

## 2.6. SMALL-ANGLE TECHNIQUES

*Surface.* The surface  $S$  of one particle is correlated with the scattering intensity  $I_1(h)$  of this particle by

$$I_1(h)|_{h \rightarrow \infty} = (\Delta\rho)^2 \frac{2\pi}{h^4} S. \quad (2.6.1.24)$$

Determination of the absolute intensity can be avoided if we calculate the specific surface  $O_s$  (Mittelbach & Porod, 1965)

$$O_s = S/V = \pi \frac{\lim_{h \rightarrow \infty} [I(h)h^4]}{Q}. \quad (2.6.1.25)$$

*Cross section, thickness, and correlation length.* By similar equations, we can find the area  $A$  of the cross section of a rod-like particle

$$A = 2\pi \frac{[I(h)h]_{h \rightarrow 0}}{Q} \quad (2.6.1.26)$$

and the thickness  $T$  of lamellar particles by

$$T = \pi \frac{[I(h)h^2]_{h \rightarrow 0}}{Q} \quad (2.6.1.27)$$

but the experimental accuracy of the limiting values  $[I(h)h]_{h \rightarrow 0}$  and  $[I(h)h^2]_{h \rightarrow 0}$  is usually not very high.

The correlation length  $l_c$  is the mean width of the correlation function  $\gamma(r)$  (Porod, 1982) and is given by

$$l_c = \frac{\pi}{Q} \int_0^{\infty} I(h)h \, dh. \quad (2.6.1.28)$$

The *maximum dimension*  $D$  of a particle would be another important particle parameter, but it cannot be calculated directly from the scattering function and will be discussed later.

*Persistence length*  $a_p$ . An important model for polymers in solution is the so-called worm-like chain (Porod, 1949; Kratky & Porod, 1949). The degree of coiling can be characterized by the persistence length  $a_p$  (Kratky, 1982*b*). Under the assumption that the persistence length is much larger than the cross section of the polymer, it is possible to find a transition point  $h^+$  in an  $I(h)h^2$  vs  $h$  plot where the function starts to be proportional to  $h$ . There is an approximation

$$h^+ a_p \simeq 2.3, \quad (2.6.1.29)$$

depending on the length of the chain (Heine, Kratky & Roppert, 1962). For further details, see Kratky (1982*b*).

*Molecular weight. Particles of arbitrary shape.* The particle is measured at high dilution in a homogeneous solution and has an isopotential specific volume  $v_2'$  and  $z_2$  mol. electrons per gram, *i.e.* the molecule contains  $z_2 M$  electrons if  $M$  is the molecular weight. The number of effective mol. electrons per gram is given by

$$\Delta z_2 = (z_2 - v_2' \rho_0), \quad (2.6.1.30)$$

where  $\rho_0$  is the mean electron density of the solvent. The molecular weight can be determined from the intensity at zero angle  $I(0)$ :

$$\begin{aligned} M &= \frac{I(0)}{P} \frac{a^2}{\Delta z_2^2 d c I_e N_L} \\ &= \frac{I(0)}{P} \frac{21.0 a^2}{\Delta z_2^2 d c} \end{aligned} \quad (2.6.1.31)$$

(Kratky, Porod & Kahovec, 1951), where  $P$  is the total intensity per unit time irradiating the sample,  $a$  [cm] is the distance between the sample and the plane of registration,  $d$  [cm] is the

thickness of the sample,  $c$  [g cm<sup>-3</sup>] is the concentration, and  $N_L$  is Loschmidt's (Avogadro's) number.

*Rod-like particles.* The mass per unit length  $M_c = M/L$ , *i.e.* the mass related to the cross section of a rod-like particle with length  $L$ , is given by a similar equation (Kratky & Porod, 1953):

$$\begin{aligned} M_c &= \frac{[I(h)h]_{h \rightarrow 0}}{P} \frac{a^2}{\pi \Delta z_2^2 d c I_e N_L} \\ &= \frac{[I(h)h]_{h \rightarrow 0}}{P} \frac{6.68 a^2}{\Delta z_2^2 d c}. \end{aligned} \quad (2.6.1.32)$$

*Flat particles.* A similar equation holds for the mass per unit area  $M_t = M/A$ :

$$\begin{aligned} M_t &= \frac{[I(h)h^2]_{h \rightarrow 0}}{P} \frac{a^2}{2\pi \Delta z_2^2 d c I_e N_L} \\ &= \frac{[I(h)h^2]_{h \rightarrow 0}}{P} \frac{3.34 a^2}{\Delta z_2^2 d c}. \end{aligned} \quad (2.6.1.33)$$

*Abscissa scaling.* The various molecular parameters can be evaluated from scattered intensities with different abscissa scaling. The abscissa used in theoretical work is  $h = (4\pi/\lambda) \sin \theta$ . The most important experimental scale is  $m$  [cm], the distance of the detector from the centre of the primary beam with the distance  $a$  [cm] between the sample and the detector plane.

$$h[\text{nm}^{-1}] = T_{hm}[\text{cm}^{-1} \text{nm}^{-1}] m[\text{cm}], \quad (2.6.1.34)$$

with

$$T_{hm} = 2\pi/\lambda a. \quad (2.6.1.35)$$

The angular scale  $2\theta$  with

$$2\theta \simeq m/a = (\lambda/2\pi)h \quad (2.6.1.36)$$

was used in the early years of small-angle X-ray scattering experiments. The formulae for the various parameters for  $m$  and the  $h$  scale can be found in Table 2.6.1.1, the formulae for the  $2\theta$  scale can be found in Glatter & Kratky (1982, p. 158).

## 2.6.1.3.2. Shape and structure of particles

In this subsection, we have to discuss how shape, size, and structure of the scattering particle are reflected in the scattering function  $I(h)$  and in the PDDF  $p(r)$ . In general, it is easier to discuss features of the PDDF, but some characteristics like symmetry give more pronounced effects in reciprocal space.

## 2.6.1.3.2.1. Homogeneous particles

*Globular particles.* Only a few scattering problems can be solved analytically. The most trivial shape is a sphere. Here we have analytical expressions for the scattering intensity

$$I(h) = \left( 3 \frac{\sin(hR) - hR \cos(hR)}{(hR)^3} \right)^2 \quad (2.6.1.37)$$

and for the PDDF (Porod, 1948)

$$p(r) = 12x^2(2 - 3x + x^3) \quad x = r/(2R) \leq 1, \quad (2.6.1.38)$$

where  $R$  is the radius of the sphere. The graphical representation of scattering functions is usually made with a semi-log plot [ $\log I(h)$  vs  $h$ ] or with a log–log plot [ $\log I(h)$  vs  $\log h$ ]; the PDDF is shown in a linear plot. In order to compare functions from particles of different shape, it is preferable to keep the scattering intensity at zero angle (area under PDDF) and the radius of

## 2. DIFFRACTION GEOMETRY AND ITS PRACTICAL REALIZATION

gyration  $R_g$  [slope of the main maximum of  $I(h)$  or the second moment of  $p(r)$ ] constant.

The scattering function of a sphere with  $R = 65$  is shown in Fig. 2.6.1.2 [dashed line,  $\log I(0)$  normalized to 12]. We see distinct minima which are typical for particles of high symmetry. We can determine the size of the sphere directly from the position of the zeros  $h_{01}$  and  $h_{02}$  (Glatter, 1972).

$$R \simeq \frac{4.493}{h_{01}} \quad \text{or} \quad R \simeq \frac{7.725}{h_{02}} \quad (2.6.1.39)$$

or from the position of the first side maximum ( $R_g \simeq 4.5/h_1$ ). The minima are considerably flattened in the case of cubes (full line in Fig. 2.6.1.2). The corresponding differences in real space are not so clear-cut (Fig. 2.6.1.3). The  $p(r)$  function of the sphere has a maximum near  $r = R = D/2$  ( $x \simeq 0.525$ ) and drops to zero like every PDDF at  $r = D$ , where  $D$  is the maximum dimension of the particle - here the diameter. The  $p(r)$  for the cube with the same  $R_g$  is zero at  $r \simeq 175$ . The function is very flat in this region. This fact demonstrates the problems of accuracy in this determination of  $D$  when we take into account

experimental errors. In any case, this accuracy will be different for different shapes.

Any deviation from spherical symmetry will shift the maximum to smaller  $r$  values and the value for  $D$  will increase [ $I(0)$  and  $R_g$  constant!]. A comparison of PDDF's for a sphere, an oblate ellipsoid of revolution (axial ratio 1:1:0.2), and a prolate ellipsoid of revolution (1:1:3) is shown in Fig. 2.6.1.4. The more we change from the compact, spherical structure to a two- and one-dimensionally elongated structure, the more the maximum shifts to smaller  $r$  values and at the same time we have an increase in  $D$ . We see that  $p(r)$  is a very informative function. The interpretation of scattering functions in reciprocal space is hampered by the highly abstract nature of this domain. We can see this problem in Fig. 2.6.1.5, where the scattering functions of the sphere and the ellipsoids in Fig. 2.6.1.4 are plotted. A systematic discussion of the features of  $p(r)$  can be found elsewhere (Glatter, 1979, 1982b).

*Rod-like particles.* The first example of a particle elongated in one direction (prolate ellipsoid) was given in Figs. 2.6.1.4 and 2.6.1.5. An important class is particles elongated in one

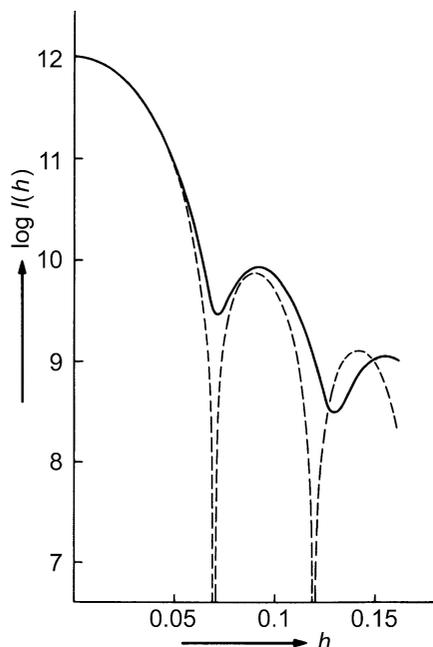


Fig. 2.6.1.2. Comparison of the scattering functions of a sphere (---) and a cube (—) with same radius of gyration.

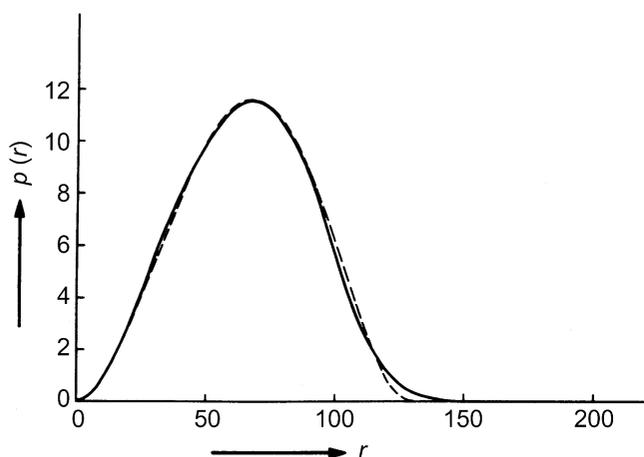


Fig. 2.6.1.3. Distance distribution function of a sphere (---) and a cube (—) with the same radius of gyration and the same scattering intensity at zero angle.

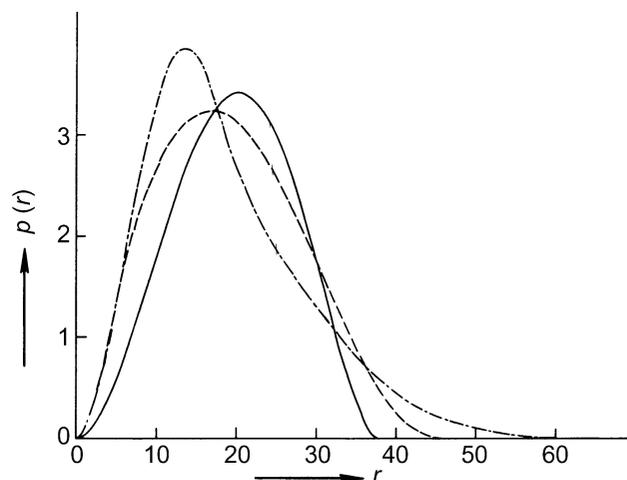


Fig. 2.6.1.4. Comparison of the  $p(r)$  function of a sphere (—), a prolate ellipsoid of revolution 1:1:3 (---), and an oblate ellipsoid of revolution 1:1:0.2 (- - -) with the same radius of gyration.

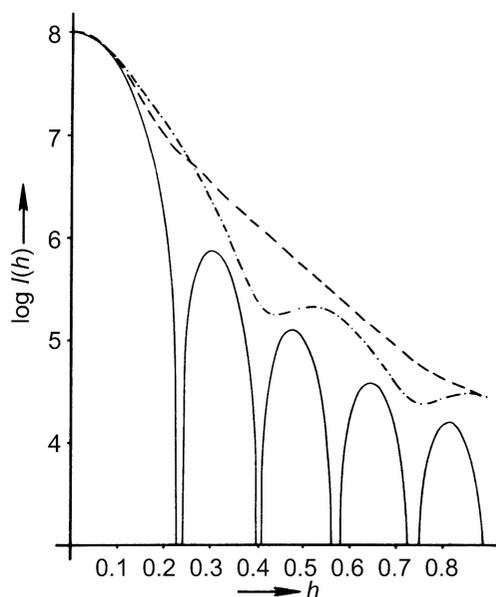


Fig. 2.6.1.5. Comparison of the  $I(h)$  functions of a sphere, a prolate, and an oblate ellipsoid (see legend to Fig. 2.6.1.4).

## 2.6. SMALL-ANGLE TECHNIQUES

direction with a constant cross section of arbitrary shape (long cylinders, parallelepipeds, *etc.*) The cross section  $A$  (with maximum dimension  $d$ ) should be small in comparison to the length of the whole particle  $L$ :

$$d \ll L \quad L = (D^2 - d^2)^{1/2} \simeq D. \quad (2.6.1.40)$$

The scattering curve of such a particle can be written as

$$I(h) = L(\pi/h)I_c(h), \quad (2.6.1.41)$$

where the function  $I_c(h)$  is related only to the cross section and the factor  $1/h$  is characteristic for rod-like particles (Kratky & Porod, 1948; Porod, 1982). The cross-section function  $I_c(h)$  is

$$I_c(h) = (L\pi)^{-1}I(h)h = \text{constant} \times I(h)h. \quad (2.6.1.42)$$

This function was used in the previous subsection for the determination of the cross-section parameters  $R_c$ ,  $A$ , and  $M_c$ . In addition, we have

$$I_c(h) = 2\pi \int_0^\infty p_c(r)J_0(hr) dr, \quad (2.6.1.43)$$

where  $J_0(hr)$  is the zero-order Bessel function and

$$p_c(r) = \frac{1}{2\pi} \int_0^\infty I_c(h)(hr)J_0(hr) dh \quad (2.6.1.44)$$

(Glatter, 1982a). The function  $p_c(r)$  is the PDDF of the cross section with

$$p_c(r) = r\gamma_c(r) = \langle \Delta\rho(\mathbf{r}_c) * \Delta\rho(-\mathbf{r}_c) \rangle. \quad (2.6.1.45)$$

The symbol  $*$  stands for the mathematical operation called convolution and the symbol  $\langle \rangle$  means averaging over all directions in the plane of the cross section. Rod-like particles with a constant cross section show a linear descent of  $p(r)$  for  $r \gg d$  if  $D > 2.5d$ . The slope of this linear part is proportional to the square of the area of the cross section,

$$\frac{dp}{dr} = -\frac{A^2\Delta\rho^2}{2}. \quad (2.6.1.46)$$

The PDDF's of parallelepipeds with the same cross section but different length  $L$  are shown in Fig. 2.6.1.6. The maximum corresponds to the cross section and the point of inflection  $r_i$  gives a rough indication for the size of the cross section. This is shown more clearly in Fig. 2.6.1.7, where three parallelepipeds with equal cross section area  $A$  but different cross-section dimensions are shown. If we find from the overall PDDF that the particle under investigation is a rod-like particle, we can use the

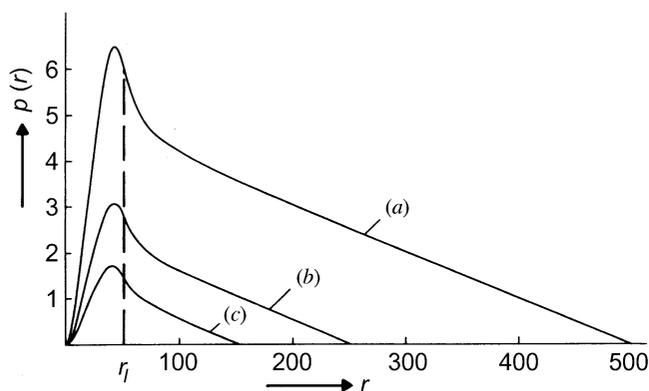


Fig. 2.6.1.6. Distance distributions from homogeneous parallelepipeds with edge lengths of: (a)  $50 \times 50 \times 500 \text{ \AA}$ ; (b)  $50 \times 50 \times 250 \text{ \AA}$ ; (c)  $50 \times 50 \times 150 \text{ \AA}$ .

PDDF of the cross section  $p_c(r)$  to obtain more information on the cross section (Glatter, 1980a).

*Flat particles.* Flat particles, *i.e.* particles elongated in two dimensions (discs, flat parallelepipeds), with a constant thickness  $T$  much smaller than the overall dimensions  $D$ , can be treated in a similar way. The scattering function can be written as

$$I(h) = A \frac{2\pi}{h^2} I_t(h), \quad (2.6.1.47)$$

where  $I_t(h)$  is the so-called thickness factor (Kratky & Porod, 1948) or

$$I_t(h) = (A2\pi)^{-1}I(h)h = \text{constant} \times I(h)h^2, \quad (2.6.1.48)$$

which can be used for the determination of  $R_t$ ,  $T$ , and  $M_t$ . In addition, we have again:

$$I_t(h) = 2 \int_0^\infty p_t(r) \cos(hr) dr \quad (2.6.1.49)$$

and

$$\begin{aligned} p_t(r) &= \gamma_t(r) - \frac{1}{\pi} \int_0^\infty I_t(h) \cos(hr) dh \\ &= \Delta\rho_t(r) * \Delta\rho_t(-r). \end{aligned} \quad (2.6.1.50)$$

PDDF's from flat particles do not show clear features and therefore it is better to study  $f(r) = p(r)/r$  (Glatter, 1979). The corresponding functions for lamellar particles with the same basal plane but different thickness are shown in Fig. 2.6.1.7(b). The marked transition points in Fig. 2.6.1.7(b) can be used to determine the thickness. The PDDF of the thickness  $p_t(r)$  can give more information in such cases, especially for inhomogeneous particles (see below).

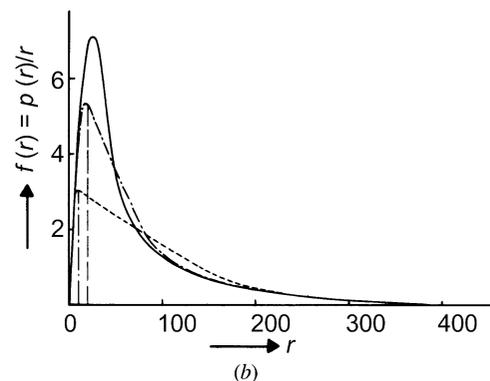
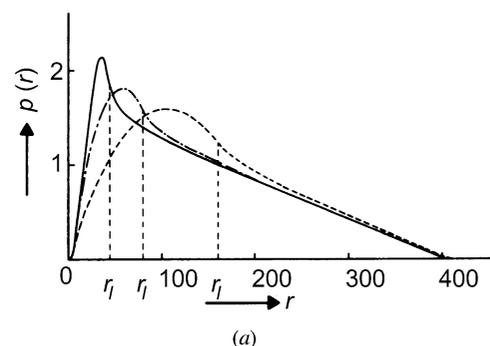


Fig. 2.6.1.7. Three parallelepipeds with constant length  $L$  ( $400 \text{ \AA}$ ) and a constant cross section but varying length of the edges: —  $40 \times 40 \text{ \AA}$ ; — · —  $80 \times 20 \text{ \AA}$ ; - - -  $160 \times 10 \text{ \AA}$ . (a)  $p(r)$  function. (b)  $f(r) = p(r)/r$ .

## 2. DIFFRACTION GEOMETRY AND ITS PRACTICAL REALIZATION

*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  $\Delta$  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:

$$A(h) = 4\pi \int_0^{\infty} r\rho(r) \frac{\sin(hr)}{h} dr \quad (2.6.1.51)$$

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

$$\rho(r) = \frac{1}{2\pi^2} \int_0^{\infty} hA(h) \frac{\sin(hr)}{r} dh \quad (2.6.1.52)$$

(Glatter, 1977a). 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, 1982b).

*Rod-like particles. Radial inhomogeneity.* If we assume radial inhomogeneity of a circular cylinder, *i.e.*  $\rho$  is a function of the radius  $r$  but not of the angle  $\varphi$  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  $0 < r \leq d$ . 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  $\rho$  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

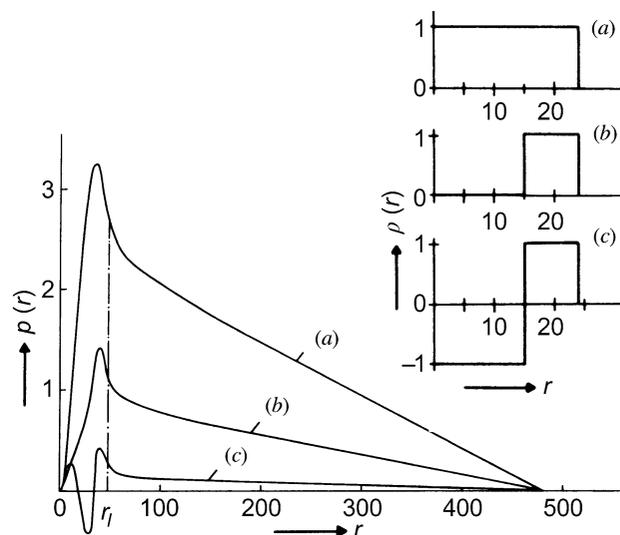


Fig. 2.6.1.8. Circular cylinder with a constant length of 480 Å and an outer diameter of 48 Å. (a) Homogeneous cylinder, (b) hollow cylinder, (c) inhomogeneous cylinder. The  $p(r)$  functions are shown on the left, the corresponding electron-density distributions  $\rho(r)$  on the right.