Crystallite Shape and the Fourier Analysis of Diffraction Line Profiles

By W. L. Smith*

Warren Spring Laboratory, Department of Industry, Stevenage, Herts, England

(Received 3 January 1975; accepted 20 December 1975)

The relation between the column distribution as determined from the Fourier analysis of diffraction line profiles and the overall size distribution is examined for mixtures of crystallites of uniform shape, but differing in size. It is concluded that for such systems Fourier analyses of a number of profiles can lead to information on the nature of the shape, but that very careful measurements will be necessary to generate useful information on the nature of the distribution of sizes. While the detailed application of the results of this model may be limited, more general consequences seem to be that (a) there is normally no superficial resemblance between the Fourier column distribution and the true size distribution and (b) information on the latter can only be extracted with difficulty from Fourier analyses.

Introduction

Measures of particle size and distribution of size are required in many areas of applied science, but such measures are only well-defined if all the particles are of known and preferably uniform shape. Difficulties can be expected in the interpretation of experimental data from systems where these conditions are not well satisfied. X-ray diffraction techniques have proved useful in providing information on crystallite sizes in the range 50–500 Å, but such data can only be correlated with other parameters such as total surface area if some assumption is made concerning crystallite shape. With the increasing automation of X-ray powder diffraction work it is becoming feasible to carry out on a routine basis more powerful data-processing methods such as the Fourier analysis of line profiles. It would be valuable if Fourier methods could supplement the detailed information which they can provide on crystallite size and size distribution by providing some insight into the dominant crystallite shape. More or less arbitrary assumptions concerning crystallite shape would then become less necessary. It also seems worth clarifying the relation between Fourier measures of size distribution and others determined, for example, by electron microscopy. These two questions are the subject of this paper.

It is well known (Warren, 1969) that the Fourier coefficients $A_n$ of a size broadened diffraction peak are related to the distribution $g(n)$ of columns of length $n$ unit cells normal to the reflecting plane $hkl$ by the relation

$$g(n) = N \left( \frac{d^2 A_n}{dn^2} \right)$$

(1)

where $N$ is the number of unit cells in the sample. For a recent application of this equation to the determination of crystallite size distributions in supported metal catalysts see Păușescu, Mănăilă, Popescu & Ijovici (1974). It is tempting to compare values of $g(n)$ determined in this way with, for example, data drawn from the scrutiny of electron micrographs of the material. However, results from the latter tend to be related to the distribution $G(A)$ of overall crystallite sizes present, as measured by a parameter $A$ such as the edge length of a cube. The distinction between $g(n)$ and $G(A)$ is best illustrated by a particular example; for a collection of uniform spheres, only a single parameter, the diameter $A$, is required to describe the size of the particles, but the column length normal to any reflecting plane varies from $n=0$ to $n=A$. No continuous distribution function $G(A)$ exists, but the column distribution $g(n)$ in such a case is a simple linear relation (see below). If all particles in a sample have the same shape, it is possible to attach a well-defined meaning to $G(A)$, and in the following sections an exploration is made of the explicit relation between the forms of $G(A)$ and $g(n)$ for some simple shapes and orders of reflexion. For simplicity of interpretation, the discussion is restricted to crystals of the cubic system.

Theory

Consider an assemblage of crystallites all of the same shape described by a parameter $A$ and a size distribution function $G(A)$ such that the number of crystallites with sizes between $A$ and $A + dA$ is $G(A)dA$. Suppose also that the number of columns with lengths between $n$ and $n + dn$ normal to the $(hkl)$ plane in a single crystallite is given by $f(n, A)dn$. The maximum value of $n$ for a given value of $A$ will be some function $n_0(A)$, and the least value of $A$ which can accommodate a column length $n$ will be a related function $A_0(n)$. For example, in the simplest case of a sphere if $A$ is identified with the diameter, $n_0 = A$ and $A_0 = n$ (for all reflexions $hkl$). The total number of columns $dN$ with lengths between $n$ and $n + dn$ is given by

$$dN = g(n)dn = \int_{A_0(n)}^{A_0(n+dn)} f(n, A)G(A)dAdn$$
or
\[ g(n) = \int_{A_0(n)}^{\infty} f(n, A) G(A) dA. \quad (2) \]

This is the general relation between the column distribution function \( g(n) \) determined from the Fourier coefficients according to (1) and the size parameter function \( G(A) \) which may be determined from a visual analysis of electron micrographs.

The next problem lies in deducing the form of \( f(n, A) \) for various shapes of crystallite and orders of reflexion. In certain simple cases it is possible to accomplish this easily from geometrical considerations, but in general such an approach is cumbersome. Fortunately all the functions can be derived easily from relations given by Stokes & Wilson (1942) in their well-known paper on size broadening. These authors introduced a volume \( V_n \) common to a crystallite and its 'ghost' shifted a distance \( n \) unit cells in a direction normal to the \((hkl)\) plane. They showed that the quantities \( V_n \) are essentially the same as the Fourier coefficients \( A_n \) of the size-broadened profile arising from diffraction from the \((hkl)\) plane of the crystallite in question. It follows that the second derivative of \( V_n \) gives the column distribution function normal to the plane \((hkl)\) of the crystallite in question. Stokes & Wilson give explicit forms for \( V_n \) for all reflexions from spheres, cubes, tetrahedra and octahedra, and a double differentiation of their results leads directly to the functions \( f(n, A) \) required above. Moreover, values of the limiting functions \( n_0 \) and \( A_0 \) are simply obtained by equating to zero the original functions \( V_n \) (for when the ghost volume just vanishes, the displacement \( n \) must be the maximum extent of the crystallite in that particular direction).

It is now possible to evaluate (2) for various shapes without difficulty.

(a) Sphere
In this case \( A \) is taken as the diameter of the sphere, and the maximum value of \( n \) is simply \( A \). Stokes & Wilson's results give for all reflexions \( hkl \),
\[ f(n, A) = \frac{\pi n}{2} \quad (3) \]
and
\[ g(n) = \frac{\pi n}{2} \int_{n_0}^{\infty} G(A) dA. \quad (4) \]
Evidently
\[ g(0) = 0 \quad (5) \]
and differentiation of (4) with respect to the lower limit* gives:
\[ \frac{\partial}{\partial n} \left[ \frac{g(n)}{n} \right] = -\frac{\pi}{2} G(n). \quad (6) \]

From this it is clear that whatever the form of the function \( G(A) \), \( g(n) \) will always be zero at the origin, and will always go through a maximum.

(b) Cube
\( A \) is taken as the edge length of the cube, and \( g(n) \) varies according to the reflecting planes chosen.

\( h00 \) reflexions: in this case it is easy to see by inspection that \( g(n) = n G(n) \) (7) and \( g(0) = 0 \). Once again \( g(n) \) always goes through a maximum.

\( hh0 \) reflexions: Stokes & Wilson's results show that
\[ f(n, A) = A \]
and
\[ g(n) = \int_{n_0, 2}^{\infty} AG(A) dA. \quad (8) \]
Clearly
\[ g(0) = \bar{A} N_c \quad (9) \]
where \( \bar{A} \) is the mean cube edge length, and \( N_c \) is the number of crystallites present in the sample. Also
\[ g'(n) = -\frac{\sqrt{3}}{2} N_c \]
Evidently here since \( g(n) \) is finite at the origin, with a slope always less than or equal to zero, it can never go through a maximum, whatever the form of \( G(A) \).

\( hhh \) reflexions:
\[ f(n, A) = 2 \left[ A - (n/\sqrt{3}) \right] \]
and
\[ g(n) = 2 \int_{n_0, 3}^{\infty} \left[ A - (n/\sqrt{3}) \right] G(A) dA. \quad (11) \]
This is a most interesting case since the form of (11) is exactly equivalent to that relating the original Fourier coefficients \( A_n \) to the column distribution function \( g(n) \), i.e. (Warren, 1969)
\[ A_n = \frac{1}{N} \int_{i=n}^{\infty} (i-n) g(i) di. \quad (12) \]
It is therefore easy to deduce the following analogues of the well-known results of the Fourier theory of line profile analysis:
\[ g(0) = 2\bar{A} N_c \quad (13) \]
\[ g'(n) = -\frac{2}{\sqrt{3}} \int_{n_0, 3}^{\infty} G(A) dA \quad (14) \]
\[ g'(0) = -\frac{2}{\sqrt{3}} N_c \quad (15) \]
\[ g''(n) = \frac{2}{3} G(n/\sqrt{3}). \quad (16) \]

Further it may be concluded:
(i) since \( g(n) \) is always negative, \( g(n) \) will decrease continuously from a finite value at the origin, whatever the form of \( G(A) \).
(ii) the second derivative of \( g(n) \) gives the crystallite size distribution \( G(n) \).
(iii) the initial slope of the second derivative of the measured Fourier coefficients $A_n$ cuts the $n$ axis at $n = A \sqrt{3}$ where $A$ is the mean cube edge length.

(c) Tetrahedra

The parameter $A$ is here the edge length of the tetrahedron; using Stokes & Wilson’s results it is found that for reflexions $hkl$ with $h > k + l$, and with $Q = h^2 + k^2 + l^2$,

$$f(n, A) = \frac{\sqrt{2(h^2)}}{Q} \left[ A - \frac{\sqrt{2(hn)}}{Q^{1/2}} \right]$$

and

$$g(n) = \frac{\sqrt{2(h^2)}}{Q} \int_{h=0}^{\infty} \left[ A - \frac{\sqrt{2(hn)}}{Q^{1/2}} \right] G(A) dA. \quad (17)$$

Similarly for $h < k + l$,

$$g(n) = \frac{(h + k + l)^2}{2Q} \int_{[h+k+l]n/(2Q)^{1/2}}^{\infty} \left[ A - \frac{(h + k + l)n}{(2Q)^{1/2}} \right] G(A) dA. \quad (18)$$

These relations are closely analogous to those deduced for the $hhh$ reflexions in cubes discussed in the preceding section, and similar conclusions can be drawn. In particular, for $h < k + l$,

$$g(0) = \frac{(h + k + l)^2}{2Q} A N_e$$

and

$$g'(n) = -\frac{(h + k + l)^3}{4Q^{3/2}} \int_{(h+k+l)n/(2Q)^{1/2}}^{\infty} G(A) dA. \quad (20)$$

$$g(0) = -\frac{(h + k + l)^3}{4Q^{3/2}} A N_e$$

$$g''(n) = \frac{(h + k + l)^4}{2Q^2} \left[ \frac{(h + k + l)n}{(2Q)^{1/2}} \right]. \quad (21)$$

In this case for all reflexions, $g(n)$ decreases continuously from a finite value at the origin, and its second derivative leads to values of $G(n)$. The intercepts of the initial slopes of $g(n)$ or of $d^2A_n/dn^2$ on the $n$ axis are $A \sqrt{2}/2$ ($h00$ reflexions), $A$ ($hh0$ reflexions) and $A \sqrt{2}/3$ ($hhh$ reflexions), where $A$ is the mean tetrahedral edge length.

The author is grateful to the referee for pointing out that this work is related to, and can be extended by, certain results given by Wilson (1971). The quantity $g(0)$ used here is proportional to Wilson’s $V''(0)$, and from equations (28) and (29) of Wilson’s paper one may show that $g(0)$ must possess a maximum when Wilson’s $L$ (taper) parameter is zero, or if Mitra’s $M$ (rotundity) parameter is negative.

Discussion

Table 1 summarizes the above results according to whether or not a maximum can exist in the function $g(n)$. It is seen that irrespective of the nature of the function $G(A)$, a maximum must always exist for all reflexions from spheres, but can never do so for any reflexion from tetrahedra. Cubes occupy an intermediate position, with the existence of a maximum depending on the particular reflexion chosen. It is hoped that the results given here will allow conclusions to be drawn about crystallite shape from the Fourier analysis of a number of reflexions. Most samples of polycrystalline materials will of course contain crystallites of various shapes, and cases where a single shape predominates will be in a minority. Nevertheless, this analysis should help to decide whether the concept of a ‘mean’ shape has any relevance; it is worth repeating that only if this is so is the correlation of size and surface area data likely to be straightforward. In the application of this theory care will be necessary to minimize the ‘hook’ effect (Warren, 1969), which artificially depresses the earlier Fourier coefficients if the line profile is truncated; otherwise a spurious maximum will occur near the origin in the second derivative of the Fourier coefficients.

Table 1. Behaviour of the function $g(n)$ for various shapes and orders of reflexion

<table>
<thead>
<tr>
<th>Reflexion</th>
<th>Shape</th>
<th>$h00$</th>
<th>$hh0$</th>
<th>$hhh$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Cube</td>
<td>✓</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Tetrahedron</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

✓: $g(n)$ always shows a maximum
x: $g(n)$ never shows a maximum

Opportunities for the detailed application of the theory presented here are likely to be restricted, but a wider validity attaches to the more general conclusions that have emerged from the analysis. These are firstly, that a size distribution function $G(A)$ estimated by electron microscopy or other means will not be simply related to the function $g(n)$ determined from the second derivative of the Fourier coefficients of the diffraction line profile. Secondly, for the shapes considered here, only in the case of the $h00$ reflexions from cubes is a single or double differentiation not necessary to provide information about $G(A)$. This implies a third or fourth differentiation of the original Fourier coefficients, and one may suspect that in general very careful measurements of diffraction data will be necessary before any useful information concerning $G(A)$ can be established.

The author is indebted to Mr D. Wood, of the BP Research Centre, Sunbury-on-Thames, for discussions which led to this work.

References


