scattering function because that leads to an increasing loss of essential information about the particle (monomer) itself.

2.6.1.4. *Polydisperse systems*

In this subsection, we give a short survey of the problem of polydispersity. It is most important that there is no way to decide from small-angle scattering data whether the sample is mono- or polydisperse. Every data set can be evaluated in terms of monodisperse or polydisperse structures. Independent *a priori* information is necessary to make this decision. It has been shown analytically that a certain size distribution of spheres gives the same scattering function as a monodisperse ellipsoid with axes a, b and c (Mittelbach & Porod, 1962).

The scattering function of a polydisperse system is determined by the shape of the particles and by the size distribution. As mentioned above, we can assume a certain size distribution and can determine the shape, or, more frequently, we assume the shape and determine the size distribution. In order to do this we have to assume that the scattered intensity results from an ensemble of particles of the same shape whose size distribution can be described by $D_n(R)$, where R is a size parameter and $D_n(R)$ denotes the number of particles of size R. Let us further assume that there are no interparticle interferences or multiple scattering effects. Then the scattering function $I(h)$ is given by

$$I(h) = c_n \int_0^\infty D_n(R) R^6 i_0(hR)\, \mathrm{d}R, \qquad (2.6.1.54)$$

where c_n is a constant, the factor R^6 takes into account the fact that the particle volume is proportional to R^3, and $i_0(hR)$ is the normalized form factor of a particle size R. In many cases, one is interested in the mass distribution $D_m(R)$ [sometimes called volume distribution $D_c(R)$]. In this case, we have

$$I(h) = c_m \int_0^\infty D_m(R) R^3 i_0(hR)\, \mathrm{d}R. \qquad (2.6.1.55)$$

The solution of these integral equations, *i.e.* the computation of $D_n(R)$ or $D_m(R)$ from $I(h)$, needs rather sophisticated numerical or analytical methods and will be discussed later.

The problems of interparticle interference and multiple scattering in the case of polydisperse systems cannot be described analytically and have not been investigated in detail up to now. In general, interference effects start to influence data from small-angle scattering experiments much earlier, *i.e.* at lower concentration, than multiple scattering. Multiple scattering becomes more important with increasing size and contrast and is therefore dominant in light-scattering experiments in higher concentrations.

A concentration series and extrapolation to zero concentration as in monodisperse systems should be performed to eliminate these effects.

2.6.1.5. *Instrumentation*

X-ray sources are the same for small-angle scattering as for crystallographic experiments. One can use conventional generators with sealed tubes or rotating anodes for higher power. For the vast majority of applications, an X-ray tube with copper anode is used; the wavelength of its characteristic radiation (Cu $K\alpha$ line) is 0.154 nm. Different anode materials emit X-rays of different characteristic wavelengths.

X-rays from synchrotrons or storage rings have a continuous wavelength distribution and the actual wavelength for the experiment is selected by a monochromator. The intensity is much higher than for any type of conventional source but synchrotron radiation is available only at a few places in the world. Reviews on synchrotron radiation and its application have been published during recent years (Stuhrmann, 1978; Holmes, 1982; Koch, 1988). In these reviews, one can also find some remarks on the general principles of the systems including cameras and special detectors.

2.6.1.5.1. *Small-angle cameras*

General. In any small-angle scattering experiment, it is necessary to illuminate the sample with a well defined flux of X-rays. The ideal condition would be a parallel monochromatic beam of negligible dimension and very high intensity. These theoretical conditions can never be reached in practice (Pessen, Kumosinski & Timasheff, 1973). One of the main reasons is the fact that there are no lenses as in the visible range of electromagnetic radiation. The refractive index of all materials is equal to or very close to unity for X-rays. On the other hand, this fact has some important advantages. It is, for example, possible to use circular capillaries as sample holders without deflecting the beam. There are different ways of constructing a small-angle scattering system. Slit, pinhole, and block systems define a certain area where the X-rays can pass. Any slit or edge will give rise to secondary scattering (parasitic scattering). The special construction of the instrument has to provide at least a subspace in the detector plane (plane of registration) that is free from this parasitic scattering. The crucial point is of course to provide the conditions to measure at very small scattering angles.

The other possibility of building a small-angle scattering system is to use monochromator crystals and/or bent mirrors to select a narrow wavelength band from the radiation (important for synchrotron radiation) and to focus the X-ray beam to a narrow spot. These systems require slits in addition to eliminate stray radiation.

Block collimation – Kratky camera. The Kratky (1982*a*) collimation system consists of an entrance slit (edge) and two blocks – the *U*-shaped centre piece and a block called *bridge*. With this system, the problem of parasitic scattering can be largely removed for the upper half of the plane of registration and the smallest accessible scattering angle is defined by the size of the entrance slit (see Fig. 2.6.1.13). This system can be integrated in an evacuated housing (Kratky compact camera) and fixed on the top of the X-ray tube. It is widely used in many laboratories for different applications. In the Kratky system, the X-ray beam has a rectangular shape, the length being much larger than the width. Instrumental broadening can be corrected by special numerical routines. The advantage is a relatively high primary-beam intensity. The main disadvantage is that it cannot be used in special applications such as oriented systems where

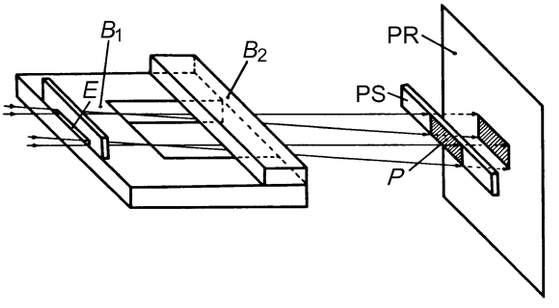

Fig. 2.6.1.13. Schematic drawing of the block collimation (Kratky camera): E edge; B_1 centre piece; B_2 bridge; P primary-beam profile; PS primary-beam stop; PR plane of registration.

the two-dimensional scattering pattern has to be recorded. For such applications, any type of point collimation can be used.

Slit and pinhole cameras. The simplest way to build a camera is to use two pairs of slits or pinholes at a certain distance apart (Kratky, 1982*a*; Holmes, 1982). The narrower the slits and the larger the distance between them, the smaller is the smallest attainable scattering angle (sometimes called the '*resolution*'). Parasitic scattering and difficult alignment are the main problems for all such systems (Guinier & Fournet, 1955). A slit camera that has been used very successfully is that of Beeman and co-workers (Ritland, Kaesberg & Beeman, 1950; Anderegg, Beeman, Shulman & Kaesberg, 1955). A rather unusual design is adopted in the slit camera of Stasiecki & Stuhrmann (1978), whose overall length is 50 m! A highly developed system is the ORNL 10 m camera at Oak Ridge (Hendricks, 1978).

Standard-size cameras for laboratory application are commercially available with different designs from various companies.

Bonse–Hart camera. The Bonse–Hart camera (Bonse & Hart, 1965, 1966, 1967) is based on multiple reflections of the primary beam from opposite sides of a groove in an ideal germanium crystal (collimator and monochromator). After penetrating the sample, the scattered beam runs through the groove of a second crystal (analyser). This selects the scattering angle. Rotation of the second crystal allows the measurement of the angle-dependent scattering function. The appealing feature of this design is that one can measure down to very small angles without a narrow entrance slit. The system is therefore favourable for the investigation of very large particles ($D > 350$ nm). For smaller particles, one obtains better results with block collimation (Kratky & Leopold, 1970).

Camera systems for synchrotron radiation. Small-angle scattering facilities at synchrotrons are built by the local staff and details of the construction are not important for the user in most cases. Descriptions of the instruments are available from the local contacts. These small-angle scattering systems are usually built with crystal monochromators and focusing mirrors (point collimation). All elements have to be operated under remote control for safety reasons. A review of the different instruments was published recently by Koch (1988).

2.6.1.5.2. *Detectors*

In this field, we are facing the same situation as we met for X-ray sources. The detectors for small-angle scattering experiments are the same as or slightly modified from the detectors used in crystallography. Therefore, it is sufficient to give a short summary of the detectors in the following; further details are given in Chapter 7.1. If we are not investigating the special cases of fully or partially oriented systems, we have to measure the dependence of the scattered intensity on the scattering angle, *i.e.* a one-dimensional function. This can be done with a standard gas-filled proportional counter that is operated in a sequential mode (Leopold, 1982), *i.e.* a positioning device moves the receiving slit and the detector to the desired angular position and the radiation detector senses the scattered intensity at that position. In order to obtain the whole scattering curve, a series of different angles must be positioned sequentially and the intensity readings at every position must be recorded. The system has a very high dynamic range, but – as the intensities at different angles are measured at different times – the stability of the primary beam is of great importance.

This drawback is eliminated in the parallel detection mode with the use of position-sensitive detectors. Such systems are in most cases proportional counters with sophisticated and expensive read-out electronics that can evaluate on-line the accurate position where the pulses have been created by the incoming radiation.

Two-dimensional position-sensitive detectors are necessary for oriented systems, but they also have advantages in the case of non-oriented samples when circular chambers are used or when integration techniques in square detectors lead to a higher signal at large scattering angles.

The simplest and cheapest two-dimensional detector is still film, but films are not used very frequently in small-angle scattering experiments because of limited linearity and dynamic range, and fog intensity.

Koch (1988) reviews the one- and two-dimensional detectors actually used in synchrotron small-angle scattering experiments. For a general review of detectors, see Hendrix (1985).

2.6.1.6. *Data evaluation and interpretation*

After having discussed the general principles and the basics of instrumentation in the previous subsections, we can now discuss how to handle measured data. This can only be a very short survey; a detailed description of data treatment and interpretation has been given previously (Glatter, 1982*a*,*b*).

Every physical investigation consists of three highly correlated parts: theory, experiment, and evaluation of data. The theory predicts a possible experiment, experimental data have to be collected in a way that the evaluation of the information wanted is possible, the experimental situation has to be described theoretically and has to be taken into account in the process of data evaluation *etc*. This correlation should be remembered at every stage of the investigation. Before we can start any discussion about interpretation, we have to describe the experimental situation carefully.

All the theoretical equations in the previous subsections correspond to ideal conditions as mentioned in the subsection on instrumentation. In real experiments, we do not measure with a point-like parallel and strictly monochromatic primary beam and our detector will have non-negligible dimensions. The finite size of the beam, its divergence, the size of the detector, and the wavelength distribution will lead to an instrumental broadening as in most physical investigations. The measured scattering curve is said to be *smeared* by these effects. So we find ourselves in the following situation.

The particle is represented by its PDDF $p(r)$. This function is not measured directly. In the scattering process it is Fourier-transformed into a scattering function $I(h)$ [equation (2.6.1.9)]. This function is smeared by the broadening effects and the final *smeared* scattering function $I_{\rm exp}(h)$ is measured with a certain experimental error $\sigma(h)$. In the case of polydisperse systems, the situation is very similar; we start from a size-distribution function $D(R)$ and have a different transformation [equations (2.6.1.54), (2.6.1.55)], but the smearing problem is the same.

2.6.1.6.1. *Primary data handling*

In order to obtain reliable results, we have to perform a series of experiments. We have to repeat the experiment for every sample, to be able to estimate a mean value and a standard deviation at every scattering angle. This experimentally determined standard deviation is often much higher than the standard deviation simply estimated from counting statistics. A blank experiment (cuvette filled with solvent only) is necessary to be able to subtract background scattering coming from the instrument and from the solvent (or *matrix* in the case of solid samples). Finally, we have to perform a series of such

references