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

experiments at different concentrations to extrapolate to zero concentration (elimination of interparticle interferences).

If the scattering efficiency of the sample is low (low contrast, small particles), it may be necessary to measure the outer part of the scattering function with a larger entrance slit and we will have to merge different parts of the scattering function. The intensity of the instrument (primary beam) should be checked before each measurement. This allows correction (normalization) for instabilities.

It is therefore necessary to have a so-called primary data-handling routine that performs all these preliminary steps like averaging, subtraction, normalization, overlapping, concentration extrapolation, and graphical representation on a graphics terminal or plotter. In addition, it is helpful to have the possibility of calculating the Guinier radius, Porod extrapolation [equations (2.6.1.24)], invariant, *etc*. from the raw data.

When all these preliminary steps have been performed, we have a smeared particle-scattering function $I_{\rm exp}(h)$ with a certain statistical accuracy. From this data set, we want to compute $I(h)$ and $p(r)$ [or $D(R)$] and all our particle parameters. In order to do this, we have to *smooth* and *desmear* our function $I_{\rm exp}(h)$. The smoothing operation is an absolute necessity because the desmearing process is comparable to a differentiation that is impossible for noisy data. Finally, we have to perform a Fourier transform (or other similar transformation) to invert equations (2.6.1.9) or (2.6.1.54), (2.6.1.55). Before we can discuss the desmearing process (collimation error correction) we have to describe the smearing process.

2.6.1.6.2. *Instrumental broadening – smearing*

These effects can be separated into three components: the two-dimensional geometrical effects and the wavelength effect. The geometrical effects can be separated into a slit-length (or slit-height) effect and a slit-width effect. The slit length is perpendicular to the direction of increasing scattering angle; the corresponding weighting function is usually called $P(t)$. The slit width is measured in the direction of increasing scattering angles and the weighting function is called $Q(x)$. If there is a wavelength distribution, we call the weighting function $W(\lambda')$ where $\lambda' = \lambda/\lambda_0$ and λ_0 is the reference wavelength used in equation (2.6.1.2). When a conventional X-ray source is used, it is sufficient in most cases to correct only for the $K\beta$ contribution. Instead of the weighting function $W(\lambda')$ one only needs the ratio between $K\beta$ and $K\alpha$ radiation, which has to be determined experimentally (Zipper, 1969). One or more smearing effects may be negligible, depending on the experimental situation.

Each effect can be described separately by an integral equation (Glatter, 1982*a*). The combined formula reads

$$\bar{I}_{\rm exp}(h) = 2 \int_{-\infty}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} Q(x)P(t)W(\lambda') \times I\left(\frac{[(m-x)^2 + t^2]^{1/2}}{\lambda'}\right) {\rm d}\lambda'\ {\rm d}t\ {\rm d}x. \quad (2.6.1.56)$$

This threefold integral equation cannot be solved analytically. Numerical methods must be used for its solution.

2.6.1.6.3. *Smoothing, desmearing, and Fourier transformation*

There are many methods published that offer a solution for this problem. Most are referenced and some are reviewed in the textbooks (Glatter, 1982*a*; Feigin & Svergun, 1987). The *indirect transformation method* in its original version (Glatter, 1977*a*,*b*, 1980*a*,*b*) or in modifications for special applications (Moore, 1980; Feigin & Svergun, 1987) is a well established method used in the majority of laboratories for different applications. This procedure solves the problems of smoothing, desmearing, and Fourier transformation [inversion of equations (2.6.1.9) or (2.6.1.54), (2.6.1.55)] in one step. A short description of this technique is given in the following.

Indirect transformation methods. The *indirect transformation method* combines the following demands: single-step procedure, optimized general-function system, weighted least-squares approximation, minimization of termination effect, error propagation, and consideration of the physical smoothing condition given by the maximum intraparticle distance. This smoothing condition requires an estimate $D_{\rm max}$ as an upper limit for the largest particle dimension:

$$D_{\rm max} \geq D. \quad (2.6.1.57)$$

For the following, it is not necessary for $D_{\rm max}$ to be a perfect estimate, but it must not be smaller than D.

As $p(r) = 0$ for $r \geq D_{\rm max}$, we can use a function system for the representation of $p(r)$ that is defined only in the subspace $0 \leq r \leq D_{\rm max}$. A linear combination

$$p_A(r) = \sum_{\nu=1}^{N} c_\nu \varphi_\nu(r) \quad (2.6.1.58)$$

is used as an approximation to the PDDF. Let N be the number of functions and c_ν be the unknowns. The functions $\varphi_\nu(r)$ are chosen as cubic B splines (Greville, 1969; Schelten & Hossfeld, 1971) as they represent smooth curves with a minimum second derivative.

Now we take advantage of two facts. The first is that we know precisely how to calculate a smeared scattering function $\bar{I}(h)$ from $I(h)$ [equation (2.6.1.56)] and how $p(r)$ or $D(R)$ is transformed into $I(h)$ [equations (2.6.1.9) or (2.6.1.54), (2.6.1.55)], but we do not know the inverse transformations. The second fact is that all these transformations are linear, *i.e*. they can be applied to all terms in a sum like that in equation (2.6.1.58) separately. So it is easy to start with our approximation in real space [equation (2.6.1.58)] taking into account the *a priori* information $D_{\rm max}$. The approximation $I_A(h)$ to the ideal (unsmeared) scattering function can be written as

$$I_A(h) = \sum_{\nu=1}^{N} c_\nu \Psi_\nu(h), \quad (2.6.1.59)$$

where the functions $\Psi_\nu(h)$ are calculated from $\varphi_\nu(r)$ by the transformations (2.6.1.9) or (2.6.1.54), (2.6.1.55), the coefficients c_ν remain unknown. The final fit in the smeared, experimental space is given by a similar series

$$\bar{I}_A(h) = \sum_{\nu=1}^{N} c_\nu \chi_\nu(h), \quad (2.6.1.60)$$

where the $\chi_\nu(h)$ are functions calculated from $\psi_\nu(h)$ by the transform (2.6.1.56). Equations (2.6.1.58), (2.6.1.59), and (2.6.1.60) are similar because of the linearity of the transforms. We see that the functions $\chi_\nu(h)$ are calculated from $\varphi_\nu(r)$ in the same way as the data $\bar{I}_{\rm exp}(h)$ were produced by the experiment from $p(r)$. Now we can minimize the expression

$$L = \sum_{k=1}^{M} [\bar{I}_{\rm exp}(h_k) - \bar{I}_A(h_k)]^2 / \sigma^2(h_k), \quad (2.6.1.61)$$

where M is the number of experimental points. Such *least-squares problems* are in most cases *ill conditioned, i.e*. additional stabilization routines are necessary to find the best

references