On Two Methods for Determination of Particle Size Distribution Functions by Means of Small-Angle X-ray Scattering

By C. G. Vonk

DSM Central Laboratory, PO-Box 18, Geleen, Netherlands

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The total X-ray intensity as a function of \( h \) (\( h \) is the radial coordinate in reciprocal space), scattered by an isotropic system of particles of equal shapes but of different sizes \( R \), can, under certain conditions, be expressed as an integral over the particle size distribution function \( D(R) \), multiplied by a common single-particle function of \( hR \) which can be calculated from the assumed particle shape. In the first method \( D(R) \) is calculated from this relation by the method of least squares, in which values of \( D \) at a limited number of particle sizes are the unknowns. To avoid oscillations in the \( D \) curve, constraints are imposed on the \( D \) values. The proper weight to be assigned to these constraints must be determined by trial and error. The method has been adapted to suit various assumptions and requirements as to the shape of the particles, the type of distribution function to be calculated, and experimental conditions (slit or pinhole focusing). The second method is essentially the one described by Schmidt, Weil & Brill [X-ray & Electron Methods of Analysis, pp. 86–100. (1968), New York: Plenum], which, however, is adapted to the use of slit-smeared intensities. Both methods may give rise to artefacts in the calculated distribution functions in the range of the smallest particle sizes, which are sensitive to the setting of the various parameters and to experimental errors. However, the position and shape of the main maxima can usually be determined quite well. The agreement between the results obtained by the two methods is satisfactory.

According to a well-known theorem from diffraction theory, the intensity of X-rays scattered by a dilute system of randomly dispersed and oriented particles can, to a good approximation, be regarded as the sum of the intensities scattered by the individual particles. If the particles are all of equal shape but differ in size, the contributing single-particle intensity functions, if plotted versus the reciprocal-space radial coordinate, can all be thought of as being derived from one of these functions by merely changing the units along the horizontal and vertical axes. If this function is known, one may expect to be able to calculate the distribution of the sizes from the scattering curve of the system.

Early methods developed for this purpose are by Roess (1946), Riseman (1952), Luzzati (1957) and Soule (1957). However, at the time of their presentation none of these was put into practice, probably because the laborious calculations they required were considered prohibitive in the pre-computer days. Other early methods involved approximations, and were only partially successful. After the advent of the computer, new rigorous methods were developed and applied by Schmidt and coworkers, a review of whose work was published by Schmidt, Weil & Brill (1968), and by a group of French workers [see Donati, Pascal & Renouprez (1967), Brusset & Donati (1969), Renouprez & Imelik (1973) for further references]. Approximate methods were improved by Motzkus (1959); by Harkness, Gould & Hren (1969), and by Mittelbach (1965); the latter method is specially suited for studying systems of particles with relatively narrow size distribution functions. Also, the early method of Roess (1946) was applied to neutron small-angle scattering by Mook (1974).

Work on the same problem in light scattering seems to have proceeded largely independently from the progress described above. A large number of papers on this subject were published by Shifrin and coworkers and reviewed by Shifrin & Perelman (1967). Furthermore, Dave (1971) and Magar (1970) described methods involving solution of the basic equation by means of least-squares procedures.

In this paper, a new method is presented which is based on ideas from Luzzati (1957) and also contains elements from the methods of Dave (1971) and Magar (1970). This is referred to as method I. Next, a further method (II) is described in which the approach of Schmidt, Weil & Brill (1968) is combined with relations given by Mérig & Tchoubar (1968), to make it accessible to the use of slit-smeared intensities. Finally, results obtained by the two methods are presented and compared.

The derivations given in both treatments are based on the use of intensity values which are on a relative scale. As a result, only relative values of the distribution functions can be determined. These can be converted to absolute values if the total volume fraction of the particles is known, which is usually the case.

**Method I**

**Outline of the method**

Let \( I_0 (h, R) \) represent the intensity in electron units of the X-rays scattered by a single particle, averaged over all orientations under the obtaining experimental
conditions. Here, \( h = 2\pi s \), \( s = (2 \sin \theta)/\lambda \), \( \theta \) = scattering angle, \( R \) = some characteristic dimension of the particle (e.g. the radius, if the particle is a sphere). According to Guinier & Fournet (1955) the following expression holds:

\[
I_o(h,R) = m Z_i o(hR)
\]  
\( (I.1) \)

in which \( m \) is the excess number of electrons in the particle over and above the number of electrons in the same volume of the surrounding medium, and \( i o(hR) \) is a function which is unity at \( h = 0 \).

In considering the total intensity scattered by a large number of particles, a number of assumptions are made, the most important of which are:

1. The chance of finding the centre of a particle in a certain volume element within the sample is independent of the position of this element relative to the positions of the other particles.

2. The particles are of the same shape but differ in size; if non-spherical, they are furthermore assumed to be oriented at random.

3. Multiple scattering can be neglected. Making these assumptions, we may write for the total intensity

\[
I(h) \propto \int_0^\infty D_o(R) m^2(R) i o(hR) \, dR
\]  
\( (I.2) \)

where \( D_o(R) \) is proportional to the number of particles defined by the size parameter \( R \) in a unit interval. (In this and the following relations the symbol \( \propto \) stands for 'is proportional to'.) In order to solve \( D_o(R) \) from this equation, the integration might be replaced by a summation over discrete intervals \( \Delta R \), of which the number is substantially smaller than the number of observed \( I(h) \) values, and the corresponding \( D \) values be found by the method of least squares. However, the interpolation procedures involved in calculating the coefficients in the normal equations may be considerably speeded up by first making, after Luzzati (1957), the following substitutions:

\[
z_o = -\log R \quad z = \log h
\]

This leads to:

\[
J(z) \propto \int_{-\infty}^{\infty} T(z_0) F(z_0) G(z-z_0) \, dz_0
\]  
\( (I.3) \)

where, here, \( J(z) = I(h) \), \( T(z_0) = R m^2(R) \), \( F(z_0) = D_o(R) \), and \( G(z-z_0) = i o(hR) \). (In other applications, to be discussed under the next heading, \( J, T, F \) and \( G \) may have different meanings.) Next, this integral is approximated by

\[
J_i \propto \sum_{k} T_k F_k G_k
\]  
\( (I.4) \)

where \( i, \) running from 1 to \( i_m \), indicates the sequence number of the intensity measurement, and \( k, \) running from 1 to \( k_m \), indicates the sequence number in a series of equidistant \( z_0 \) values. On the assumption that \( i_o > k_m \), \( F \) is calculated according to the method of least squares, by solving the normal equations:

\[
AF = H
\]  
\( (I.5) \)

in which the matrix elements are given by

\[
A_{ki} = \sum_{1}^{i_m} w_i T(z_0) T(z_0) G(z_i-z_0) G(z_i-z_0)
\]

\[
F_k = F(z_0)
\]

\[
H_k = \sum_{1}^{i_m} w_i T(z_0) G(z_i-z_0) J(z_i)
\]

and \( w_i \) is the weight to be attached to intensity number \( i \).

In practice, the \( F(z_0) \) functions found in this way show large oscillations, which, however, can be suppressed by applying suitable constraints to the values of \( F_k \). This was done with the aid of a method described by Waser (1963), according to which (I.5) must be modified as follows:

\[
(A + \sum_{1}^{p_m} g_p B_p) F = H
\]  
\( (I.6) \)

Here, \( B_p \) is a matrix derived from the equations expressing the \( p \)th constraint and \( p_m \) is the total number of constraints. The parameters \( g_p \) serve to vary the severity of the constraints.

**Additional features**

In this section it will be shown how the present method can be applied to various structural models and can be used for calculating several types of distribution function, starting from either slit-smeared or pinhole intensity values.

(a) If the intensity is recorded with the aid of slit collimation, the following relation holds for the observed, slit-smeared intensity \( I_o(x) \) due to a single particle:

\[
I_o(x) = \int_{-\infty}^{\infty} I_o(r) L(y) \, dy
\]

where, here, \( x, y \) and \( r \) are related to each other as shown in Fig. 1, and \( L(y) \) represents the intensity distribution along the trace of the primary beam. Changing to the variable \( hR \) and applying (I.1), we get:

\[
\tilde{I}_o(hR) \propto m^2 i o(hR)/R
\]

where

\[
\tilde{I}_o(hR) = \int_{-\infty}^{\infty} i o(h, R) L(h, R) \, dh \, dr
\]

Fig. 1. Coordinates in the plane of registration of a camera with slit collimation. \( PQ \) represents the trace of the primary beam, \( R \) the position at which the intensity is measured and \( O \) the origin.
Here, $h_r$ and $h_y$ are the $h$ values corresponding to $r$ and $y$ respectively. Consequently, if slit-smeared intensities are used, $G$ in (I,3) should be defined as $I_0$, $J(z)$ as $I(h)$ and $T(z_0)$ as $m^2(R)$.

(b) If the electron density within all particles is uniform and of the same value (two-phase structure), one may write $m^2 \propto R^6$. If the particles are spherical, $I_0$ is given by (Guinier & Fournet, 1955)

$$I_0, \text{spher} = \left[3(\sin hR - hR \cos hR)/h^3 R^3 \right]^2.$$

(c) Equation (I,2) may also be expressed in terms of the distribution by length $D_4(R)$, by surface $D_3(R)$, or by volume $D_2(R)$. These are related to $D_n(R)$ as follows:

$$D_4(R) \propto RD_4(R) \quad D_3(R) \propto R^2 D_3(R) \quad D_2(R) \propto R^3 D_2(R).$$

(d) If the diffracting units are needle-like objects of equally shaped cross section characterized by some dimension $R$, the distribution of $R$ may be found from the two-dimensional analogue of (I,2). To this end, $I(h)$ is replaced by $I_2(h)$, the sum of the intensities in the equatorial planes of all needles. If the needles are oriented at random, $I_2(h)$ is found from $I_2(h) \propto hI(h)$. Furthermore, $m$ must be redefined as the excess number of electrons in one unit of needle length; if the electron density within the needles is uniform and equal in all needles, $m$ is proportional to $R^2$. Also, $I_0$ should be replaced by $I_{02}$, the corresponding two-dimensional equatorial intensity diffracted by one needle of the shape under consideration. For needles of uniform electron density and circular cross section, $I_{02}$ is given by (Hosemann & Bagchi, 1962)

$$I_{02, \text{cyl}} = J_1^2(hR)/h^2 R^2,$$

where $J_1$ is the first-order Bessel function.

(e) Entirely analogous considerations can be followed to find the equivalent of (I,2) relating the sum $I_1(h)$ of the one-dimensional intensities of the X-rays diffracted by an assembly of plate-like objects to the distribution of the thicknesses of these plates and to the intensity function $I_{01}$ of a single plate. In this case, $m$ is the excess number of electrons per unit surface of a plate, which for plates of equal and uniform electron densities is proportional to $R$. For such a plate of thickness $2R$, $I_{01}$ is given by:

$$I_{01, \text{pl}} = \sin^2 (hR)/h^2 R^2.$$

Furthermore, if the plates are oriented at random, $I_1(h) \propto h^2 I(h)$.

It should be emphasized that in this and the previous case only pinhole-collimated intensities can be used in the relations derived here.

(f) Linear polymer molecules in dilute solution are known to possess an approximately Gaussian density distribution. If this is characterized by the radius of gyration $R_g$, the intensity of a single molecule can be expressed by

$$I_0(h) = (2m^2/u^2) \left( e^{-u^2} - (1 - u) \right) = m^2 I_{0, \text{pl}}(hR_g)$$

where $u = h^2 R_g^2$ (Debye, 1947). According to Tanford (1963), $R_g$ is related to the molecular weight $M$ of the molecule by

$$R_g^2 = \alpha^2 \beta^2 M/(6M_0)$$

where $M_0$ is the molecular weight of the repeat unit in the polymer chain, and $\alpha$ and $\beta$ are constants varying in value with the type of polymer and solvent. Consequently, if $\alpha$ and $\beta$ are known, the present method may be used to derive the molecular-weight distribution by number $E_n$ or by weight $E_w$ from the SAXS intensity of a dilute solution. If the parameters $\alpha$ and $\beta$ are not known, the shape of one of these distributions may be determined and be brought to the proper scale with the aid of the corresponding average molecular weight determined by some other method.

The various calculations corresponding to the cases just mentioned may all be performed with the same procedure, based on (I,4) and (I,6), provided the functions $J$, $F$, $T$ and $G$ are properly defined. A survey of the definitions to be used is given in Table 1.

**Practical considerations**

In the following, some practical aspects met in developing and operating a computer program based on the present procedure will be discussed.

In solving the normal equations (I,5), two constraints were imposed on vector $F_k$: first, the sum

$$\sum_{k=1}^{k_m} \left[ (F_{k-1} + F_{k+1})/2 - F_k \right]^2$$

was minimized to suppress oscillations in the $F$ curve; second, the values of $F_k^2$ and $F_{km}^2$ were minimized to prevent the $F$ curve from increasing to absurdly high values at the extremities.

The first constraint gives rise to a matrix $B_1$ in

### Table 1. Definition of the various functions occurring in (I,3)

<table>
<thead>
<tr>
<th>Scattering units</th>
<th>Type of collimation</th>
<th>$J$</th>
<th>$G$</th>
<th>Values of $q$ in $T=R_q^2$ if $F=$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical particles, uniform density</td>
<td>Pinhole</td>
<td>$I(h)$</td>
<td>$I_0, \text{spher}$</td>
<td>7 5 4</td>
</tr>
<tr>
<td>Cylindrical rods, uniform density</td>
<td>Slit</td>
<td>$I(h)$</td>
<td>$I_0, \text{spher}$</td>
<td>6 4 3</td>
</tr>
<tr>
<td>Plates, uniform density</td>
<td>Pinhole</td>
<td>$I(h)$</td>
<td>$I_{01, \text{pl}}$</td>
<td>5 4 3</td>
</tr>
<tr>
<td>Spherical particles, Gaussian density distribution</td>
<td>Slit</td>
<td>$I(h)$</td>
<td>$I_{0, \text{pl}}$</td>
<td>3 3 2</td>
</tr>
</tbody>
</table>

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(I, 6) in which all elements are zero, except the elements $B_{k, k-2}, B_{k, k-1}, B_{k, k}, B_{k, k+1}$ and $B_{k, k+2},$ which are $\frac{1}{3}, -2, 3, -2$ and $\frac{1}{3}$ respectively. In matrix $B_2,$ corresponding to the second constraint, the elements $B_{1, 1}$ and $B_{km, km}$ are 1, whereas all others are zero.

Special consideration must be given to the weights $g_p$ to be assigned to these constraints. Mathematical arguments that may serve to determine these weights are difficult to find, but the shape of (I, 6) suggests that the $g$ values should be related to the ratio of the magnitudes of the elements in $A$ and $B$ respectively. This led to the following equation for the weight $g_1:

$$g_1 = A_{1, 1} A_{km, km}^{1-v}$$

in which $v$ is a parameter between 0 and 1, the best value of which must be determined by trial. If $v$ is too low, the calculated $F$ curve will still show oscillations, whereas too high a value will lead to loss of significant detail. In practice, two or three trial calculations with different values of $v$ suffice to find the best value, which usually is between 0.3 and 0.6. An example of this procedure is shown in Fig. 2. The weight $g_2$ to be assigned to the second constraint was set at 100 $g_1,$ which effectively prevents the distribution function from exploding at its lower and upper ends.

According to theory the weights $w_i$ to be assigned to the intensity measurements should be inversely proportional to the square of the standard deviation of the intensity. In the case where the intensities are measured by direct counting, this leads to $w_i \propto 1/I_i.$ Because of the background intensity, which is present in all intensities, the relation $w_i \propto 1/(I_i + c)$ was used, where $c$ is a small constant.

The sampling points $z_{0k},$ at which the distribution functions were calculated, were so selected as to correspond to all multiples of 0.1 or 0.2 within the $z$ range in which the intensities were measured. Furthermore, the density of the measuring points on the $z$ scale was made to exceed the density of the sampling points $z_{0k}$ by a factor of at least 1.4.

Owing to the high value of the exponent of $R$ in the final expression of the intensity that has to be used in most applications (see Table 1), the accuracy of the shape of the distribution functions obtained is the lowest in the range of the lowest $R$ values. Within this range maxima and minima may be introduced by small errors in the level of the background that has to be subtracted from the measured intensities. Usually, such spurious details can be recognized in that they are much more sensitive to changes in the parameter $v$ than are the main features of the distribution function. However, if there exists a genuine maximum in the distribution curve at low $R$ values, its shape and position may well be affected by such details.

As the present method is based on a least-squares procedure, random intensity errors are accounted for in a natural way and should not seriously affect the results. This was confirmed by comparing in a number of cases the distribution functions obtained with and without previous smoothing of the scattering curve; these distribution functions were found to be essentially equal. Consequently, the raw intensity values, if corrected for background radiation, may be used, which, in fact, was done in all examples of the application of method I discussed further on.

In the computer program the intensities are calculated back from the calculated distribution function with the aid of (I, 3). By comparison of these with the original intensities systematic differences may be detected, which, if not due to systematic errors of some kind, may have to be attributed to deviations of the assumptions from reality. The most obvious deviations are: insufficient dilution of the particles, differences between assumed and real particle shape, and the occurrence of multiple scattering. Furthermore, too high weights $g_1$ and $g_2$ assigned to the constraints may give rise to oscillations of the calculated intensity curve around the observed one. A special example of this is encountered if the distribution function extends beyond the diameter $2R$ corresponding to $z_1,$ which is the $z$ value of the first intensity measurement. A decrease of $g_2$ should improve the situation, but usually this does not lead to acceptable shapes of the calculated distribution functions. These may however be obtained by first extrapolating the intensity curve to lower $z$ values according to the equation $I_1(\bar{h}) = a_1 \exp(-a_2 h^2),$ where $a_1$ and $a_2$ are adjusted so as to make the extrapolated curve fit the first five intensity measurements of the scattering curve. The extrapolated curve is extended to a point where $\exp(-a_2 h^2)$ is larger than 0.95.

Method II

Outline of the method

This method is restricted to two-phase systems, for which a number of relations have been derived by Porod (1952), Soulé (1957) and Debye, Anderson & Brumberger (1957). One of these is

$$C_q(r) = \gamma^{F(r)}$$
in which \( C_s(r) \) is the so-called ‘chord distribution function’ and \( \gamma(r) \) the correlation function. By combining this with the general relation

\[
\gamma(r) \propto \mathcal{F}\{I(h)\}
\]

where \( \mathcal{F} \) is the operator for Fourier transformation, one obtains in the case of an isotropic scattering system

\[
C_s(r) \propto \int_0^\infty h^4 I(h) [\sin \zeta/\zeta] \, dh \quad (II, 1)
\]

where \( \zeta = hr \). Another relation valid in two-phase systems is Porod’s law, which states that \( h^4 I(h) \) approaches a constant value, here called \( c_4 \), as \( h \) increases. In view of this, (II, 1) is divided as follows:

\[
C_s(r) \propto \int_0^\infty \left[ P(h)[\sin \zeta/\zeta] - c_4[\sin \zeta/\zeta] \right] \, dh \quad (II, 2)
\]

with \( P(h) = h^4 I(h) - c_4 \). It can be shown that the second term on the right-hand side in this equation is zero at all non-zero values of \( r \). Donati, Pascal & Renouprez (1967) furthermore have shown that in the case of spherical particles of radius \( R \) the distribution function \( D_s(R) \) is related to \( C_s(r) \) as follows:

\[
D_s(R) = \frac{1}{2} [C_s(r) - rC_s(r)] \big|_{r=R} = c_5 \quad (II, 3)
\]

Combination of the last two relations, and subsequent development of the second derivative of \( \sin \zeta/\zeta \), leads to

\[
D_s(R) \propto \int_0^\infty P(h)[(4 \sin \zeta/\zeta)(1 - 2/\zeta^2) - \cos \zeta(1 - 8/\zeta^2)] \, dh \quad (II, 4)
\]

which was also derived by Brill & Schmidt (1968) in a somewhat different way.

A relation similar to (II, 1) was derived by Mérign & Tchoubar (1968, equation 1-11) for use with intensities smeared by a slit of infinite length. Combining this with (II, 3) one obtains the equivalent of (II, 4), which is

\[
D_s(R) \propto \int_0^\infty Q(h)[2J_0(\zeta) + (\zeta - 3/\zeta)J_1(\zeta)] \, dh \quad (II, 5)
\]

where \( J_0 \) and \( J_1 \) are zero and first-order Bessel functions respectively and \( Q(h) = h^3 I(h) - c_3 \), \( c_3 \) being the limiting value of \( h^3 I(h) \).

Other relations, which are useful in establishing the correct shape of \( P(h) \) or \( Q(h) \) are, in the first place, an extension of Porod’s law given by Brill & Schmidt (1968), which is valid if \( D_s \) has a definite lower boundary:

\[
\lim_{h \to -\infty} I(h) = c_4 h^{-4} + c_6 h^{-6} \quad ,
\]

and second, a relation found by the same authors as well as by Mérign & Tchoubar (1968):

\[
\int_0^\infty P(h) \, dh = 0 \quad ,
\]

which holds for spherical particles. The equivalents of these relations, which must be used if the measured intensities are smeared by a slit of infinite length, are:

\[
\lim_{h \to -\infty} I(h) = c_3 h^{-3} + c_5 h^{-5} \quad (II, 6)
\]

and

\[
\int_0^\infty Q(h) \, dh = 0 \quad . \quad (II, 7)
\]

**Practical considerations**

As the use of slit focusing entails a large gain in intensity compared to the use of pinhole focusing, the relations derived for slit-smeared intensities were employed in all applications to be described here.

Like method I, the present method is very sensitive to small errors in the background subtracted from the observed intensities. For this reason (II, 6) was extended as follows:

\[
\lim_{h \to -\infty} I(h) = c_3 h^{-3} + c_5 h^{-5} + c_0 \quad , \quad (II, 6a)
\]

in which \( c_0 \) represents an error of this type. Values of \( c_0 \) and \( c_5 \) were in the first instance found from plots of \( \bar{I} \) versus \( 1/h^6 \) prepared from the tail part of the scattering curve; an example of such a plot is shown in Fig. 3. If in this plot an interval could be indicated in which a linear relation could be assumed to hold, \( c_5 \) was set to zero and \( c_0 \) and \( c_3 \) were determined with the aid of a least-squares procedure from the data points within this interval. The interval chosen in Fig. 3 runs from \( 1/h^3 = 0 \) to \( 40 \, \text{Å}^3 \).

Next, the intensities were corrected by subtracting \( c_0 \) and smoothed with the aid of a procedure described previously (Vonk, 1975). Furthermore, the smoothed \( \bar{I} \) curve was made to join the lower end curve of the interval just mentioned without introducing discontinuities into either \( \bar{I}(1/h^3) \) or \( d\bar{I}/d(1/h^3) \); but for these precautions spurious oscillations would occur in the \( D_s \) curves, calculated with (II, 5), especially at large \( R \) values. Generally the \( D_s \) curves so obtained

![Fig. 3. Plot of \( \bar{I} \) versus \( 1/h^3 \) for the data points in the tail part of the scattering curve from the Pd particles of sample 2.](image-url)
did not fall to zero at $R=0$ owing to deviations of the integral in (II, 7) from zero.

If no linear relation was obvious in the $I$-versus-$1/h^3$ plot, it was assumed to be hidden in the scatter of the data points near the origin of the plot. In that case an interval was selected in which (II.6a) was assumed to be obeyed. The $I$-versus-$h$ curve was smoothed and $c_0$, $c_2$ and $c_4$ were determined on the basis of the conditions that the curves for $I$ and $I_{lim}$ join smoothly and (II, 7) is obeyed. In the following the two ways of dealing with the tail of the SAXS-curve just discussed will be referred to as methods IIa and IIb respectively.

Clearly, method II contains an element of arbitrariness because the interval for replacing $I$ by $I_{lim}$ has to be chosen, and a choice must be made between method IIa and method IIb. Further, the degree of smoothing can be varied at will. As in the application of method I, a wrong choice of the value of any parameter will affect the calculated distribution function the most strongly at low values of $R$. Here false maxima and minima may be introduced, which, however, will not seriously affect the shape and position of the main maximum, as long as this occurs at sufficiently large $R$ values.

**Comparison and illustration of the methods**

**Samples**

The samples used for comparing the two methods are a colloidal solution of aerosil in dilute HCl and three home-made catalysts containing 1000 Pd (by weight) dispersed on activated carbon. Furthermore, a catalyst containing 1000 CrO$_3$, dispersed on aerosil is used for illustrating some features of method I.

Additional information on the samples is presented in Table 2, where also the specific surface of the Pd particles in the samples 2–4 are given. These were measured with the aid of CO adsorption as described by Scholten & van Montfoort (1962).

**SAXS measurements**

The intensities were measured with a Kratky camera, adjusted to satisfy the requirement of ‘infinite’ slit height. Monochromatization was simulated with the aid of K$\beta$ filter together with pulse-height discrimination; the copper-target X-ray tube was operated at 35 kV. Entrance and exit slits were 80 and 150 $\mu$m respectively. The diffraction angle was varied between 0.0015 and 0.14 radians in steps of at most 0.001 radian. As a rule, each diffraction curve was measured a number of times in succession, in altogether 24 h.

The amount of sample was so chosen that it absorbed no more than 150% of the Cu K$\alpha$ radiation. In order to reduce the scattering from the carrier materials in the catalyst samples, these were impregnated with a solution of 50% of paraffin oil in toluene. After evaporation of the toluene the SAXS from the empty carrier materials had fallen to 10–25% of its original value, whereas the absorption of Cu K$\alpha$ radiation had only gone up slightly.
Processing of the scattering data

The scattering data were processed with the aid of the computer program \textit{FFSAXS} described previously (Vonk, 1975). All diffraction curves were corrected for blind scattering; the curve obtained from sample 1 was also corrected for solvent scattering.

The SAXS from the carrier materials used in the samples 2, 3 and 4 extended to larger scattering angles than the scattering from the Pd particles. Therefore, the curve from the empty carrier could be scaled to the curve from the complete catalyst by comparing the intensities at the high-angle limit. The scattering from the Pd particles was then obtained by subtraction of the two curves. This procedure could not be applied to sample 5, as in this case the scattering from the CrO$_3$ particles extended beyond the scattering from the silicon carrier.

Calculations by method I were performed with the aid of a subroutine \textit{DISTR}, which was added to the operation subroutines forming part of the computer program \textit{FFSAXS}. Application of method II was made possible by extending the subroutines for determination of the background and of the correlation function accordingly.

Results

The surface distribution functions $D_s$ obtained by the two methods on the samples 1–4, after elimination of the scattering from the solvent or from the carrier material are presented in the Fig. 4(a),(b),(c) and (d). In this figure, as well as in the Figs. 5 and 6, those parts of the curves which show pronounced sensitivity to the setting of the various parameters, and therefore must be considered to be not very reliable, are indicated by dotted lines.

As can be seen in Fig. 4, the agreement as to shape and position of the main maxima is quite satisfactory; serious divergence between the curves only occurs in the range of low diameter values, where the curves are indicated as being unreliable.

In Table 2 the specific surfaces of the Pd particles in samples 2–4, as calculated from the Pd content of these samples, together with the surface averages of the diameters obtained from the $D_s$ curves, are presented in column 4. The values found from CO adsorption are 0.6 to 0.8 times as large; this difference might be ascribed to the circumstance that the part of the Pd surface that is in contact with the carrier is inaccessible to gas absorption.

Table 2. Description and specific surfaces of samples

| Sample | Description | Specimen surface, m$^2$ g$^{-1}$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>from CO adsorption</td>
</tr>
<tr>
<td>1</td>
<td>Colloidal silica</td>
<td>103</td>
</tr>
<tr>
<td>2</td>
<td>Pd, 9.5% on activated carbon</td>
<td>59</td>
</tr>
<tr>
<td>3</td>
<td>Pd, 100% on activated carbon</td>
<td>36</td>
</tr>
<tr>
<td>4</td>
<td>CrO$_3$, 100% on porous silica</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5 shows the $D_s$ curve obtained by applying method I to sample 2, this time without correcting the scattering curve for the contribution from the carrier. Also shown in this figure are the separate, suitably scaled $D_s$ curves of the carrier and the Pd particles. Ignoring the parts of the curves at low diameter values, one may conclude that in this case the distribution functions are additive to a fair approximation. (In calculation of the $D_s$ curves shown in Fig. 5, the diffracting entities in the carbon carrier were assumed to be spherical objects, which is probably far from reality. Though this would imply that the corresponding $D_s$ curves are essentially meaningless, one may expect them to contain at least qualitative information about the size of the inhomogenities present in the carbon.)

As mentioned above, the $D$ curve of the CrO$_3$ particles in sample 5 cannot be calculated separately. The $D_s$ functions obtained by method I from the CrO$_3$ + carrier combination and the pure carrier (see Fig. 6) show a similar maximum at 150–180 Å, which therefore must be attributed to the inhomogenities in the...
carrier material. Consequently, the (only partly reliable) maximum at 20 Å must be due to the CrO₃ particles.

The examples concerning catalysts dispersed on porous carriers show that in certain cases one may obtain information about the active component from SAXS analysis without resorting to the use of pore-masking liquids like those discussed by Whyte, Kirklin, Gould & Heinemann (1972). Application of such techniques may however be inevitable if the concentration of the active component is very low.

So far, no experiments have been made to check the usefulness of method I for determining molecular-weight distributions of macromolecules. The relatively large extension of the polymer coils, which requires the use of very dilute solutions, together with the low contrast of the electron density in most polymer solutions, must lead to very low intensity contributions from the macromolecules, which would be difficult to measure with the conventional apparatus at our disposal.

Conclusion

Although the two methods differ largely as regards the underlying theoretical approaches, the agreement between the results is gratifying and justifies confidence in the reliability of particle distribution functions derived from SAXS data. The distribution curves calculated by the two methods are liable to some arbitrariness in choosing the various parameters involved, but, especially after gaining some experience, one can usually distinguish the artefacts from the true features.

In view of the large number of possibilities offered by method I (see Table 1), this method is of a wider scope than method II. In addition it is easier to execute as it does not require previous processing of the intensity data like smoothing or curve fitting. The computation times for the two methods are similar: 20–30 s on a Univac 1108 computer.

Copies of the program FFSAXS (Vonk, 1975), including the extensions for executing methods I and II, as well as examples of input and output, can be obtained from the author on request. Also, a program FFDISTR for performing method I separately is available.

I am greatly indebted in the first place to Dr O. Glatter of Graz University, who called my attention to the possibility of using constraints in the method of the least squares, and secondly to Professor J. J. Scholten and Mr A. P. Pijpers of this laboratory, for providing the samples together with the CO-absorption data and for the experimental work respectively, also to Professor R. Koningsveld from this laboratory, and to Professor P. W. Schmidt of the University of Missouri for providing a number of references to important literature.

References