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

$$I(h) = c_n \int\limits_0^\infty D_n(R)R^6 i_0(hR)\,\mathrm{d}R, \qquad (2.6.1.54)$$

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

$$I(h) = c_m \int\limits_0^\infty D_m(R)R^3 i_0(hR)\,\mathrm{d}R. \qquad (2.6.1.55)$$

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

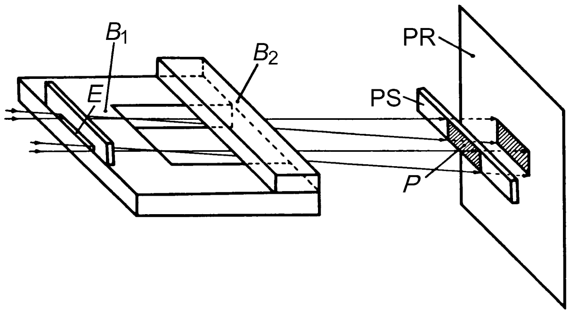

Fig. 2.6.1.13. Schematic drawing of the block collimation (Kratky camera): E edge; B_1 centre piece; B_2 bridge; P primary-beam profile; PS primary-beam stop; PR plane of registration.

references