Recent Developments in X-ray and Neutron Small-Angle Scattering Instrumentation and Data Analysis*†

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The developments in instrumentation and data analysis that have occurred in the field of small-angle X-ray and neutron scattering since 1973 are reviewed. For X-rays, the cone camera collimation system was invented, synchrotrons and storage rings were demonstrated to be intense sources of X-radiation, and one- and two-dimensional position-sensitive detectors were interfaced to cameras with both point and line collimation. For neutrons, the collimators and detectors on the Jülich and Grenoble machines were improved, new D11-type instruments were built or are under construction at several sites, double-crystal instruments were set up, and various new machines have been proposed. Significant progress in data analysis and evaluation has been made through application of mathematical techniques such as the use of spline functions, error minimization with constraints, and linear programming. Several special experiments, unusual in respect to the anisotropy of the scattering pattern, gravitational effects, moving scatterers, and dynamic fast time slicing, are discussed.

I. Introduction

From the earliest developments of small-angle scattering, it was recognized that the technique could be widely applied in various fields such as metallurgy, biophysics, polymer science, and physical chemistry. In the first three decades (1940–1970) there was a steady growth along well-established principles, using for the most part long-slit cameras. This growth is evidenced by conferences such as the 1958 Kansas City meeting (Guinier, 1959), the first and second international conferences held in Syracuse, USA (Brumberger, 1965), and Graz, Austria (Guinier & Brumberger, 1971) and by the now-classical texts of Guinier & Fournet (1955) and Hendricks, 1976. The Kratky cone camera (1972). Despite the tremendous improvement in the design and performance of one- and two-dimensional position-sensitive detectors had been achieved for both X-rays and neutrons (e.g. Hendricks, 1976). The first application of a linear PSD with the advantage of much faster data collection in small-angle X-ray experiments was reported by Dupont, Gabriel, Chabre, Gulik-Krezwicki & Schlechter (1972). Despite the tremendous improvement in data acquisition, at the time of the Grenoble conference small-angle X-ray scattering was still performed for the most part in the traditional long-slit geometry.

In 1973 the situation for neutrons was quite different. The Jülich machine with its six linear PSDs, first announced at the Graz conference in 1970, had been in routine use for three years. The D11 instrument at the Institut Laue–Langevin in Grenoble with its two-dimensional PSD had been operating at the High-Flux Reactor (HFR) for about a year (Schmatz, Springer, Schelten & Ibel, 1974; Ibel, 1976). In contrast to the X-ray situation, neutron experiments on both instruments were performed in point geometry with only minor resolution corrections. These developments are for the most part responsible for the dramatic transition in emphasis from X-rays to neutrons. This transition is evidenced by the fact that only one neutron paper was presented at the 1970 Graz meeting while just three years later.
fully 30% of the contributions to the Grenoble conference dealt with neutrons. By 1973 it was already clear that position-sensitive detectors and high-flux reactors had revolutionized small-angle scattering with neutrons. Such a revolution had not yet taken place with X-rays even though one- and two-dimensional position-sensitive detectors were available and very powerful rotating-anode X-ray generators (50–100 kW) and synchrotron radiation could serve as high intensity sources of radiation. That it should occur was obvious. It was also apparent in 1973 that SANS instruments which fully utilized all of the new technology were large and expensive. Thus, researchers could no longer perform experiments in their own small-scale laboratories as was then common in X-ray SAS; rather, there would be a shift to the use of a few large-scale central facilities, a mode already common amongst high-energy physicists. A similar observation could be made for the anticipated analogous X-ray machines.

In parallel with these instrumentation developments significant progress in the analysis of scattering was being made. The expansion of the shape and electron density distribution of non-spherical scatterers as developed by Stuhrmann (1970) turned out to be an appropriate method to obtain quantitative information from SAS patterns of macromolecules in solution. New mathematical techniques involving spline functions for series expansion, minimization procedures with constraints to stabilize matrix inversions, and linear programming techniques to insure solutions with physical meaning became fashionable in the field of small-angle scattering. They were applied to the problems of obtaining the desmeared scattering function itself (Stallmann, 1970; Schelten & Hossfeld, 1971; Glatter, 1974) or model parameters from real scattering data with statistical errors (Sjöberg, 1978).

The brief historical survey of small-angle scattering instrumentation and analysis given above describes the situation at the time of the last international small-angle scattering conference (1973). Our present purpose is to review in some detail the technological developments which have occurred during the past four years. In the three following papers Stuhrmann & Miller (1978) review the recent developments in the application of the technique to biological materials, Higgins & Stein (1978) cover polymers, and Gerold & Kostorz (1978) cover materials science. It is our goal that these four review papers taken together will provide a summary of the recent development of the whole field of small-angle scattering, and will help place the research papers of the fourth conference, at Gatlingburg (1977), in perspective.

§ II of this paper reviews the progress in both X-ray and neutron position-sensitive detectors. § III considers the development of new small-angle X-ray scattering facilities. Among these are the cone collimation system, collimation systems for use at synchrotron and storage-ring sources, the application of linear PSDs to both long-slit and pinhole collimation instruments and the development of a fully computerized facility with pinhole geometry and a two-dimensional PSD. § IV reports the instrumental developments for small-angle neutron scattering. There the efficiency of a double-crystal instrument is compared with that of a conventional long instrument, new facilities at various reactor centers and improvements to existing facilities are described, and proposed instruments at pulsed and steady sources are cited. In § V examples are given to illustrate the advantages to combined X-ray and neutron small-angle scattering experiments with the same specimen. The progress in scattering-data analysis with techniques such as collimation corrections and such as particle size distribution or electron density determination is considered in § VI. Finally, special applications of small-angle scattering are considered in § VII. Among these are (1) the measurement of anisotropic scattering in a rotation experiment, (2) the determination of the velocity of moving scatterers from the analog of the astronomical aberration effect, (3) a fundamental experiment which demonstrates that the angle of reflection of neutrons from the boundary between two domains in a magnetic material (Bloch walls) is a function of the magnitude of the magnetic induction |B|, (4) an attempt to measure inelastic neutron small-angle scattering due to the anisotropy of the scattering pattern caused by gravitational effects, (5) dynamic X-ray studies of the contraction of muscle and the crystallization of polyethylene, and (6) some considerations of the correlation between inelastic scattering experiments (e.g. with neutrons) and fast time-slicing dynamic experiments. We conclude with some speculations about the future development of small-angle scattering.

II. Position-sensitive detectors

From the point of view of small-angle scattering one of the most significant technological achievements of the past decade has been the invention of both one- and two-dimensional position-sensitive X-ray and neutron detectors. It is clear that these devices have revolutionized the field of small-angle scattering. The development of position-sensitive detectors for diffraction research has followed several lines, the most prominent techniques of which involve the use of channel plates, solid-state detectors, television-based systems, and gas-filled ionization and proportional counters. However, to date it is for the most part only the ionization and proportional counters which have been applied in either X-ray or neutron small-angle scattering. In this section, we review briefly the operation of such detectors. More detailed reviews have been given by Dehme & Pepelyshev (1973), Hendricks (1976), Arndt & Faruqi (1977), and Faruqi (1977).

II.1 One-dimensional proportional counters

The simplest device is the straight one-dimensional proportional counter. In this device, as in the non-position-sensitive proportional counter, the incident radiation creates electrons and positive ions either by direct ionization of the fill gas (X-rays) or in the case of neutrons by a secondary process in which the neutron is absorbed in a gas such as $^4$He or BF$_3$ and the resultant proton or $\alpha$-particle indirectly ionizes another component of the fill gas, such as Ar. The electrons are accelerated towards the anode, and in the case of the proportional counter, the field strength at the anode is large enough for the electrons to gain sufficient energy to cause further ionization and produce a gas amplification of the signal. For the X-ray detector, the total charge created either with or without amplification is proportional to the energy of the incident photon. Such is not the case for the neutron detector because the energy of the resultant proton or $\alpha$-particle is essentially independent of the energy of the incident thermal neutron. In the non-position-sensitive detector the charge created in the detector is processed through pulse-shaping electronics and is counted in a scaler.

In the position-sensitive detector, the current which results from the movement of the positive ions in the fill gas causes a current to flow from both ends of the detector. Three techniques have been developed for position encoding:
appropriate coincidence circuitry, (2) orthogonal wires connected which is connected a separate set of electronics and appro-
riate to the sum of the pulse heights from both ends is a linear function of the arrival coordinate of the incident particle. This method has not been widely used, because at the time the detectors were developed charge-division circuits with adequate speed and linearity had not been developed. This objection is no longer valid (Alberi, Fischer, Radeka, Rogers & Schoenborn, 1975). In the pulse-shape method, the detector is treated as a distributed RC line. It can be shown that the position of the incident particle can be obtained from the difference in rise times (slopes) of the signals from each end of the detector. Such measurements can be performed with commercially available timing circuits, and the technique has become the standard method for linear detectors. In the delay-line method, the cathode wires are connected to taps on specially constructed delay lines. The anode signal is used to start a time-to-amplitude converter, and the stop signal, which is generated on the cathode, is delayed by an amount proportional to the position coordinate of the event. In an interesting variant of the RC (pulse-shape) position-encoding method, Gabriel (1977) has developed an L-C (inductance-capacitance) pulse-shape position-sensitive detector which utilizes a metal anode.

Spatial resolutions of about 500 μm for X-rays and 5 mm for neutrons are now commonplace, while with special techniques (e.g. high gas pressures) resolutions of 100 μm for X-rays (Faruqi, 1975b) and 2 mm for neutrons can now be achieved. These developments are the subject of other papers given at the Gatlinburg conference (Allemand, Bourdel, Farnoux & Gagelin, 1977; Borkowski & Kopp, 1978; Kreutz, Fritz & Henne, 1977; Sand & Crist, 1977).

Such detectors are now commercially available from several manufacturers and are becoming widely applied in both X-ray and neutron small-angle scattering.

II.2 Two-dimensional proportional counters

The development of the two-dimensional position-sensitive detectors has been more complex (Hendricks, 1976; Faruqi, 1977). For devices now in use in small-angle cameras, three methods have been used. In each the detector consists of an array of anode wires sandwiches between two cathode planes. The cathode planes consist of (1) orthogonal strips, to each of which is connected a separate set of electronics and appropriate coincidence circuitry, (2) orthogonal wires connected to delay lines and timing circuits, or (3) continuous orthogonal arrays of wires, the signals from which are processed by either charge-division or pulse-shape analysis. In each of these detectors use is made of what is known as 'center-of-gravity' position encoding. Here, use is made of the fact that the charge collected on the anode wires induces a charge on each cathode plane, the spatial extent of which is approximately the dimension of the anode-cathode plane spacing, usually 6–20 mm. This is sufficiently broad to cover several wires or strips in the cathode plane. Hence, by measuring the charge from each strip or wire and calculating the center of gravity of the distribution it is possible to inter-

polate the position of the event with accuracy greater than the cathode wire spacing. This interpolation technique may be done via software (very slowly!) or via special hardware (Parkman, Hajduk, Jeavons, Ford & Lindberg, 1975) for strip cathodes. The interpolation is automatically performed in the charge-division, delay-line, and pulse-shape analysis methods. Currently the spatial resolution of the X-ray detectors is about 1 mm FWHM, while for neutrons it is 2–5 mm. A serious problem associated with the high-resistance anode linear PSD and the continuous-cathode two-dimensional PSDs has been that of pulse pile-up limitations on the count-rate capability of the system. Recently, Kopp (1975, 1977) has solved this difficulty with the development of a preamplifier with output stabilization by pole-zero cancellation in the feedback circuit. With these new preamplifiers, which are now routinely used with all Oak Ridge National Laboratory (ORNL) position-sensitive detectors, count rates of about 10^5 s^-1 can be achieved with only minimal loss in spatial resolution.

II.3 Imaging detector

We cannot leave the topic of position-sensitive detectors without commenting on a recent development which may be of great importance to X-ray small-angle scattering in the near future. This is the recent announcement of a high-resolution imaging X-ray detector (Kellog, Henry, Murray & Van Spraybroeck, 1976) and the Photicon (Kellog, Murray, Briel & Bardas, 1977). The high-resolution X-ray detector uses a pair of cascaded microchannel plates (MCPs) with 16 μm bore as a photocathode followed by a pair of orthogonal grids of cathode wires, which perform as a two-dimensional position-sensitive detector. About 10% of the incident photons create a photoelectron in a tube: the potentials across the tube create a cascade with a gain of 10^7–10^8. The charge cloud emanating from the back of the MCP is collected over several wires in the crossed-wire grid which consists of 100 μm wires on 200 μm centers. Center-of-gravity position encoding is performed by charge division with a resolution of 10 μm FWHM! Since the detector is 26 × 26 mm the system can, in principle, resolve 6.8 × 10^6
interest in SAS and the lack of energy resolution.

The most serious problems at present are the poor quantum efficiency of the channel plate for radiations of a wavelength equal to or shorter than 1 Å (cutoff at 10 Å). The count-rate capability is currently about $10^4$ counts s$^{-1}$ The cathode and imaging electrostatic optics are used in front of the MCP. Thereafter, the system performs as the device described above. A schematic is shown in Fig. 1. For X-rays, and the application of one- and two-dimensional position-sensitive detectors of X-ray small-angle scattering.

In this section we shall consider the invention of a totally new collimation system (the Kratky cone camera), the development of synchrotrons and storage rings as intense sources of X-rays, and the application of one- and two-dimensional position-sensitive detectors of X-ray small-angle scattering.

### III.1 The Kratky cone camera

Perhaps the only invention of a new collimation geometry for SAS in the past two decades has been the development of the cone camera (Kratky, 1969; Kratky, Stabinger, Wrentschur & Zipper, 1976). This device is designed to overcome both the problems of difficult slit-length collimation corrections in the weak tails of scattering curves obtained in long-slit geometry and the problems of the weak scattering in point geometry. The principle of the new collimation geometry is illustrated in Fig. 2 and is as follows: a diverging cone of radiation is created in a cylindrically symmetric collimation system (K) in which a tapered needle (N) is centered in a hollow cone (HK) and is followed by a cylindrical edge (B). The divergence of the radiation in the cone is controlled by the spacing of the needle (N) and the cone (HK). The edge B provides a parasitic-scattering-free region along the camera axis. A slit (LB) and a detector (D) are positioned on the camera axis about 35 cm from B. The radiation scattered into the pinhole LB by the sample P makes an angle 20 with the incident ray. The scattering angle is changed by moving the sample along the axis (in the original unit, the sample was fixed and the detector was moved). Since all radiation entering the slit LB makes the same angle 20 with the incident beam, the system is a pseudo pinhole device. However, it must be recalled that the diffraction vectors created by all rays in the cone are uniformly distributed in all directions of the plane of the sample. Thus the system is not capable of recording data from anisotropic scatterers. Its strong advantage is a very low-background for a point-averaged system of weak, low-resolution scattering patterns.

### III.2 Small-angle scattering at synchrotron and storage-ring sources

It has been known for some time that the electromagnetic radiation emitted by relativistic electrons circulating in synchrotrons or storage rings can be used as an intense source of X-rays for diffraction research (e.g. Perlman, Rowe & Watson, 1974). Internationally there are now some half-dozen such facilities, all of which operate in a parasitic fashion on machines designed for high-energy physics (Table 1).

In recent years, it has become clear that facilities designed for high-energy physics are not optimized for diffraction research, and that the potential of such sources is so promising that dedicated facilities should be constructed. Two such dedicated facilities which emit photons at X-ray energies are now either in the design phase (the Brookhaven National Synchrotron Light Source in the USA) or already under construction (SRS, at the Daresbury Laboratory in the UK).

Although the details of the radiation spectra vary among machines, there are three properties common to all of these.

<table>
<thead>
<tr>
<th>Location</th>
<th>Type</th>
<th>Critical wavelength (Å)</th>
<th>Flux (at 1 Å, Å$^{-1}$)</th>
<th>Operating conditions (GeV, mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NINA, Daresbury, UK</td>
<td>Syn</td>
<td>0.84</td>
<td>2.5 × 10$^{15}$</td>
<td>(5, 20)</td>
</tr>
<tr>
<td>DESY, Hamburg, BRD</td>
<td>Syn</td>
<td>0.74</td>
<td>5.0 × 10$^{14}$</td>
<td>(6, 40)</td>
</tr>
<tr>
<td>DCI, Orsay, France</td>
<td>SR</td>
<td>2.73</td>
<td>3.0 × 10$^{15}$</td>
<td>(1.8, 500)</td>
</tr>
<tr>
<td>SPEAR, Stanford, USA</td>
<td>SR</td>
<td>1.24</td>
<td>4.5 × 10$^{15}$</td>
<td>(3.5, 500)</td>
</tr>
<tr>
<td>DORIS, Hamburg, BRD</td>
<td>SR</td>
<td>1.90</td>
<td>1.8 × 10$^{16}$</td>
<td>(3, 1000)</td>
</tr>
<tr>
<td>BNSLS, Brookhaven, USA</td>
<td>SR</td>
<td>3.0</td>
<td>6.0 × 10$^{15}$</td>
<td>(2.5, 500)</td>
</tr>
<tr>
<td>VEPP-3, Novosibirsk, USSR</td>
<td>SR</td>
<td>3.26</td>
<td>1.0 × 10$^{15}$</td>
<td>(2.2, 100)</td>
</tr>
<tr>
<td>SRS, Daresbury, UK</td>
<td>SR</td>
<td>3.9</td>
<td>5.0 × 10$^{15}$</td>
<td>(2.0, 500)</td>
</tr>
<tr>
<td>CESR, Cornell, USA</td>
<td>SR</td>
<td>3.35</td>
<td>1.2 × 10$^{16}$</td>
<td>(8, 100)</td>
</tr>
</tbody>
</table>

* Shut down 1977.
sources: (1) they are pulsed, generally with frequencies near 1 MHz, (2) the radiation is almost linearly polarized, and (3) the spectrum is continuous.

In the synchrotron, electrons are injected into the ring at low energies, accelerated to the desired energy, and then extracted for the physics experiment. This process is then repeated with a new injection of electrons. It is only near the end of the acceleration stage that the electrons have sufficient energy to emit radiation in the range 0.5–20 Å. Thus, X-rays are produced with a time structure which is long compared to the circulating frequency of the electrons. Haselgrove, Faruqi, Huxley & Arndt (1977) have suggested some potential dynamic experiments which utilize this feature. In a storage ring, on the other hand, electrons are injected and accelerated to their final energy but are not extracted from the ring. Thus, the radiation remains at its maximum value, and is pulsed with the frequency of the electron bunch circulating past the photon port. (Because of machine losses, the beam decays by 50% in typically 4–8 h, at which time the ring is refilled). There are, of course, several difficulties associated with utilizing such radiation for small-angle scattering, the most important of which are those associated with radiation safety, which force experiments to be performed by remote control, and those associated with beam heating, which can become severe for biological samples. These difficulties are compensated by the brilliance of the source, its wavelength tunability, and its high degree of collimation. Further properties of synchrotron radiation may be found in various reviews (e.g., Codling, 1973; Perlman et al., 1974; Kunz, 1975; Lindau & Winick, 1976).

The first small-angle scattering experiment using synchrotron radiation was reported by Rosenbaum et al. (1971). Further developments are presented by Barrington Leigh, Holmes & Rosenbaum (1972; Barrington Leigh & Rosenbaum, 1974, 1976). In this instrument, two 20 cm-long polished total-reflection glass mirrors were bent to a radius of 1 km and were placed in the horizontal plane to focus the slightly diverging radiation, and a quartz crystal, set at 26°, was used to select 1.5 Å radiation from the spectrum reflected by the mirrors. With proper adjustment the mirrors can be used to eliminate shorter wavelengths in order that harmonics are not diffracted by the crystal. Appropriate collimation slits were placed at the sample position and either film or a linear position-sensitive detector was used for data recording. A schematic of the instrument is shown in Fig. 3. A difficulty with this instrument is the rather high parasitic scattering. This has been determined to result not only from slit-edge scattering, but also from the mirrors and from the monochromator crystal (Barrington Leigh & Rosenbaum, 1976). A possible source of difficulty with quartz monochromators arises because, when they are irradiated to high fluences of X-radiation, color centers (presumably formed at OH- ions) agglomerate at room temperature into defects with \( R_t \approx 30 \) Å (R. W. Hendricks, unpublished research). These defects cause the crystal to turn black, and their small-angle scattering would be expected to contribute to the background. There are conflicting reports that the parasitic scattering is decreased by using perfect Si or Ge crystals.

Similar mirror–monochromator instruments have been constructed for use at NINA (Haselgrove et al., 1977) and SPEAR (Webb, Samson, Stroud, Gamble & Baldeschweiler, 1976, 1977). In each of these instruments, new developments such as gold-plated mirrors, monochromator crystals bent in a logarithmic spiral, etc. were employed. [Apparently Au is evaporated rapidly from the mirror surfaces due to beam heating, while Pt is relatively stable (A. R. Faruqi, private communication).] In all cases, although mirrors having dimensions of up to 2 m were desirable in order to intercept...
Table 2. Summary of operating parameters of small-angle scattering cameras constructed at synchrotron and storage-ring sources

<table>
<thead>
<tr>
<th>Location</th>
<th>Collimation system</th>
<th>Angular aperture (vertical/horizontal)</th>
<th>Ring conditions (GeV, mA)</th>
<th>Observed power (photons s⁻¹)</th>
<th>Calculated power (photons s⁻¹)</th>
<th>Beam size at sample (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DESY</td>
<td>Mirror/mono</td>
<td>1 x 3</td>
<td>(7.2, 11)</td>
<td>5 x 10⁶</td>
<td>1.7 x 10⁸</td>
<td>3 x 3</td>
</tr>
<tr>
<td>NINA</td>
<td>Mirror/mono</td>
<td>~-3.3 x 3.3</td>
<td>(5.15)</td>
<td>1.2 x 10⁶</td>
<td>5 x 10⁸</td>
<td>5 x 5</td>
</tr>
<tr>
<td>NINA</td>
<td>Ge crystal</td>
<td>0.5 x 0.5</td>
<td>(4.10)</td>
<td>1 x 10⁶</td>
<td>0.25 x 0.25</td>
<td>5 x 5</td>
</tr>
<tr>
<td>SPEAR</td>
<td>Mirror/mono</td>
<td>~-3.5 x 3.5</td>
<td>(3.7, 20)</td>
<td>6 x 10⁶</td>
<td>6.8 x 10⁸</td>
<td>5 x 5</td>
</tr>
<tr>
<td>SPEAR</td>
<td>Double-curved mirror/channel cut crystal</td>
<td>0.6 x 6</td>
<td>(3.2, 20)</td>
<td>1 x 10¹²</td>
<td>1 x 10¹²</td>
<td>2 x 3</td>
</tr>
<tr>
<td>DORIS</td>
<td>Mirror/Ge mono</td>
<td>4 x 4</td>
<td>(2.1, 180)</td>
<td>1.5 x 10⁹</td>
<td>4 mm</td>
<td></td>
</tr>
</tbody>
</table>


The full vertical aperture of the beam, usually pairs of 40 cm mirrors were used (120 cm at SPEAR). The parasitic scattering from the instruments has also been disappointing high (Beaumont, Grime & Hart, 1976; Haselgrove et al., 1977; Rubin, 1977). The application of these instruments to biophysical research is reviewed in the companion paper by Stuhrmann & Miller (1978), as well as the recent reviews of Holmes (1974, 1976), Barrington Leigh & Rosenbaum (1976), and Barrington Leigh et al. (1977).

It is important to note that the performance of the mirror-monochromator systems described above has been disappointing in that the actual power on the specimen is a decade or more below that anticipated from theoretical calculations (see Table 2). However, the results of Hastings, Kincaid & Eisenberg (1978) at SPEAR, in which they mounted a channel-cut crystal after a focusing mirror, have shown that the calculated results are not far from correct, and that the discrepancy between calculated and observed power in the other systems is real, as may be seen in Table 2. This suggests that the complex mirror-monochromator systems are not as efficient as simple physics suggests. Bordas (private communication) has suggested that the problem is probably associated with the focusing properties of the monochromating crystals and not with the mirrors.

There has been some discussion regarding the optimum monochromator design for small-angle scattering facilities which utilize synchrotron light. Barrington Leigh & Rosenbaum (1976) and Webb et al. (1977) have discussed the essential need for mirror-monochromator systems in order to utilize effectively the full divergence of the synchrotron beam. However, a serious difficulty with such systems is the complexity of remote alignment procedures (e.g. Vibert, Craig & Cohen, 1977). Beaumont et al. (1976) have argued convincingly in favor of a focusing system using only a planar Ge crystal. It has the advantage of being cheap and simple to align. In this design the beam size is determined by the size of the aperture at the crystal. This system is claimed to have significantly lower parasitic scattering than the mirror-monochromator systems. A machine using a flat Ge crystal monochromator has been recently installed at the DORIS storage ring in Orsay (Rousseaux, Tchoubar, Pons & Lemonnier, 1977), while Kretschmar, Mendelson & Morales (1976) have used a double-crystal spectrometer system with a linear position-sensitive detector at SPEAR in Stanford.

A completely different approach to X-ray powder diffraction was proposed by Giessen & Gordon (1968). Their idea was to hold the scattering angle fixed and use a solid-state detector with excellent energy resolution and a multichannel analyzer to record the variation of energy (wavelength) of the scattered radiation. Sparks & Gedke (1972) have given further quantitative details. Schultz & Long (1975) were the first to apply this idea to small-angle scattering where they mounted a Si(Li) detector on a Kratky camera. The white radiation from a tungsten target was used as a source. Bordas, Munro & Glazer (1976) recognized the immense potential of this technique for use with synchrotron radiation because, unlike the systems described above in which a monochromator is used to select only a small fraction of the incident spectrum (which is ideal for sources with intense characteristic radiation peaks), this method fully utilizes all of the intense white spectrum. The principle of the system is illustrated in Fig. 4. Here, a plane parallel source of white radiation is incident upon the sample. If we utilize the equation

\[ E = 12.4/\lambda, \]

which relates the energy \( E \) (in keV) and wavelength \( \lambda \) (Å) of the radiation, then from Bragg's law it is readily shown that

\[ E = 12.4n/2d \sin \theta. \]

Hence, if the energy of the scattered radiation is measured at fixed scattering angle, there is an inverse relationship between the energy of the scattered radiation and the \( d \) spacing. As an example, Bordas et al. (1976) were able to record the first five orders of the diffraction pattern from rat-tail collagen using energies between 5 and 30 keV. By increasing \( \theta \), the energy at which a given reflection occurs can be decreased and higher-order reflections will then appear at

![Fig. 4. Energy-dispersive small-angle X-ray scattering system used at NINA in Daresbury Laboratory. UK (taken from Bordas et al., 1976).](image-url)
higher energies. Thus, in analogy to decreasing the specimen-to-detector distance in a normal camera in order to record lower-resolution data, in this system one simply moves the energy-dispersive detector to higher angles. Further details of this technique are given in the paper by Bordas & Randall (1978). The analogy of such a system to the time-of-flight (TOF) neutron-scattering spectrometers being developed at pulsed neutron sources will be discussed in § IV.2.

Present limitations of this technique result from (i) the low count-rate capabilities of the detector electronics and (ii) slow analog-to-digital converters (ADCs). A potential solution is to manufacture multiple solid-state detectors on the same chip. In this way, several θ angles can be measured simultaneously. Realistically, a linear array of 20 such detectors could provide an instrument which could cover a ~ resolution, the incident power on the sample, and to a lesser extent, the size of the beam at the specimen. We have summarized the available data for each of the instruments mentioned above in Table 2. In order to have a valid intercomparison of the power incident on the sample, it is essential to scale the data to the same angular resolution.

In most small-angle scattering experiments not only the power on the specimen (at the desired angular resolution) but also the total data acquisition rate must be considered as important parameters. The latter is the product of the incident beam power, the efficiency of the detector, and the number of data points simultaneously recorded. Thus, to utilize effectively the very high fluxes available from synchrotron radiation, it has been clear for some time that position-sensitive detectors must be used. To date, only linear detectors have been utilized at the three Western synchrotron centers (e.g., Holmes, 1974; Yu et al., 1976; Kretzschmar et al., 1976; Barrington Leigh & Rosenbaum, 1976) while only at VEPP-3 in Novosibirsk has an area detector been used (Baru, Mokul’skaya, Mokul’ski, Sidorenko & Khabakhpashev, 1976). If the specimen under investigation shows a k range of 5 × 10^{-3} to 5 Å^{-1} [k=(4π/λ)sinθ] with a count-rate capability of 500000 cps. Area detectors of this type are foreseeable, although the cost of electronics will be high.

What are ultimately the only parameters of importance in any small-angle scattering camera are the angular resolution (or k resolution), the incident power on the sample, the signal-to-noise ratio of the system, the speed of data acquisition, and to a lesser extent, the size of the beam at the specimen. We have summarized the available data for each of the instruments mentioned above in Table 2. In order to have a valid intercomparison of the power incident on the sample, it is essential to scale the data to the same angular resolution.

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The long instruments described above are simple X-ray analogues of the much larger neutron machines at the FRJ-2 reactor in Jülich (Schelten, 1972) and the HFR in Grenoble (Schmatz et al., 1974; Ibel, 1976). What remained for X-ray small-angle scattering was the construction of the X-ray analog of these machines. This was accomplished by Hendricks (1978) between 1974 and 1976, who constructed a 10-meter camera which utilizes a 6 kW rotating-anode X-ray source, incident-beam graphite monochromator, pinhole collimation, and a two-dimensional position-sensitive detector. The detector is a Borkowski-Kopp continuous-cathode device in which the anode and cathode wire spacings are 2 mm, the fill gas is 1 atm of Ar-5% CO₂† and there is a 10 cm drift field in front of the detector planes. Position encoding is via the RC-line method. The flight path is totally evacuated (5 μm Hg), and is mounted on a box beam which pivots directly under the monochromator crystal, thus allowing for changes in either the incident wavelength (Cu Kα or Mo Kα) or monochromator crystal. The angular resolution of the camera is changed by removing sections of the beam pipes to shorten the spacing between the entrance slit, the collimating slit at the sample, and the sample-to-detector distance. Perhaps the most significant feature of this machine is its advanced data-acquisition and analysis system, as shown schematically in Fig. 5. A medium-scale minicomputer having 65 K words of 16-bit 800-ns core memory (a ModComp II) is interfaced to the detector electronics via a high-speed microcomputer (Twichell & Hendricks, 1976, 1978; Hendricks, 1978). This interface allows for high-speed memory switching (~2 μs) between different data arrays, thus opening the possibility for fast dynamic experiments heretofore not possible.

A complete description of the camera is presented elsewhere (Hendricks, 1978), while examples of its performance are presented in several other papers submitted to the Gatlinburg conference. Among these are studies of voids in neutron-irradiated molybdenum (Liu, Moteff, Hendricks & Lin, 1978), plastically deformed polyethylene (Baczek, Stein, Carlson & Hendricks, 1978), crystallization kinetics of polyethylene (Schultz, Hendricks & Lin, 1978), and microporosity and micromineralogy of a bituminous coal (Lin, Hendricks, Harris & Yust, 1978). Experience with the ORNL 10 m X-ray camera, as with the D11 neutron camera, is indicating that one of its most powerful features is the ability to record and analyze quantitatively anisotropic scattering patterns.

Another small-angle X-ray scattering system with an area detector is under development by Hashizume, Amemiya, Mase & Kohra (1977a).

Before we leave the subject of new X-ray cameras, a quantitative comparison of various collimation systems would be instructive. For this comparison, we consider the neutron scattering facility at the FRJ-2 reactor in Jülich with its bank of five linear PSD's (Schelten, 1972), a commercially available Kratky camera operating on a specially designed X-ray tube in the long-slit geometry, a 2 m pinhole camera with a single linear PSD (Schelten & Hendricks, 1975), and the new 10 m camera with its area PSD. There are several parameters which are important for such an intercomparison; the X-ray source, its monochromatization and apparent brilliance, the collimation conditions and the resulting power incident on the sample, the effective resolution of the collimation system in terms of both the minimum angle, θ_{min}, to which data can be recorded and the spread of wave vector, Δk, within a given resolution element, and finally the number of data points simultaneously recorded and the total solid angle subtended by the detector on the sample, which gives a measure of the total data rate capability of the system. With the use of data developed by Schelten & Hendricks (1975) and Hendricks (1978) such a comparison is presented in Table 3. In the comparison of the Kratky camera and the linear PSD system, the resolution of the Kratky camera was set to be a little poorer than that of the PSD system. Thus it takes about twice as long to record a scattering pattern from a polyethylene (Lupolen) standard sample containing the same total number of photons with the 2 m camera as with the Kratky camera.

Several significant observations may be drawn from the data of Table 3. First, although the power incident on the sample is about a decade higher for the long-slit geometry, the use of the linear (one-dimensional) PSD for simultaneous data recording allows the measurement of a true scattering pattern, free of the need for collimation corrections, in approximately the same experimental time as that required to measure the slit-smeared data in the Kratky camera. Second, it is seen that by full use of the total area of the focal spot it was possible to achieve over a factor of two better resolution with the 10 m machine with less than a factor of two loss in incident beam intensity as compared to the earlier 2 m camera. Experience indicates that with the

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Fig. 5. Schematic drawing of the ORNL 10 m small-angle X-ray scattering camera control and data acquisition system.
Table 3. Comparison of X-ray and neutron small-angle scattering facilities
Based on data taken from Schelten & Hendricks (1975) and Hendricks (1978).

| Radiation characteristics | Facility: |(lonely camera | One-dimensional | Two-dimensional |
|---------------------------|----------|---------------|-----------------|-----------------|-----------------|
| Source                    | Siemens special Kratky tube with 2.8 x 7 mm focal spot (40 kV, 30 mA) | Rigaku-Denki 6 kW rotating anode with 1 x 10 mm focal spot (45 kV, 100 mA) | Rigaku-Denki 6 kW rotating anode with 1 x 10 mm focal spot (45 kV, 100 mA) |
| Monochromatization        | Compression-annealed pyrolytic graphite in diffracted beam (Δλ/λ ≈ 10^{-3}) | Compression-annealed pyrolytic graphite in incident beam (Δλ/λ ≈ 10^{-3}) | Compression-annealed pyrolytic graphite in incident beam (Δλ/λ ≈ 10^{-3}) |
| λ, wavelength (Å)         | 1.542    | 1.542         | 1.542           | 1.542           |
| φ, apparent source brilliance (particles s^{-1} sterad^{-1} mm^{-1}) | 0.32 x 10^{12} | 10.7 x 10^{12} | 8.0 x 10^{12} | 5.5 x 10^{6} |
| Collimation conditions    | F_{1}, area of entrance slit (mm²) | 0.098 x 10 = 0.98 | π (1/2)^2 = 0.20 | π (2)^2 = 3.14 | 20 x 80 = 1600 |
| ΔΩ₁, solid angle of incident beam (sterad) | 0.222 x 18 (288)^2 = 48 x 10^{-6} | π (1/2)² 3 1/500 = 0.78 x 10^{-6} | (1)^2 (5000)^2 = 0.04 x 10^{-6} | 10 x 30 (6000)^2 = 8.3 x 10^{-6} |
| ΔΩ₂, solid angle of receiving slit (sterad) | 0.633 x 10 (259)^2 = 94 x 10^{-6} | 0.9 x 5 (2055)^2 = 0.95 x 10^{-6} | 3.13 x 1.13 (5000)^2 = 0.4 x 10^{-6} | 8 x 40 (5000)^2 = 13.0 x 10^{-6} |
| I₀, power incident on specimen (particles s^{-1}) | 150 x 10^5 | 16 x 10^5 | 10 x 10^5 | 0.75 x 10^5 |
| Resolution                | Δκ₁, spread in wave vector of incident beam (Å^{-2}) | □ | 1.3 x 10^{-6} | 0.66 x 10^{-6} | 5.1 x 10^{-6} |
| Δκ₂, spread in wave vector of scattered beam (Å^{-2}) | □ | 1.6 x 10^{-6} | 6.5 x 10^{-6} | 8.0 x 10^{-6} |
| κₘᵟ, smallest scattering vector for this geometry (Å^{-1}) | 10 x 10^{-3} | 6.0 x 10^{-3} | 2.9 x 10^{-3} | 4.7 x 10^{-3} |
| Nₘ, number of data points simultaneously recorded | 1 | 90 | 64 x 64 = 4096 | 50 x 5 = 250 |
| Data recording            | ΔΩ₁, total solid angle subtended by the detector (sterad) | 9.4 x 10^{-5} | 72 x 5 (2055)^2 = 8.5 x 10^{-5} | 200 x 200 (5000)^2 = 160 x 10^{-5} | 400 x 40 (5000)^2 = 65 x 10^{-5} |

* The X-ray values do not include the effects of Be window absorption, monochromator efficiency (0.1-0.3) or take-off angle (6°). They are the apparent values at the entrance slit, and not the true brilliance of the focal spot.
† The resolution of the detector is 1 mm FWHM, thus giving up to 200 x 200 = 40,000 resolution elements. However, the data acquisition system can handle only 64 x 64 or 128 x 128.
‡ Meaningless quantity in long-slit geometry.
§ There are five parallel one-dimensional PSDs.
¶ The smallest possible κₘᵟ for this instrument is 0.9 x 10^{-4} Å^{-1} and may be achieved by moving the detector from 6 to 20 m and increasing the neutron wavelength from 8 to 12 Å.
proved performance of the 10 m collimation plus the additional increase in data acquisition speed resulting from the use of an area detector, equivalent patterns from polyethylene to those obtained on the 2 m machine can now be obtained in approximately 60 s. It is this increase in performance which has made possible for the first time real-time dynamic experiments on the crystallization of polyethylene (Schulz et al., 1978).

As was pointed out earlier (Schelten & Hendricks, 1975) although the apparent brilliance of the neutron source at the Jülich SANS facility is over six orders of magnitude lower than that of the X-ray sources, because of the use of long-wavelength neutrons and thus the ability to use large slits and samples and still achieve good \( \kappa \) resolution, the actual flux of neutrons on the sample is only about one decade less than that of photons in the X-ray machines. Thus, depending on the ratio of the X-ray to neutron scattering cross sections for the sample under investigation, the neutron facility may be even faster than the X-ray facility for recording a pattern to the same statistical accuracy. Finally, although it is commonly assumed that long wavelengths are necessary to achieve good \( \kappa \)-space resolution, it can be seen from the data of Table 3 that it is possible to achieve excellent resolution with 1.54 Å X-rays and still maintain very satisfactory incident beam intensities by fully utilizing the total area of the focal spot and long collimation distances.

We conclude this section on X-ray instrumentation with a brief discussion of the calibration of absolute intensities. Although a wide variety of calibration procedures have been developed (for examples, see the review by Hendricks, 1972) only few intertechnique comparisons have been published (e.g. Shaffer & Hendricks, 1974). The problem of precision in measurements of absolute intensity, and the need for a comparison of the different techniques with a common standard sample, were discussed by an \( ad \) hoc group of participants from 21 laboratories during the Second International Conference on Small-Angle Scattering of X-rays, which was held in Graz, Austria in 1970. It was concluded that an international project should be established with the aims of (1) testing the precision of reproducibility and comparative accuracy of the various calibration techniques in current use, and (2) clarifying the areas of difficulty in absolute intensity calibration. The project was accepted as an official function of the Commission on Crystallographic Apparatus of the IUCr. In the project, the absolute differential X-ray scattering cross sections for two different standard samples were measured using five different calibration techniques and two different X-ray wavelengths by fifteen investigators from eight different laboratories in six countries. The results were intercompared using various statistical methods. It was concluded that angularly dependent errors associated with determining the zero of angle, dead-time corrections, collimation corrections, and insufficiently close data-point spacing are more important in accounting for discrepancies between laboratories than are differences in the absolute-intensity calibration methods or the collimation geometries. Complete details of the project are given in their final report (Hendricks et al., 1978).

### IV. Instrument development in SANS

Nowadays one tends to denote the concept of the small-angle scattering instruments at the reactors in Jülich and Grenoble as the traditional one for building SANS instruments. As described by Schmatz et al. (1974) the main features of this concept are (1) large cross sections for sample and entrance slits to benefit from the huge source area of a reactor and (2) an optimization of the \( \kappa \) resolution which requires that all contributions to the total \( \kappa \) resolution have about the same magnitude. This leads to very long instruments for high-resolution experiments, allows the use of mechanical velocity selectors to monochromatize the neutron beam, and demands a large area detector in the case of simultaneous detecting of the scattered beam.

#### IV.1 Double-crystal instrument

At various reactors in the US small-angle scattering measurements have been done quite differently by utilizing the double-crystal technique. Based on the early work of Shull, Billman & Wedgewood (1967) and Schneider & Shull (1971), Werner, Wiener (Aynear), Gürmén & Arrott (1970) and Gürmén, Werner & Arrott (1971, 1975) developed a high-resolution two-crystal spectrometer for measuring inelastic small-angle scattering from spin waves in Fe and Fe-Ni alloys. The monochromator and analyzer crystals were silicon single crystals of \( \sim 2.5 \)° mosaic spread with the analyzer cooled to liquid-N\(_2\) temperature to reduce background scattering from phonons. Following these ideas, Mook (1974) developed an instrument using two good-quality Ge crystals. In these instruments, the sample is placed between the two crystals which are set in the parallel rocking curve geometry as shown in Fig. 6(a). From the polychromatic neutron beam in front of the first crystal a neutron wavelength \( \lambda \) is selected by Bragg reflection from it with a diffraction angle \( 2\theta \). Without the specimen between the crystals a narrow rocking curve is measured if the second crystal is rotated about an axis perpendicular to the scattering plane of the first one. The rocking curve can be very narrow even though the neutron beam divergence is fairly large. This is due to the fact that there is a direct relationship between the neutron wavelength and the scattering angle, as can be seen from Fig. 6(b). This connection is in such a

![Fig. 6.](image-url)
The factor of a cold source if there is one installed in the reactor, different ways on the instrumental design and are related

specimen is represented by its attenuation factor $T$, its

thickness $t$ and its cross section per unit volume $d\Sigma(K)/d\Omega$.

$\frac{\Delta k_y}{\Delta k_0} = \frac{\Delta k'_y}{\Delta k'_0} = \delta k$

$\frac{\Delta k_x}{\Delta k_0} = \frac{\Delta k'_x}{\Delta k'_0} = \delta k$

$\frac{\Delta k_x}{\Delta k_0} = \frac{\Delta k'_x}{\Delta k'_0} = \delta k$

and for the double-crystal instrument:

where the resolution is $\delta k = \omega k_0$ as long as $\omega /\nu$ and $\omega \sim \nu$

in point-like geometry. Inserting these values into (1), one obtains for the ratio of the scattered intensities from the double-crystal and the traditional instruments

$$\frac{\Delta I_{de}}{\Delta I_{rad}} = \exp\left(-\frac{k_0^2}{k_Z^2}\right) \frac{g A f}{\delta \kappa^2}$$

where the primes refer to the double-crystal instrument. For simplicity it will be assumed that the instrumental attenuation

factors $A'$ and $A$ are identical for the two instruments

and furthermore that both exponential factors are approximately 1. This latter approximation is good for sub-thermal

neutrons with $\lambda \gtrsim 4$ Å, which are used in the long instruments, and is moderate for $\lambda = 2.5$ Å, which was the wave-

length chosen in the double-crystal instrument. For neutrons of the latter wavelength the gain from a cold source

is very little and thus $g$ can be set to 1. With these simplifications and approximations the intensity ratio becomes

$$\frac{\Delta I_{de}}{\Delta I_{rad}} \sim \frac{1}{F} \frac{\omega_k}{\omega} \frac{\delta \kappa}{\delta \kappa'} .$$

(2)

Thus, from equation (2) the two reasons why a double crystal instrument becomes more efficient than a traditional

instrument with increasing resolution are seen. The first

reason is that the scattered intensity of the double-crystal

instrument decreases with the third power of the resolution

$\delta k$ while in the long instrument the decrease is with the

fourth power. The second reason is that for a given finite

length of the long instrument and for a given sample cross

section a $\delta \kappa_{min}$ exists, beyond which the resolution cannot

be improved further without narrowing down all slits. Thus,

beyond this resolution the sample cross section $F$ decreases

proportionally to $\delta k^2$ while in the double-crystal instrument

the whole specimen can be illuminated. At the 20 m instru-

ment in Jülich, with 10 Å neutrons $\delta \kappa_{min}$ has a value of

$0.6 \times 10^{-3}$ Å$^{-1}$ for a 1 cm$^2$ illuminated specimen cross section. This resolution is obtained in a double-crystal instru-

ment for 2.5 Å neutrons with a crystal mosaic spread of

45°. In the experiment of Mook (1974) an extreme high re-

solution was not desired and therefore the Ge crystals used

in the spectrometer were deliberately distorted so that a rock-

ing curve width of 2° was obtained.

Up to now, in comparing the double-crystal instrument with

a conventional SAS instrument the advantages of the double-

crystal instrument have been emphasized. There are, how-

ever, also serious disadvantages which will be briefly men-

tioned now. The simultaneous detection of the scattered

neutrons by large area detectors cuts down considerably the time required to record a SAS pattern and allows the measurement of weak scatterers in the conventional long instrument. Unfortunately, simultaneous detecting of the SAS pattern is virtually impossible in the double-crystal instru-

ment and because of this its efficiency is more than 100
times less than that of the long instruments at which position-sensitive detectors are routinely used. In the conventional

instruments where the neutron beam is simply col-

limated by two slits the instrumental background does not

usually cause any problems. Experience has shown that only a few millimeters away from the geometrical boundary of the primary beam the neutron intensity is down to $10^{-5}$ or even $10^{-6}$ of the maximum intensity at the beam center.
Such a contrast cannot be achieved in the double-crystal instrument because of the wings of the rocking curves resulting from the mosaic spread of the crystals and thermal diffuse scattering. A reduction of the background can be achieved by cooling the crystals to at least liquid-N₂ temperature to diminish the inelastic scattering and by rotating more than one crystal (e.g. channel-cut crystals) since the resulting rocking curve is sharpened by multiple reflections. Finally, it should be mentioned that the problem of double Bragg scattering in the SAS specimen can arise in the double-crystal instrument because fairly-small-wavelength neutrons are used. However, in the case that perfect crystals with large d spacings and high reflectivities are developed this shortcoming can be circumvented. The application of this instrument to a high-resolution study of flux lines in type II superconductors is described in this issue by Christen, Spooner, Thorel & Kercner (1978).

IV.2 New SANS instruments

At the end of 1973, when the third SAS conference was held in Grenoble, the situation for SAS with neutrons could be characterized in the following way. The Jülich instrument had been in operation 24 hours a day for several years, and the famous D11 camera at the High Flux Reactor (HFR) in Grenoble had operated routinely for almost a year. At that time it became clear that the demand for SAS with neutrons was tremendous and that it seemed to be impossible that all the required scattering data could be measured by only a few instruments. As a consequence, new instruments for SAS were designed or even constructed at various places and, in addition, the existing instruments were improved so that their operation became more efficient. For instance, at D11 the original multidetector, which was operated in the ionization chamber mode and which was used until November 1974 (Allemand et al., 1975), was replaced by a multidetector of the same size but which operates with gas amplification (Ibel, 1974). This replacement was a considerable improvement, because the detector’s spatial response was made to be stable and therefore it became possible to correct for the differences in the efficiency of different detector cells. In addition, the electronic noise was brought down to 1 count h⁻¹ cm⁻² which resulted in a much better signal-to-noise ratio than before.

The SAS facility in Pisa, which is essentially used for applied research, was drastically improved by the installation of a multidetector identical to that at D11. This SAS instrument, described by Galotto et al. (1976), utilizes neutrons produced with a hydrocarbon cold source on the 5 MW Galileo reactor. It has an acceptable angular resolution according to its total length of 11 m.

In Jülich the existing instrument has been improved in several respects. The major change was made at the primary flight path, where more flexibility for an adequate collimation of the neutron beam was achieved by installing a new device with movable neutron guides. Its design is identical to that of the collimation system at D11 in Grenoble (Degenholbe & Greiss, 1973). Collimation lengths of 1, 2, 4, 6, and 11 m are now available with the Jülich instrument.

In addition to these major improvements of existing instruments, which have been made since 1973, new instruments have either been constructed or at least designed.

In Geesthacht, Germany a long SAS instrument has been put into operation mainly for materials research (Frisius & Naraghi, 1977). Because of the small reactor and the lack of a cold source, the measurements are usually performed in slit geometry. The minimum k value at which scattered neutrons were measured is about 3 x 10⁻³ Å⁻¹. The usefulness of the instrument was demonstrated by a study of radiation-induced defect clusters in samples of pressure-vessel steels used in nuclear reactors. Scattering curves with an intensity range of several orders of magnitude could be measured.

At the HFR in Grenoble a second SAS instrument D17 is now operating. It was designed for small-angle scattering and diffraction experiments in biology. Since usually only small amounts of biological sample substances are available the instrumental design was emphasized by a smaller sample cross section than at D11. As a consequence, shorter distances between the collimating slits and between sample and detector are demanded for a given resolution and the detector resolution elements must have a smaller cross section of about the same magnitude as the illuminated sample area. At D17 the collimation distances are about 4 m and the multidetector has detector cells of 0.5 x 0.5 cm cross section instead of 1 x 1 cm as at D11. For higher-angle diffraction experiments it is very useful that the area detector can be rotated about the specimen axis in order that diffraction patterns can also be measured at large k values with almost the same high resolution as at the smallest k values. At large k values the resolution δk, which is determined by

\[ \delta k^2 = k^2 \left( \frac{\Delta \lambda}{\lambda} \right)^2 + \left( \frac{\Delta \theta}{\theta} \right)^2, \]

has its major contribution from the wavelength distribution achieved with a mechanical velocity selector, while the angular resolution \( \Delta \theta/\theta \) becomes negligible. \textit{Vice versa}, at the smallest k values \( \Delta \theta/\theta \) plays the important role, while the contribution of \( \Delta \lambda/\lambda \) is less significant.

For the purposes of biological research a SAS spectrometer has been constructed at the Brookhaven National Laboratory with a two-dimensional position-sensitive detector having a spatial resolution of 0.27 x 0.27 cm (Alberi et al., 1975; Alberi, 1975). The design parameters of this instrument were to achieve moderate resolution, as is required to study ordered lamellar samples with spacings up to 300 Å with small specimens of 10 mm² cross section, within a convenient total instrument length of 8 m. A unique feature of this machine is the use of a thin detector filled to high gas pressures (10 atm) in order to avoid parallax at higher k values. Further details are presented in this issue by Schoenborn, Alberi, Saxena & Fisher (1978). Another new long SAS spectrometer with a two-dimensional detector has been assembled at ORNL, as is described by Spooner, Child, Kopp & Madden (1976) and Child & Spooner (1978). The first results on voids in neutron-irradiated niobium obtained from this instrument have been presented (Spoonier, Child & Wiffen, 1978).

The design of the small-angle scattering spectrometer now under construction at the Research Reactor Facility at the University of Missouri (Brugger, King, Werner & Yelon, 1976) is unusual in that the size of the containment building constrains the flight path to be vertical. This is achieved by Bragg scattering upward through 90° from a set of three slightly misaligned pyrolytic graphite crystals. The primary beam is defined by two matched variable-aperture irises located 4.5 m apart, and the scattered flight tube is also 4.5 m. An array of 43 one-dimensional position-sensitive detectors with a minimum spatial resolution of 1.25 x 0.5 cm² will be used as an economical alternative to a two-dimensional multi-detector. The area-averaged detector efficiency is about 79% and the front-wall background scattering is
can be reflected with 80% reflectivity for glancing angles between 0 and 30°, where 0° is the critical glancing angle constructed. It has been demonstrated that a neutron beam These devices have promising theoretical properties (Mezei, of materials having different scattering-length densities.

Soller collimators because they become very long but also experiments, in which the $k$ values are reduced by an order of magnitude, will offer some significant advantages, as discussed in the next section.

The difficult aspect of the traditional SAS instruments is the extreme lengths of evacuated flight paths which are required in order to achieve high resolutions and reasonable intensities with large specimens. A well-known alternative, circumventing long distances for high resolution but still utilizing big samples, is a system of Soller slits as collimators before and behind the specimen. Unfortunately, this alternative, which was used in Saclay (Cribier, Jacrot, Rao & Farnoux, 1967), has the serious disadvantage that simultaneous recording of the scattered beam with position-sensitive detectors is not possible; thus one is limited to single-detector scans over the scattering pattern. Nunes (1974) and Nunes & Zaccai (1975) solved this problem by introducing a converging Soller slit system in front of the specimen to focus the neutron beam at the detector plane. A focusing Soller collimator with nonreflecting cadmium vanes was constructed and was shown experimentally to be of a quality similar to that of a conventional Soller collimator for $k$ values larger than $2 \times 10^{-2}$ Å$^{-1}$. For high-resolution experiments, in which the $k$ values are reduced by an order of magnitude, it is not only much more difficult to construct Soller collimators because they become very long but also much worse to have them in the primary beam because scattering from the surfaces of the vanes will drastically reduce the signal-to-noise ratio in this $k$ range.

Another possible way to focus neutron beams is with supermirrors which are formed from alternating thin layers of materials having different scattering-length densities. These devices have promising theoretical properties (Mezei, 1972, 1976, 1977), and the first prototypes have already been constructed. It has been demonstrated that a neutron beam can be reflected with 80% reflectivity for glancing angles between 0 and $30\theta$, where $\theta_1$ is the critical glancing angle for total reflection from an interface between the two different materials which form the layers of the supermirror. This result is preliminary and the glancing-angle interval for reflection can be extended.

In direct analogy to the energy-dispersive small-angle X-ray scattering experiments described in the previous section, small-angle neutron scattering can be performed by measuring the energy of neutrons scattered at a fixed angle. However, in contrast to the X-ray technique, where the energy of the scattered radiation is determined from the charge created in the detector, the neutron energy is determined by using a pulsed neutron source and performing time-of-flight (TOF) measurements. For conventional diffraction experiments, a wide wavelength band of $k$ between 0.1 and 10 Å can be utilized with this technique, and as with X-rays, overlapping $k$ ranges of the diffraction pattern can be simultaneously recorded by detectors at various scattering angles. Such a system has been in operation at the IBR-30 pulsed reactor in Dubna for several years (Gladkikh, Kozlov, Ostanevitch & Cser, 1974; Gladkikh, Ostanevitch & Cser, 1975; Cser, 1975); others are planned for future pulsed reactors (Bauer et al., 1976; Mildner, 1978). A special complication arises in TOF SAS experiments because of the long flight time of 10 Å neutrons over the large sample-to-detector distance of more than 20 m which is required for high-resolution experiments with large specimens. The flight time under these conditions is more than 50 ms, while the duty cycle of pulsed neutron sources is usually such that every 20 ms there is a new neutron burst. Thus, TOF recording would be considerably blurred if the detector obtained from a given neutron pulse arrive at the detector at times during which slower neutrons from the previous neutron pulse are also arriving at the detector. Many of these problems have been described by Cser (1975) and Mildner (1978). To avoid the frame overlap with the slow neutrons, which are the most valuable neutrons in SAS experiments, shorter sample-to-detector distances are required. This means that for a given resolution either smaller sample sizes at the expense of intensity, or Soller slit collimators, at the expense of simultaneous detecting, must be used (Bauer et al., 1976). Another way to take advantage of the pulsed nature of the neutron source using a SAS instrument with a multidetector is discussed by Bauer et al. (1976) and by Carpenter & Faber (1978).

### V. Combined X-ray and neutron experiments

Several years ago, when the earliest neutron small-angle scattering results were obtained, an attitude of competition developed between the few people who dealt with neutrons and the rest of the SAS community who dealt with X-rays. The power of a neutron SAS facility was compared with that of X-ray machines by pointing to the maximum achievable resolution, to the scattered intensity expected for a typical sample, or to the long neutron wavelengths with which double Bragg scattering could be avoided. In addition, scattering problems were known which could be solved by only one method because of vanishing or too little contrast in the other method. These arguments are reminiscent of similar discussions among materials scientists regarding the applicability of small-angle X-ray scattering vis a vis transmission electron microscopy (i.e. Fourier-space versus real-space information) to solid-state problems as is so clearly stated in Thomas's (1970) letter commenting on Guinier's (1969) review. Of course, in both cases it has be,

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* See reference, National Science Foundation (1978).
come clear that the techniques are complementary, not competitive.

In this section, we discuss the application of both SAS methods to the same specimen or to two similarly treated specimens which differ only in their cross sections (e.g. different isotopes) or thicknesses. Because of the rapid development of the neutron scattering technique and because of the good access scientists in Europe have had to the SAS instruments in Grenoble such combined X-ray and neutron SAS experiments have been realized only recently. Even so, numerous experiments have already been performed. The following discussion is far from complete and is meant only to give examples of what can be accomplished.

V.1 Phase-separating systems

Phase-separating systems have been investigated by SAS in order to obtain the limits of the metastable miscibility gap from the integrated scattered intensity. If we define the integrated intensity as

$$Q_0 = \frac{4\pi}{(2\pi)^2} \int \frac{1}{N} \frac{d\sigma}{d\Omega} (x)k^2 dx,$$

where \(1/N)d\sigma/d\Omega\) is the SAS cross section per lattice site, and if the material has separated into two phases, 1 and 11, then the following identities can be written for \(Q_0\):

$$Q_0 = \Omega_0 \langle q - <q> \rangle^2,$$

and

$$Q_0 = \Omega_0 \langle q - <q> \rangle \langle q - \eta_1 \rangle,$$

where \(\Omega_0\) is the volume per lattice site, \(\eta_1\) and \(\eta_{11}\) are the scattering length densities of the two phases, and \(\langle q \rangle\) is the mean scattering length density of the system (Gerold, 1967).

Let us restrict ourselves to a binary system of components \(B\) in \(A\), and denote their coherent scattering lengths by \(b_B\) and \(b_A\), respectively. Also let \(x\) represent the overall mean atomic fraction of \(B\) in the system while \(x_1\) and \(x_{11}\) represent the concentrations of \(B\) in the two separated phases. If there is no lattice misfit, we may thus write

$$\langle q \rangle = \frac{1}{\Omega_0} \left[ x b_B + (1-x) b_A \right]$$

with similar expressions for \(\eta_1\) and \(\eta_{11}\).

Thus, the integrated intensity is

$$Q_0 = \frac{\Delta b^2}{\Omega_0} \Delta x_1 \Delta x_{11},$$

where

$$\Delta b = b_B - b_A,$$

$$\Delta x_1 = x_1 - x,$$

and

$$\Delta x_{11} = x - x_{11}.$$
Only a few combined SAS experiments with two-phase systems have been performed, among which are Al(Zn), Al(Zn, Mg), voids in neutron-irradiated Al, and the phase-separating sodium- and aluminum-silicate glasses. For comparison purposes, the $\beta_x$ and $\beta_n$ values shown in Table 4 have been calculated. For the two glass systems, all scattering lengths refer to an oxygen site. Stimulated by Professor Guinier, Raynal, Schelten & Schmatz (1971) performed the first combined X-ray and neutron SAS measurements on Al(Zn). Here the importance of considering lattice misfit in a two-phase system was pointed out and an estimate of $\varepsilon$ was deduced from the comparison of the X-ray and neutron integrated intensities measured in absolute units. More recently, Gerold, Epperson, Gerstenberg & Kostorz (1978) performed another combined experiment with an Al(Zn) specimen, which demonstrated the validity of Vegard's rule for this binary alloy. The experimental values of $Q_{ox}$ and $Q_{nx}$ were found to agree within 5% of the theoretical values calculated from equation (10) with $\varepsilon$ calculated from Vegard's rule. Similarly, agreement within experimental errors of 10% (which resulted mainly from the conversion of the scattered intensities into absolute units) has been obtained by Hendricks, Schelten & Schmatz (1974) and Schelten & Hendricks (1975) in the SAS study of voids in neutron-irradiated aluminum single crystals. The experimental finding was $R_x^2 = 1$. This does not imply that there is no lattice misfit, since in the particular case of voids $\beta_x = \beta_n = -1$ and hence, by equation (11) $R_x^2 = 1$ for all $\varepsilon$. Because of this coincidence, specimens containing voids (e.g. glassy carbon or neutron-irradiated aluminum) should be selected as standard samples for future absolute intensity projects which intercompare X-ray and neutron SAS results.

A third metallic system, ternary Al(Mg, Zn) alloys, was investigated in a combined X-ray and neutron SAS study. As long ago as 1969 it had already been suggested by Guinier that it should be possible to extend the well-established method of determining miscibility gap limits in binary alloys to ternary alloys by combining X-ray SAS data with those from neutrons. The theory for this was worked out by Gerold (1977). For ternary alloys, assumptions have to be made concerning lattice misfit and then the ratio $R_x^2$ can be used to determine the tie-line. The experimental part of it was partially successful since the data analysis lead to reasonable results for the miscibility gap (Gerold, Epperson & Kostorz, 1977).

The glass system SiO$_2$-Na$_2$O was investigated by Roth & Zarzycki (1974) by neutron SAS, while years before X-ray SAS studies were performed in different laboratories (Nelson, 1969; Tomozawa, MacCrone & Herman, 1970). It was recognized with the neutron experiments that the molecular composition fluctuations were not seen by X-rays, since SiO$_2$ and Na$_2$O molecules have essentially the same scattering length of 30 electrons, in contrast to the neutron case, where the molecules have different scattering lengths (see Table 4). In addition, Roth & Zarzycki made the rather artificial distinction between molecular composition fluctuations and density fluctuations. In any SAS experiment it is solely the coherent scattering length density which counts and $q$ is a ratio of scattering length (composition) and molar volume (density).

A second glass system, SiO$_2$-Al$_2$O$_3$, for which parameters are found in Table 4, was investigated by neutron and X-ray SAS measured with the same specimens. As is reported by Jantzen, Schwahn, Schelten & Herman (1978) elsewhere in this issue, by combining neutron data with X-ray data the volume-change parameter was shown to be non-zero and its value was determined in accordance with interpolations of density measurements. It was not possible to explain the original neutron scattering data even by assuming a complete two-phase decomposition if there were no lattice misfit. As a result of this discrepancy, X-ray experiments were performed and the anticipated non-zero value of $\varepsilon$ was found.

V.2 Biological systems

The complementary properties of neutron and X-ray small-angle scattering are also demonstrated by the following combined experiments on myoglobin in dilute aqueous solution, polyethylene in its partially crystallized state, and polystyrene copolymers in concentrated solution.

The contrast-variation method, developed to a large extent by Stuhrmann (1970; 1975) and described in more detail in the review of Stuhrmann & Miller (1978), was tested in a combined X-ray and neutron scattering experiment on myoglobin in dilute solution by Ibel & Stuhrmann (1975). The excess scattering-length densities between solvent and solute were varied by choosing different mixtures of H$_2$O/D$_2$O and of water/glycerol or water/sugar in the neutron and X-ray experiments respectively. By comparing the X-ray and neutron results for the molar volumes deduced from $\rho_{solv}$ for vanishing forward scattering $I(0)$, the ratios $[I(0)]^{1/2}/\langle q \rangle$, and the radius of gyration $R_g$ at infinite contrast, quantitative information concerning H/D exchange was obtained. A few results for myoglobin were: at the matching condition ($\langle q \rangle = 0$) 105 H atoms were exchanged; exchange occurred predominantly in a region close to the surface of the myoglobin molecule, and its volume fraction amounted to 20%. In the treatment of Stuhrmann (1970; 1975), the observed scattering function $I(\kappa)$ was separated into three components which result from the particle shape
The X-ray and neutron values of \( I_s(k) \) are shown in Fig. 8 as a function of the scattering vector \( k \). The differences between the two curves are considerable except at very small \( k \) values where both curves must coincide. These remarkable differences imply that the structural units of myoglobin are differently weighted by X-rays and neutrons. Thus, we may presume that a combined X-ray and neutron SAS experiment is the key to obtaining more structural details of macromolecules in dilute solution.

V.3 Polymeric systems

The SAS of neutrons from tagged, protonated polyethylene in a deuterated polyethylene matrix should yield information about the molecular conformation from the scattering by the tagged molecules and information about the \( d \) spacing of the periodic arrangement of the crystalline and amorphous regions from the scattering by the scattering-length density fluctuations of the two phases. The first experiments were not successful, however, because an extremely intense background scattering from voids (created during specimen preparation) completely masked the two scattering effects. The effect of voids could be avoided in the reversed system created by blending deuterated tagged molecules into a protonated matrix, although the incoherent background is significantly increased. Since the scattering length density of a specimen with fractions \( x \) and \( 1-x \) of \( CD_2 \) and \( CH_2 \) components, respectively, vanishes for \( x = 4 \times 10^{-4} \), it is now clear why the void scattering almost completely disappeared in specimens with tagged molecule concentrations between 2 and 6\% (Schelten, Wignall, Ballard & Schmatz, 1974). The coherent scattering from the tagged molecules, however, does not depend on whether the matrix is deuterated or protonated. Thus, it was possible to determine molecular configurational parameters. Simultaneously, it became impossible to measure the \( d \) spacings of the lamellae, because the contrast given by the scattering length density difference \( \rho_c - \rho_a \) between the crystalline and amorphous regions became too small. Therefore it was necessary to perform an X-ray experiment on the same specimens to measure the crystallinity parameters (Schelten, Ballard, Wignall, Longman & Schmatz, 1976). It is evident that the X-ray contrast is the same irrespective of whether the bulk is protonated or deuterated, and that there is no scattering contribution from molecular conformation.

In another experiment on polyethylene in which chlorine atoms were statistically attached to the chains the amount of Cl in the amorphous and crystalline regions could be determined from integrated intensities measured with X-rays and neutrons for the same specimens (Kalepky, 1977). Both results are required since it is unreasonable to expect that the change in specific volume between the amorphous and crystalline states for the tagged polymer is the same as in pure polyethylene. Preliminary experiments have shown that Cl is preferentially found in the amorphous part of the specimen, thus implying that special molecular arrangements must occur during the crystallization of the tagged material.

As a final example of the power of combined X-ray and neutron experiments, we consider the remarkable idea of Hayashi, Hamada & Nakajima (1976, 1977) from Kyoto University, who tagged polystyrene molecules with statistically attached iodine. By this tagging method conformational studies of polystyrene in concentrated solutions and in the bulk could also be investigated with X-rays. A straightforward calculation shows that the scattering law for such a randomly and only sparsely tagged molecule is, apart from trivial constants, identical to that of a continuously tagged molecule as obtained for neutron experiments by deuteration. In fact, if a tag is attached at \( n \) sites out of \( N \) and if \( N \gg n \gg 1 \), the scattered intensity for such a statistical tagging is

\[
I_s(k) \sim \langle F^2(k) \rangle + \frac{1-n/N}{n-1},
\]

where \( \langle F^2(k) \rangle \) is the form factor of the molecules averaged over all conformations. The term \( \langle F^2(k) \rangle \) is also the scattered intensity (normalized to unity at \( k = 0 \)) for continuous tagging as measured with neutrons. Thus, the only difference between the two tagging methods (and therefore between the X-ray and neutron methods) is a \( k \)-independent Laue monochromatic-type scattering contribution which plays only a minor role at small \( k \) values. It is only at very high \( k \) values that the sensitivity of the method of statistical tagging for X-rays is weakened because of this additive background. The experiments were performed in such a way that the scattering curve itself, or parameters determined from it, could be extrapolated to zero degree of tagging \( t = n/N \rightarrow 0 \) and zero concentration of tagged molecules \( c_t \rightarrow 0 \) as is shown for the radius of gyration in Fig. 9. The authors believe that these double-extrapolated values were the results for (untagged) polystyrene itself. The validity of this presumption is strengthened because the extrapolated X-ray results from tagged polystyrene copolymers were, within experimental uncertainties, the same as the neutron results from deuterated tagged polystyrene. It is our feeling that the scientific community would be less inclined to believe these X-ray results if it were not for the cross checks that were obtained from neutron scattering with the much better established deuterium tagging method. This feeling is supported by the historical example of the results of Krigbaum & Godwin (1965) on the conformation of polystyrene in the solid state. Unfortunately, their work was ignored for almost a decade until the results were confirmed by neutrons.
VI. Scattering data analysis

The most serious problems which arise during the analysis of data from SAS experiments and their partially successful solutions will be discussed in this section. Among these still survives the very old problem of finding a new resolution correction procedure which is at least slightly better than all the other already existing procedures. Other more significant problems are the determination of general real-space functions such as the scattering-density function of a particle, the particle-shape function, or the particle-size distribution by evaluating either the raw scattering data or the resolution-corrected values. The experience in this field seems to indicate that the Fourier-type back-transformation should be performed only once and not in consecutive steps. This means that more reliable results can be expected if the required model parameters (e.g., the particle-size distribution itself or a few geometrical quantities which describe the particle shape) are directly fitted to the measured data (Sjöberg, 1978). If this observation is correct, one loses interest in utilizing an exact solution of an integral equation which enables one to do just one step in a few special cases. In the following paragraphs, a selection of a few data evaluation procedures which have been developed during the last three years are described.

VI.1 Collimation corrections

The various techniques which have been developed for collimation corrections, especially to correct for the slit-length effect, were recently reviewed by Schmidt (1975). If slit-width smearing can be neglected, as is often the case in long-slit geometry instruments, then the observed scattering function \( I(\theta) \) and the true scattering functions \( I(\theta) \) are related by

\[
F(\theta) = \int_{-\infty}^{\infty} W_{l}(u) \frac{1}{\sqrt{\theta^2 + u^2}} du ,
\]

where \( W_{l}(u) \) is the slit-length weighting function (Hendricks & Schmidt, 1967, 1973) determined only by the geometry of the collimation system. For many years an exact solution of equation (13) for a given weighting function was known only for the two cases in which \( W_{l}(u) \) is a constant or in which \( W_{l}(u) \) is a Gaussian function. An exact, explicit solution for an arbitrary weighting function was developed very recently by Deutsch & Luban (1978a) who started from the well-known implicit solution of Kratky, Porod & Kuhovec (1951). In the latter work, it was shown that

\[
I(\theta) = -\frac{1}{\pi} \int_{0}^{\infty} du V_{l}(u) \left( \frac{1}{\sqrt{\theta^2 + u^2}} \right)^{1/2} F\left[ \left( \frac{1}{\theta^2 + u^2} \right)^{1/2} \right] ,
\]

where \( V_{l}(u) \) must be determined from the integral equation

\[
\int_{0}^{\infty} d\theta W_{l}(x \sin \theta) V_{l}(x \cos \theta) = \frac{\pi}{2}
\]

and \( x \) is a dummy variable.

The first key step of Deutsch & Luban was to rewrite equation (14b) in such a way that the left-hand side becomes a Faltung integral which is immediately solvable by Laplace transformation. The solution is

\[
V_{l}(u) = \pi u \left[ \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{dse^{-sw^2}}{se-\pi i} \right] ,
\]

where

\[
W_{l}(s) = 2 \int_{0}^{\infty} du e^{-su^2} W_{l}(u) .
\]

Equation (15b) is the Laplace transform of the slit-length weighting function. Their second key step was to get rid of the derivative of \( F \) in equation (14a), because reliable values of \( F \) cannot be calculated from a discrete set of data points without additional information. By partial integration, the derivative was transferred from \( F(\theta) \) to \( V_{l}(u) \) and the following expression was obtained

\[
I(\theta) = F(\theta) + \frac{1}{\pi} \int_{0}^{\infty} du \left( \frac{1}{\sqrt{\theta^2 + u^2}} - F(\theta) \right) \frac{d}{du} V_{l}(u) .
\]

An evaluation of the true scattering function, \( I(\theta) \), from this equation, after calculation of \( V_{l}(u) \) from the known weighting function \( W_{l}(u) \) (Deutsch & Luban, 1978a), requires additional information besides the given set of measured data points \( \theta, F(\theta) \). \( F(\theta) \) must be interpolated between consecutive data points for numerical integration, must be extrapolated to \( \theta = \infty \) by a reasonably chosen function in order to minimize truncation errors, and must be very carefully extrapolated to \( \theta = 0 \). For the latter extrapolation it is necessary to have zero slope and an 'accurate' measure of the second derivative at \( \theta = 0 \); otherwise, unreasonable scattering functions are obtained. It is demonstrated with the examples given in Deutsch & Luban (1978a) that more accurate results were obtained than with the iterative technique of Lake (1967). However, the question should be raised of whether the better results may have been obtained because of the additional information which was provided by extrapolating \( F(\theta) \). It is quite clear that every collimation-correction procedure needs additional information to avoid truncation errors and numerical noise in the scattering function because the integral equation (equation 14) is not well conditioned and must be stabilized. Therefore one should judge the quality of a solution procedure not only from the results which are obtained but also from the a priori information which has to be added. If our knowledge of this additional information is limited, then techniques which rely on it can yield accurate but uncertain results. In the application of the exact solution of Deutsch & Luban, unfortunately, information about the scattering pattern which cannot be
obtained without making serious assumptions for the solution function itself must also be provided.

VI.2. Particle-size distributions

The numerical problems associated with finding the particle-size distribution from the scattering curve are similar to the problems which have been discussed above for the collimation correction. Let us assume an ensemble of particles of the same shape whose size distribution can be described by $H(y)$, where $y$ is a size parameter, and let us assume further that there are no interparticle-interference or multiple-scattering effects. Then, the scattering function $I(\kappa)$ is

$$I(\kappa) = \int_0^\infty dyH(y)F_2(\kappa y), \quad (17)$$

where $F_2(\kappa y)$ is the scattering function of a particle and is assumed to be known. For the particular case of spherical particles an explicit solution for $H(y)$ has been found (Letcher & Schmidt, 1966):

$$H(y) = \frac{1}{y^2} \int_0^\infty \, dk \, [k^4 I(\kappa) - C] z(\kappa y) \, dk,$$  \quad (18)

with

$$\sigma(z) = \left(1 - \frac{8}{z^2}\right) \cos z - \frac{4 \sin z}{z} \left(1 - \frac{2}{z^2}\right), \quad (19a)$$

and

$$C = \lim_{\kappa \to \infty} k^4 I(\kappa). \quad (19b)$$

Because the $\kappa$ integration ranges to infinity and because the Porod constant $C$ is involved, it is immediately recognized that a reasonable extrapolation of $I(\kappa)$ to infinity is absolutely necessary as additional information, since the solution function $H(y)$ is very sensitive to the extrapolated part of $I(\kappa)$. A discussion of extrapolation procedures was given by Brill & Schmidt (1968) and more recently by Federova (1977). Experience indicates that the convergence of the integral in equation (18) is quite sensitive to the shape of the observed scattering curve, and that a reliable computer program for general scattering curves is difficult to write (J. S. Lin, private communication). Federova (1977) also developed similar, exact and explicit solutions for oriented and nonoriented cylindrical particles.

An alternative approach, which was selected mainly because only scattering values which had been measured were used, was developed by Harkness, Gould & Hren (1969) and Shuin (1977), who assumed that the particle-size distribution function could be approximated by a log-normal function with only two adjustable parameters. It is apparent that the size distribution so determined is biased to a considerable extent by the a priori information which was assumed for the particle-size distribution of the physical system.

More general approaches to the particle-size distribution problem have been made by representing the distribution function $H(y)$ by a basis of functions $h_x(y)$ according to

$$H(y) = \sum_{i=1}^N c_i h_x(y). \quad (20)$$

In this case it is assumed that the actual size distribution can be described with sufficient accuracy by $N$ adjustable coefficients $c_i$. For computational reasons the number of $h_x(y)$ functions is kept low, usually $N \leq 20$. Available fundamental knowledge about the size distribution can be taken into account by choosing an appropriate set of functions and by adding constraints to the procedure of finding the $c_i$ values from fitting

$$I(\kappa) = \sum_{i=1}^N c_i I(\kappa) \quad (21)$$

with

$$I(\kappa) = \int_0^\infty h_x(y)F_2(\kappa y)dy$$

to $M$ experimental data points $(\kappa, I_j)$ $(1 \leq j \leq M)$. Plavnik, Kozhevnikov & Shishkin (1976), for instance, demanded continuity and smoothness for $H(y)$ controlled by the norm of the second derivative of $H(y)$ as a constraint. However, nothing is said in the paper about the functions $h_x(y)$, which were used to represent $H(y)$. The use of the curvature of the size distribution is similar to the constraint used by Stallmann (1970) in solving the collimation-correction problem.

Vonk (1976) represented $H(y)$ by a histogram, i.e. $h_x(y) = 1$ for $y \in [Y_{i-1}, Y_i]$ and zero elsewhere, and minimized either the sum $S_1$:

$$S_1 = \sum_{i=2}^{N-1} (c_{k-1} - 2c_k + c_{k+1})^2 \quad (22a)$$

or the sum $S_2$:

$$S_2 = \sum_{i=1}^N c_i^2 \quad (22b)$$

to suppress, in the first place, oscillations in the histogram, * or the best assigned values to be determined by trial and error from the resulting histograms.

From the experience of Hendricks et al. (1974) it is known that Vonk's procedure does not necessarily guarantee reasonable particle-size distributions. The occurrence of negative $c_i$ values is not prevented by his minimization procedure and hence nonphysical size distributions with negative $H(y)$ are still possible. This problem can be overcome by using the methods of linear programming (e.g. Simonnard, 1966) through which it is possible to find the minima of functions which are subject to constraints defined by inequalities. Standard computer subroutines are available for such operations (e.g. Westley & Watts, 1970). Hendricks et al. (1974) developed a procedure to determine particle size distributions in which, with Vonk (1976), they approximated the size distribution function by a histogram and then minimized $S_1$ as defined in equation (22a) subject to the $N$ constraints

$$c_i \geq 0, \quad (23)$$

with the additional $(N + 1)$th constraint,

$$1 - \frac{1}{M} \sum_{j=1}^{M} \left| I(\kappa_j) - I_j \right|^2 \sigma_j^2 < 1 + \frac{1}{M}, \quad (24)$$

* An analogous constraint to that of minimizing the integral of the second derivative.
where \( M \) is the number of data points and the \( \sigma_i \) are the estimated errors of the scattering data \( I_j \) at \( K_j \). Equation (24) is the mathematical expression for data fidelity.

The concepts of linear programming have not previously been applied to either the particle-size distribution or to the collimation-correction problem. Unfortunately, Hendricks et al. (1974) did not publish the results of their experience with test functions, nor did they perform a direct comparison with other available methods. Despite this, the concept seems to be an excellent compromise because:

1. Stabilization is achieved by minimizing the second derivative (equation 22a), which does not bias unreasonably the size distribution.
2. Definite knowledge about the size distribution is introduced by the \( N \) inequality constraints of equations (23).
3. The experimental data are taken into account according to their uncertainties (equation 24) and no speculative interpolations or extrapolations are required.

VI. 3 Real-space information

The correlation function \( \gamma(r) \) of a particle, which is defined by

\[
\gamma(r) = \langle g(r') + r g(r') \rangle_{r'},
\]  

(25)

where \( g(r') \) is the local scattering-length density, can be evaluated by a method developed by Glatter (1977) where again all available information about the solution function was incorporated into the procedure. The solution function \( p(r) = \gamma(r) r^2 \) was approximated by a linear combination of a finite number of cubic B-splines

\[
pA(r) = \sum_{j=1}^{N} \left( \sum_{k=1}^{J} c_{jk} B_j(r) \right).
\]  

(26)

This representation was wisely chosen for several reasons. By properly adjusting the knots of the spline functions one ensures that the solution function can differ from 0 only for \( r < D \), where \( D \) is the maximum distance within a particle. In addition, the spline functions represent curves with minimum second-order derivatives. Thus, smooth slowly varying solution functions are created, which is the behavior expected for the true \( p(r) \). Data fidelity and stability were achieved by minimizing the weighted sum,

\[
S = S_1 + \lambda S_2,
\]  

(27)

where \( S_1 \) is an expression of the norm of the first derivative

\[
S_1 = \sum_{k=1}^{N-1} (c_{k+1} - c_k)^2,
\]  

(28)

\( S_2 \) is the mean standard deviation,

\[
S_2 = \frac{1}{M} \sum_{j=1}^{M} \left( \prod_{k=1}^{K} \left( \sum_{j=1}^{N} c_{jk} B_j(r) \right) - I_j \right)^2 \frac{1}{\sigma_j^2},
\]  

(29)

and \( \lambda \) is a Lagrangian multiplier. In equation (29) \( \prod \) is the operator which relates \( p(r) \) to the observed scattering data. For the simplest case \( \prod \) is given by

\[
\prod[p(r)] = 4\pi \int p(r) \frac{\sin kr}{kr} dr.
\]  

(30)

An optimum value of the Lagrangian multiplier \( \lambda \) can be determined from the dependence of \( S_1 \) and \( S_2 \) during the minimization of the function \( S \). The optimum \( \lambda \) is a compromise between sufficient stability and an appropriate description of the experimental data. Criteria to find \( \lambda_{opt} \) are given by Glatter (1977). A similar procedure has been given (Glatter, 1978) for \( g(r) \) for centrosymmetric particles. In this case, the observables are scattering amplitudes \( A(k) \) which are real values because of the assumed centrosymmetry \( [A(k) = \pm I(k)^{1/2}] \). Whether there are sign changes within the experimental \( k \) range cannot be decided in a scattering experiment, and reasonable guesses have to be made.

The power of the data evaluation procedures described above is that, once the back-transformation from \( l(K) \) to \( p(r) \) or from \( A(K) \) to \( g(r) \) has been performed, other more usually desired quantities can then be obtained directly. As examples, the radius of gyration \( R_g \), the forward scattering \( I(0) \), the integrated intensity \( Q_0 \), and interpolated or even extrapolated \( I(K) \) values are obtained from \( p(r) \) by the following operations:

\[
R_g^2 \frac{1}{6} \int_0^\infty p(r)r^2 dr / \int_0^\infty p(r) dr,
\]  

(31)

\[
I(0) = 4\pi \int_0^{\infty} p(r) dr,
\]  

(32)

\[
Q_0 = \frac{(2\pi)^3}{4\pi} \lim_{r \to 0} p(r),
\]  

(33)

\[
I(K) = 4\pi \int_0^{\infty} p(r) \frac{\sin kr}{kr} dr.
\]  

(34)

The advantages of determining \( R_g \) and \( I(0) \) in this way are twofold: (1) equations (31) and (32) are integral operations, which are always superior to the differential operations required in more traditional methods, and (2) in the calculation of \( p(r) \), additional information was incorporated \([p(r) \neq 0 \forall r \leq D, p(r) \) is smooth and has minimum curvature, etc.\]. That these procedures result in more accurate (biased) values is illustrated in Fig. 10 for simulated scattering data with a 5% statistical error. The radius of gyration was calculated from \( p(r) \) according to equation (31) with an uncertainty of 2% while an uncertainty of at least 10% is estimated if \( R_g \) is determined from the Guinier plot which is also shown in Fig. 10.
VI. 4 Porod analysis

A discussion of data analysis procedures would not be complete without a discussion of the information contained in the Porod region of the scattering curve for a two-phase system. It has generally been assumed that the observation of a $k^{-4}$ dependence was an indication that the boundaries between the phases were sharp. Recently, this has been checked by Kranjc (1976), who calculated the tails for various interface profiles. She was able to show that a partially sharp boundary was also sufficient to get a Porod-type $k^{-4}$ dependence. Ruland (1977) has developed an elaborate procedure for evaluating SAXS patterns from partially crystallized polyethylene. The widely accepted model of a two-phase lamellar stacking with sharp boundaries was generalized by allowing fluctuations of the interfaces between different phases, which were described by interface distribution functions. This model is certainly much more problem-specific than anything else we have discussed in this section. However, because of the almost structureless SAS patterns from density fluctuations in polymers such a highly specified model is demanded to deduce reasonable results from the data, as was demonstrated by Ruland (1977). Further results are presented elsewhere in this issue (Stribeck & Ruland, 1978).

In all of the preceding discussion, it has been assumed that the background-free and collimation-corrected true scattering curve is available for analysis. Although it had been discovered very early that surface roughness and/or oxides could produce a parasitic small-angle scattering (Li & Smoluchowski, 1955; Robinson & Smoluchowski, 1956; Gerold, 1967), these results appear to have been neglected. More recent experiments, with both X-rays (Parker, 1972; Liu et al., 1978) and neutrons (Roth, 1977), have indicated that serious surface scattering effects can obscure the true scattering curve in that they may be so uncontrollable as to be different for the specimen and the blank. It is clear that for weakly scattering specimens, these effects must be given careful consideration.

VII. Special SAS experiments

In the normal SAS experiment scattering data are recorded as a function of the magnitude of the scattering vector $k$ and the measured scattering pattern is then interpreted in terms of long-range correlations in real space. In contrast to this type of experiment, there are other experiments in which the dependence of the scattering data on parameters other than $k$ is emphasized. Such parameters are the azimuthal angle $\phi$ of $\mathbf{k}$ for anisotropic scatterers, the angle $\phi$ of specimen rotation for planar scatterers, or the time $t$ of a process with changing scattering patterns. Because of this different emphasis one can expect to deduce quite different information from the scattering data. It is the purpose of this section to describe a selected few experiments in order to illustrate the breadth of applicability of the SAS method. It is also hoped that the discussion will stimulate and encourage the invention of new ways of utilizing the SAS method, anticipating that a new approach to a problem generally leads to new information.

VII. 1 Rotation experiments

With the development of two-dimensional PSDs and their gradually increasing use in SAS instruments, anisotropies in scattering patterns can now be discovered directly. One of the principal advantages of simultaneous recording is that the scattering pattern is not affected by instabilities of the SAS instrument. For very anisotropic scatterers – such as, for instance, flux lines in type II superconductors (e.g. Lippmann, Schelten, Hendricks & Schmatz, 1973) – it must be recalled that scattered intensities are not measured in a certain plane in reciprocal space, but along the surface of the Ewald sphere of radius $k_0$ (see Fig. 11). The distance $\delta$ between the surface of the Ewald sphere and its tangential plane through the origin of reciprocal space is, for small $k$ values, very small ($\delta = \frac{1}{2}k^2/k_0^2 = \frac{1}{2}k_0^2v^2$). Nevertheless, there are known cases where $\delta$ is larger than characteristic half-widths of the intensity rods in reciprocal space and where therefore the anisotropy cannot be detected simultaneously by an area detector. In this case it is recommended that a specimen-rotation experiment be performed – i.e. to record the scattered intensity at fixed $|k|$ values as a function of the rotation angle $\phi$. Rotating the specimen about an axis perpendicular to the scattering plane as indicated in Fig. 11 has the advantage over any other rotation axis in that the measured scattering data belong to the same (scattering) plane in reciprocal space even for different absolute values of $k$. The experimental arrangement as sketched in Fig. 12 was used to measure the anisotropic scattering from oriented voids in neutron-irradiated aluminum single crystals (Hendricks, Schelten & Lippmann, 1977). Since the SAS instrument was not equipped with a two-dimensional area detector, this rotation experiment was the only way to measure an anisotropic scattering pattern. For two fixed $k$ values it was possible to record simultaneously the $|k|$ dependence of the scattered intensity. Typically, two peaks in $\langle 111 \rangle$ and a single peak in $\langle 100 \rangle$ directions were measured as shown in Fig. 13. This indicated a faceting of voids by $\langle 111 \rangle$ planes and to some extent by $\langle 100 \rangle$ planes. From the ratio of the intensity peaks it was then possible to deduce the ratio of the area of $\langle 100 \rangle$ to $\langle 111 \rangle$ void surfaces.

VII. 2 Moving scatterers

Essentially the same rotation experiment as sketched in Fig. 12 was used to determine flux-line velocities in a superconductor (Schelten, Ulmaier & Lippmann, 1975). A transport current flowing perpendicular to flux lines in an ideal type-II superconducting slab causes a motion of the flux lines. Provided the same basic assumptions are made as were made to describe the Josephson effect, the following vector equation holds for the flux-line velocity $V_L$:

$$\mathbf{E} = -(\mathbf{V}_L \times \mathbf{B}).$$

(35)

Here, $\mathbf{E}$ is the voltage drop per unit length in the current

![Fig. 11. Sketch of elastic scattering with the wave-number vectors $k_0$ and $k_1$ and the scattering angle $\nu.$](image-url)
direction and \( B \) is the flux density. Several earlier attempts to measure \( V_L \) had been made by other methods. However, it was only possible to verify the concept of flux-line motion, but not to determine the velocity.

The idea of the experiment of Schelten et al. (1975) for determining the flux-line velocity by SAS with neutrons is based on the aberration effect, which can be described with reference to Fig. 14. In Fig. 14(a), the flux lines are assumed to be at rest and a well-collimated neutron beam of velocity \( V_0 \) (wavelength \( \lambda = h/mV_0 \)) enters the periodic flux-line arrangement which is positioned in such a way that the neutron beam is Bragg diffracted. Thus, the glancing angle \( \theta \) is given by Bragg's law, \( 2d \sin \theta = \lambda \), where \( d \) is the spacing of (10) flux-line lattice planes. If the flux lines are set in motion the neutron beam will no longer be diffracted for reasons indicated in Fig. 14(b). In order to return to the Bragg condition the flux-line lattice planes must be rotated about an axis perpendicular to the diffraction plane by an angle \( \Delta \phi \) which is related to the flux line velocity \( V_L \) as indicated in Fig. 14(b) by the expression

\[
\Delta \phi = V_L / V_0.
\]

(36)

For an achievable flux-line velocity of 1 m s\(^{-1}\) the small angular shift \( \Delta \phi \approx 8' \) for 9 Å neutrons. Such \( \Delta \phi \) values were determined from the angular shifts of the measured rocking curves in the low-temperature experiment of Schelten et al. (1975) for various transport currents and various flux densities. From these \( \Delta \phi \) values, flux-line velocities \( V_L \) were determined with equation (36). These directly determined velocities are compared with the expected velocities given by equation (35) as found from the experimental \( E/B \) ratios determined from voltage drop and flux density, as shown in Fig. 15. The conclusions deduced from Fig. 15 were: (1) flux lines move under the influence of transport current, (2) the direction of motion was in accordance with that predicted by equation (35), and (3) within the admittedly large experimental uncertainty of \( \pm 0.2 \) m s\(^{-1}\) the absolute value of \( V_L \) is in accordance with equation (35).

VII. 3 Neutron refraction

To study neutron refraction from Bloch walls in ferromagnetic domains, it was necessary to use a double-crystal spectrometer with perfect silicon crystals with very high resolution. The purpose of this fundamental magnetic experiment by Schärf (1976) was to demonstrate that the angle...
of deflection due to magnetic refraction at a boundary between magnetic domains of different $B$ vectors is a function solely of the magnitude of $B$.

Nuclear and magnetic scattering of neutrons are usually treated in the first Born approximation (Marshall & Lovesy 1971). An essential result of this treatment is that the magnetic scattering-length density of a particle of magnetization $M$ is proportional to the component $M^2$ perpendicular to the scattering vector $\mathbf{k}$. Since the refraction of a neutron wave is the result of the interference of scattered waves it is apparent that it must be assumed that the refractive index depends on the $B$ component perpendicular to the scattering vector. This is, for refraction, the component parallel to the wall separating the two domains. Such arguments and a calculation of the index of refraction were given by De Benedetti (1964). His results must be questioned because the first Born approximation is not a legitimate approximation for a quantitative description of refraction phenomena. In the past the only refraction experiments which were performed were made with the $B$ vectors of the two domains perpendicular to the wall normal. Hence, it was not possible to decide whether the relevant quantity for the index of refraction is $|B|$ or $B^2$.

In the experiment of Schärf (1976) the well-known regular domain structure in an iron single crystal with 90° Bloch walls (Fig. 16) was used for a measurement of deflection angles. By applying a small magnetic field parallel to the wall normal, the 90° angle between $B$ vectors of neighboring domains (Fig. 16) could be changed to any value between 90 and 0°. This enabled him to vary the $B^2$ component while the magnitude of $B$ was kept constant. The deflection angle $\alpha$ was measured as a function of the grazing angle $\theta$ (see Fig. 16) for 90° and 56° Bloch walls. As can be seen in Fig. 17, the data points measured for the two cases of $B^2 = 0.71 |B|$ and $B^2 = 0.47 |B|$ follow a common curve. Thus, the experimental finding is that the index of refraction does not depend on $B^2$. Also shown in Fig. 17 is the $\theta$ dependence of $\alpha$ as would be expected for 180°, 90°, and 56° Bloch walls if one assumes, as was done by De Benedetti, that the relevant quantity for the index of refraction is $B^2$. The overlap of the measured data points and the theoretical curve for 180° Bloch walls ($B^2 = |B|$) is remarkable, and the discrepancy with the other curves for 90° and 56° Bloch walls is outside the experimental errors. A significant consequence of this experiment is that the deflection angle remains even though the angle between the $B$ vectors of neighboring domains tends to zero as is the case for 180° Bloch walls. It is only the intensity of the refracted beam which tends to zero when the 0° Bloch wall is reached. These results, which are of fundamental interest, were theoretically confirmed by an exact solution of the Schrödinger equation for neutron waves in $B$ fields which satisfies the domain structure boundary conditions (Schärf, 1976). Further details are given in papers elsewhere in this issue (Schärf, 1978a, b).

VII. 4 Gravitational effects

Another unique small-angle neutron scattering experiment was that of Murani, Goeltz & Ibel (1976) on the temperature dependence of the scattered intensity of spin glasses as determined by a change of the frequency spectrum of spin clusters. So-called freezing temperatures were determined, below which spin relaxations died out. The gravitational effect was utilized for the observation of energy changes of inelastically scattered neutrons. Accordingly, a neutron with a certain energy loss from an inelastic scattering process arrives at a detector position which is lower than that for a neutron scattered with an energy gain, provided both scattering processes take place for the same scattering angle.

The authors are not confident that Murani et al. (1976) were able to deduce freezing temperatures of spin glasses from the measured SAS signal. Nevertheless, the experiment stimulated us to explore thoroughly the chances of detecting inelastic scattering processes by utilizing gravitational effects. First, consider the sensitivity of the method. If an experimental arrangement as shown in Fig. 18 with a 40 m sample-to-detector distance is used, the drop (distance from the center line) is given by

$$x = 0.05 \lambda^2.$$

where $x$ is in cm if the neutron wavelength $\lambda$ is in Å units. Thus, there is a 5 cm drop for a 10 Å unscattered neutron beam, which arrives at $D_0$ in the detector plane. If neutrons are inelastically scattered in the forward direction ($\theta = 0$) these neutrons will arrive at different vertical positions $x_i$ at the detector. Two examples of energy loss scattering are shown and values are tabulated in Fig. 18. For instance, for

![Diagram](image-url)
neutrons with the already enormous 20% energy loss, the additional spatial drop \( \Delta x_i \) is only 1-25 cm. This is only slightly larger than the spatial resolution of PSDs. A sufficient spatial separation of an inelastically scattered beam from the primary beam is clearly not achieved for small energy changes. Thus the method is very insensitive and the inelastic processes required for sufficient separation are coupled with fairly large momentum transfers. These are given as scattering vectors \( q_i \) and \( q_j \) in Fig. 18 and must be compared with scattering vectors \( \kappa_1 \) and \( \kappa_2 \) for the elastic scattering processes by which neutrons can also arrive at the detector positions \( D_1 \) and \( D_2 \). As seen from the two examples given in Fig. 18 the \( \kappa \) values for elastic scattering are almost four orders of magnitude smaller than the \( q \) values for inelastic scattering into \( D_1 \) and \( D_2 \), still assuming for the latter \( v = 0 \). Because of this, it is apparent that it is possible to find a scattering angle \( \theta(\omega) \) for the inelastic scattering process with energy loss \( h\omega \) such that any given detector element is reached. In addition, even for the largest energy changes, the \( \theta(\omega) \) angles are very small (< 1 mrad). The only exception is the special case in which the neutron energy \( E_0 \) after the scattering process is very close to zero. Because the \( \theta(\omega) \) are very small scattering angles, each detector element \( D_1 \) and \( D_2 \) records essentially the same proportion of inelastically scattered neutrons and integrates over all energies \( h\omega \) which are consistent with the laws of conservation of energy and momentum for scattering processes at small scattering angles. Therefore, changes in the frequency spectrum within the broad range \( |h\omega| < E_0 \) cannot be determined from intensity changes. In light of this discussion, it is conceivable to us that elastic scattering was measured in the experiment of Murani et al. (1976) and that the temperature dependence of the SAS signal was instead caused by a continuous increase in the size of the spin cluster with decreasing temperature.

VII. 5 Dynamic experiments

The increased intensities provided by new X-ray sources and the increased efficiency of data acquisition made possible by PSDs have stimulated interest in dynamic experiments, in which changes in structure are examined following the application of an external stimulus. Several potential examples come immediately to mind: structural changes in membranes resulting from light stimulation; the kinetics of phase transformations in metals and glasses. To date, the major effort in these directions has been the application of linear PSDs to study the mechanisms of muscle contraction as described by Faruqi (1975a), Faruqi & Leigh (1975), Hashizume et al. (1975, 1976, 1977a, b), Podosky et al. (1976), and Amemiya, Hashizume, Kohra & Sigui (1977). In each of these systems elaborate techniques were developed to synchronize switching in the data acquisition system memory with the applied stress. The data acquisition system was usually a multichannel analyzer, although a computer system is used by the Japanese group. To date, only two area PSDs have been developed for time-resolved diffraction studies (Hashizume et al., 1977a; Hendricks, 1978). The latter has been applied to a transient experiment to determine the kinetics of crystallization of polyethylene from the melt, as is reported in this issue by Schultz, Lin & Hendricks (1978). In these experiments an entire diffraction pattern was obtained in 30 s, and with increased power of the X-ray source measurement times of < 1 s appear to be possible. The area of dynamic experiments appears to us to be on the threshold of an explosion of activity.

Finally, we discuss the relationships between a time-slicing dynamical X-ray SAS experiment and inelastic neutron scattering processes. On the one hand, because of high-flux X-ray sources from synchrotrons and storage rings and because of two-dimensional area detectors with high data-acquisition rates, it is conceivable that dynamic experiments with microsecond time slicing will be performed in the near future. On the other hand, new techniques are being developed to achieve very high energy resolution (0.03 \( \mu \)eV) in inelastic neutron scattering experiments (Alefeld, 1972; Heidemann, 1974; Mezei, 1972). In such high-resolution experiments dynamic processes with relaxation times of 0.2 \( \mu \)s or faster can be investigated. To some extent, the information obtainable from inelastic neutron scattering experiments is similar to the information desired from dynamical X-ray experiments. However, the two methods complement each other because they are practical on significantly different time scales.

The double-differential scattering cross section for \( N \) scatterers (atoms and molecules) of coherent scattering length \( b \) is given by

\[
\frac{d\sigma}{d\Omega d\omega} = \frac{b^2}{2\pi k_0} \int \{\exp[-i(\kappa \cdot r + \omega t)]\} G(r,t) dr dt , \tag{38}
\]

where \( r \) is the distance between two scatterers. This equation is a relationship between the scattering cross section and the space and time correlation function \( G(r,t) \). Because our primary interest is concerned with the time dependence of \( G(r,t) \), it is convenient to perform the space Fourier transformation of equation (38). This leads to the intermediate scattering function \( \chi(\kappa,t) \) and gives

\[
\frac{d\sigma}{d\Omega d\omega} = \frac{b^2}{2\pi k_0} \int \chi(\kappa,t)e^{-i\kappa \cdot r} dr , \tag{39}
\]

It can be shown that the intermediate scattering function is given by

\[
\chi(\kappa,t) = \sum_{i,j=1}^{N} \langle \exp[i\kappa \cdot R_i(0)] \exp[-i\kappa \cdot R_j(t)] \rangle , \tag{40}
\]

where \( R_i \) and \( R_j \) are position operators at times 0 and \( t \) of the \( i \)th and \( j \)th scatterers, respectively, and \( \langle \rangle \) means an average over the positions at time \( t = 0 \). The observable differences between scattering experiments performed with X-rays as opposed to slow neutrons arises from the much...
smaller interaction time during the scattering for X-rays than for neutrons. This interaction time is given by

\[ t_1 = \frac{(1/k_0)}{v}. \]

where \( k_0 = 1/N_0 \) is the range for coherent scattering and \( v \) is the photon or neutron velocity. If we select \( k_0 = 0.01 \text{ Å}^{-1} \) as typical of SAS experiments, then for X-rays \( t_1 = 3.3 \times 10^{-14} \text{ s} \), while for 10 Å neutrons the interaction time is \( t_1 = 2.5 \times 10^{-11} \text{ s} \). These two interaction times, which are different by six orders of magnitude, must be considered in relationship to the characteristic time \( t_0 \) for relaxation processes described by \( \chi(K,t) \). For all practical cases it may be assumed that the interaction time \( t_1 \) is smaller than the relaxation times \( t_0 \), which are of physical interest, by many orders of magnitude. As a consequence in the usual SASX-ray experiment, which has only little energy discrimination, the static approximation holds. The measurements are performed as though an instantaneous photograph were taken and the scattering pattern is, for all practical purposes, proportional to

\[ \exp \left[ iK \cdot R_0(z) \right]. \]

In other words, because the time during which a photon is scattered is much shorter than the relaxation time, the photon does not feel the motion of the ensemble. Thus, unless data are recorded in time slices, information about the dynamics is lost because the scattering pattern is an average over a very large number of snapshots taken throughout the whole measuring time. However, by measuring separately in various time intervals \([t, t + dt]\), snapshots averaged over these time intervals yield a scattered intensity

\[ I(K,t) \sim \langle \chi(K,0) \rangle_{t=0}^{t=dt}. \]

The analogous situation would exist for neutrons in a real-time experiment if the relaxation time \( t_0 \), which is many orders of magnitude longer than neutron interaction time \( t_1 \), and if no energy analysis of the scattered neutron beam were made. In reality, the situation is quite different in SANS experiments in which there is a capability for especially high-resolution energy analysis and in which there are fast relaxation processes \( < 1 \mu s \). From Fourier transformation of the measured differential cross section (equation 39), the intermediate scattering function can be obtained directly. Thus, the information concerning dynamic behavior is, for the neutron experiment

\[ I_N(K,t) \sim \exp \left[ iK \cdot R(t) \right] \exp \left[ iK \cdot R(t + dt) \right] \exp \left[ iK \cdot R_0(z) \right] \exp \left[ iK \cdot R_0(z) \right]. \]

while for the real-time X-ray experiment

\[ I_X(K,t) \sim \exp \left[ iK \cdot R(t) \right] \exp \left[ iK \cdot R(t + dt) \right] \exp \left[ iK \cdot R_0(z) \right] \exp \left[ iK \cdot R_0(z) \right]. \]

The \( K \) and \( t \) dependences of \( I_N \) and \( I_X \) can be quite different. As an instructive example, consider a rigid ensemble which moves sinusoidally back and forth, i.e.

\[ R(t) = R(0) + r_0 \sin \left( \frac{2\pi t}{t_r} \right). \]

In this case \( I_N(K,t) \) is a periodic function of \( t \) with period \( t_r \), while \( I_X(K,t) \) does not depend on \( t \). It is clear from these results that when it becomes possible to perform time-slicing X-ray experiments in which \( \Delta t \) is of the order of magnitude of the relaxation times \( t_0 \) of the ensemble, comparative X-ray and neutron experiments should yield significant information which is new and different. Certainly, there are other aspects of this problem which have not been discussed. It was the purpose of this brief consideration to stimulate experiments in which \( I_N \) and \( I_X \) are measured for the same relaxation process. Such experiments should become possible in the near future.

VIII. Conclusions

The past four years have seen numerous developments in both X-ray and neutron small-angle scattering. Many of them are recorded in the following papers in this issue. Of these, perhaps the most significant are the one- and two-dimensional position-sensitive detectors, and the utilization of synchrotron radiation as an intense X-ray source. It was the efficiency of PSDs which totally changed the design of SAS facilities by allowing one to operate in point rather than line geometry. Their impact was especially great on SANS because from the beginning, long-slit collimation in which the ratio of slit length to slit width is typically 10:1 to 100:1 was not feasible at reactors. Thus, PSDs have allowed routine measurements, and especially at medium-flux reactors, when otherwise scattering patterns would have required days or months. The full potential of the high synchrotron intensity has not yet been reached in that the performance of current mirror/crystal monochromators has not been as good as expected, and because appropriate PSDs and associated electronics have not yet been developed.

It is interesting and possibly useful to speculate on the future of SAS. The most significant developments which we foresee will be the use of extremely intense synchrotron radiation from dedicated storage rings coupled with ultra-fast electronics for PSDs. With such devices, SAS patterns will be obtained more than 1000 times faster than at present. Such systems will allow very fast time-slicing dynamic experiments on a wide variety of physical problems. To achieve these goals expensive developments in detector design and especially in digital data-acquisition systems will be required. Of course, only a few such large counters will be constructed and the user community will be required to travel to these facilities, as is now the usual case for use of SANS. On the other hand, the commercial development of linear PSDs at reasonable prices will ensure the continued development and installation of a large number of smaller pinhole and line-geometry machines. Such instruments will be valuable not only for more routine experiments but will also be necessary to perform exploratory experiments for the large synchrotron facilities.

We cannot be so optimistic about the continued revolutionary development of SANS: it appears to us to have already reached a high plateau. We do not foresee the construction of significantly higher-flux continuous reactors in the near future, and believe that, although time-of-flight SANS will be an interesting development, it will by no means have the profound effect on the field that synchrotron radiation is expected to have on SAXS. Thus, we suggest that big improvements in data acquisition rate will not be forthcoming.

The remarkable advances in computer technology and their ever-decreasing prices and increasing performance lead us to believe that fully automated small-angle scattering facilities, in which automatic specimen loading and decision making regarding data analysis are performed on-line, will
appear in the near future. Thus SAS should become a reliable tool in the arsenal of sophisticated analytical techniques.

Perhaps the most encouraging observation of all is that coupled with the new instrumental and analytical techniques, we have seen some truly original and ingenious developments in experimental design. We are encouraged that the remarkable explosion in SAS activity of the past several years will lead to numerous additional such experiments. Among these, it should be anticipated that the wealth of information contained in anisotropic scattering patterns, which two-dimensional PSDs now make routinely available, will be more thoroughly utilized.

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References


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