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sample is detectable by neutron low-Q scattering. The neutron spins need not be oriented themselves, although important contributions can be expected from measuring the difference between the scattering of neutron beams with opposite spin orientation. At present, several low-Q instruments are being planned or even built including neutron polarization and polarization analysis.

Studies of magnetic SANS without (and rarely with) neutron polarization include dislocations in magnetic crystals and amorphous ferromagnets [see the review of Kostorz (1988)].

Janot & George (1985) have pointed out that it is important to apply contrast variation for suppressing surface-roughness scattering and/or volume scattering in order to isolate magnetic scattering contributions by matching the scattering-length density of the material with that of a mixture of heavy and light water or oil, *etc*.

2.6.2.3.1. *Spin-contrast variation*

For a long time, the magnetic properties of the neutron have been neglected as far as 'nonmagnetic' matter is concerned. Spin-contrast variation, proposed by Stuhrmann (Stuhrmann *et al.*, 1986; Knop *et al.*, 1986), takes advantage of the different scattering lengths of the hydrogen atoms in its spin-up and spin-down states. Normally, these two states are mixed, and the cross section of unpolarized neutrons with the undirected spins gives rise to the usual value of the scattering amplitude of hydrogen. If, however, one is able to orient the spins of a given atom, and especially hydrogen, then the interaction of *polarized* neutrons with the two different oriented states offers an important contribution to the scattering amplitude:

$$A = b + 2B\mathbf{I}\cdot\mathbf{s}, \qquad (2.6.2.5)$$

where b is the isotropic nuclear scattering amplitude, B is the spin-dependent scattering amplitude, $\mathbf{s}$ is the neutron spin, and $\mathbf{I}$ the nuclear spin. For hydrogen, $b = -0.374 \times 10^{-12}$ cm, $B = 2.9 \times 10^{-12}$ cm.

The sample protons are polarized at very low temperatures (order of mK) and high magnetic fields (several tesla) by dynamic nuclear polarization, *i.e.* by spin–spin coupling with the electron spins of a paramagnetic metallo-organic compound present in the sample, which are polarized by a resonant microwave frequency. It is clear that the principles mentioned above also apply to other than biological and chemical material.

2.6.2.4. *Long wavelengths*

An important aspect of neutron scattering is the ease of using long wavelengths: Long-wavelength X-rays are produced efficiently only by synchrotrons, and therefore their cost is similar to that of neutrons. Unlike neutrons, however, they suffer from their strong interaction with matter. This disadvantage, which is acceptable with the commonly used Cu $K\alpha$ radiation, is in most cases prohibitive for wavelengths of the order of 1 nm.

Very low Q values are more easily obtained with long wavelengths than with very small angles, as is necessary with X-rays, since the same Q value can be observed further away from the direct beam. Objects of linear dimensions of several 100 nm, *e.g.* opals, where spherical particles of amorphous silica form a close-packed lattice with cell dimensions of up to several hundreds of nm, can still be investigated easily with neutrons. X-ray double-crystal diffractometers (Bonse & Hart, 1966), which may also reach very low Q, are subject to transmission problems, and neutron DCD's again perform better.

2.6.2.5. *Sample environment*

Important new fields of low-Q scattering, such as dynamic studies of polymers in a shear gradient and time-resolved studies of samples under periodic stress or under high pressure, have become accessible by neutron scattering because the weak interaction of neutrons with (homogeneous) matter permits the use of relatively thick (several mm) sample container walls, for example of cryostats, Couette-type shearing apparatus (Lindner & Oberthür, 1985, 1988), and ovens. Air scattering is not prohibitive, and easy-to-handle standard quartz cells serve as sample containers rather than very thin ones with mica windows in the case of X-rays.

Unlike with X-rays, samples can be relatively thick, and nevertheless be studied to low Q values. This is particularly evident for metals, where X-rays are usually restricted to thin foils, but neutrons can easily accept samples 1–10 mm thick.

2.6.2.6. *Incoherent scattering*

Incoherent scattering is produced by the interaction of neutrons with nuclei that are not in a fixed phase relation with that of other nuclei. It arises, for example, when molecules do not all contain the same isotope of an element (isotopic incoherent scattering). The most important source of incoherent scattering in SANS, however, is the spin-incoherent scattering from protons. It results from the fact that only protons and neutrons with identical spin directions can form an intermediate compound nucleus. The statistical probabilities of the parallel and antiparallel spin orientations, the similarity in size of the scattering lengths for spin up and spin down and their opposite sign result in an extremely large incoherent scattering cross section for ^{1}H, together with a coherent cross section of normal magnitude (but negative sign). Incoherent scattering contributes a background that can be by orders of magnitude more important than the coherent signal, especially at larger Q. On the other hand, it can be used for the calibration of the incoming intensity and of the detector efficiency (see below).

2.6.2.6.1. *Absolute scaling*

Wignall & Bates (1987) compare many different methods of absolute calibration of SANS data. Since the scattering from a thin water sample is frequently already being used for correcting the detector response [see §2.6.2.6.2], there is an evident advantage for performing the absolute calibration by H_2O scattering.

For a purely isotropic scatterer, the intensity scattered into a detector element of surface ΔA spanning a solid angle $\delta\Omega = \Delta A/4\pi L^2$ can be expressed as

$$\Delta I = I_0(1 - T_i)\delta\Omega g/4\pi, \qquad (2.6.2.6)$$

with T_i the transmission of the isotropic scatterer, *i.e.* the relation of the number of neutrons in the primary beam measured within a time interval Δt after having passed through the sample, I_{Tr}, and the number of neutrons I_0 observed within Δt without the sample. In practice, T_i is measured with an attenuated beam; typical attenuation factors are about 100 to 1000. g is a geometrical factor taking into account the sample surface and the solid angle subtended by the apparent source, *i.e.* the cross section of the neutron guide exit.

Vanadium is an incoherent scatterer frequently used for absolute scaling. Its scattering cross section, however, is more than an order of magnitude lower than that of protons. Moreover, the surface of vanadium samples has to be handled with much care in order to avoid important contributions from surface scattering by scratches. The vanadium sample has to be hermetically sealed to prevent hydrogen incorporation (Wignall & Bates, 1987).

The coherent cross sections of the two protons and one oxygen in light water add up to a nearly vanishing *coherent*-scattering-length density, whereas the incoherent scattering length of the water molecule remains very high. The (quasi)isotropic incoherent scattering from a thin, *i.e.* about 1 mm or less, sample of ^1H_2O, therefore, is an ideal means for determining the absolute intensity of the sample scattering (Jacrot, 1976; Stuhrmann *et al.*, 1976), on condition that the sample-to-detector distance L is not too large, *i.e.* up to about 10 m. A function $f(\sigma_t[H_2O], \lambda)$ that accounts for deviations from the isotropic behaviour due to inelastic incoherent-scattering contributions of ^1H_2O and for the influence of the wavelength dependence of the detector response has to be multiplied to the right-hand side of equation (2.6.2.6) (May, Ibel & Haas, 1982). f can be determined experimentally and takes values of around 1 for wavelengths around 1 nm.

Since the intensity scattered into a solid angle $\Delta\Omega$ is

$$I(Q) = P(Q)NT_sI_0g\big(\textstyle\sum b_i - \rho_s V\big)^2, \qquad (2.6.2.7)$$

where $P(Q)$ is the form factor of the scattering of one particle, and the geometrical factor g can be chosen so that it is the same as that of equation (2.6.2.6) (same sample thickness and surface and identical collimation conditions), we obtain

$$I(Q) = 4\pi P(Q)NT_sf(\sigma_t[H_2O], \lambda)\big(\textstyle\sum b_i - \rho_s V\big)^2/(1 - T[H_2O]). \qquad (2.6.2.8)$$

Note that the scattering intensities mentioned above are scattering intensities corrected for container scattering, electronic and neutron background noise, and, in the case of the sample, for the solvent scattering.

2.6.2.6.2. *Detector-response correction*

For geometrical reasons (*e.g.* sample absorption), and in the case of 2D detectors also for electronic reasons, the scattering curves cannot be measured with a sensitivity uniform over all the angular region. Therefore, the scattering curve has to be corrected by that of a sample with identical geometrical properties, but scattering the neutrons with the same probability into all angles (at least in the forward direction). As we have seen previously, such samples are vanadium and thin cells filled with light water. Again, water has the advantage of a much higher scattering cross section, and is less influenced by surface effects.

At large sample-to-detector distances (more than about 10 m), the scattering from water is not sufficiently strong to enable its use for correcting sample scattering curves obtained with the same settings. Experience shows that it is possible in this case to use a water scattering curve measured at a shorter sample-to-detector distance. This should be sufficiently large not to be influenced by the deviation of the (flat) detector surface from the spherical shape of the scattered waves and small enough so that the scattering intensity per detector element is still sufficient, for example about 3 m. It is necessary to know the intensity loss factor due to the different solid angles covered by the detector element and by the apparent source in both cases. This can be determined, for instance, by comparing the global scattering intensity of water on the whole detector for both conditions (after correction for the background scattering) or from the intensity shift of the same sample measured at both detector distances in a plot of the logarithm of the intensity *versus* Q.

2.6.2.6.3. *Estimation of the incoherent scattering level*

For an exact knowledge of the scattering curve, it is necessary to subtract the level of incoherent scattering from the scattering curve, which is initially a superposition of the (desired) coherent sample scattering, electronic and neutron background noise, and (sometimes dominant) incoherent scattering.

A frequently used technique is the subtraction of a reference sample that has the same level of incoherent scattering, but lacks the coherent scattering from the inhomogeneities under study. Although this seems simple in the case of solutions, in practice there are problems: Very often, the $^1H/^2H$ mixture is made by dialysis, and the last dialysis solution is taken as the reference. The dialysis has to be excessive to obtain really identical levels of ^1H, and in reality there is often a disagreement that is more important the lower the sample concentration is. If the concentration is high, then the incoherent scattering from the sample atoms (protons) themselves becomes important.

For dilute aqueous solutions, there is a procedure using the sample and reference transmissions for estimating the incoherent background level (May, Ibel & Haas, 1982): The incoherent scattering level from the sample, $I_{i,s}$, can be estimated as

$$I_{i,s} = I[H_2O]f_\lambda(1 - T_s)/(1 - T[H_2O]), \qquad (2.6.2.9)$$

where $I[H_2O]$ is the scattering from a water sample, $T[H_2O]$ is transmission, T_s that of the sample. f_λ is a factor depending on the wavelength, the detector sensibility, the solvent composition, and the sample thickness; it can be determined experimentally by plotting $I_{i,s}/I[H_2O]$ *versus* $(1 - T_s)/(1 - T[H_2O])$ for a number of partially deuterated solvent mixtures.

This procedure is justified because of the overwhelming contribution of the incoherent scattering of ^1H to the macroscopic scattering cross section of the solution, and therefore to its transmission. The procedure should also be valid for organic solvents. The precision of the estimation is limited by the precision of the transmission measurement, the relative error of which can hardly be much better than about 0.005 for reasonable measuring times and currently available equipment, and by the (usually small) contribution of the coherent cross section to the total cross section of the solution. A modified version of (2.6.2.9) can be used if a solvent with a transmission close to that of a sample has been measured, but the factor f_λ should not be omitted.

An equation similar to (2.6.2.9) holds for systems with a larger volume occupation c of particles in a (protonated) solvent with a scattering level $I_{\rm inc}$ in a cell with identical pathway (without the particles):

$$I_{i,s} = I_{\rm inc}(1 - T_{\rm inc}^{1-c})/(1 - T_{\rm inc}). \qquad (2.6.2.9a)$$

In this approximation, the particles' cross-section contribution is assumed to be zero, *i.e.* the particles are considered as bubbles.

In the case of dilute systems of monodisperse particles, the residual background (after initial corrections) can be quite well estimated from the zero-distance value of the distance-distribution function calculated by the indirect Fourier transformation of Glatter (1979).

2.6.2.6.4. *Inner surface area*

According to Porod (1951, 1982), small-angle scattering curves behave asymptotically like $I(Q) = \text{constant} \times A_sQ^{-4}$ for large Q, where A_s is the inner surface of the sample. Theoretically, fitting a straight line to $I(Q)Q^4$ *versus* Q^4 ('Porod plot') *at sufficiently large* Q therefore yields a zero intercept, which is proportional to the internal surface; a slope

references