = 2 \arcsin \left(\frac{\lambda}{2d} \right)$.

In the case of a crystal (periodic lattice in three dimensions \vec{a} , \vec{b} , \vec{c}), the Bragg directions are given by the vectors of the «reciprocal lattice»: $\vec{Q} \equiv \vec{G} \equiv h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$

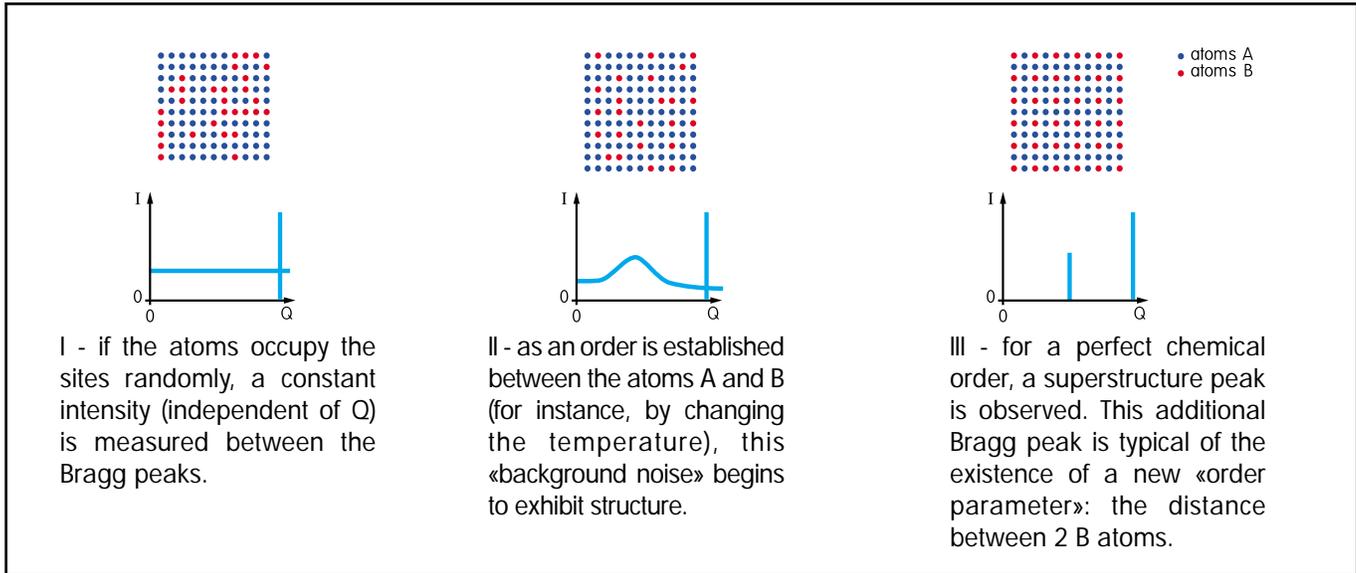
The relative intensity of the successive peaks (h,k,l) enables the scientist to determine the position of all the atoms in the unit cell.



Scattered intensity curve $I = f(2\theta)$, measured by the detector when passing through a Bragg reflection.

- Deviations from the perfect order are, according to their nature, revealed by different modifications in the angular distribution of the scattered neutrons.

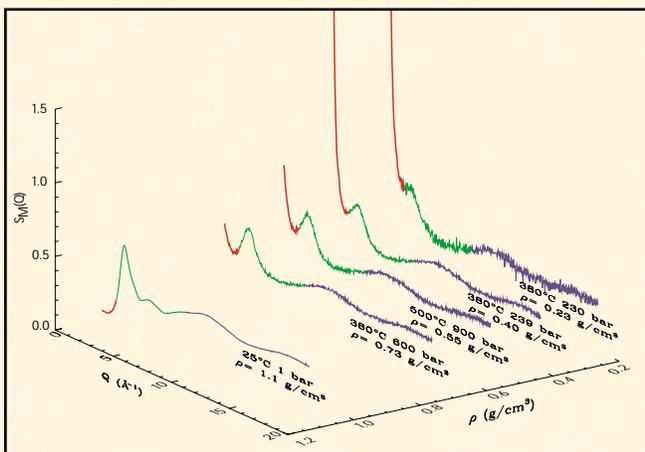
In a crystalline alloy A_3B the distribution at each site of the atoms A (•) and B (•) may be more or less random (chemical order or disorder):



Representation of the scattering diagrams of a crystalline alloy A_3B : influence of a chemical order.

Supercritical Water

In the (Temperature-Pressure) plane, the liquid-gas transition occurs at precise (P, T) points. This transition only exists below the critical point (P_c, T_c); thus, starting in the liquid state, a path in the (P, T) diagram surrounding the critical point allows one to obtain a gas without crossing the boiling curve. The region of the plane ($P > P_c; T > T_c$) corresponds to the so-called supercritical fluid state. In their supercritical state, fluids have frequently new physico-chemical properties. For instance, supercritical water is chemically very active: it can degrade by oxidation most organic compounds with production of carbon dioxide and water. This property could be useful in the treatment of household rubbish.

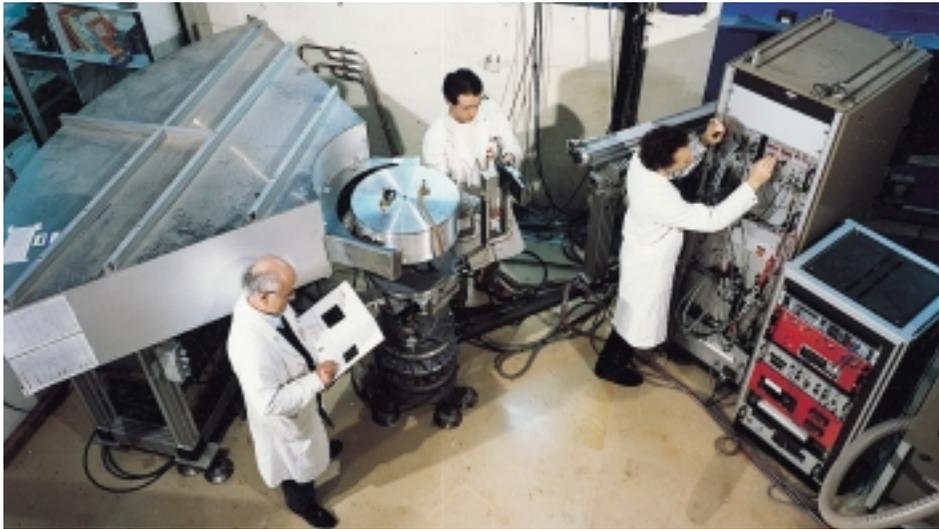


Structure factor of water (D_2O) for various temperatures and pressures. Critical point $T_c = 371^\circ C$, $P_c = 218 \text{ bar}$, $\rho_c = 0,36 \text{ g/cm}^3$.

The evolution with the pressure of the structure factor, measured over a large Q range, leads to 3 results:

- $Q > 5 \text{ \AA}^{-1}$ (molecular dimension; in blue)
 \Rightarrow the curves, which are very similar, show that the structure of the molecule is unchanged when crossing the critical point.
- $5 > Q > 1 \text{ \AA}^{-1}$ (intermolecular distances; in green)
 \Rightarrow when the density decreases, the main peak becomes larger and shifts; the molecules are less localised and the distance between them increases.
- $Q < 1 \text{ \AA}^{-1}$ (local density; in red)
 \Rightarrow in the vicinity of the critical point, the strong intensity observed at small q values is due to the onset of density fluctuations (critical scattering).

❑ Two-axis diffractometer for powders and liquids



The «powder» diffractometer G41 and its 800 cells multidetector

- ❑ An isotropic powder is made of small crystals that are randomly oriented in every direction. The diffraction pattern does not depend on the direction of the incident beam since, by definition, the angular distribution of small crystals is the same relative to all axes. The scattering is distributed uniformly on a cone of axis parallel to the incident beam and open angle 2θ . The diffraction spectrum (Bragg peaks and/ or diffuse scattering between the peaks) is obtained by measuring the distribution of intensities reaching the detector when it moves in the horizontal plane on a circle centred at the sample (or more efficiently by using a multidetector). A second rotational axis, around the monochromator, allows the scientist to choose the incident wavelength λ_0 and, therefore, the range of momentum transfer $q = |\vec{Q}|$ that is analysed. In one direction, the intensity scattered is the sum of the scattering by each crystallite (powder averaging):

$$I(2\theta) = I(q) = \int_0^{2\pi} I(\vec{Q}) \sin \beta \, d\beta$$

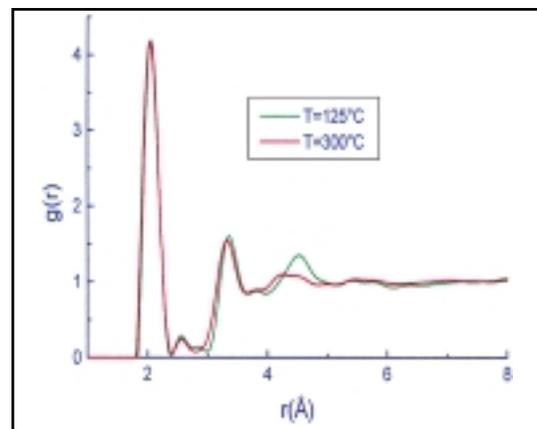
- ❑ In a textured powder the distribution of the crystallite is non-isotropic. By measuring the scattered intensity versus the relative orientation of the sample with respect to the incident beam, the scientist can deduce the orientational distribution of the crystallite (texture).
- ❑ In a liquid, the measurement of the angular distribution of the scattered intensity allows the scientist to obtain the pair distribution function $g(r)$ that characterises the local order of atoms:

$$g(r) = 1 + \frac{1}{2\pi^2 \rho_0} \int_0^\infty q^2 [I(q) - I(\infty)] \frac{\sin qr}{qr} \, dq$$

ρ_0 = average density

$I(\infty)$ = scattered intensity for very large q

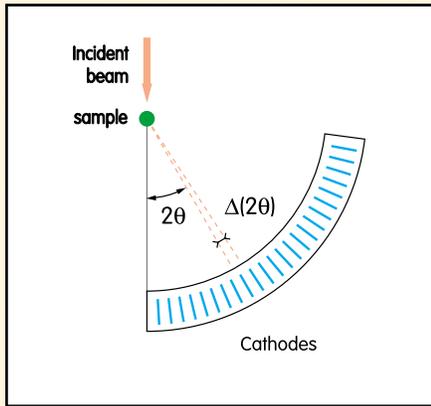
Around 160°C, liquid sulphur exhibits a discontinuity that affects numerous properties: viscosity, density, specific heat,... Measured at 125° and 300°C, $g(r)$ shows the disappearance of a correlation peak around 4.5 Å. These results are well reproduced in a model in which liquid sulphur, made of S_8 rings at low temperatures, transforms into a liquid with long S_n chains at temperatures above 160° C.



Polymerization transition of liquid sulphur.

«Banana» type multidetector

This multidetector allows scientists to measure the distribution of the scattered intensity over a wide angular region in one single step.



In the volume between 2 sections of concentric cylinders (with a common axis perpendicular to the scattering plane and passing through the sample), a series of N cathodes, separated by an angle $\Delta(2\theta)$ have been set. The volume is filled with a detecting gas (BF_3 ou ^3He). Appropriate electronics indicate, for each detected neutron, the specific cathode from which the pulse comes (see P. 30). The content of the channel « n », which represents the number of scattered neutrons within the angle $n \times \Delta(2\theta)$, is thus incremented by one unit.

3 types of «banana» multidetectors exist at LLB:

$N = 400$ cells on 80 degrees $\Rightarrow \Delta(2\theta) = 12$ arc minutes

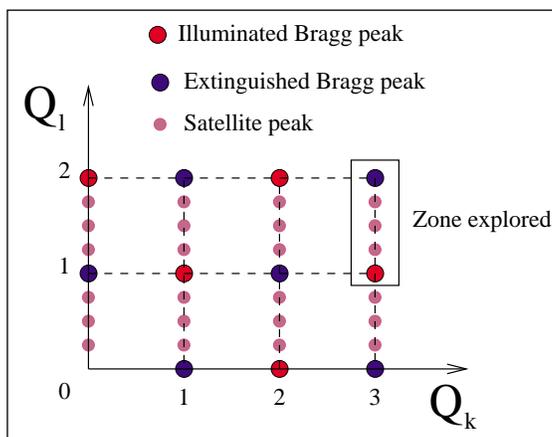
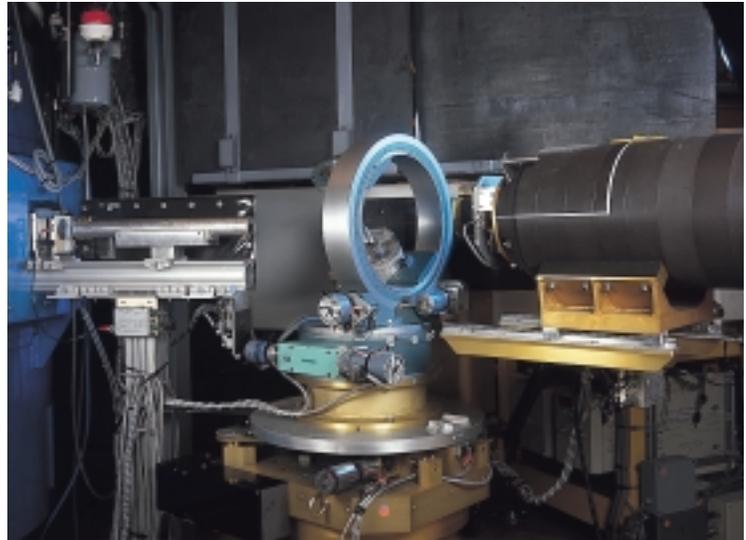
$N = 800$ cells on 80 degrees $\Rightarrow \Delta(2\theta) = 6$ arc minutes

$N = 640$ cells on 128 degrees $\Rightarrow \Delta(2\theta) = 12$ arc minutes

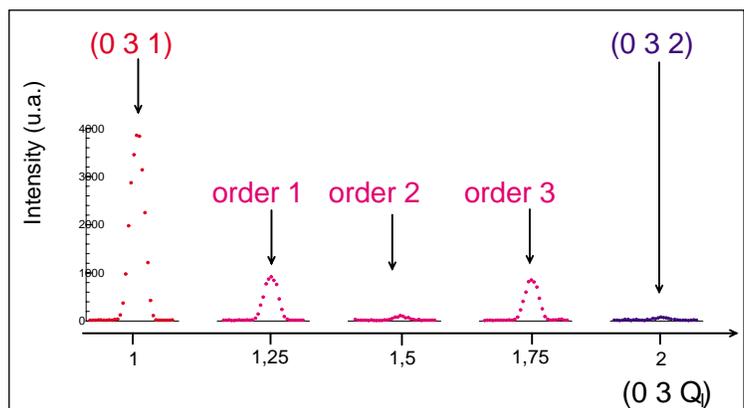
Four circle diffractometer for single crystals

When the sample is a single crystal, the orientation of its crystalline axes relative to the directions \vec{k}_i and \vec{k}_f becomes an essential parameter of the measurement. This is why, besides the axis of rotation around the monochromator (choice of the incident wavelength λ_0), 4 rotation axes are needed that intersect at the sample position: 3 rotations (Euler angles) allow all possible orientations of the crystalline axes relative to the incident direction \vec{k}_i ; the rotation of the detector defines the scattering angle 2θ .

Diffractometer 6T2



Modulated structure of calcium and dihydrated betaine chloride (BCCD).



\vec{Q} scan along the \vec{c}^* axis between Bragg peaks $(0\ 3\ 1)$ and $(0\ 3\ 2)$ in the modulated phase $\vec{q} = \frac{1}{4}\vec{c}^*$ of BCCD at $T = 100\text{ K}$: one can see intense satellite peaks of order 3. The measurement of the intensity of the diffraction on a single crystal allows scientists to refine the structure in real space.

2 - Spectrometers for inelastic scattering

If, in addition to the average structure, the scientist wants to study the dynamics of the atoms or of the magnetic moments in the sample, the spectrometer must measure the number of neutrons that have undergone an energy change $\hbar\omega$ during the scattering process; that is to say the fraction of particles that, arriving on the sample with energy E_i , leaves in the direction \vec{k}_f (forming angle ψ with direction \vec{k}_i of the incident neutrons) with energy E_f (conservation law $\hbar\omega = E_i - E_f$). However, there are no physical phenomena that measure (or select) directly the energy of neutrons:

Neutron = wave \rightarrow energy \Leftrightarrow wavelength λ
 Neutron = particle \rightarrow energy \Leftrightarrow speed V

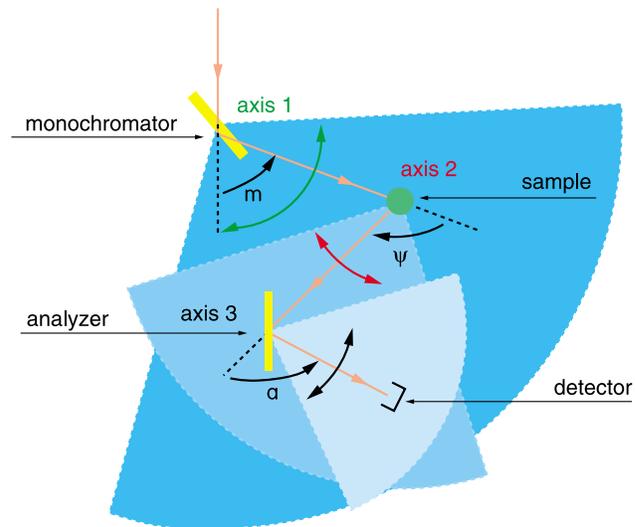
These two points of view are the basis for the 2 kinds of spectrometers that measure inelastic scattering (i.e. «triple axis» and «time of flight» types)

□ Triple-axis spectrometer

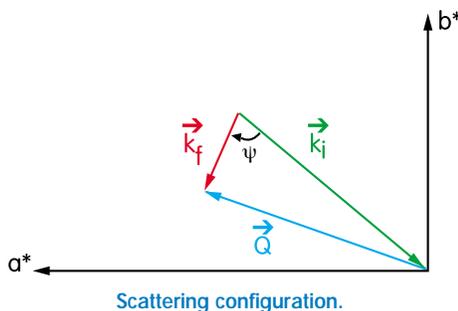
Before the sample, neutrons with a specific energy are selected; then, after scattering their energy is measured by their wavelength.

The parallel and monochromatic (λ_0) incident beam is obtained by Bragg reflection on a single crystal (monochromator). It is possible to vary λ_0 by rotating the entire spectrometer (angle m) around the vertical axis passing through the monochromator (1st axis).

The analysis of the scattered intensity is performed as a function of the angle ψ measured around the vertical axis passing through the sample (2nd axis). Finally, in the direction ψ the energy of the neutrons is analysed by a second single crystal and a mobile detector rotating with angle «a» around the corresponding vertical axis (3rd axis).



Outline of the principle of a 3-axis spectrometer.



Provided that the sample is a single crystal, the analysis of the scattering diagram shows that the degrees of freedom available allow one to move at will in the chosen plan of the reciprocal lattice.

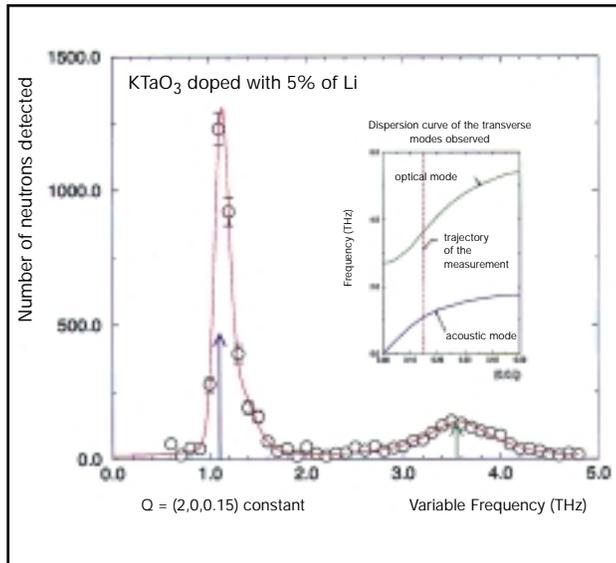
Plane a^* , b^* is the plane of the reciprocal lattice defined by the scattered and incident beams (scattering plane).



Triple-axis spectrometer 1T

Depending on the particular case, a path can be followed keeping $\vec{k}_i - \vec{k}_f = c^{te}$ [measure of $S(\vec{Q} = c^{te}, \omega)$], or $E_i - E_f = c^{te}$ [$S(\vec{Q}, \omega = c^{te})$]. These possibilities are extremely advantageous when using a single crystal of the material under study.

Constant \vec{Q} method: observation of an acoustic mode and of an optical mode.

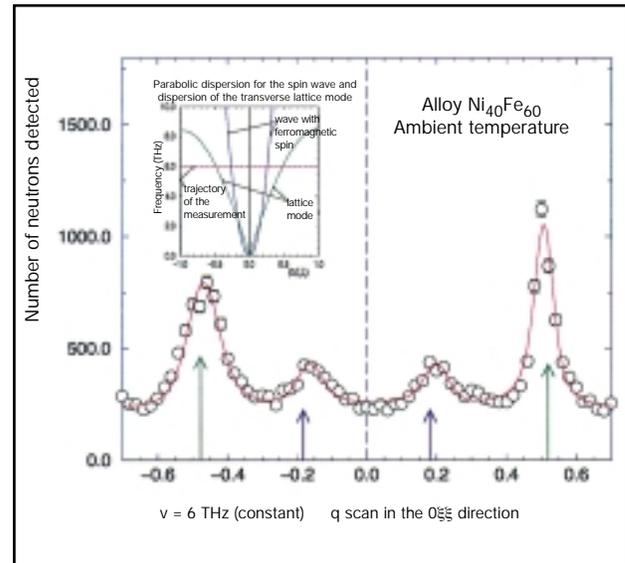


By probing the reciprocal space of the crystal lattice, the 3-axis spectrometer is able to measure the energy of the modes of vibration and their dispersion curves.

Neutrons are scattered when the measurement trajectory intersects the curves $\omega = f(\vec{Q})$ which are characteristics of the lattice dynamics of the crystalline system. The figure gives an example of a measurement at constant \vec{Q} .

It shows 2 modes (1 acoustic and 1 optic) with transverse polarization.

Constant energy method: observation of a lattice vibration mode and of a spin wave mode.



When the vibration modes exhibit a strong dispersion in \vec{Q} , the 3-axis spectrometer allows to follow a trajectory with constant energy (or frequency).

The figure gives an example of the simultaneous determination of a lattice vibration mode (green arrow) and of a spin wave mode (blue arrow) in a ferromagnetic alloy $Ni_{40}Fe_{60}$.

The $+\vec{Q}$ and $-\vec{Q}$ scans reveal the effect of the instrumental resolution.

□ The time-of-flight spectrometer

The speed V , or more precisely the time t used to travel along a given distance ($t = \frac{L}{V}$), measures the neutron energy before and after scattering by the sample.

The monoenergetic incident beam (V_i) is formed in bursts or pulses by a chopper monochromator. The moment when the burst passes through the sample is known thanks to the production of an electric impulse synchronised with the opening of the last chopper. By activating at this very moment a «chronometer», one can measure the time each neutron takes to «fly» across from the sample to the detector situated at a distance L in the direction ψ . Obviously, the measurement is repeated identically for each burst produced by the monochromator (for each turn of the chopper wheel).

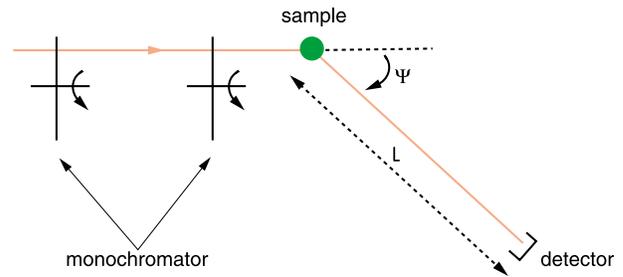
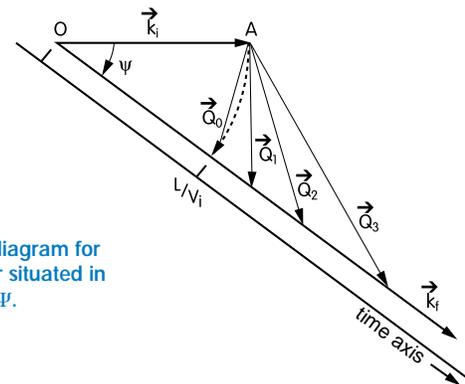
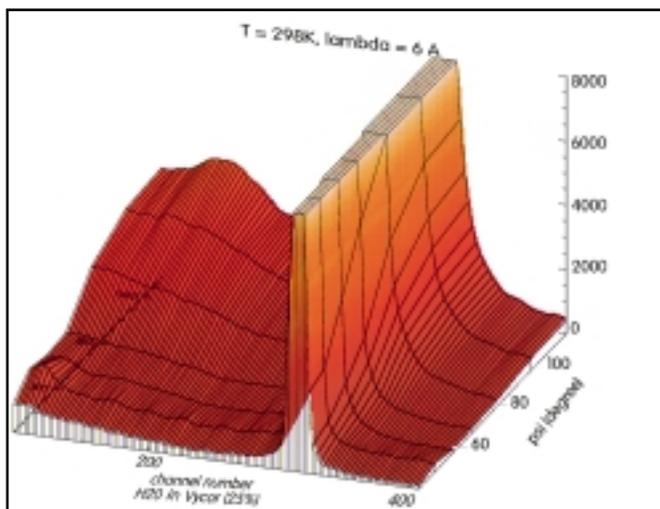


Diagram of a time-of-flight spectrometer.

The scattering diagram shows that each arrival time in the detector corresponds to a transfer of momentum Q which changes in module and direction. The path in the reciprocal space is complicated so that the Q dependence of the scattering function may be difficult to study accurately. If the sample is isotropic (powder or liquid) one shall measure the $S(\vec{Q}_0 | \psi, \omega)$ function in the direction (ψ). Then by setting up numerous detectors, the inelastic transfers for several $|Q_0|$ may be simultaneously measured.



Scattering diagram for the detector situated in a direction ψ .



Time-of-flight spectrum of confined water.

Vycor is a silicate glass with high porosity corresponding to a network of interconnected cylindrical pores (diameter 50 Å). In these internal volumes, numerous molecules can be adsorbed; there, they are confined in a very small space. This confinement influences their dynamics and, therefore their thermodynamic properties. The spectrum of neutrons scattered by water molecules adsorbed in vycor is measured by time-of-flight method as a function of the scattering angle and of the energy exchanged. The analysis of the quasi-elastic components indicates that the model of diffusion by jumps which is applicable to liquid water remains valid. By contrast, the long range diffusion coefficient at 25°C is about 10 times weaker than for non-confined water, but it remains measurable at -15 °C.

□ Measuring very low energy transfers: the «spin-echo» spectrometer

The magnetic moment (spin) of a neutron provides the opportunity to precisely measure very weak energy changes that may take place during the scattering process. Immersed into a magnetic field H , the neutron spin rotates around the field (Larmor precession) with an angular speed $\Omega = \gamma H$ (γ = gyromagnetic ratio $\simeq 2.10^8$ rd/s.T). Used as a chronometer, this rotation is interesting for two reasons:

- By counting the number of turns, we know precisely the amount of time the neutron spends in the magnetic field. If the neutron travels along the axis of a solenoid with length L (precession coil) traversed by a current (that creates the field), one can deduce its speed V .
- Each neutron carries its own «clock» that is activated when it penetrates the coils and is deactivated when it comes out.



The «Spin-echo» spectrometer, MESS.

The long cylinders that are found before and after the sample are precession coils. They are identical but create opposite magnetic fields. If during scattering, the neutron does not change speed, its spin undergoes N_1 turns before the sample and $-N_1$ after; on exiting it will have the same orientation as it did on entering (echo). On the other hand, if the speed changes, the orientation of the spin will be different. By measuring this orientation we can detect a change of speed ($\Delta V/V_0 \simeq 10^{-5}$).

3 - The reflectometers

In the preceding chapter we mentioned that every medium is characterised, from the point of view of wave propagation, by an index n (whose value depends on the nature of the wave). In the case of neutron propagation, we can show that this index depends only on **the scattering length density** of the material, which is the product of its density (ρ) by the mean scattering length (b_{coh}) of the different atomic species present.

$$n = 1 - \frac{\lambda^2 \rho}{2\pi} b_{\text{coh}}$$

Let us note immediately that, even in a material that is dense and made of atoms having a large scattering length, the index n always remains in the neighbourhood of 1 for the range of available wavelengths; in nickel for example:

$$\lambda = 10 \text{ \AA} \Rightarrow \frac{\lambda^2 \rho}{2\pi} b_{\text{coh}} \approx 10^{-4}.$$

The laws describing the passage of the neutron wave from a medium with index n_1 ($n_1=1$ for air or vacuum) to the sample medium with index n_2 are the same as for light. They are known since the 19th century (Fresnel, Maxwell). In particular, there is always the appearance of a **reflected beam**.

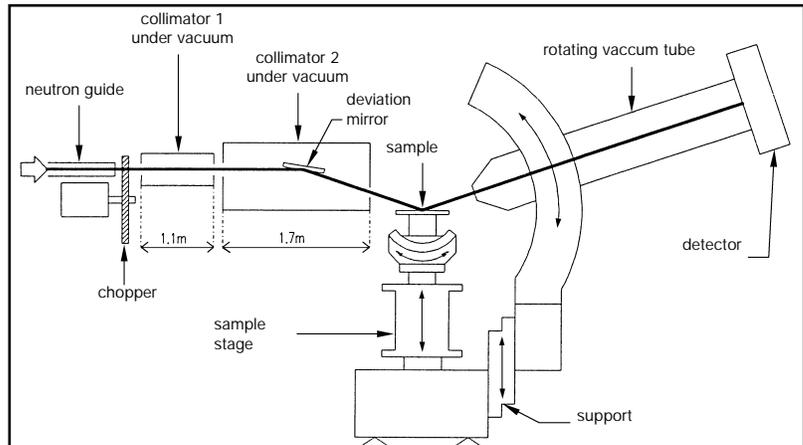


Diagram of the time-of-flight reflectometer DESIR (G5 bis).

If $n_2 < 1$, there exists a critical angle θ_c such that, for $\theta < \theta_c$ the beam undergoes a **total reflection**:

$$\theta_c \sim \frac{\lambda}{\sqrt{\pi}} \sqrt{\epsilon_2 b_2}$$

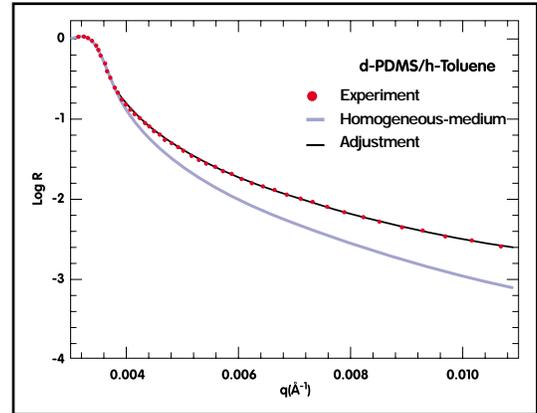
For $\theta > \theta_c$ the beam splits into a refracted and a reflected beam. The distribution of the intensity into these 2 components depends on the incident angle θ and on the variation of the index $n_2(z)$ with the distance (z) to the interface.

- If the medium is homogeneous ($n_2(z) = \text{constant}$), the reflected intensity is given by Fresnel's formula:

$$I_r = I_0 \left| \frac{1-x}{1+x} \right|^2 ; x = \sqrt{1 - \left(\frac{q_c}{q} \right)^2} ; q = \frac{4\pi}{\lambda} \sin \theta$$

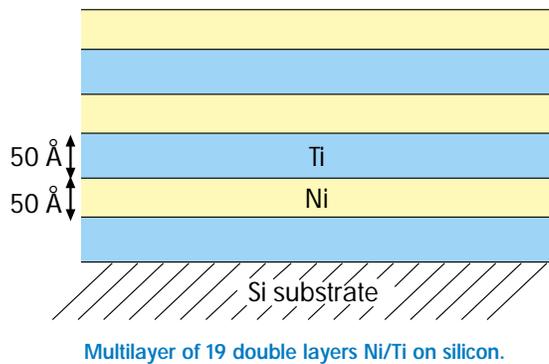
- If $\frac{d n_2}{dz} \neq 0$ (index gradient), a deviation from this distribution will be measured. Choosing a particular form for $n_2(z)$, different theoretical curves can be calculated and compared with the experimental results.

Reflected intensity at the interface between air and a solution of PDMS in toluene.

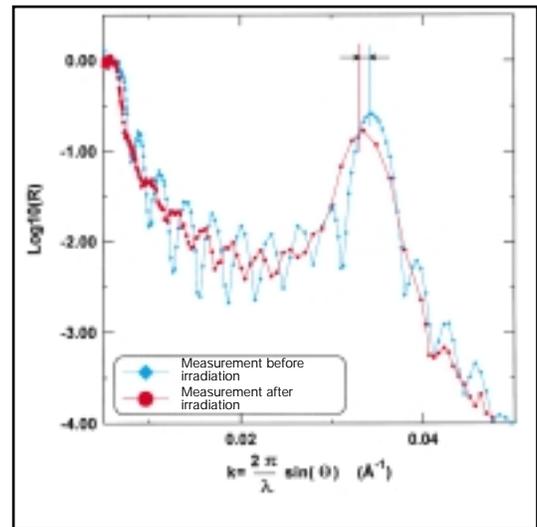


The deviation from the curve «homogeneous medium» is due to the concentration gradient of polymer molecules near the surface. The theoretical prediction $\varnothing(z) = z^{-4/3}$ is in good agreement with the experimental result ($\varnothing(z) = \text{polymer concentration}$).

- For a layered structure, the index undergoes abrupt changes (steps of a staircase) evidenced by a series of peaks in the decreasing part of the reflected intensity. These peaks come from interferences between the different rays reflected by successive interfaces. The number of peaks and their angular distances allow the scientist to measure the thickness of the layers and the quality of the interfaces (roughness, inter-diffusion,...).



Treatment: irradiation with thermal neutrons under a dose of $6 \cdot 10^{19} \text{ n.cm}^{-2}$.



Reflectivity curve of the multilayer measured before and after irradiation.

The shift of the peak is typical of a swelling of the layers. The lowering of its intensity is characteristic of the increase (from 5 to 30 Å) in the roughness between the layers.

4 - Spectrometers for «small angle scattering» (SANS)



The small-angle spectrometer PAXE.

Built to characterise large size objects (1 to 50 nm), these spectrometers measure the quantity of neutrons scattered «near the forward direction», that is to say resulting from a process characterised by very small transfers of momentum.

These spectrometers must satisfy 2 conditions: a very well collimated incident beam with a long wavelength λ_0 ; a wide planar detector located far from the sample (between 1 and 7 m).

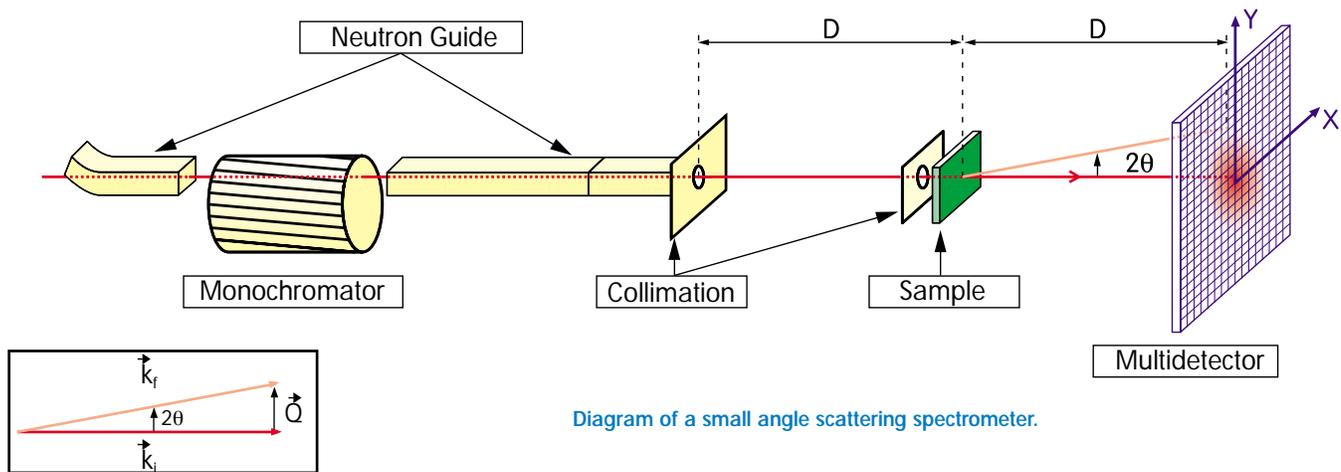


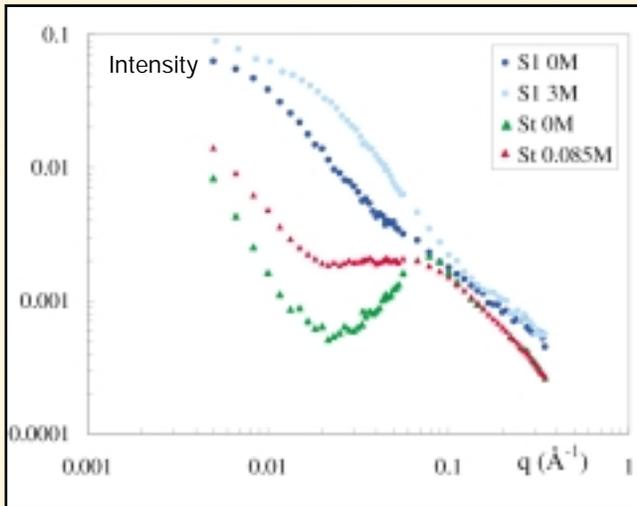
Diagram of a small angle scattering spectrometer.

Scattering diagram.

The impact point of each detected neutron is located by its coordinates (X, Y) in a system of orthogonal axes linked to the detector. The origin of the axes is chosen at the impact point of the direct beam (not deviated by the sample). Therefore, a neutron detected at the point with coordinates (X, Y) has undergone a momentum transfer:

$$Q = \frac{4\pi}{\lambda_0} \sin \theta \sim \frac{2\pi}{\lambda_0} \frac{\sqrt{X^2 + Y^2}}{D} \quad (\theta \text{ small}), \text{ where } D \text{ is the distance from the sample to the detector.}$$

Inter and intra-chain electrostatic interaction in a poly-electrolyte solution



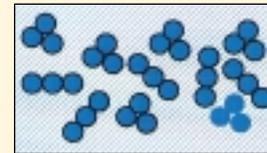
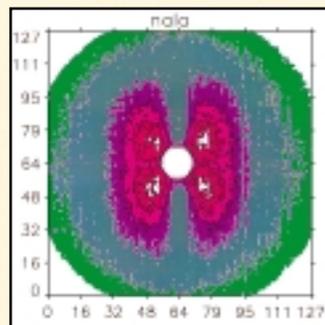
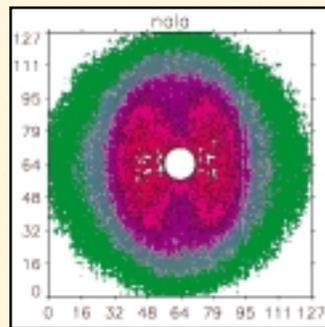
Intensity scattered by a solution of poly-electrolyte, with and without added salt.

Intensity measured in the direction 2θ (abscissa: $q = \frac{4\pi}{\lambda} \sin \theta$) for poly-electrolyte solutions (charged polymers in water, 0.17 moles/liter):

- If all the chains are deuterated, the scattered intensity (green triangles) shows a peak around $q = 0,1 \text{ \AA}^{-1}$ characteristic of a repulsion between chains. This interaction is «screened» by the strong density of charges when salt is added (red triangles).
- If half the chains are deuterated and the other half hydrogenated, and if the index of the solvent is adjusted to an average value (mixture of heavy water and light water), one measures the signal from a single chain directly. In the absence of salt (dark blue circles), the repulsion stretches the chain and, as a result, its signal decreases more quickly with angle. In the presence of salt (light blue circles), this repulsion disappears and the chain has the same rigidity as in its neutral state.

The stretching effect in a composite material

Experimental proof of the correlations between nanometric silica particles in a stretched polymer matrix: Intensity mapping on a bi-dimensional multidetector perpendicular to the beam. The progressive distortion of the originally isotropic signal (ring) evidences the displacement of the particles caused by the stretching; this enables scientists to understand the reinforcement of polymers by hard particles.



Isotropic



Moderate stretch:
displacement of the hard parts
(Opposite spectrum, 2 lobes)



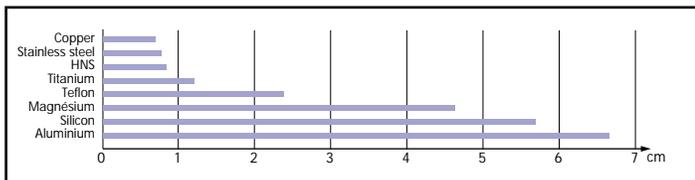
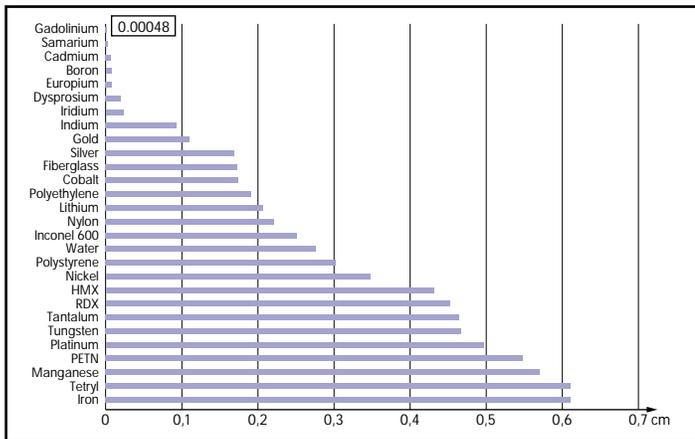
Avoidance by local shearing
(Opposite spectrum, 4 lobes)

Observation by SANS of the relative displacement of hard particles in a stretched polymer matrix.

5 - Neutron radiography

Totally different in its principle and in its goals, neutron radiography is a direct imaging technique.

A wide neutron beam is sent to the object to be observed. A photographic detector, which is sensitive to neutrons, is placed behind it. After exposure, an image of the «neutron transparency» averaged on the thickness of the object is obtained.

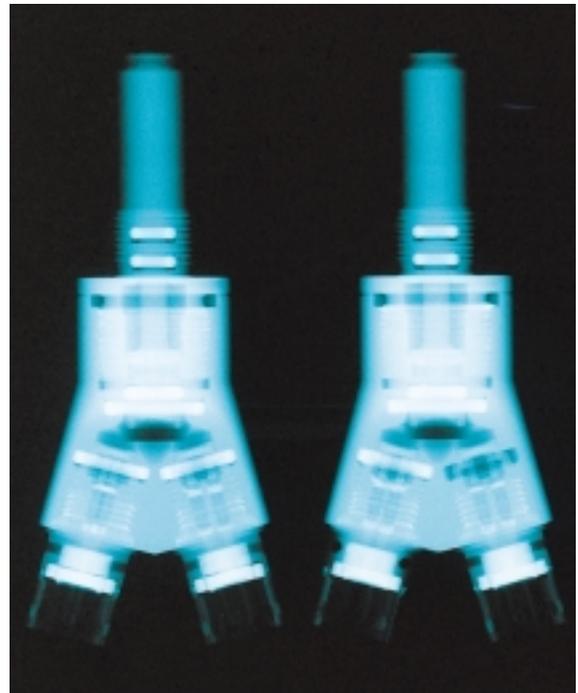


This transparency is a function of the probability that the neutron passes through the object without «disappearing» from the original beam, in other words without being either absorbed (in this case it would disappear completely) or scattered (then it would have been deviated from its initial trajectory and consequently it would not reach the photo plate). The result of a neutron radiography is related to the interaction of the neutron with the atoms (see P. 8-10) and thus is very complementary to the X-ray radiography.

Thickness of various materials which gives a beam attenuation of 50% ($\lambda = 1.8 \text{ \AA}$).

Space technology requires as much control as possible of a lot of critical equipment. This includes devices that make use of pyrotechnology (explosives) employed to ensure essential functions like the separation into stages and the release of satellites. The great sensitivity of neutron to hydrogen makes neutron radiography a trustworthy way to detect, across metallic envelopes, eventual defects in the placement of these explosives or in the final assembly.

In the photograph we see that a rubber joint (in black) is missing in the element to the right.



Neutron radiography of some pyrotechnic jacks used in the rocket «ARIANE» (DASSAULT-AVIATION).