

ANALYTICAL EXPRESSION FOR DIFFRACTION LINE PROFILE FOR POLYDISPERSIVE POWDERS

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An analytical expression for the diffraction line profile for polydisperse powders (particularly, nanopowders) with Gamma Grain Size Distribution is derived. The expression consists of elementary functions only and can readily replace standard functions (like Gaussian, Lorentzian or Pearson) for diffraction peak fitting purposes. This allows for direct Grain Size Distribution determination using standard fitting software.

1 Introduction

X-ray diffraction is a well established experimental method sensitive to both (i) crystal structure, (ii) size and shape of the crystallites. The latter property of diffraction is especially appreciated in case of nanocrystals, when small size of the objects makes diffraction techniques a feasible tool for crystallite size determination.

Theory of powder diffraction describes^a diffraction pattern as a set of diffraction peaks (located in reciprocal space according to Bragg law, with intensities defined by the structure factor) convoluted with some line profile (defined by crystal shape and size).

An analytical formula for the line profile for spherical crystallites of same size (monodisperse powder) was given by Wilson¹. Later, similar formulas were given for other crystallites shapes^{2,3,4}.

In the present paper formula for line profile for polydisperse powder consisting of spherical grains with the Gamma Grain Size Distribution (GSD) is presented.

2 Debye formula for crystals

Debye formula⁵ for intensity of X-rays scattered by a cluster of atoms is given by:

$$I(q) = \sum_{i=1}^N \sum_{j=1}^N F_i F_j \frac{\sin(q \cdot r_{ij})}{q \cdot r_{ij}}, \quad (1)$$

where F_i i F_j are atomic factors of atoms i th and j th, $q = \frac{4\pi \sin \theta}{\lambda}$ is scattering vector, r_{ij} is distance between atoms i th and j th and N is a number of atoms in the cluster. Consider a compound containing L elements e.g. Si and C in case of SiC , ($L = 2$). Set of all possible atomic pairs can be divided into L^2 subsets of pairs of same kind^b, e.g. $(Si - Si)$, $(C - C)$, $(Si - C)$ i $(C - Si)$. Let's index all kinds as (mn) , where $m, n \in (1 \div L)$ describe pair contents, e.g. $(11) \Leftrightarrow Si - Si$,

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^aFor consistency of the paper some other phenomena like diffuse scattering or Compton effect are intentionally neglected.

^bObviously, pairs (mn) and (nm) , e.g. $(Si - C)$ and $(C - Si)$ are equivalent in sense of interatomic distances, so instead of L^2 subsets we could create only $\frac{L(L+1)}{2}$. We stay at L^2 for simplicity.

(22) $\Leftrightarrow C - C$, (12) $\Leftrightarrow Si - C$ and (21) $\Leftrightarrow C - Si$. Thus, Debye equation can be rewritten as:

$$I(q) = \frac{1}{q} \sum_{m=1}^L \sum_{n=1}^L F_m F_n \sum_{i=1}^{N_L} \sum_{j=1}^{N_L} \frac{\sin(q \cdot r_{(mn)ij})}{r_{(mn)ij}}, \quad (2)$$

where first two summations run over all kinds of pairs, two latter - run over all pairs of same kind. Since the same interatomic distance $r_{(mn)ij}$ corresponds to many^c pairs i, j in the inner summation, the distances can be consolidated by introduction of a histogram of interatomic distances, so called Pair Correlation Function (*PCF*):

$$PCF_{(mn)}(r) = \sum_{i=1}^{N_L} \sum_{j=1}^{N_L} \delta_{r, r_{(mn)ij}}, \quad (3)$$

where δ is Dirac or Kronecker delta (depending on context). Modified Debye equation (2) takes form:

$$I(q) = \frac{1}{q} \sum_{m=1}^L \sum_{n=1}^L F_m F_n \int_0^R \frac{PCF_{(mn)}(r)}{r} \sin(q \cdot r) dr, \quad (4)$$

where R is size, from Polish word „Rozmiar”, (usually diameter) of the grain. Since:

$$\bigwedge_{r \notin (0, R)} PCF(r) = 0,$$

the integral in (4) is a Fourier transform of $PCF(r)/r$. In practice Fast Fourier Transform (*FFT*) is used:

$$I(q) = \frac{1}{q} \sum_{m=1}^L \sum_{n=1}^L F_m F_n \cdot FFT \left(\frac{PCF_{(mn)}(r)}{r} \right) \quad (5)$$

Gierlotka and Marciniak⁶ found that *PCF* differs from Radial Distribution Function (*RDF*) by a factor depending on size and shape of the grain, see Fig.1. This factor, called Shape Distribution (*SD*) of the grain, contains entire information concerning powder microstructure available from the diffraction image (cf. ⁷). It can be shown⁸, that in general case, i.e. for finite crystals, the following relation exists:

$$PCF(r) = RDF(r) \cdot SD(r; R),$$

where *shape distribution* *SD* is analytically known for many solids (grain shapes)⁸. Therefore (5) can be written in the form:

$$I(q) = \frac{1}{q} \sum_{m=1}^L \sum_{n=1}^L F_m F_n \cdot FFT \left(\frac{RDF_{(mn)}(r)}{r} \cdot SD(r; R) \right). \quad (6)$$

The above expression describes line profile as a Fourier transform of the product of two functions: *radial distribution function of the (infinite) crystalline structure*

^cParticularly in crystals.

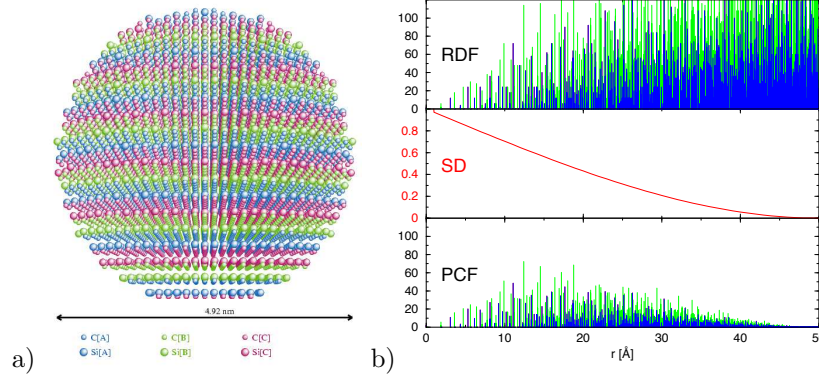


Figure 1. (a) A model of crystalline grain of SiC of diameter 50\AA . (b) Radial Distribution Function (RDF) of the (infinite) atomic structure multiplied by Shape Distribution of the grain (SD) becomes atomic Pair Correlation Function (PCF) of the grain.

$RDF(r)$ divided by r and shape distribution of the grain $SD(r; R)$. Basing on Stokes theorem we can replace transform of the product with convolution of appropriate transforms, obtaining Debye formula for crystals:

$$I(q) = \frac{1}{q} \sum_{m=1}^L \sum_{n=1}^L F_m F_n \cdot \left[FFT \left(\frac{RDF_{(mn)}(r)}{r} \right) * FFT (SD(r; R)) \right] \quad (7)$$

In this form, Debye equation is a convolution of two functions: the Fourier transform of $\frac{RDF(r)}{r}$ and transform of the shape distribution SD . Fourier transforms of both $\frac{RDF(r)}{r}$ and SD functions describe some physical quantities (see below), thus only real parts of these transforms are meaningful. Expanding first of these transforms we have:

$$\begin{aligned} Re \left[FFT \left(\frac{RDF(r)}{r} \right) \right] &= \int_0^{\infty} \frac{RDF(r)}{r} \cos(q \cdot r) dr = \int_0^{\infty} \sum_{hkl} \sum_i \frac{1}{r} \delta(r - i \cdot d_{hkl}) \cos(q \cdot r) dr \\ &= \sum_{hkl} \sum_i \int_0^{\infty} \frac{1}{r} \delta(r - i \cdot d_{hkl}) \cos(q \cdot r) dr = \sum_{hkl} \sum_i \frac{1}{i \cdot d_{hkl}} \cos(i \cdot q \cdot d_{hkl}) \end{aligned} \quad (8)$$

Series (8) does not vanish while the following condition is satisfied:

$$q \cdot d_{hkl} = 2n\pi, \quad (9)$$

which is Bragg equation. This condition is fulfilled for a countable set of scattering vector values $q_{hkl} = \frac{2n\pi}{d_{hkl}}$ that determine locations of the Bragg lines. It is known from integral test for convergence that series $\sum_i \frac{1}{i}$ (Riemann's zeta function for $m = 1$) are divergent to $+\infty$. Therefore sum of series (8) for q_{hkl} (i.e. at Bragg

maxima) is:

$$Re \left[FFT \left(\frac{RDF(r)}{r} \right) \right]_{q=q_{hkl}} = \sum_{hkl} \sum_i^{\infty} \frac{\delta_{q,q_{hkl}}}{i \cdot d_{hkl}} \cos(i \cdot q \cdot d_{hkl}) = \sum_{hkl} \delta_{q,q_{hkl}} \sum_i^{\infty} \frac{1}{i \cdot d_{hkl}} = \sum_{hkl} \delta(q_{hkl}) \quad (10)$$

It turns out that transform of $\frac{RDF(r)}{r}$ is a series (“a comb”) of Dirac delta functions $\sum_{hkl} \delta(q_{hkl})$ placed at the Bragg maxima of diffraction pattern $q = q_{hkl}$. This „comb” is convoluted (basing on (7)) with the transform of the *shape distribution SD*. Therefore, transform of the *shape distribution SD* is the diffraction line profile, while the *shape distribution SD* itself is so called „ghost” function described already by Stokes and Wilson ⁹ (see also ^{10,11,3,4,2}).

3 Diffraction Line Profile for polydispersive powders

Assume a powder consisting of spherical grains. It can be shown (e.g. ⁸) that the *shape distribution SD* of sphere is:

$$SD(r; R) = \begin{cases} 0 & r < 0 \\ \frac{(R-r)^2(2R+r)}{2R^3} & 0 \leq r \leq R \\ 0 & R < r \end{cases}, \quad (11)$$

where R is grain size (here: diameter). Diffraction line profile for monodispersive powder consisting of spherical grains is:

$$LP(q) = Re [FFT(SD(r; R))] = \frac{3}{\sqrt{2\pi}} \frac{2 + q^2 R^2 - 2 \cos qR - 2qR \sin qR}{q^4 R^3}. \quad (12)$$

Consider Gamma *grain size distribution GSD*:

$$GSD(R; R_0, m) = \frac{R_0^{-m-1}}{\Gamma(m+1)} R^m e^{-R/R_0}, \quad (13)$$

where Γ is Euler Gamma function, R_0 and m are some parameters (see below). Average grain size (moment of the first order) for this distribution is:

$$\langle R \rangle = \int_0^{\infty} GSD(R; R_0, m) R dR = \int_0^{\infty} \frac{R_0^{-m-1}}{\Gamma(m+1)} R^m e^{-R/R_0} R dR = (m+1)R_0, \quad (14)$$

moment of the second order:

$$\langle R^2 \rangle = \int_0^{\infty} GSD(R; R_0, m) R^2 dR = \int_0^{\infty} \frac{R_0^{-m-1}}{\Gamma(m+1)} R^m e^{-R/R_0} R^2 dR = (m+1)(m+2)R_0^2, \quad (15)$$

and dispersion:

$$\sigma = \sqrt{\langle R^2 \rangle - \langle R \rangle^2} = \sqrt{(1+m)R_0^2} = R_0 \sqrt{m+1}. \quad (16)$$

Parameters R_0 and m of the distribution (13) are related to its mean and dispersion by:

$$R_0 = \frac{\sigma^2}{\langle R \rangle} \quad (17)$$

$$m = \frac{\langle R \rangle^2}{\sigma^2} - 1 \quad (18)$$

Parameter m (more precisely: $m + 1$) can be considered as a measure of relative width of the size distribution (13). Large values of m correspond to a narrow distribution, small - to a wide one. Last two expressions allow to rewrite (13) as a function of physically significant parameters $\langle R \rangle$ and σ instead of R_0 and m :

$$GSD(R; \langle R \rangle, \sigma) = \frac{R^{\frac{\langle R \rangle^2}{\sigma^2} - 1} \left(\frac{\langle R \rangle}{\sigma^2} \right)^{\frac{\langle R \rangle^2}{\sigma^2}}}{e^{\frac{R \langle R \rangle}{\sigma^2}} \Gamma \left(\frac{\langle R \rangle^2}{\sigma^2} \right)}, \quad (19)$$

where both $\langle R \rangle$ and σ are given in [\AA]. Expression for the line profile for polydisperse powder can be derived as an average $\langle LP \rangle$ of (12) taken with probability distribution (13):

$$\langle LP(q; R_0, m) \rangle = \frac{3}{\sqrt{2\pi}} \int_0^\infty \frac{R_0^{-1-m}}{\Gamma(1+m)} R^m e^{-R/R_0} \frac{2 + q^2 R^2 - 2 \cos qR - 2qR \sin qR}{q^4 R^3} dR \quad (20)$$

Integral (20) exists if q , $(m + 1)$ and R_0 are real and positive, which conforms to physical requirements for those quantities. After integration we have:

$$\begin{aligned} \langle LP(q; R_0, m) \rangle = & \frac{3}{\sqrt{2\pi} q^4 R_0 \Gamma(m+1)} \cdot \\ & \left\{ \frac{2\Gamma(m-2)}{R_0^2} - \frac{2(1+q^2 R_0^2)^{1-\frac{m}{2}} \cos[(m-2) \arctan qR_0] \Gamma(m-2)}{R_0^2} \right. \\ & \left. + q^2 \Gamma(m) - \frac{2q(1+q^2 R_0^2)^{\frac{(1-m)}{2}} \sin[(m-1) \arctan qR_0] \Gamma(m-1)}{R_0^2} \right\}. \end{aligned} \quad (21)$$

From (21) we obtain simplest available expression for the diffraction line profile $\langle LP \rangle$ for polydisperse powder consisting of spherical grains with Gamma size distribution:

$$\begin{aligned} \langle LP(q; R_0, m) \rangle = & \frac{(1+q^2 R_0^2)^{-\frac{m+1}{2}}}{\sqrt{2\pi} q^4 R_0^3 m(m-1)(m-2)} \cdot \\ & \left\{ 3(1+q^2 R_0^2)^{\frac{m+1}{2}} (2+q^2 R_0^2(m-1)(m-2)) \right. \\ & - 6(1+q^2 R_0^2)^{\frac{3}{2}} \cos[(m-2) \arctan qR_0] \\ & \left. - 6qR_0(1+q^2 R_0^2)(m-2) \sin[(m-1) \arctan qR_0] \right\}. \end{aligned} \quad (22)$$

Formula (22) contains only elementary functions and may be easily used either in numerical or symbolic calculations. Maximum intensity of the diffraction line profile can be obtained from (22) in the limit $q \rightarrow 0$:

$$\lim_{q \rightarrow 0} \langle LP(q; R_0, m) \rangle = \frac{3(m+1)R_0}{4\sqrt{2\pi}} = \frac{3}{4\sqrt{2\pi}} \langle R \rangle, \quad (23)$$

which shows that the peak height does not depend on dispersion of the grain sizes. After substitution of (17) and (18) into (22) we finally obtain **expression for the diffraction line profile $\langle LP \rangle$ for polydisperse powders as a function of quantities $\langle R \rangle$ and σ having direct physical interpretation:**

$$\begin{aligned} \langle LP(q; \langle R \rangle, \sigma) \rangle = & \frac{\langle R \rangle^3}{\sqrt{2\pi}q^4\sigma^6 \left(1 + \frac{q^2\sigma^4}{\langle R \rangle^2}\right)^{\frac{\langle R \rangle^2}{2\sigma^2}} (\frac{\langle R \rangle^2}{\sigma^2} - 1) (\frac{\langle R \rangle^2}{\sigma^2} - 2) (\frac{\langle R \rangle^2}{\sigma^2} - 3)} \\ & \left\{ 3 \left(1 + \frac{q^2\sigma^4}{\langle R \rangle^2}\right)^{\frac{\langle R \rangle^2}{2\sigma^2}} \left(2 + \frac{q^2\sigma^4}{\langle R \rangle^2} \left(\frac{\langle R \rangle^2}{\sigma^2} - 2\right) \left(\frac{\langle R \rangle^2}{\sigma^2} - 3\right)\right) \right. \\ & \quad \left. - 6 \left(1 + \frac{q^2\sigma^4}{\langle R \rangle^2}\right)^{\frac{3}{2}} \cos \left[\left(\frac{\langle R \rangle^2}{\sigma^2} - 3\right) \arctan \frac{q\sigma^2}{\langle R \rangle} \right] \right. \\ & \quad \left. - 6 \frac{q\sigma^2}{\langle R \rangle} \left(1 + \frac{q^2\sigma^4}{\langle R \rangle^2}\right) \left(\frac{\langle R \rangle^2}{\sigma^2} - 3\right) \sin \left[\left(\frac{\langle R \rangle^2}{\sigma^2} - 2\right) \arctan \frac{q\sigma^2}{\langle R \rangle} \right] \right\}. \end{aligned} \quad (24)$$

Above formula is a generalization of, and should converge to (12) in a special case of vanishing dispersion. Indeed, from (24) in the limit $\sigma \rightarrow 0$, we obtain:

$$\lim_{\sigma \rightarrow 0} \langle LP(q; \langle R \rangle, \sigma) \rangle = \frac{3}{\sqrt{2\pi}} \frac{2 + q^2 \langle R \rangle^2 - 2 \cos q \langle R \rangle - 2q \langle R \rangle \sin q \langle R \rangle}{q^4 \langle R \rangle^3}. \quad (25)$$

Formula (24) can be readily used for *grain size distribution* determination from a single powder diffraction peak.

4 Concluding remarks

Function (24) can be used in its explicit form for fitting experimentally measured powder diffraction lines. Existing, commercially available software can be employed for this purpose^d. Fitting of the line profile function (24) instead of a standard functions (like Gaussian or Lorentzian) benefits in meaningful fit parameters $\langle R \rangle$ and σ , thus immediate determination of the *grain size distribution*, Fig.2. *Grain size distribution* can be plotted using determined $\langle R \rangle$, σ and the Gamma function (19) as shown on Fig.2b. This procedure performed for several diffraction maxima allows for average grain shape resolution.

^dMost of fitting software allows for user defined functions.

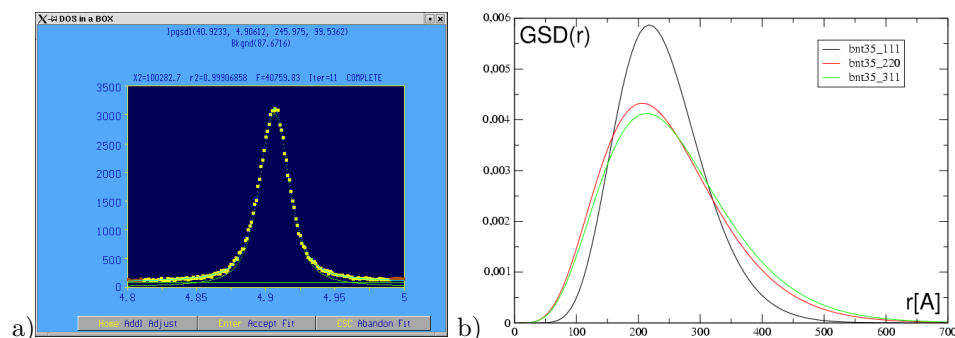


Figure 2. (a) An experimental diffraction data fitted by the derived line profile function (24). Obtained profile parameters $\langle R \rangle$ and σ (here $\langle R \rangle = 245.975 \text{ \AA}$ and $\sigma = 99.5362 \text{ \AA}$ are seen) directly define Grain Size Distribution of the powder being examined. (b) Grain Size Distribution (GSD) plotted using determined $\langle R \rangle$ and σ values for several diffraction maxima.

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