

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 μs 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 ^1H -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° for $\text{Cu K}\alpha$ radiation, but amounts to 9.1° 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 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 cm^2 , moves within an evacuated tube of 1.6 m diameter and a length of 40 m. Thus, a Q range of 5×10^{-3} to 5 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} 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 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_{min} of some 10^{-4} nm^{-1} , corresponding to particles of several μm 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 (1982*b*); 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

2.6. SMALL-ANGLE TECHNIQUES

form factor does not decay like the atomic form factor, an isotropic background from the nuclei is present in all SANS measurements.

While X-ray scattering amplitudes increase regularly with the atomic number, neutron coherent-scattering amplitudes that give rise to the interference scattering necessary for structural investigations vary irregularly (see Bacon, 1975). Isotopes of the same element often have considerably different amplitudes owing to their different resonant scattering. The most prominent example of this is the difference of the two stable isotopes of hydrogen, ^1H and ^2H (deuterium). The coherent-scattering length of ^2H is positive and of similar value to that of most other elements in organic matter, whereas that of ^1H is negative, *i.e.* for ^1H there is a 180° phase shift of the scattered neutrons with respect to other nuclei.

This latter difference has been exploited vastly in the fields of polymer science (*e.g.* Wignall, 1987) and structural molecular biology (*e.g.* Timmins & Zaccai, 1988), in mainly two complementary respects, contrast variation and specific isotopic labelling.

In the metallurgy field, other isotopes are being used frequently for similar purposes, for example the nickel isotope ^{62}Ni , which has a negative scattering length, and the silver isotopes ^{107}Ag and ^{109}Ag (see the review of Kostorz, 1988).

2.6.2.2.1. Contrast variation

The easiest way of using the scattering-amplitude difference between ^1H and ^2H is the so-called contrast variation. It was introduced into SANS by Ibel & Stuhrmann (1975) on the basis of X-ray crystallographic (Bragg & Perutz, 1952), SAXS (Stuhrmann & Kirste, 1965), and light-scattering (Benoit & Wippler, 1960) work. Most frequently, contrast variation is carried out with mixtures of light ($^1\text{H}_2\text{O}$) and heavy water ($^2\text{H}_2\text{O}$), but also with other solvents available in protonated and deuterated form (ethanol, cyclohexane, *etc.*). The scattering-length density of H_2O varies between $-0.562 \times 10^{10} \text{ cm}^{-2}$ for normal water, which is nearly pure $^1\text{H}_2\text{O}$, and $6.404 \times 10^{10} \text{ cm}^{-2}$ for pure heavy water.

The scattering-length densities of other molecules, in general, are different from each other and from pure protonated and deuterated solvents and can be matched by $^1\text{H}/^2\text{H}$ mixture ratios characteristic for their chemical compositions. This mixture ratio (or the corresponding absolute scattering-length density) is called the scattering-length-density match point, or, semantically incorrect, contrast match point. If a molecule contains non-covalently bound hydrogens, they can be exchanged for solvent hydrogens. This exchange is proportional to the ratio of all labile ^1H and ^2H present; in dilute aqueous solutions, it is dominated by the solvent hydrogens. A plot of the scattering-length density *versus* the $^2\text{H}/(^2\text{H}+^1\text{H})$ ratio in the solvent shows a linear increase if there is exchange; the value of the match point also depends on solvent exchange. The fact that many particles have high contrast with respect to $^2\text{H}_2\text{O}$ makes neutrons superior to X-rays for studying small particles at low concentrations.

The scattered neutron intensity from N identical particles without long-range interactions in a (very) dilute solution with solvent scattering density ρ_s can be written as

$$I(Q) = [d\sigma(Q)/d\Omega]NTA I_0 \Delta\Omega, \quad (2.6.2.1)$$

with the scattering cross section per particle and unit solid angle

$$d\sigma(Q)/d\Omega = \left\langle \left| \int [\rho(\mathbf{r}) - \rho_s] \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} \right|^2 \right\rangle. \quad (2.6.2.1a)$$

The angle brackets indicate averaging over all particle orientations. With $\rho(\mathbf{r}) = \sum b_i/V_p$ and $I(0) = \text{constant} \times \langle \left| \int [\rho(\mathbf{r}) - \rho_s] d\mathbf{r} \right|^2 \rangle$, we find that the scattering intensity at zero angle is proportional to

$$\Delta\rho = \sum b_i/V_p - \rho_s, \quad (2.6.2.2)$$

which is called the contrast. The exact meaning of V_p is discussed, for example, by Zaccai & Jacrot (1983), and for X-rays by Luzzati, Tardieu, Mateu & Stuhrmann (1976).

The scattering-length density $\rho(\mathbf{r})$ can be written as a sum

$$\rho(\mathbf{r}) = \rho_0 + \rho_F(\mathbf{r}), \quad (2.6.2.3)$$

where ρ_0 is the average scattering-length density of the particle at zero contrast, $\Delta\rho = 0$, and $\rho_F(\mathbf{r})$ describes the fluctuations about this mean. $I(Q)$ can then be written

$$I(Q) = (\rho_0 - \rho_s)^2 I_c(Q) + (\rho_0 - \rho_s) I_{cs}(Q) + I_s(Q). \quad (2.6.2.4)$$

I_s is the scattering intensity due to the fluctuations at zero contrast. The cross term $I_{cs}(Q)$ also has to take account of solvent-exchange phenomena in the widest sense (including solvent water molecules bound to the particle surface, which can have a density different from that of bulk water). This extension is mathematically correct, since one can assume that solvent exchange is proportional to $\Delta\rho$. The term I_c is due to the invariant volume inside which the scattering density is independent of the solvent (Luzzati, Tardieu, Mateu & Stuhrmann, 1976). This is usually not the scattering of a homogeneous particle at infinite contrast, if the exchange is not uniform over the whole particle volume, as is often the case, or if the particle can be imaged as a sponge (see Witz, 1983).

The method is still very valuable, since it allows calculation of the scattering at any given contrast on the basis of at least three measurements at well chosen $^1\text{H}/^2\text{H}$ ratios (including data near, but preferentially not exactly at, the lowest contrasts). It is sometimes limited by ^2H -dependent aggregation effects.

2.6.2.2.2. Specific isotopic labelling

Specific isotope labelling is a method that has created unique applications of SANS, especially in the polymer field. Again, it is mainly concerned with the exchange of ^1H by ^2H , this time in the particles to be studied themselves, at hydrogen positions that are not affected by exchange with solvent atoms, for example carbon-bound hydrogen sites.

With this technique, isolated polymer chains can be studied in the environment of other polymer chains which are identical except for the hydrogen atoms, which are either ^1H or ^2H . Even if some care has to be taken as far as slightly modified thermodynamics are concerned, there is no other method that could replace neutrons in this field.

Inverse contrast variation forms an intermediate between the two methods described above. The contrast with respect to the solvent of a whole particle or of well defined components of a particle, for example a macromolecular complex, is changed by varying its degree of deuteration. That of the solvent remains constant. Since solvent-exchange effects remain practically identical for all samples, the measurements can be more precise than in the classical contrast variation (Knoll, Schmidt & Ibel, 1985).

2.6.2.3. Magnetic properties of the neutron

Since the neutron possesses a magnetic moment, it is sensitive to the orientation of spins in the sample [see, for example, Abragam *et al.* (1982)]. Especially in the absence of any other (isotopic) contrast, an inhomogeneous distribution of spins in the