

## 2.6. SMALL-ANGLE TECHNIQUES

## 2.6.2. Neutron techniques (By R. May)

## Symbols used in the text

$A$	sample area
$A_s$	inner sample surface
$b_i$	coherent scattering length of atom $i$
$B_i$	spin-dependent scattering length of atom $i$
$C$	sample concentration in $\text{g l}^{-1}$
$c$	volume fraction occupied by matter
$d$	sample thickness
$D$	particle dimension
DCD	double-crystal diffractometer
$d_0$	Bragg spacing
$\mathbf{e}, \mathbf{e}_0$	unit vectors along the diffracted and incident beams
$\mathbf{I}$	nuclear spin
IFT	indirect Fourier transformation
$N$	number of particles in the sample
$N_A$	Avogadro's number
$Q$	momentum transfer $[= (4\pi/\lambda) \sin \theta]$
$r$	radius of a sphere
$R_G$	radius of gyration
$s$	neutron spin
SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
$T$	transmission
TOF	time of flight
$v$	partial specific volume
$V_p$	particle volume
$V_s$	sample volume
$\Delta\Omega$	solid angle subtended by a detection element
$\lambda$	wavelength
$\rho$	scattering-length density
$2\theta$	full scattering angle
$d\sigma(Q)/d\Omega$	scattering cross section per particle and unit solid angle

## 2.6.2.1. Relation of X-ray and neutron small-angle scattering

X-ray and neutron small-angle scattering (SAXS and SANS, respectively) are dealing with the same family of problems, *i.e.* the investigation of 'inhomogeneities' in matter. These inhomogeneities have dimensions  $D$  of the order of 1 to 100 nm, which are larger than interatomic distances, *i.e.* 0.3 nm. The term inhomogeneities may mean clusters in metals, a small concentration of protonated chains in an otherwise identical deuterated polymer – or *vice versa* – but also particles as well defined as purified proteins in aqueous solution.

In most cases, the inhomogeneities are not ordered. This is where small-angle scattering is most useful: many systems are not crystalline, cannot be crystallized, or do not exhibit the same properties if they are. One field, if one may say so, of SANS where samples are ordered is low-resolution crystallography of biological macromolecules. It will not be treated further here. In the case of crystalline order, the scattering of the single particle is observed with an amplification factor of  $N^2$  for  $N$  identical particles in the crystal, but only for those scattering vectors observing the Bragg condition  $n\lambda = 2d_0 \sin \theta$ . For disordered, randomly oriented particles, the amplification is only  $N$ , and the scattering pattern is lacking all information on particle orientation. Moreover, the real-space information on the internal arrangement of atoms within the inhomogeneities is reduced to the 'distance distribution function', a sine Fourier transform of the scattering intensity.

The mathematical descriptions of SAXS and SANS are either identical or hold with equivalent terms. The reader is referred to

Section 2.6.1 on X-ray small-angle scattering techniques for a general description of low- $Q$  scattering. An abundant treatment of SAXS can be found in the book edited by Glatter & Kratky (1982), and in Guinier & Fournet (1955) and Guinier (1968). A general introduction to SANS is given, for example, by Kostorz (1979) and by Hayter (1985). This section deals mainly with the differences between the techniques.

Altogether, neutrons are used for low- $Q$  scattering essentially for the same reasons as for other neutron experiments. These reasons are:

(1) neutrons are sensitive to the isotopic composition of the sample;

(2) neutrons possess a magnetic moment and, therefore, can be used as a magnetic probe of the sample; and

(3) because of their weak interaction with and consequent deep penetration into matter, neutrons allow us to investigate properties of the bulk;

(4) for similar reasons, strong transparent materials are available as sample-environment equipment.

The fact that the kinetic energies of thermal and cold neutrons are comparable to those of excitations in solids, which is a reason for the use of neutrons for inelastic scattering, is, with the exception of time-of-flight SANS (see §2.6.2.1.1), not of importance for SANS.

The information obtained from low- $Q$  scattering is always an average over the irradiated sample volume and over time. This average may be purely static (in the case of solids) or also dynamic (liquids). The limited  $Q$  range used does not resolve interatomic scattering contributions. Thus, a 'scattering-length density'  $\rho$  can be introduced,  $\rho = \sum b_i/V$ , where  $b_i$  are the (coherent) scattering lengths of the atoms within a volume  $V$  with linear dimensions of at least  $\lambda/\pi$ . Inhomogeneities can then be understood as regions where the scattering-length density deviates from the prevailing average value.

## 2.6.2.1.1. Wavelength

In the case of SANS – as in that of X-rays from synchrotron sources – the wavelength dependence of the momentum transfer  $Q$ ,  $Q = (4\pi/\lambda) \sin \theta$ , where  $\theta$  is half the scattering angle and  $\lambda$  is the wavelength, has to be taken into account explicitly.  $Q$  corresponds to  $k$ ,  $h$ , and  $2\pi s$  used by other authors.

SANS offers an optimal choice of the wavelength: with sufficiently large wavelengths, for example, first-order Bragg scattering (and therefore the contribution of multiple Bragg scattering to small-angle scattering) can be suppressed: The Bragg condition written as  $\lambda/d_{\max} = (2 \sin \theta)/n < 2$  cannot hold for  $\lambda \geq 2d_{\max}$ , where  $d_{\max}$  is the largest atomic distance in a crystalline sample. For the usually small scattering angles in SANS, even quite small  $\lambda$  will not produce first-order peaks.

The neutrons produced by the fuel element of a reactor or by a pulsed source are moderated by the (heavy) water surrounding the core. Normally, the neutrons leave the reactor with a thermal velocity distribution. Cold sources, small vessels filled with liquid deuterium in the reactor tank, permit the neutron velocity distribution to be slowed down ('cold' neutrons) and lead to neutron wavelengths (range 0.4 to 2 nm) which are more useful for SANS.

At reactors, a narrow wavelength band is usually selected for SANS either by an artificial-multilayer monochromator or – more frequently, owing to the slow speed of cold neutrons – by a velocity selector. This is a rotating drum with a large number (about 100) of helical slots at its circumference, situated at the entrance of the neutron guides used for collimation. Only neutrons of the suitable velocity are able to pass through this

## 2. DIFFRACTION GEOMETRY AND ITS PRACTICAL REALIZATION

drum. The wavelength resolution  $\Delta\lambda/\lambda$  of velocity selectors is usually between 5 and 40% (full width at half-maximum, FWHM); 10 and 20% are frequently used values.

Alternatively, time-of-flight (TOF) SANS cameras have been developed on pulsed neutron sources (*e.g.* Hjelm, 1988). These use short bunches (about 100  $\mu\text{s}$  long) of neutrons with a 'white' wavelength spectrum produced by a pulsed high-energy proton beam impinging on a target with a repetition rate of the order of 10 ms. The wavelength and, consequently, the  $Q$  value of a scattered neutron is determined by its flight time, if the scattering is assumed to be quasi-elastic. The dynamic  $Q$  range of TOF SANS instruments is rather large, especially in the high- $Q$  limit, owing to the large number of rapid neutrons in the pulse. The low- $Q$  limit is determined by the pulse-repetition rate of the source because of frame overlap with the following pulse. It can be decreased, if necessary with choppers turning in phase with the pulse production and selecting only every  $n$ th pulse. This disadvantage does not exist for reactor-based TOF SANS cameras, where the pulse-repetition rate can be optimally adapted to the chosen maximal and minimal wavelength. A principal problem for TOF SANS exists in the 'upscattering' of cold neutrons, *i.e.* their gain in energy, by  $^1\text{H}$ -rich samples: The background scattering may not arrive simultaneously with the elastic signal, and may thus not be attributed to the correct  $Q$  value (Hjelm, 1988).

### 2.6.2.1.2. Geometry

With typical neutron wavelengths, low  $Q$  need not necessarily mean small angles: The interesting  $Q$  range for an inhomogeneity of dimension  $D$  can be estimated as  $1/D < Q < 10/D$ . The scattering angle corresponding to the upper  $Q$  limit for  $D = 10\text{ nm}$  is  $1.4^\circ$  for  $\text{Cu K}\alpha$  radiation, but amounts to  $9.1^\circ$  for neutrons of 10 nm wavelength. Consequently, it is preferable to speak of low- $Q$  rather than of small-angle neutron scattering.

'Pin-hole'-type cameras are the most frequently used SANS instruments; an example is the SANS camera D11 at the Institut Max von Laue-Paul Langevin in Grenoble, France (Ibel, 1976; Lindner, May & Timmins, 1992), from which some of the numbers below are quoted. Since the cross section of the primary beam is usually chosen to be rather large (*e.g.*  $3 \times 5\text{ cm}$ ) for intensity reasons, pin-hole instruments tend to be large. The smallest  $Q$  value that can be measured at a given distance is just outside the image of the direct beam on the detector (which either has to be attenuated or is hidden behind a beamstop, a neutron-absorbing plate of several  $10\text{ cm}^2$ , *e.g.* of cadmium). Very small  $Q$  values thus require long sample-to-detector distances. The area detector of D11, with a surface of  $64 \times 64\text{ cm}$  and resolution elements of  $1\text{ cm}^2$ , moves within an evacuated tube of 1.6 m diameter and a length of 40 m. Thus, a  $Q$  range of  $5 \times 10^{-3}$  to  $5\text{ nm}^{-1}$  is covered. The geometrical resolution is determined by the length of the free neutron flight path in front of the sample, moving sections of neutron guide into or out of the beam ('collimation'). In general, the collimation length is chosen roughly equal to the sample-to-detector distance. Thus, the geometrical and wavelength contributions to the  $Q$  resolution match at a certain distance of the scattered beam from the direct-beam position in the detector plane. In order to resolve scattering patterns with very detailed features, *e.g.* of particles with high symmetry, longer collimation lengths are sometimes required at the expense of intensity.

Much more compact double-crystal neutron diffractometers [described for X-rays by Bonse & Hart (1966)] are being used to reach the very small  $Q$  values of some  $10^{-4}\text{ nm}^{-1}$  typical of static light scattering. The sample is placed between two crystals. The

first crystal defines the wavelength and the direction of the incoming beam. The other crystal scans the scattered intensity. The resolution of such an instrument is mainly determined by the Darwin widths of the ideal crystals. This fact is reflected in the low neutron yield. Slit geometry can be used, but not 2D detectors.

A recent development is the ellipsoidal-mirror SANS camera. The mirror, which needs to be of very high surface quality, focuses the divergent beam from a small (several  $\text{mm}^2$ ) source through the sample onto a detector with a resolution of the order of  $1 \times 1\text{ mm}$ . Owing to the more compact beam image, all other dimensions of the SANS camera can be reduced drastically (Alefeld, Schwahn & Springer, 1989). Whether or not there is a gain in intensity as compared with pin-hole geometry is strongly determined by the maximal sample dimensions. Long mirror with cameras (*e.g.* 20 m) are always superior to double-crystal instruments in this respect (Alefeld, Schwahn & Springer, 1989), and can also reach the light-scattering  $Q$  domain ( $Q_{\text{min}}$  of some  $10^{-4}\text{ nm}^{-1}$ , corresponding to particles of several  $\mu\text{m}$  dimension).

### 2.6.2.1.3. Correction of wavelength, slit, and detector-element effects

Resolution errors affect SANS data in the same way as X-ray scattering data, for which one may find a detailed treatment in an article by Glatter (1982b); there is one exception to this; namely, gravity, which of course only concerns neutron scattering, and only in rare cases (Boothroyd, 1989). Since SANS cameras usually work with pin-hole geometry, the influences of the slit sizes, *i.e.* the effective source dimensions, on the scattering pattern are small; even less important is, in general, the pixel size of 2D detectors. The preponderant contribution to the resolution of the neutron-scattering pattern is the wavelength-distribution function after the monochromatizing device, especially at larger angles. The situation is more complicated for TOF SANS (Hjelm, 1988).

As has been shown in an analytical treatment of the resolution function by Pedersen, Posselt & Mortensen (1990), who also quote some relevant references, resolution effects have a small influence on the results of the data analysis for scattering patterns with a smooth intensity variation and without sharp features. Therefore, one may assume that a majority of SANS patterns are not subjected to desmearing procedures.

Resolution has to be considered for scattering patterns with distinct features, as from spherical latex particles (Wignall, Christen & Ramakrishnan, 1988) or from viruses (Cusack, 1984). Size-distribution and wavelength-smearing effects are similar; it is evident that wavelength effects have to be corrected for if the size distribution is to be obtained.

Since measured scattering curves contain errors and have to be smoothed before they can be desmeared, iterative indirect methods are, in general, superior: A guessed solution of the scattering curve is convoluted with known smearing parameters and iteratively fitted to the data by a least-squares procedure. The guessed solution can be a simply parameterized scattering curve, without knowledge of the sample (Schelten & Hossfeld, 1971), but it is of more interest to fit the smeared Fourier transform of the distance-distribution function (Glatter, 1979) or the radial density distribution (*e.g.* Cusack, Mellema, Krijgsman & Miller, 1981) of a real-space model to the data.

### 2.6.2.2. Isotopic composition of the sample

Unlike X-rays, which 'see' the electron clouds of atoms within a sample, neutrons interact with the point-like nuclei. Since their