

## 2.6. SMALL-ANGLE TECHNIQUES

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.

## 2. DIFFRACTION GEOMETRY AND ITS PRACTICAL REALIZATION

### 2.6.1.7.2. Model calculation

In the section on data evaluation and interpretation, we have seen that we obtain a rough estimate for the structure of the particles under investigation directly from the experimental data. For further refinement, we have to compare our results with scattering functions or PDDF's from models

### 2.6.1.7.3. Calculation of scattering intensities

The scattering curves can be calculated semi-analytically for simple triaxial bodies and for models composed of some of these bodies. The scattering amplitude for regular bodies like ellipsoids, parallelepipeds, and cylinders can be calculated analytically for any orientation. The spatial averaging has to be performed numerically. Such calculations have been performed for a large number of different models by Porod (1948), Mittelbach & Porod (1961*a,b*, 1962), and by Mittelbach (1964). More complicated structures can be described by models composed of several such triaxial bodies, but the computing time necessary for such calculations can be hours on a mainframe computer.

Models composed only of spherical subunits can be evaluated with the Debye formula (Debye, 1915):

$$I(h) = i_{\text{el}}(h) \sum_{i=1}^N \sum_{k=1}^N \rho_i V_i \rho_k V_k \Phi_i(h) \Phi_k(h) \frac{\sin(hd_{ik})}{hd_{ik}}, \quad (2.6.1.67)$$

where the spatial average is carried out analytically. Another possibility would be to use spherical harmonics as discussed in the previous section but the problem is how to find the expansion coefficients for a certain given geometrical structure.

### 2.6.1.7.4. Method of finite elements

Models of arbitrary shape can be approximated by a large number of very small homogeneous elements of variable electron density. These elements have to be smaller than the smallest structural detail of interest.

*Sphere method.* In this method, the elements consist of spheres of equal size. The diameter of these spheres must be chosen independently of the distance between nearest neighbours, in such a way that the total volume of the model is represented correctly by the sum of all volume elements (which corresponds to a slight formal overlap between adjacent spheres). The scattering intensity is calculated using the Debye formula (2.6.1.67), with  $\Phi_i(h) = \Phi_k(h) = \Phi(h)$ .

The computing time is mainly controlled by the number of mutual distances between the elements. The computing time can be lowered drastically by the use of approximate  $d_{ik}$  values in (2.6.1.67). Negligible errors in  $I(h)$  result if  $d_{ik}$  values are quantized to  $D_{\text{max}}/10000$  (Glatter, 1980*c*). For the practical application (input operation), it is important that a certain number of elements can be combined to form so-called substructures that can be used in different positions with arbitrary weights and orientations to build the model.

The sphere method can also be used for the computation of scattering curves for macromolecules from a known crystal structure. The weights of the atoms are given by the effective number of electrons

$$Z_{\text{eff}} = Z - \rho_0 V_{\text{eff}}, \quad (2.6.1.68)$$

where  $V_{\text{eff}}$  is the apparent volume of the atom given by Langridge, Marvin, Seeds, Wilson, Cooper, Wilkins & Hamilton (1960).

*Cube method.* This method has been developed independently by Fedorov, Ptitsyn & Voronin (1972, 1974*a,b*) and by Ninio & Luzzati (1972) mainly for the computation of scattered intensities for macromolecules in solution whose crystal structure is known. In the cube method, the macromolecule is mentally placed in a parallelepiped, which is subdivided into small cubes (with edge lengths of 0.5–1.5 Å). Each cube is examined in order to decide whether it belongs to the molecule or to the solvent. Adjacent cubes in the  $z$  direction are joined to form parallelepipeds. The total scattering amplitude is the sum over the amplitudes from the parallelepipeds with different positions and lengths. The mathematical background is described by Fedorov, Ptitsyn & Voronin (1974*a,b*). The *modified cube method* of Fedorov & Denesyuk (1978) takes into account the possible penetration of the molecule by water molecules.

### 2.6.1.7.5. Calculation of distance-distribution functions

The PDDF can be calculated analytically only for a few simple models (Porod, 1948; Goodisman, 1980); in all other cases, we have to use a finite element method with spheres. It is possible to define an analogous equation to the Debye formula (2.6.1.67) in real space (Glatter, 1980*c*). The PDDF can be expressed as

$$p(r) = \sum_{i=1}^N \rho_i^2 p_0(r, R_i) + 2 \sum_{i=1}^{N-1} \sum_{k=i+1}^N \rho_i \rho_k p(r, d_{ik}, R_i, R_k). \quad (2.6.1.69)$$

$p_0(r, R_i)$  is the PDDF of a sphere with radius  $R_i$  and electron density equal to unity,  $p(r, d_{ik}, R_i, R_k)$  is the cross-term distance distribution between the  $i$ th and  $k$ th spheres (radii  $R_i$  and  $R_k$ ) with a mutual distance  $d_{ik}$ .

Equation (2.6.1.69) [and (2.6.1.67)] can be used in two different ways for the calculation of model functions. Sometimes, it is possible to approximate a macromolecule as an aggregate of some spheres of well defined size representing different globular subunits (Pilz, Glatter, Kratky & Moring-Claesson, 1972). The form factors of the subunits are in such cases real parameters of the model. However, in most cases we have no such possibility and we have to use the method of finite elements, *i.e.* we fit our model with a large number of sufficiently small spheres of equal size, and, if necessary, different weight. The form factor of the small spheres is now not a real model parameter and introduces a limit of resolution.

Fourier transformation [equation (2.6.1.10)] can be used for the computation of the PDDF of any arbitrary model if the scattering function of the model is known over a sufficiently large range of  $h$  values.

### 2.6.1.8. Suggestions for further reading

Only a few textbooks exist in the field of small-angle scattering. The classic monograph *Small-Angle Scattering of X-rays* by Guinier & Fournet (1955) was followed by the proceedings of the conference at Syracuse University, 1965, edited by Brumberger (1967) and by *Small-Angle X-ray Scattering* edited by Glatter & Kratky (1982). The several sections of this book are written by different authors being experts in the field and representing the state of the art at the beginning of the 1980's. The monograph *Structure Analysis by Small-Angle X-ray and Neutron Scattering* by Feigin & Svergun (1987) combines X-ray and neutron techniques.