Composite structures – aggregates, subunits. The formation of dimers can be analysed qualitatively with the $p(r)$ function (Glatter, 1979). For an approximate analysis, it is only necessary to know the PDDF of the monomer. Different types of aggregates will have distinct differences in their PDDF. Higher aggregates generally cannot be classified unambiguously. Additional information from other sources, such as the occurrence of symmetry, can simplify the problem.

Particles that consist of aggregates of a relatively large number of identical subunits show, at low resolution, the overall structure of the whole particle. At larger angles (higher resolution), the influence of the individual subunits can be seen. In the special case of globular subunits, it is possible to determine the size of the subunits from the position of the minima of the corresponding shape factors using equation (2.6.1.39) (Glatter, 1972; Pilz, Glatter, Kratky & Moring-Claesson, 1972).

2.6.1.3.2.2. *Hollow and inhomogeneous particles*

We have learned to classify homogeneous particles in the previous part of this section. It is possible to see from scattering data [$I(h)$ or $p(r)$] whether a particle is globular or elongated, flat or rod-like, *etc.*, but it is impossible to determine uniquely a complicated shape with many parameters. If we allow internal inhomogeneities, we make things more complicated and it is clear that it is impossible to obtain a unique reconstruction of an inhomogeneous three-dimensional structure from its scattering function without additional *a priori* information. We restrict our considerations to special cases that are important in practical applications and that allow at least a solution in terms of a first-order approximation. In addition, we have to remember that the $p(r)$ function is weighted by the number of excess electrons that can be negative. Therefore, a minimum in the PDDF can be caused by a small number of distances, or by the addition of positive and negative contributions.

Spherically symmetric particles. In this case, it is possible to describe the particle by a one-dimensional radial excess density function $\Delta\rho(r)$. For convenience, we omit the Δ sign for excess in the following. As we do not have any angle-dependent terms, we have no loss of information from the averaging over angle. The scattering amplitude is simply the Fourier transform of the radial distribution:

$$A(h) = 4\pi \int\limits_0^\infty r\rho(r)\frac{\sin(hr)}{h}\,\mathrm{d}r \qquad (2.6.1.51)$$

$[I(h) - A(h)^2]$ and

$$\rho(r) = \frac{1}{2\pi^2}\int\limits_0^\infty hA(h)\frac{\sin(hr)}{r}\,\mathrm{d}h \qquad (2.6.1.52)$$

(Glatter, 1977*a*). These equations would allow direct analysis if $A(h)$ could be measured, but we can measure only $I(h)$. $\rho(r)$ can be calculated from $I(h)$ using equation (2.6.1.10) remembering that this function is the convolution square of $\rho(r)$ [equations (2.6.1.5) and (2.6.1.8)]. Using a *convolution square-root* technique, we can calculate $\rho(r)$ from $I(h)$ *via* the PDDF without having a 'phase problem' like that in crystallography; *i.e.* it is not necessary to calculate scattering amplitudes and phases (Glatter, 1981; Glatter & Hainisch, 1984; Glatter, 1988). This can be done because $p(r)$ differs from zero only in the limited range $0 < r < D$ (Hosemann & Bagchi, 1952, 1962). In mathematical terms, it is again the difference between a Fourier series and a Fourier integral.

Details of the technique cannot be discussed here, but it is a fact that we can calculate the radial distribution $\rho(r)$ from the scattering data assuming that the spherical scatterer is only of finite size. The hollow sphere can be treated either as a homogeneous particle with a special shape or as an inhomogeneous particle with spherical symmetry with a step function as radial distribution. The scattering function and the PDDF of a hollow sphere can be calculated analytically. The $p(r)$ of a hollow sphere has a triangular shape and the function $f(r) = p(r)/r$ shows a horizontal plateau (Glatter, 1982*b*).

Rod-like particles. Radial inhomogeneity. If we assume radial inhomogeneity of a circular cylinder, *i.e.* ρ is a function of the radius r but not of the angle φ or of the value of z in cylindrical coordinates, we can determine some structural details. We define $\bar{\rho}_c$ as the average excess electron density in the cross section. Then we obtain a PDDF with a linear part for $r > d$ and we have to replace $\Delta\rho$ in equation (2.6.1.46) by $\bar{\rho}_c$ with the maximum dimension of the cross section d. The $p(r)$ function differs from that of a homogeneous cylinder with the same $\bar{\rho}_c$ only in the range $0 < r \le d$. A typical example is shown in Fig. 2.6.1.8. The functions for a homogeneous, a hollow, and an inhomogeneous cylinder with varying density $\rho_c(r)$ are shown.

Rod-like particles. Axial inhomogeneity. This is another special case for rod-like particles, *i.e.* the density is a function of the z coordinate. In Fig. 2.6.1.9, we compare two cylinders with the same size and diameter. One is a homogeneous cylinder with density $\bar{\rho}$, diameter $d = 48$ and length $L = 480$, and the other is an inhomogeneous cylinder of the same size and mean density $\bar{\rho}$, but this cylinder is made from slices with a thickness of 20 and alternating densities of $1.5\bar{\rho}$ and $0.5\bar{\rho}$, respectively. The PDDF of the inhomogeneous cylinder has ripples with the periodicity of 40 in the whole linear range. This periodicity leads to reflections in reciprocal space (first and third order in the h range of the figure).

Flat particles. Cross-sectional inhomogeneity. Lamellar particles with varying electron density perpendicular to the basal plane, where ρ is a function of the distance x from the central plane, show differences from a homogeneous lamella of the same size in the PDDF in the range $0 < r < T$, where T is the

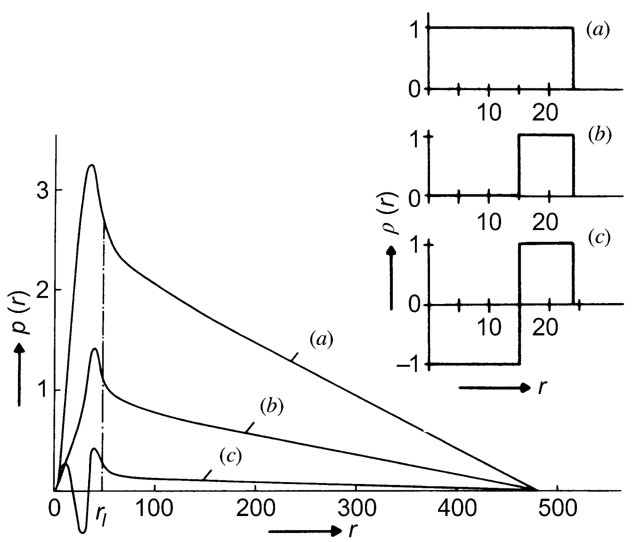

Fig. 2.6.1.8. Circular cylinder with a constant length of 480 Å and an outer diameter of 48 Å. (*a*) Homogeneous cylinder, (*b*) hollow cylinder, (*c*) inhomogeneous cylinder. The $p(r)$ functions are shown on the left, the corresponding electron-density distributions $\rho(r)$ on the right.

references