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):

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

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 $D_{max}/10000$ (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

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

where V_{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 mutal 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 Gunier & 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.

references