

## 2.6. SMALL-ANGLE TECHNIQUES

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  $I_{\text{exp}}(h)$  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  $I_{\text{exp}}(h)$ . 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  $\lambda_0$  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, 1982a). The combined formula reads

$$\bar{I}_{\text{exp}}(h) = 2 \int_{-\infty}^{\infty} \int_0^{\infty} \int_0^{\infty} Q(x)P(t)W(\lambda') \times I \left( \frac{[(m-x)^2 + t^2]^{1/2}}{\lambda'} \right) d\lambda' dt dx. \quad (2.6.1.56)$$

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, 1982a; Feigin & Svergun, 1987). The *indirect transformation method* in its original version (Glatter,

1977a,b, 1980a,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  $D_{\text{max}}$  as an upper limit for the largest particle dimension:

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

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

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

$$p_A(r) = \sum_{v=1}^N c_v \varphi_v(r) \quad (2.6.1.58)$$

is used as an approximation to the PDDF. Let  $N$  be the number of functions and  $c_v$  be the unknowns. The functions  $\varphi_v(r)$  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  $D_{\text{max}}$ . The approximation  $I_A(h)$  to the ideal (unsmeared) scattering function can be written as

$$I_A(h) = \sum_{v=1}^N c_v \Psi_v(h), \quad (2.6.1.59)$$

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

$$\bar{I}_A(h) = \sum_{v=1}^N c_v \chi_v(h), \quad (2.6.1.60)$$

where the  $\chi_v(h)$  are functions calculated from  $\psi_v(h)$  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  $\chi_v(h)$  are calculated from  $\varphi_v(r)$  in the same way as the data  $\bar{I}_{\text{exp}}(h)$  were produced by the experiment from  $p(r)$ . Now we can minimize the expression

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

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

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solution. This problem is far from being trivial, but it can be solved with standard routines (Glatter, 1977a,b; Tikhonov & Arsenin, 1977).

The whole process of data evaluation is shown in Fig. 2.6.1.14. Similar routines cannot be used in crystallography (periodic structures) because there exists no estimate for  $D_{\max}$  [equation (2.6.1.57)].

*Maximum particle dimension.* The sampling theorem of Fourier transformation (Shannon & Weaver, 1949; Bracewell, 1986) gives a clear answer to the question of how the size of the particle  $D$  is related to the smallest scattering angle  $h_1$ . If the scattering curve is observed at increments  $\Delta h \leq h_1$  starting from a scattering angle  $h_1$ , the scattering data contain, at least theoretically, the full information for all particles with maximum dimension  $D$

$$D \leq \pi/h_1. \quad (2.6.1.62)$$

The first application of this theorem to the problem of data evaluation was given by Damaschun & Pürschel (1971a,b). In practice, one should always try to stay below this limit, *i.e.*

$$h_1 < \pi/D \text{ and } \Delta h \ll h_1, \quad (2.6.1.63)$$

taking into account the loss of information due to counting statistics and smearing effects. An optimum value for  $\Delta h = \pi/(6D)$  is claimed by Walter, Kranold & Becherer (1974).

*Information content.* The number of independent parameters contained in a small-angle scattering curve is given by

$$N_{\max} \leq h_2/h_1, \quad (2.6.1.64)$$

with  $h_1$  and  $h_2$  being the lower and upper limits of  $h$ . In practice, this limit certainly depends on the statistical accuracy of the data. It should be noted that the number of functions  $N$  in equations (2.6.1.58) to (2.6.1.60) may be larger than  $N_{\max}$  because they are not independent. They are correlated by the stabilization

routine. An example of this problem can be found in Glatter (1980a).

*Resolution.* There is no clear answer to the question concerning the smallest structural details, *i.e.* details in the  $p(r)$  function that can be recognized from an experimental scattering function. The limiting factors are the maximum scattering angle  $h_2$ , the statistical error  $\sigma(h)$ , and the weighting functions  $P(t)$ ,  $Q(x)$ , and  $W(\lambda')$  (Glatter, 1982a). The resolution of standard experiments is not better than approximately 10% of the maximum dimension of the particle for a monodisperse system. In the case of polydisperse systems, resolution can be defined as the minimum relative peak distance that can be resolved in a bimodal distribution. We know from simulations that this value is of the order of 25%.

*Special transforms.* The PDDF  $p(r)$  or the size distribution function  $D(R)$  is related to  $I(h)$  by equations (2.6.1.9) or (2.6.1.54), (2.6.1.55). In the special case of particles elongated in one direction (like cylinders), we can combine equations (2.6.1.41) and (2.6.1.43) and obtain

$$I(h) = 2\pi^2 L \int_0^\infty p_c(r) \frac{J_0(hr)}{h} dr. \quad (2.6.1.65)$$

This Hankel transform can be used in the indirect transformation method for the calculation of  $\psi_v(h)$  in (2.6.1.59). Doing this, we immediately obtain the PDDF of the cross section  $p_c(r)$  from the smeared experimental data. It is not necessary to know the length  $L$  of the particle if the results are not needed on an absolute scale. For this application, we only need the information that the scatterers are elongated in one direction with a constant cross section. This information can be found from the overall PDDF of the particle or can be *a priori* information from other experiments, like electron microscopy. The estimate for the maximum dimension  $D_{\max}$  (2.6.1.57) is related to the cross

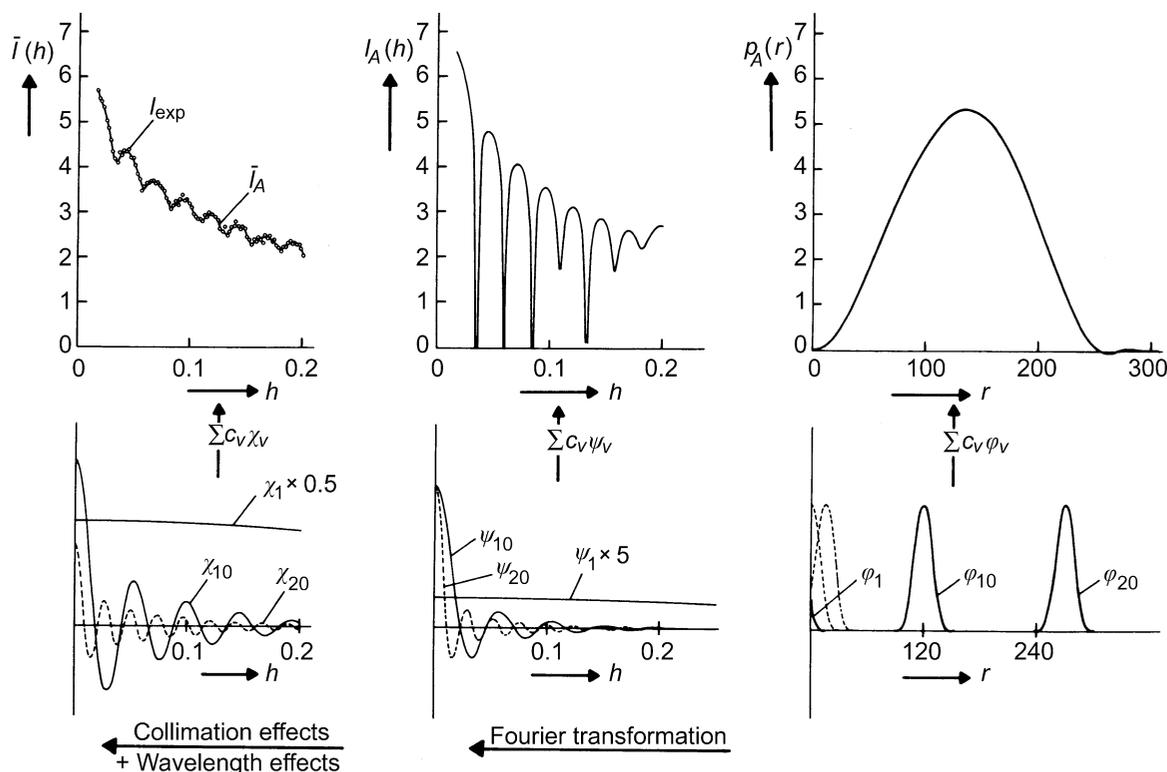


Fig. 2.6.1.14. Function systems  $\varphi_v(r)$ ,  $\Psi_v(h)$ , and  $\chi_v(h)$  used for the approximation of the scattering data in the indirect transformation method.

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section in this application, *i.e.* the maximum dimension of the cross section must not be larger than  $D_{\max}$ .

The situation is quite similar for flat particles. If we combine (2.6.1.47) and (2.6.1.49), we obtain

$$I(h) = 4\pi A \int_0^{\infty} p_t(r) \frac{\cos(hr)}{h^2} dr, \quad (2.6.1.66)$$

$p_t(r)$  being the distance distribution function of the thickness. We have to check that the particles are flat with a constant thickness with maximum thickness  $T \leq D_{\max}$ .  $A$  is the area of the particles and would be needed only for experiments on an absolute scale.

### 2.6.1.6.4. Direct structure analysis

It is impossible to determine the three-dimensional structure  $\rho(\mathbf{r})$  directly from the one-dimensional information  $I(h)$  or  $p(r)$ . Any direct method needs additional *a priori* information – or assumptions – on the system under investigation. If this information tells us that the structure only depends on one variable, *i.e.* the structure is in a general sense *one dimensional*, we have a good chance of recovering the structure from our scattering data.

Examples for this case are particles with spherical symmetry, *i.e.*  $\rho$  depends only on the distance  $r$  from the centre, or particles with cylindrical or lamellar symmetry where  $\rho$  depends only on the distance from the cylinder axis or from the distance from the central plane in the lamella. We will restrict our discussion here to the spherical problem but we keep in mind that similar methods exist for the cylindrical and the lamellar case.

*Spherical symmetry.* This case is described by equations (2.6.1.51) and (2.6.1.52). As already mentioned in §2.6.1.3.2.2, we can solve the problem of the calculation of  $\rho(r)$  from  $I(h)$  in two different ways. We can calculate  $\rho(r)$  *via* the distance distribution function  $p(r)$  with a *convolution square-root* technique (Glatter, 1981; Glatter & Hainisch, 1984). The other way goes through the amplitude function  $A(h)$  and its Fourier transform. In this case, one has to find the right phases (signs) in the square-root operation  $\{A(h) = \pm[I(h)^{1/2}]\}$ . The *box-function refinement* method by Svergun, Feigin & Schedrin (1984) is an iterative technique for the solution of the phase problem using the *a priori* information that  $\rho(r)$  is equal to zero for  $r \geq R_{\max}$  ( $D_{\max}/2$ ). The same restriction is used in the convolution square-root technique. Under ideal conditions (perfect spherical symmetry), both methods give good results. In the case of deviations from spherical symmetry, one obtains better results with the convolution square-root technique (Glatter, 1988). With this method, the results are less distorted by non-spherical contributions.

*Multipole expansions.* A wide class of homogeneous particles can be represented by a boundary function that can be expanded into a series of spherical harmonics. The coefficients are related to the coefficients of a power series of the scattering function  $I(h)$ , which are connected with the moments of the PDDF (Stuhrmann, 1970*b,c*; Stuhrmann, Koch, Parfait, Haas, Ibel & Crichton, 1977). Of course, this expansion cannot be unique, *i.e.* for a certain scattering function  $I(h)$  one can find a large variety of possible expansion coefficients and shapes. In any case, additional *a priori* information is necessary to reduce this number, which in turn influences the convergence of the expansion. Only compact, globular structures can be approximated with a small number of coefficients.

This concept is not restricted to the determination of the shape of the particles. Even inhomogeneous particles can be described

using all possible radial terms in a general expansion (Stuhrmann, 1970*a*). The information content can be increased by contrast variation (Stuhrmann, 1982), but in any event one is left with the problem of how to find additional *a priori* information in order to reduce the possible structures. Any type of symmetry will lead to a considerable improvement. The case of axial symmetry is a good example. Svergun, Feigin & Schedrin (1982) have shown that the quality of the results can be further improved when upper and lower limits for  $\rho(r)$  can be used. Such limits can come from a known chemical composition.

### 2.6.1.6.5. Interpretation of results

After having used all possible data-evaluation techniques, we end up with a desmeared scattering function  $I(h)$ , the PDDF  $p(r)$  or the size-distribution function  $D(R)$ , and some special functions discussed in the previous subsections. Together with the particle parameters, we have a data set that can give us at least a rough classification of the substance under investigation.

The interpretation can be performed in reciprocal space (scattering function) or in real space (PDDF *etc.*). Any symmetry can be detected more easily in reciprocal space, but all other structural information can be found more easily in real space (Glatter, 1979, 1982*b*).

When a certain structure is estimated from the data and from *a priori* information, one has to test the corresponding model. That means one has to find the PDDF and  $I(h)$  for the model and has to compare it with the experimental data. Every model that fits within the experimental errors can be true, all that do not fit have to be rejected. If the model does not fit, it has to be refined by trial and error. In most cases, this process is much easier in real space than in reciprocal space. Finally, we may end up with a set of possible structures that can be correct. Additional *a priori* information will be necessary to reduce this number.

### 2.6.1.7. Simulations and model calculations

#### 2.6.1.7.1. Simulations

Simulations can help to find the limits of the method and to estimate the systematic errors introduced by the data-evaluation procedure. Simulations are performed with exactly known model systems (test functions). These systems should be similar to the structures of interest. The model data are transformed according to the special experimental situation (collimation profiles and wavelength distribution) starting from the theoretical PDDF (or scattering function). ‘*Experimental data points*’ are generated by sampling in a limited  $h$  range and adding statistical noise from a random-number generator. If necessary, a certain amount of background scattering can also be added. This simulated data set is subjected to the data-evaluation procedure and the result is compared with the starting function. Such simulation can reveal the influence of each approximation applied in the various evaluation routines.

On the other hand, simulations can also be used for the optimization of the experimental design for a special application. The experiment situation is characterized by several contradictory effects: a large width for the functions  $P(t)$ ,  $Q(x)$ , and  $W(\lambda')$  leads to a high statistical accuracy but considerable smearing effects. The quality of the results of the desmearing procedure is increased by high statistical accuracy, but decreased by large smearing effects. Simulations can help to find the optimum for a special application.