Applicabilities of the Warren–Averbach Analysis and an Alternative Analysis for Separation of Size and Strain Broadening

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Abstract
The validities of the Warren–Averbach analysis and of an alternative analysis for separation of size and strain contributions to diffraction line broadening are investigated. The analyses are applied to simulated and experimental line profiles. The Fourier coefficients of the simulated line profiles are derived from expressions for the distortion field around specific lattice defects: misfitting inclusions and small-angle grain boundaries. Applicability tests are also performed on experimental powder diffraction line profiles taken from plastically deformed specimens: thin aluminium layers and ball-milled molybdenum powders. It is concluded that for both methods finite but different classes of specimen exist for which they give meaningful results. In practice, each time an analysis is performed the results must be tested against common (physical) sense and all information available on the specimens.

I. Introduction
Broadening of (X-ray) diffraction line profiles is caused by nonideal optics of the instrument, wavelength dispersion and structural imperfections of the specimen. The structural line broadening is often subdivided into size broadening and strain broadening. Size broadening is caused by the finite size of ‘domains diffracting essentially incoherently with respect to one another’ (Warren, 1959). Strain broadening is caused by varying displacements of the atoms with respect to their reference-lattice positions.

Line broadening is frequently characterized by means of one or two breadth measures and separation of size and strain contributions has been performed on this basis (Hall, 1949; de Keijser, Langford, Mittemeijer & Vogels, 1982; Langford, 1992). In principle, a more detailed analysis is possible by taking into account the complete shape of a line profile by expressing it in terms of Fourier coefficients. Both breadth and Fourier methods gain in reliability if more than one order of reflection is used for a given set of lattice planes.

The classical method to separate size and strain broadening using Fourier coefficients of multiple orders of reflection was developed by Warren & Averbach (1950, 1952) (WA). For the case of polycrystalline cold-worked metals, the WA analysis yields average size values that are considerably smaller than the grain sizes of the materials under study. Such observations have been interpreted as being caused by ‘some sort of a domain structure’ within the grains caused by the cold deformation (Warren, 1959). However, it has also been argued that the assumptions underlying the WA analysis are incompatible with the nature of the strains in cold-worked metals and that therefore the results of the WA analysis can deviate significantly from the true values (Williamson & Smallman, 1954; Wilkens, 1979, 1984).

With assumptions other than those made in the WA analysis, alternative methods can be developed that are in general equally valid. Here, one recently developed alternative is discussed that may be of interest for cold-worked metals (van Berkum, Vermeulen, Delhez, de Keijser & Mittemeijer, 1993).

The WA analysis and the alternative analysis are applied to simulated and experimental Fourier coefficients of broadened line profiles. In the case of simulations, extracted parameters can be compared with true ones. For the experiments, the meaning of the separation results can be discussed in terms of the physics pertaining to the specimens. On this basis, the ranges of validity of the two methods are investigated.

II. Theory
A measured diffraction line profile \( P_l(\Delta S) \), where the rank number \( l \) serves to distinguish profiles from each
other, can be expressed as a Fourier series:

\[ P_h(\Delta S) = K \sum_{L=\infty}^{+\infty} A(L, S_i) \cos (2\pi L \Delta S) + B(L, S_i) \sin (2\pi L \Delta S), \tag{1} \]

where \( K \) is (approximately) a constant, \( A \) and \( B \) are the cosine and sine Fourier coefficients and \( L \) is a distance perpendicular to the diffracting planes. In practice, \( L \) takes specific discrete values \( n \Delta L \), where \( n \) is an integer and \( \Delta L \) is inversely proportional to the length of the measurement range in reciprocal space.

The line profile according to (1) is defined with respect to a distance \( S_i \) to the origin in reciprocal space, related to a diffraction angle \( 2\theta \) by \( S_i = 2\sin \theta_0/\lambda \), where \( \lambda \) is the wavelength. The deviation from \( S_i \) is denoted \( \Delta S \), where \( \Delta S = 2(\sin \theta - \sin \theta_0)/\lambda \). Usually, for \( 2\theta \), the location of the centroid of the line profile is chosen. Any pair of line profiles \( P_1 \) and \( P_2 \) with \( S_2 = 2S_1 \) is called a first and second order of reflection. In the present paper, only the cosine Fourier coefficients \( A(L, S_i) \) are considered because usually the sine coefficients are not physically interpreted [exceptions are the work of Mittemeijer & Delhez (1978) and Ungár, Groma & Wilkens (1989)].

The profile measured from a structurally imperfect specimen can be considered as the convolution of a structurally broadened line profile with an instrumental line profile. Fourier coefficients of a measured profile are therefore the products of Fourier coefficients of the structural and the instrumental line profiles. The instrumental line profile can be measured using a 'standard' specimen that is (essentially) free of lattice defects. By division of Fourier coefficients of the line profiles of the imperfect and the 'standard' specimens, Fourier coefficients of the structurally broadened line profile are obtained (Stokes, 1948). If no standard specimen is available, two broadened line profiles can be treated analogously by assignation of the role of the instrumental profile to the profile with the smaller broadening. The resulting Fourier coefficients then represent the differences in lattice imperfection (size and strain) (de Keijser & Mittemeijer, 1980). This procedure is used in §IV.A.

The Fourier cosine coefficients of a structurally broadened line profile can be written as the products of order-independent size coefficients \( A^S(L) \) and order-dependent strain coefficients \( A^D(L, S_i) \) (subscripts \( S \) for size and \( D \) for distortion). If the specimen is considered to consist of columns parallel to the diffraction vector, \( A^S(L) \) is determined by the column-length (size) distribution \( p(D) \), where \( D \) is the column length. The average column length (size) is denoted \( \langle D \rangle \). Further, \( A^D(L, S_i) \) is determined by the strain distributions \( p(e_L) \) (one for each \( L \)), where \( e_L \) is the average of the true (local) strain \( e_0 \) over a length \( L \). All distributions are normalized to unit area. In summary (Warren, 1959),

\[ A(L, S_i) = A^S(L)A^D(L, S_i), \tag{2} \]

\[ A^S(L) = (1/\langle D \rangle) \int_0^{\infty} \langle D - |L| \rangle p(D) dD, \tag{3} \]

\[ A^D(L, S_i) = \int_{-\infty}^\infty p(e_L) \cos (2\pi LS_i e_L) de_L. \tag{4} \]

To obtain information on \( A^S(L) \) and \( A^D(L, S_i) \) separately, at least two orders of reflection have to be measured and the \( L \) and/or \( S_i \) dependence of \( A^S(L) \) and/or \( A^D(L, S_i) \) has to be specified by making assumptions on \( p(D) \) and/or \( p(e_L) \). The latter can be done in different ways, leading to different separation methods, and in practice one must try to choose the one most suited to the specimen to be investigated.

A. The Warren–Averbach analysis

In the WA analysis, an approximation is used for the \( S_i \) dependence of \( A^D(L, S_i) \). It can be shown by a Taylor-series expansion that, for small \( L \) and \( S_i \) (Warren & Averbach, 1950; see Appendix A),

\[ \ln [A^D(L, S_i)] \approx -2\pi^2 L^2 S_i^2 \langle e_L^2 \rangle \]

\[ \approx (S_i/S_i)^2 \ln [A^D(L, S_i)], \tag{5} \]

where \( \langle e_L^2 \rangle \) is the mean squared strain. If all \( p(e_L) \) are Gaussian, (5) is exact for all values of \( L \) and \( S_i \) (Warren & Averbach, 1950). The more the \( p(e_L) \) deviate from being Gaussian, the smaller the range in \( L \) for which (5) is valid [see after (A2)].

From (5) and the order independence of \( A^S(L) \), the WA analysis is derived from taking the logarithm on both sides of (2) (Warren & Averbach, 1952):

\[ \ln [A(L, S_i)] = \ln [A^S(L)] - 2\pi^2 L^2 S_i^2 \langle e_L^2 \rangle. \tag{6} \]

Here, for the sake of comparison with the other separation method [cf. (10)], the following form of the basic equation for the WA analysis is preferred:

\[ \ln [A(L, S_i)] = \ln [A^S(L)] + (S_i/S_i)^2 \ln [A^D(L, S_i)]. \tag{7} \]

From plots of \( \ln [A(L, S_i)] \) versus \( (S_i/S_i)^2 \), the size Fourier coefficients are obtained from the intercepts and the strain Fourier coefficients of the profile \( P_1 \) are acquired from the slopes. If application of the WA analysis is justified, mean squared strains \( \langle e_L^2 \rangle \) can be calculated from \( A^D(L, S_i) \) using (5) and can be

* In textbooks (e.g. Warren, 1969), the notations \( P(h) \) and \( A(n, l) \) are often used. For that notation, it is necessary to choose a unit-cell dimension \( a_3 \) in the direction of the diffraction vector. Then, \( n = L/a_3 \), \( l = S_i a_3 \) and \( a_3 = (S_i + \Delta S)\). We prefer the present notation for practical purposes.
physically interpreted in terms of \(\langle e_{0}^2 \rangle, \langle e_{0}^2 \rangle\) etc. using (A3) (Turunen, de Keijser, Delhez & van der Pers, 1983).

**B. An alternative analysis**

As indicated above, the WA analysis breaks down at a certain value of \(L\) if the strain distributions are not Gaussian. The breakdown may occur so early that in practice size and strain parameters become very unreliable. For this reason, an alternative analysis has been developed. This alternative analysis also breaks down at a certain \(L\) value, which can be smaller or larger than for the WA analysis owing to the different approximations used. Hence, specimens for which the WA analysis is problematic may be reliably analysed by the alternative analysis and vice versa (van Berkum, Vermeulen, Delhez, de Keijser & Mittemeijer, 1993).

The first approximation used in the alternative analysis concerns the \(L\) and \(S_i\) dependences of \(A^0(L, S_i)\). By the expression of \(A^0(L, S_i)\) in terms of the local strain \(e_0\) and its derivatives, it can be shown that for small \(L\) the strain gradients within the columns can be neglected [this is sometimes called the Stokes–Wilson approximation; see Stokes & Wilson (1944) and Wilson (1955)]. Then, the following relation can be derived for small \(L\) and \(S_i\) (see Appendix A):

\[
A^0(L, S_i) \simeq A^0(L_1, S_i), \quad \text{where} \quad L_i = (S_i/S_i)L_1. \tag{8}
\]

The smaller the average strain gradients in the columns, the larger the range in \(L\) for which (8) holds [see (A6)]. For specimens for which the lattice spacing is constant within each grain, but varies from grain to grain (e.g. owing to differences in composition), the strain gradients are zero, the \(p(e_0)\) are independent of \(L\) and (8) is exact at least for \(L_1\) up to the smallest grain size [cf. (4)]. In that case, the strain profiles of all orders of reflection have the same shape and a breadth proportional to the order (Eastabrook & Wilson, 1952).

A size–strain separation method based on (8) requires an additional equation specifying the \(L\) dependence of \(A^q(L)\). For \(L \ll \langle D \rangle\), the Taylor series of \(\ln[A^q(L)]\) can be restricted to the first term and it can be shown that (see Appendix B)

\[
\ln[A^q(L)] \simeq (S_i/S_i) \ln[A^q(L_1)],
\]

where

\[
L_i = (S_i/S_i)L_1. \tag{9}
\]

The range over which this equation is applicable depends on the shape of the distribution \(p(D)\). It is exact for all \(L\) if the column-length distribution obeys \(p(D) = (1/\langle D \rangle) \exp[-D/\langle D \rangle]\). From (2), (8) and (9), the basic equation for the alternative analysis becomes

\[
\ln[A(L, S_i)] = \ln[A^0(L_1, S_i)] + (S_i/S_i) \ln[A^q(L_1)],
\]

where

\[
L_i = (S_i/S_i)L_1. \tag{10}
\]

From plots of \(\ln[A(L, S_i)]\) versus \(S_i/S_i\), the strain Fourier coefficients of the profile \(P_1\) are obtained from the slopes and the size Fourier coefficients are acquired from the slopes. Calculation of \(\langle e_{0}^2 \rangle\) from \(A^0(L, S_i)\) obtained by this alternative analysis is not useful, because the method is designed for specimens that do not permit neglect of the influence on \(A^0(L, S_i)\) of \(\langle e_{0}^2 \rangle, \langle e_{0}^4 \rangle\) etc. (see Appendix A). In the case of appropriate applications of the alternative method, \(A^0(L, S_i)\) can be interpreted in terms of \(\langle e_{0}^2 \rangle, \langle e_{0}^4 \rangle\) etc. by fitting the first column of terms of (A5) to \(A^0(L, S_i)\).

**C. Remarks**

(i) **Linear versions of the analyses.** It has been argued that, instead of a truncated Taylor series of \(\ln[A(L, S_i)]\), simply that of \(A(L, S_i)\) can be used in the WA analysis (Delhez & Mittemeijer, 1976) (see Appendix A):

\[
A^0(L, S_i) \simeq 1 - 2\pi^2 S_i^2 \langle e_{0}^2 \rangle
\]

\[
\simeq 1 - (S_i/S_i)^2 [1 - A^0(L, S_i)], \tag{11}
\]

leading to the following equivalent of (7):

\[
A(L, S_i) = A^q(L) - (S_i/S_i)^2 A^q(L) [1 - A^0(L, S_i)]. \tag{12}
\]

From plots of \(A(L, S_i)\) versus \(S_i/S_i^2\), the size Fourier coefficients are obtained from the intercepts and the strain Fourier coefficients of the profile \(P_1\) can be deduced from the slopes.

Just like (5), (11) is correct for small \(L\) and \(S_i\). Unlike (5), no distributions \(p(e_0)\) exist for which (11) holds exactly. It can be shown that the first term neglected in the derivation of (11) is always larger than the one in (5) (see Appendix A). This disadvantage of the WA analysis executed according to (12) is countered by an important advantage: (12) is less sensitive to the inevitable random errors in \(A(L, S_i)\) owing to the counting statistics in the measured profiles. Variances in Fourier coefficients \(A(L, S_i)\) and \(A(L, S_2)\) propagate into variances in \(A^q(L)\) and \(A^0(L, S_i)\) smaller by the use of (12) than by the use of (7) (see Appendix C).

For the alternative analysis, introduced in §II.B, a comparable equivalent exists. Instead of the Taylor series of \(\ln[A^q(L)]\), that of \(A^q(L)\) can be used (see Appendix B):

\[
A^q(L_i) \simeq 1 - (L_i/\langle D \rangle) \simeq 1 - (S_i/S_i)[1 - A^q(L_1)],
\]

where

\[
L_i = (S_i/S_i)L_1. \tag{13}
\]
leading to the following equivalent of (10):
\[ A(L_1, S_1) = A^0(L_1, S_1) - (S_1/S_0)A^0(L_1, S_1)[1 - A^5(L_1)], \]
where
\[ L_1 = (S_1/S_0)L_0. \]  

From plots of \( A(L_1, S_1) \) versus \( S_1/S_0 \), the strain Fourier coefficients of the profile \( P_1 \) are obtained from the intercepts and the size Fourier coefficients can be deduced from the slopes.

In general, (13) is not inferior to (9). Which of the two is best depends on the width of the size distribution in the specimen under study. For the infinitely narrow \( \delta \)-type distribution, (13) is best; for the very broad exponential distribution [see after (9)], (9) is best. For any distribution, both (13) and (9) describe at least the initial behaviour of \( A^5(L) \). Again, the linear version of the separation method has the advantage of being less sensitive to the propagation of random errors (see Appendix C).

The choice between the logarithmic separation methods and the linear versions should depend on the priorities of the study: for minimal random error choose linear methods; for minimal systematic error choose the logarithmic WA analysis and the logarithmic or linear alternative analysis, depending on the expected width of the size distribution. In this paper, only the logarithmic versions of the separation methods are used.

(ii) Recursive analysis. In principle, with (8), no additional series expansion of \( A^5(L) \) is necessary to separate size and strain coefficients. By guessing only one value of either \( A^5(L) \) or \( A^0(L, S_1) \) for \( L \neq 0 \), many others can be successively obtained. For example, suppose two sets \( A(L, S_1) \) and \( A(L, S_2) \) with \( S_2 = 2S_1 \) are available and the value of \( A^5(\Delta L) \) is guessed. Then, from the product relation \( A(L, S_1) = A^5(L)A^0(L, S_1) \), one can calculate \( A^0(\Delta L, S_1) \) and \( A^0(\Delta L, 2S_1) \). From (8), it follows that \( A^0(2\Delta L, S_1) = A^5(\Delta L, 2S_1) \), so that \( A^5(2\Delta L) \) [from \( A(2\Delta L, S_1) = A^5(2\Delta L)A^0(2\Delta L, S_1) \)] and subsequently \( A^0(2\Delta L, 2S_1) \) [from \( A(2\Delta L, S_2) = A^5(2\Delta L)A^0(2\Delta L, 2S_2) \)] can be calculated. In the same way, size and strain coefficients for \( L = 4\Delta L \), \( 8\Delta L \) and so on are obtained. This procedure was first proposed by Eastabrook & Wilson (1952).

The method can be applied several times with different initial guesses for \( A^5(\Delta L) \). The possible values of \( A^5(\Delta L) \) lie between \( A(\Delta L, S_1) \) and 1. In general, the sets of Fourier coefficients obtained with all possible guesses \( A^5(\Delta L) \) are not very different and converge with increasing \( L \). An important disadvantage of this method of size–strain separation, compared with the WA analysis and the alternative analysis, is the lack of exactness for \( L \downarrow 0 \). A determination of \( \langle D \rangle \) from the initial slope of \( A^5(L) \) or of stored energy from \( \langle e^2 \rangle \) (see §II.B) may therefore be problematic. Another disadvantage is that only Fourier coefficients at \( L = 2^n\Delta L \) are obtained if \( S_2 = 2S_1 \) or, in general, at \( L = (S_2/S_1)^n\Delta L \), where \( n \in \mathbb{Z} \).

From \( L \) equal to a few times \( \Delta L \) onwards, the results obtained by this recursive analysis must resemble those obtained by the alternative analysis. For small \( L \), the alternative analysis is independent of an arbitrary initial guess and therefore more accurate. For larger \( L \), the results using the alternative analysis may become less accurate if the assumption regarding \( A^5(L) \) [see (9)] becomes invalid. In this range, the recursive analysis, which does not use an assumption regarding \( A^5(L) \) apart from the value of \( A^5(\Delta L) \), can be used to specify a band of possible results [by variation of the initial guess of \( A^5(\Delta L) \)] for the alternative analysis or any other separation method relying on the neglect of strain gradients. Thus, if strain gradients are known to be small and the detailed results of the alternative analysis lie within the band of the recursive analysis, the application of the alternative analysis is justified.

(iii) Interpolation of Fourier coefficients. A remarkable difference between the WA analysis and the alternative analysis is that the former uses Fourier coefficients of different profiles at the same \( L \) value, whereas the latter uses Fourier coefficients of different profiles at different \( L \) values. Specifically, for a first and second order of reflection, the alternative analysis uses \( A(L_1, S_1) \) and \( A(L/2, 2S_1) \). In practice, Fourier coefficients of a line profile are obtained only at specific \( L \) values, where the step size \( \Delta L \) is inversely proportional to the length of the measurement range in reciprocal space. The WA analysis is performed most easily with identical measurement ranges for a first and a second order of reflection, so that \( \Delta L_2 = \Delta L_1 \). For the alternative analysis, it would be easiest to measure the second order over a range twice as long, so that \( \Delta L_2 = 2\Delta L_1 \). In practice, however, the length of the measurement range is usually adapted to the width of the line profiles and limited by neighbouring reflections. Then, both methods require interpolation of Fourier coefficients for the analysis to be performed.

III. Application to simulated profiles

In the first presentation of the alternative analysis, simulated Fourier coefficients of line profiles were used to determine the ranges of applicability of the WA analysis and the alternative analysis (van Berkum, Vermeulen, Delhez, de Keijser & Mittemeijer, 1993). The relative amounts of size and strain broadening, the shape of the strain distributions \( p(e_L) \) and the degree of strain variation within the columns...
were the three parameters varied in that investigation. The WA and alternative analyses were applied to the simulated Fourier coefficients and the quality of the separation was evaluated on the basis of the deviations of the extracted size and strain Fourier coefficients from the true values. The combinations of parameter values for which the results of the WA and alternative analyses were acceptable are indicated schematically in Fig. 1.

In the investigation mentioned above, the size and strain distributions used were considered as realistic, without correspondence to an actual specimen. In this paper, the merits of both methods are again discussed using simulated Fourier coefficients, but this time the simulations represent a specific specimen in a detailed way. Complete expressions for the elastic strain fields associated with certain microstructural defects are taken as a starting point.

A. Misfitting inclusions

Suppose a specimen consists of misfitting inclusions in a matrix: the inclusions and the surrounding matrix are in a state of stress. The volume misfit may result, for example, from cooling from fabrication to room temperature if a difference exists between the thermal-expansion coefficients of the inclusions and the matrix. With the assumption of spherical inclusions and matrix crystallites of uniform size, purely elastic accommodation of the misfit and elastic isotropy and with neighbouring distortion fields being ignored, the Fourier coefficients of line profiles of the distorted matrix can be calculated. An additional calculation with zero misfit and all other parameters unchanged yields the size coefficients for the system and then the strain coefficients can be inferred. Using this model, the Fourier coefficients of experimental aluminium line profiles of two-phase AlSi alloys have been described to a good level of accuracy (van Berkum, Delhez, de Keijser & Mittemeijer, 1992).

As a realistic and representative example, Fourier coefficients of broadened Al 200 and Al 400 reflections were calculated for a composite of 12.5 vol.% silicon inclusions in an aluminium matrix. The radii of the inclusions and the matrix crystallites were 759 and 1518 Å, respectively. The linear misfit was $2.3 \times 10^{-3}$. The Fourier coefficients were defined with respect to the centroid of the profiles as the origin. The results obtained with the WA and alternative analyses are shown in Fig. 2(a).

From Fig. 2(a), it is clear that both the WA and the alternative analysis provide a good separation up to a high value of the correlation length $L$ (about 750 Å). For the WA analysis, this is probably because of the
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small strains ($\langle \epsilon_L^2 \rangle^{1/2} \simeq 5 \times 10^{-4}$) and the moderate deviation from a Gaussian distribution for $p(\epsilon_L)$ (e.g. $k_2 \simeq 3$ to 6, cf. Appendix A). Then, the higher-order terms in the series expansion of $\ln A^0(L, S_1)$ [see (A2)] are small. The two assumptions applied in the alternative analysis are apparently justified for correlation lengths up to about 750 Å. Indeed, the weak dependence of the true $\epsilon_L^2$ on $L$ (see Fig. 2b) indicates, amongst other things (see van Berkum, Delhez, de Keijser & Mittemeijer, 1992), that strain gradients in the columns are small. Further, the true $A^0(L)$ (see Fig. 2a) satisfies 9 within 10% for $L_1 < 750$ Å.

In Fig. 2(b), values of $\langle \epsilon_L^2 \rangle$ calculated from the $A^0(L, S_1)$ as obtained by the WA analysis using the approximation (5) are shown. These are compared with (i) true values of $\langle \epsilon_L^2 \rangle$ directly calculated from the strains in the crystallites, and (ii) values of $\langle \epsilon_L^2 \rangle$ calculated from the true $A^0(L, S_1)$ using (5). In general, the distributions $p(\epsilon_L)$ are non-Gaussian, (5) is not exact and the values (ii) deviate from the values (i). Then, the values ‘experimentally obtained’ obviously deviate from the values (i): even a perfect separation of size and strain Fourier coefficients would yield the values (ii) not (i). The differences between (ii) and (i) are small in the present case.

By fitting (A3) to the $\langle \epsilon_L^2 \rangle$ as obtained by the WA analysis, the strain broadening is physically interpreted (see §II.A). Depending on the length of the fitting range (30 to 300 Å) and the number of terms fitted (2 to 5), one obtains $\langle \epsilon_L^2 \rangle = 2.6 \times 2.8 \times 10^{-7}$ (true value is $2.8 \times 10^{-7}$) and $\langle \epsilon_L^2 \rangle = 0.7$ to $4 \times 10^{-11}$ Å$^{-2}$ (true value is $0.49 \times 10^{-11}$ Å$^{-2}$). Higher derivatives become rapidly more inaccurate owing to the deviations of the obtained $\langle \epsilon_L^2 \rangle$ from the true $\langle \epsilon_L^2 \rangle$.

The $A^0(L, S_1)$ as obtained by the alternative analysis can be interpreted by relating the coefficients of a polynomial fit to moments of $p(\epsilon_L)$ [first column of (A5); see §II.B]. Depending on the length of the fitting range (60 to 600 Å) and the number of terms fitted (1 to 4), the results are $\langle \epsilon_L^2 \rangle = 2.3$ to $2.6 \times 10^{-7}$ (true value is $2.8 \times 10^{-7}$) and $\langle \epsilon_L^4 \rangle = 2 \times 7 \times 10^{-13}$ (true value is $5.2 \times 10^{-13}$). Because of the errors introduced by the neglect of strain gradients, the inaccuracy of higher moments increases rapidly.

The results obtained using these simulations can also be compared with the applicability regions indicated in Fig. 1. In this example, comparable amounts of size and strain broadening are present, strains are slowly varying with distance and the shapes of $p(\epsilon_L)$ are not too far from Gaussian. Therefore, this case should be compared with a location indicated by ‘inclusions’ in Fig. 1. According to the validity regions indicated, both size-strain separation methods should yield reliable results for not too large $L$, in agreement with the above.

B. Small-angle grain boundaries

As a second example, Wilkens’s diffraction model for an array of small-angle grain boundaries is used (Wilkens, 1979). The symmetrical pure tilt boundary, discussed here, is an array of parallel edge dislocations with their Burgers vectors $b$ perpendicular to the boundary. The model consists of a periodic repetition of such small-angle boundaries with alternating ‘sign’ (extra half-planes upward/downward). The crystal containing the small-angle boundaries is taken to be infinitely large and hence the line broadening can be considered as pure strain broadening [$A^0(L) = 1$ for all $L$]. The diffraction vector is taken parallel to $b$. For the calculation of the Fourier coefficients of the line profiles, the procedure described by Wilkens is followed.

The results of the WA and the alternative analysis depend significantly on the configuration of the small-angle boundaries, characterized by the ratio $\Delta/\delta$, where $\Delta$ is the spacing between the small-angle boundaries and $\delta$ is the spacing between dislocations within a boundary (see Wilkens, 1979). Here, the results for $\Delta/\delta = 2$ are discussed. Poisson’s ratio was set to $\frac{1}{3}$ and first and second orders of reflection were calculated using $S_1b = 1$ and $S_2b = 2$, where $b = |b|$. The results of both separation methods in terms of $A^0(L)$, $A^0(L, S_1)$ and, for the WA analysis, $\langle \epsilon_L^2 \rangle$ are shown in Fig. 3.

Both the WA and the alternative analysis yield results that deviate significantly from the true values. Only in the limit $L \downarrow 0$ do both methods function properly. Both methods yield an extensive concave part in $A^0(L)$, corresponding to physically impossible negative values of $p(D)$. In practice, where true values are unknown, this concave part is one of the rare indicators that assumptions in the method applied are incompatible with the specimen analysed. Neither an extrapolation of $\langle \epsilon_L^2 \rangle$ to $L = 0$ for the WA analysis nor a polynomial fit to $A^0(L, S_1)$ for the alternative analysis (see §II.B) yields physically meaningful information.

The reason for the failure of both methods even at relatively small $L$ is violation of the (different) assumptions underlying the methods. The range of $L$ for which the WA analysis is valid depends on the deviation of the actual strain distributions $p(\epsilon_L)$ from a Gaussian [see after (A2)]. In the present case, the distributions are much more ‘peaked’ than a Gaussian (e.g. $k_2 > 100$ for small $L$, cf. Appendix A). Therefore, the neglect of the term containing $\langle \epsilon_L^2 \rangle$ in the expansion of $\ln A^0(L, S_1)$ [see (A2)] is already problematic for small $L$ [cf. deviation of curve (ii) from (i) in the $\langle \epsilon_L^2 \rangle$ plot in Fig. 3(b)]. The range of $L$ for which the alternative analysis is valid depends on the shape of the size distribution and on the magnitude of the strain gradients (see §II.B). Since
there is no size broadening simulated in this example (the crystal is taken to be infinitely large), the failure of the alternative analysis is caused by large strain gradients. Indeed, with respect to isolated dislocations, ordering of dislocations in small-angle boundaries decreases the average strains in the specimen but increases the strain gradients close to the boundary [see Fig. 2(b) of Wilkens (1979)]. The very strong increase in the true \( \langle e^2 \rangle \) with decreasing \( L \) in Fig. 3(b) confirms this.

In terms of the three broadening dimensions indicated in Fig. 1, the example discussed must be compared with the location labelled ‘SABs’ in this figure: pure strain, strongly non-Gaussian \( p(e_L) \) and significant strain gradients. This location pertains to the region where neither of the two size–strain separation methods is applicable, in agreement with the above.

One may question if the example discussed has to be considered as one of pure strain broadening. It might be argued that the small-angle boundaries break up the crystal into domains that diffract incoherently with respect to each other. However, it can be shown that this phenomenon only occurs when lattice defects produce very large local strains concentrated in very small isolated parts of a specimen (van Berkum, Delhez, de Keijser & Mittemeijer, 1994). If this were to occur in the present case, the \( A^0(L) \) values to be obtained using the size–strain separation methods would satisfy \( A^0(L) = 1 - |L|/\Delta \) for \( |L| \leq \Delta \). Clearly, for \( \Delta/\delta = 2 \), this result is not obtained either. However, for much larger values of \( \Delta/\delta \), the small-angle boundaries do tend to act as coherence boundaries. In this case, the WA analysis yields approximately \( \Delta \) for the average crystallite size, a result that can again be interpreted in a physically meaningful way. The results obtained by the alternative analysis remain ambiguous for large \( \Delta/\delta \).

IV. Applications to experimental profiles

To test newly developed methods of analysis, it is always desirable to use experimental data in addition to simulated data. Unexpected complications may arise owing to the experimental circumstances. Experimental line profiles allow investigation of the (combined) effects of counting statistics, background removal, peak overlap, imperfect standards and deconvolution procedure, which do not occur using simulated data. However, for experimental data, no true values are known to check the separation results. A general test on the results is to probe their physical plausibility: values of \( A^0(L) \) or \( A^0(L, S_1) \) larger than 1 are impossible, a downward curvature of \( A^0(L) \) is unrealistic, \( A^0(L, S_1) \) rising with increasing \( L \) is unlikely etc.

For the present purpose, especially suitable data are those from specimens of which some information on the size or strain is known, either obtained from experiments other than diffraction line broadening or derived from characteristics of the preparation, deformation or other treatment the specimen has been subjected to. Then, the size and strain parameters obtained using the separation methods can be compared with this information.

A. Microstructural change in thin aluminium layers

Thin aluminium layers were prepared by physical vapour deposition in high vacuum onto \( \text{Si}(100) \) single-crystal wafers and subsequently annealed at 723 K (for details see Vermeulen, Delhez, de Keijser & Mittemeijer, 1994). During cooling to room temperature, the aluminium layers are plastically deformed owing to the development of high thermal stresses. At room temperature, considerable relaxation of the residual stresses occurs within a few days. The relaxation process is accompanied by a measurable change in line breadth related to changes in the dislocation density and arrangement (Vermeulen, Delhez & Mittemeijer, 1992). After 12 and 110 h of
relaxation at room temperature, the Al 111 and 222 reflections were recorded on a Siemens D500 diffractometer, equipped with a scanning position-sensitive detector and an incident-beam monochromator set to Co Kα1. For all four line profiles, the background was subtracted.* The remainder of the α2 component of the Kα doublet (about 2% of α1) was removed and a Fourier transformation was performed. No ideal 'standard' specimen was available for the thin aluminium layers. Therefore, a direct comparison of the line profiles after 12 and 110 h of relaxation was made (see §II): the profiles with the larger line breadths (12 h) were deconvoluted with the ones with the smaller line breadths (110 h). Finally, the WA and alternative analyses were applied. The results, representing the decrease in lattice imperfection evoked by relaxation from 12 to 110 h, are shown in Fig. 4. Owing to the relatively small decrease in line broadening during the relaxation, the Fourier coefficients after deconvolution \( A(L, S) \) [the product of \( A^S(L) \) and \( A^D(L, S) \) in Fig. 4] drop only from 1 to about 0.85 with \( L \) increasing from 0 to 1000 Å.

It is unlikely that the relaxation at room temperature could cause a change in the crystallite sizes. Hence, the values of \( A^D(L) \) after 12 and 110 h should be equal. Then, in the above-described comparison (12 h data deconvoluted with 110 h data), the size coefficients drop out completely. After size–strain separation, the ‘size’ coefficients, in this case representing the difference in size broadening, should be equal to unity.

The WA analysis yields the expected results \([A^S(L) \approx 1]\) up to \( L \approx 100 \) Å. For larger values of \( L \), before the results start to scatter owing to the effects of counting statistics (at \( L \approx 600 \) Å), a significant deviation of \( A^S(L) \) from unity is observed. These values are considered to be incorrect because they indicate an unlikely change in the size distribution during the relaxation. In conclusion, only a small portion of the statistically reliable data can be interpreted by the WA analysis.

The alternative analysis yields the expected results \([A^S(L) \approx 1]\) over a longer range than the WA analysis: up to \( L \approx 350 \) Å. Again, for larger \( L \) values, \( A^S(L) \) starts to deviate from unity, indicating that the results become incorrect. In conclusion, a substantial portion of the statistically reliable data can be interpreted by the alternative analysis.

Finally, note that the tangents at \( L = 0 \) to the \( A^S(L) \) curves obtained by both methods are clearly horizontal. Since both methods yield correct \( A^S(L) \) for \( L \perp 0 \), this observation supports the assumption, made in advance, of negligible changes in the average crystallite size during relaxation.

A discussion of the line broadening in terms of dislocation density and arrangement will be given by Vermeulen, Delhez, de Keijser & Mittemeijer (1994).

### B. Ball-milled molybdenum powder

A very different set of experimental line profiles was taken from molybdenum powder plastically deformed by ball milling. The powder was milled for 45 min in a horizontally moving cylinder with two balls. From scanning-electron-microscopy observations, the average particle diameter before milling was estimated to be between 0.5 and 1 μm; after milling, it was approximately halved. Lattice-parameter measurements did not indicate any contamination of the molybdenum powder.

A very thin and flat X-ray diffraction specimen was prepared from the milled powder. The procedure employed was analogous to that used for the standard specimen, which was prepared from annealed silicon powder (see van Berkum, Sprong, de Keijser, Sonneveld, Vermeulen & Delhez, 1992). The Mo 110

![Fig. 4. Results of (a) the WA analysis and (b) the alternative (ALT) analysis applied to the 111 and 222 reflections of an aluminium layer after 12 h of relaxation at room temperature using measurements after 110 h as 'standard' profiles. The Fourier coefficients represent only the change in the microstructure owing to the relaxation between 12 and 110 h. Dashed lines indicate the expected values for \( A^D(L) \). Note the vertical scale values.](image-url)
The 220 and Si 220 and 422 reflections were recorded on a Siemens D500 diffractometer using Cu Kα radiation.

For all line profiles, the background was subtracted, the α₂ component of the Kα doublet was removed and a Fourier transformation was performed. The Si 220 reflection was used as standard profile for Mo 110; Si 422 was used for Mo 220. The Si 220 and Mo 110 reflections do not correspond very well in 2θ position but their combination is possible because the breadth of the α₂-stripped instrumental line profile for the experimental set-up used here has a flat minimum in this range. Finally, the WA and alternative analyses were applied. The results are shown in Fig. 5.

The two methods yield opposing results: the WA analysis attributes most of the broadening to size [extrapolation of the linear part of \( A^D(L) \) to the abscissa yields \( \langle D \rangle = 340 \text{ Å} \)], whereas the alternative analysis detects dominant strain broadening with only a small size contribution (\( \langle D \rangle = 830 \text{ Å} \)). For the following reasons, the results obtained using the alternative analysis seem to have greater credibility.

Firstly, the value of \( \langle D \rangle \) obtained by the WA analysis (340 Å) is very small. The particles of the milled powder are probably still single-crystalline, so that the crystalline diameter is not much smaller than the particle diameter (between 0.25 and 0.5 μm, see above). The area-averaged column length \( \langle D \rangle \) for a polyhedral crystallite is about \( \frac{1}{10} \) to \( \frac{1}{4} \) times its 'diameter' (cf. \( K_k \) in Langford & Wilson, 1978). Therefore, an average column length of 1 to 4 × 10³ Å is to be expected. Hence, the value of \( \langle D \rangle \) according to the alternative analysis (830 Å) is closer to the expected value than the value according to the WA analysis.

A second reason for considering the results of the alternative analysis to be more realistic is the behaviour of the obtained \( A^D(L, S_1) \). It has been shown for a random distribution of dislocations (Krivoglaz, 1969) and for other distributions (Wilkins, 1970; Krivoglaz, Martynenko & Ryaboshapka, 1983; Groma, Ungár & Wilkens, 1988) that the elastic strains around dislocations give rise to the following behaviour of \( A^D(L, S_1) \) for small to moderate \( L \) values:

\[
-L^{-2} \ln [A^D(L, S_1)] = (\pi/2)CR_0^2S_1^2L^2 \ln (C'R_e/bS_1L),
\]

(15)

where \( \rho \) is the dislocation density, \( C \) and \( C' \) are dimensionless constants depending on the angles between the diffraction vector and the Burgers and line vectors of the dislocations and \( R_e \) is a length parameter depending on the configuration of the dislocations. From (15), it follows that a plot of \( -L^{-2} \ln [A^D(L, S_1)] \) versus \( \ln L \) should yield a straight line. In Fig. 6, it can be seen that this behaviour might be present in the \( A^D(L, S_1) \) according
to the WA analysis for $90 < L < 250\,\text{Å}$. For the alternative analysis, such behaviour of $A^0_1(L, S_1)$ is definitely present over a much larger range: $90 < L < 500\,\text{Å}$ (a physical interpretation according to (15) yields $C_P = 6.6 \times 10^{14}\,\text{m}^{-2}$ and $C_R_e = 1.1 \times 10^{13}\,\text{Å}$).

A third indication that the results of the present WA analysis may be less reliable is provided by checking the assumptions underlying the methods. The WA analysis is possible if either $(2\pi L S_1)^2 \langle e_1^2 \rangle \ll 1 \text{ or the } p(e_1) \text{ close to Gaussian} \text{ [see after (42)]}$. For, say, $L = 100\,\text{Å}$ (approximately the third data point) and $S_1 = 0.90\,\text{Å}^{-1}$ (Mo 220), it follows that $\langle e_1^2 \rangle = 5 \times 10^{-6}$ and, therefore, that $(2\pi L S_1)^2 \langle e_1^2 \rangle = 1.6$, so that the first condition is not met. The second condition is also not met, because for strains around dislocations the $p(e_1)$ deviate significantly from being Gaussian: they have tails proportional to $|e_1|^3$ (Wilkens, 1984). The alternative analysis is applicable if both $L \ll \langle D \rangle$ (see Appendix B) and $(2\pi L S_1)^2 \langle e_1^2 \rangle \ll 12 \langle e_1^2 \rangle$ [i.e. (46)]. For the same $L$ value as above (100Å), the first condition is met by a factor of 8. A check on the second condition is impossible here because values of $\langle e_1^2 \rangle$ and $\langle e_1^2 \rangle$ are not available.

A 'hook effect' (physically impossible concave part close to $L = 0$) is obtained in $A^0_1(L)$ if the WA analysis is applied. Extrapolation to $L = 0$ of the linear part of the corresponding $A^0_1(L)$ curve gives an ordinate value of 1.08 (see Fig. 5a). The $A^0_1(L)$ curve obtained by the alternative analysis does not show a systematic 'hook effect'. The inevitable truncation of the measured line profiles may cause the 'hook effect' in the WA analysis; the effects of such truncation on the results of the alternative analysis have not yet been investigated. On the other hand, the 'hook effect' in the WA analysis may indicate systematic errors owing to violation of the underlying assumption.

WA analyses yielding hook effects and surprisingly small crystallite sizes have often been found in the past for comparably plastically deformed metallic specimens (Warren, 1959; Klug & Alexander, 1974, and references therein). Such results may be erroneous because the assumptions inherent in the WA analysis are violated; the alternative analysis may provide more reliable data for such cases.

Also, the recursive analysis, described in §II.C(ii), was applied to the line profiles of the ball-milled molybdenum powder. The results are compared with those obtained using the alternative analysis in Fig. 7. From the two extreme values for the initial guess of $A^0_1(\Delta L)$, a range of possible results for the alternative analysis is calculated [cf. §II.C(iii)]. The results obtained here by using the alternative analysis fall approximately within this range for $L$ values up to 500Å. This means that, if the neglect of strain gradients was justified for this specimen (this assumption is inherent in both the recursive and the alternative analyses), the assumption applied to $A^0_1(L)$ did not introduce significant errors in the size-strain separation.

V. Concluding remarks

Using different assumptions for the distributions of crystallite sizes and elastic strains, different methods to interpret diffraction line broadening are possible. The frequently applied Warren–Averbach analysis relies on either small strains or approximately Gaussian strain distributions. The alternative analysis discussed in this paper relies on small strain gradients and large crystallite sizes or a broad size distribution.

For both the Warren–Averbach and the alternative analysis, a logarithmic and a linear version can be derived. The linear versions are less sensitive to propagation of random errors (e.g. due to counting statistics); in many cases, the logarithmic ones introduce less systematic errors.

Specimens exist for which both methods yield comparable and correct results up to large correlation lengths $L$, e.g. a matrix containing misfitting inclusions. The reverse is also possible: both methods already give erroneous results at small $L$, e.g. crystals containing small-angle grain boundaries. Erroneous results for size and strain are always paired: overestimation of the size broadening goes with underestimation of the strain broadening and vice versa. Certainty about the reliability of results obtained in practice is impossible. At least, the results should be in accordance with the assumptions used in the method. In addition, external information available on the specimen concerned can be used to assess the plausibility of the results.

[Fig. 7. Results of the recursive (markers and dashed lines) and alternative (full lines) analyses applied to the 110 and 220 reflections of ball-milled molybdenum. For the recursive analysis, the two extreme initial guesses $A^0_1(\Delta L) = 1$ and $A^0_1(\Delta L) = A(\Delta L, S_1)$, where $\Delta L = 31\,\text{Å}$, were used. Note the increasing step size in $L$ for the recursive analysis.]
Specimens subjected to severe plastic deformation appear to be analysed more reliably by the alternative analysis. Owing to increased violation of the underlying assumption, with increasing $L$ the Warren-Averbach analysis attributes ever more broadening incorrectly to size, yielding a too small average crystallite size and a too rapid decrease in the mean-squared strains $\langle \varepsilon_i^2 \rangle$. The assumptions used in the alternative analysis appear to be applicable up to relatively large $L$ for such specimens.

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**APPENDIX A**

**Series expansion of $A^0(L, S_i)$**

Expansion of the cosine in the general expression (4) for $A^0(L, S_i)$ in a Taylor series yields

$$A^0(L, S_i) = 1 - \frac{y^2}{2!} \langle \varepsilon_i^2 \rangle + \frac{y^4}{4!} \langle \varepsilon_i^4 \rangle - \frac{y^6}{6!} \langle \varepsilon_i^6 \rangle + \ldots$$

$$= 1 - \frac{1}{2!} y^2 \langle \varepsilon_i^2 \rangle + \frac{k_2}{4!} \left[ y^2 \langle \varepsilon_i^2 \rangle \right]^2$$

$$- \frac{k_3}{6!} \left[ y^2 \langle \varepsilon_i^2 \rangle \right]^3 + \ldots,$$

where $y = 2\pi LS_i$ and $k_1 = \langle \varepsilon_i^2 \rangle/\langle \varepsilon_i \rangle^2$ $(i \geq 2)$. Substitution of (A1) in a Taylor series for $\ln [A^0(L, S_i)]$ in $A^0(L, S_i) = 1$ yields

$$\ln [A^0(L, S_i)] = \frac{1}{2!} y^2 \langle \varepsilon_i^2 \rangle + \frac{(k_2 - 3)}{4!} \left[ y^2 \langle \varepsilon_i^2 \rangle \right]^2$$

$$- \frac{(k_3 - 15k_2 + 30)}{6!} \left[ y^2 \langle \varepsilon_i^2 \rangle \right]^3 + \ldots.$$  

(A2)

Restriction of the right-hand side of (A2) to the first term leads to (5). This approximation is reasonable if $y^2 \langle \varepsilon_i^2 \rangle < 1$ or if the values of $k_i$ are not too far from those for a Gaussian distribution: $k_2 = 3$, $k_3 = 15$, ... (assuming that $\langle \varepsilon_i \rangle = 0$, which is always the case if $S_i$ corresponds to the centroid of the structural profile). The two conditions are related: the values of $k_i$ determine the range of $y$ for which the approximation is valid. Fourth, sixth and higher moments of $p(\varepsilon_i)$ are increasingly influenced by the tails of the distribution. Many distributions have more pronounced tails than a Gaussian and therefore (much) higher values of $k_i$.

Restriction of the right-hand side of (A1) to the first two terms leads to (11). The conditions for this approximation are $y^2 \langle \varepsilon_i^2 \rangle < 1$ or $k_i$ small (as small as possible). The smallest possible value of $k_2$ for a unimodal distribution is $\frac{7}{2}$ (van Berkum, 1994). The term containing $y^4$ (usually the term that will limit the applicability of the approximation) is therefore always smaller in (A2) than in (A1).

To derive the explicit $L$ dependence of $A^0(L, S_i)$, the moments of $p(\varepsilon_i)$ are expressed in terms of the local strain $\varepsilon_0$ and its derivatives. With the assumption that averages of $\varepsilon_0$ and its derivatives at the column ends vanish, the following expression has been derived (Turunen, de Keijser, Delhez & Pers, 1983):

$$\langle \varepsilon_i^2 \rangle = \langle \varepsilon_0^2 \rangle - \frac{1}{12} \langle \varepsilon_0^2 \rangle L^2 + \frac{1}{360} \langle \varepsilon_0^2 \rangle L^4 + \ldots.$$  

(A3)

A comparable expression for the fourth moment of $p(\varepsilon_i)$ can be analogously derived:

$$\langle \varepsilon_i^4 \rangle = \langle \varepsilon_0^4 \rangle - \frac{1}{2} \langle \varepsilon_0^2 \rangle \langle \varepsilon_0^2 \rangle L^2 + \frac{1}{60} \langle \varepsilon_0^2 \rangle \langle \varepsilon_0^4 \rangle L^4 + \ldots.$$  

(A4)

Substitution of such expressions into (A1) yields

$$A^0(L, S_i) = 1 - \frac{y^2}{2!} \langle \varepsilon_0^2 \rangle + \frac{y^4}{4!} \langle \varepsilon_0^4 \rangle - \frac{y^6}{6!} \langle \varepsilon_0^6 \rangle + \ldots$$

(A5)

If $\varepsilon_0$ is slowly varying in space, the derivatives are small on the average and, for small $L$, the series between square brackets in (A5) are dominated by their first terms. In this case, $A^0(L, S_i)$ can be written as a function of $y$ only, which means that (8) is valid.

With increasing $L$, the term limiting the applicability of (8) is in general the second term in the first series in (A5). Thus, the range of $L$ for which (8) is valid is determined by the condition

$$\langle \varepsilon_0^2 \rangle L^2 \ll 12 \langle \varepsilon_0^2 \rangle.$$  

(A6)

This means that (8) holds for $L$ up to the order of magnitude of the spatial width of the peaks or humps in $\varepsilon_0$. 
The difference between the assumptions used in the WA and alternative analyses \((5) \text{ and } (8), \) respectively\] can be discussed as follows. The terms between square brackets in \((A5)\) can be considered to form an infinitely large matrix of terms. The rows of this matrix represent \(\langle e_3^2 \rangle, \langle e_3^4 \rangle, \) etc. \(\text{cf. } (A3), (A4).\) Expansion of \(\ln [A^P(L, S)]\) results in a similar matrix. For either the logarithmic or linear version, in the WA analysis only the first row of the matrix is taken into account and in the alternative analysis only the first column is taken into account. The additional rows are determined by the shape of the frequency distribution \(p(e_1)\); the additional columns are determined by the spatial distribution of \(e_0.\) For \(L\) decreasing to zero, \(A^P(L, S)\) approaches \(1 - \frac{1}{2} y^2 \langle e_0^2 \rangle\) and both approximations used are valid regardless of the nature of the spatial distribution or the frequency distribution of the strain.

**APPENDIX B**

Series expansion of \(A^S(L)\)

In the general expression (3) for \(A^S(L),\) the distribution \(p(D)\) can be expanded in a Taylor series. Integration of the individual terms yields

\[
A^S(L) = 1 - \frac{|L|}{\langle D \rangle} + \frac{|L|^2 p(0)}{2! \langle D \rangle} + \frac{|L|^3 p'(0)}{3! \langle D \rangle} + \ldots \quad (B1)
\]

Substitution of \((B1)\) in a Taylor series for \(\ln [A^S(L)]\) in \(A^S(L) = 1\) yields

\[
\ln [A^S(L)] = -\frac{1}{\langle D \rangle} \left[ 1 - \frac{p(0)}{2} - \frac{1}{2 \langle D \rangle} \right] - \frac{1}{\langle D \rangle} \left[ \frac{p'(0)}{3!} + \frac{p(0)}{2! \langle D \rangle} - \frac{1}{3 \langle D \rangle^2} \right] - \ldots \quad (B2)
\]

If the term between square brackets on the right-hand side of \((B2)\) is approximated from \((B2)\). This approximation is valid if \(|L|/\langle D \rangle \ll 1\) or if the size distribution \(p(D)\) is not too far from the exponential distribution \(p(D) = (1/\langle D \rangle) \exp (-D/\langle D \rangle).\) As for \(A^P(L, S),\) the two conditions are related: the more \(p(D)\) deviates from the exponential distribution, the shorter the range of \(L\) for which the approximation is valid. However, for \(A^S(L),\) very large values of the coefficients in the expansion, determined by the derivatives \(p^{(n)}(0),\) seem physically unrealistic, whereas in the case of \(A^P(L, S)\) large values of \(k_i\) may occur in practice.

Restriction of \((B1)\) to two terms on the right-hand side is the basis for \((13).\) This approximation is justified if \(|L|/\langle D \rangle \ll 1\) or if \(p(0)\) and all derivatives \(p^{(m)}(0)\) are small. Here, the ideal distribution is \(p(D) = \delta(D - \langle D \rangle),\) i.e. the \(\delta\)-type distribution, representing a monodisperse system, for which the approximation is exact up to \(D = \langle D \rangle.\)

**APPENDIX C**

Propagation of random errors

I. Warren–Averbach analysis

Suppose Fourier coefficients of a first and a second order of reflection \(A(L, S_1)\) and \(A(L, S_2)\) with \(S_2 = 2S_1\) are used to separate size and strain broadening. For the logarithmic version of the WA analysis \((7),\) the size Fourier coefficients are calculated from

\[
A^S(L)_{\log} = \left[ \frac{A(L, S_1)^2}{A(L, 2S_1)} \right]^{1/3} \quad (C1)
\]

(subscripts \(\log\) and \(\text{lin}\) are used to distinguish between values obtained by the logarithmic and the linear versions, respectively). If the random errors in the Fourier coefficients are not too large, the variance of \(A^S(L),\) \(\sigma^2[A^S(L)],\) can be expressed in the variances of both original coefficients \(\sigma^2[A(L, S_1)]\) and \(\sigma^2[A(L, 2S_1)]\) as follows \((\text{Arley & Buch, } 1950):\)

\[
\sigma^2[A^S(L)] \approx \left[ \frac{\partial A^S(L)}{\partial A(L, S_1)} \right]^2 \sigma^2[A(L, S_1)] + \left[ \frac{\partial A^S(L)}{\partial A(L, 2S_1)} \right]^2 \sigma^2[A(L, 2S_1)] \quad (C2)
\]

Substitution of the partial derivatives as calculated from \((C1)\) into \((C2)\) yields

\[
\sigma^2[A^S(L)]_{\log} \approx (16/9) \sigma^2[A(L, S_1)] + (1/9) \sigma^2[A(L, 2S_1)] \quad (C3)
\]

where \(\sigma^2[x]\) denotes the ‘relative variance’ \(\sigma^2[x]/x^2.\)

Using the linear version of the WA analysis \((12),\)

\[
A^S(L)_{\text{lin}} = (1/3)[4A(L, S_1) - A(L, 2S_1)] \quad (C4)
\]

Substitution of the partial derivatives as calculated from \((C4)\) into \((C2)\) yields

\[
\sigma^2[A^S(L)]_{\text{lin}} \approx \frac{16}{9} \left[ \frac{A(L, S_1)}{A^S(L)_{\text{lin}}} \right]^2 \sigma^2[A(L, S_1)] + \left[ \frac{A(L, 2S_1)}{A^S(L)_{\text{lin}}} \right]^2 \sigma^2[A(L, 2S_1)] \quad (C5)
\]

The differences between \((C3)\) and \((C5)\) are the fractions between large square brackets in \((C5).\) Since \(A(L, S_1) \leq A^S(L)\) and \(A(L, 2S_1) \leq A^S(L)\) (otherwise the strain Fourier coefficients exceed unity and the WA analysis is nonsensical), it follows that \(\sigma^2[A^S(L)]_{\text{lin}} \leq \sigma^2[A^S(L)]_{\log}.\) For not too large errors in the experimental Fourier coefficients, the relative variance \(\sigma^2[A^P(L, S_1)]\) approximately equals the relative variance \(\sigma^2[A(L)]\) [since \(A^S(L)A^P(L, S_1) = A(L, S_1)]\) and the conclusion that \(\sigma^2[A^P(L, S_1)]_{\text{lin}} \leq \sigma^2[A^P(L, S_1)]_{\log}\) is reached. Thus, the linear version of the WA analysis is less
sensitive to propagation of random errors in the experimental Fourier coefficients than the logarithmic one.

II. Alternative analysis

In the logarithmic version of the alternative analysis [(10)], $A^y(2L)$ is calculated from

$$A^y(2L)_{\log} = \frac{A(2L, S_1)}{A(L, 2S_1)}.$$  (C6)

From (C2), the relative variance of $A^y(2L)_{\log}$ is

$$\sigma^2_y[A^y(2L)_{\log}] \approx 4\{\sigma^2_y[A(2L, S_1)] + \sigma^2_y[A(L, 2S_1)]\}.  \quad (C7)$$

Using the linear version of the alternative analysis [(14)], one can calculate $A^x(2L)$ from

$$A^x(2L)_{l\in} = \frac{A(2L, S_1)}{2A(L, 2S_1) - A(2L, S_1)}  \quad (C8)$$

and, from (C2), the relative variance of $A^x(2L)_{l\in}$ is

$$\sigma^2_x[A^x(2L)_{l\in}] \approx 4\left[\frac{A(L, 2S_1)}{2A(L, 2S_1) - A(2L, S_1)}\right]^2 \times \sigma^2_y[A(2L, S_1)] + \sigma^2_y[A(L, 2S_1)]. \quad (C9)$$

The difference between (C7) and (C9) is the term between large square brackets in (C9). Since $A(L, 2S_1) \geq A(2L, S_1)$ (otherwise $A^x(2L) > 1$ and the alternative analysis is nonsensical), it follows that $\sigma^2_y[A^y(2L)]_{\log} \leq \sigma^2_x[A^x(2L)]_{l\in}$. The relative variance of $A^y(2L, S_1)$ approximately equals that of $A^y(2L)$ (cf. Appendix C, §I), so that $\sigma^2_x[A^x(2L, S_1)]_{l\in} \leq \sigma^2_y[A^y(2L, S_1)]_{\log}$. Thus, as for the WA analysis, the linear version is less sensitive to propagation of random errors in the experimental Fourier coefficients into the size and strain Fourier coefficients.

References


