with the definitions already given in equations (3.6.24) and (3.6.25).

The functional forms of equations (3.6.28) and (3.6.29) clearly suggest that the profile for a log-normal distribution of domains (which is frequently encountered in practice) is not Voigtian: all traditional line-profile analysis methods (based on Voigt or pseudo-Voigt functions) are therefore unable to correctly deal with a log-normally dispersed powder.

By analogy to the monodisperse case, it is possible to relate the parameters of the polydisperse system to the size obtained with traditional methods (Warren–Averbach and Williamson–Hall, respectively). The following holds (Krill & Birringer, 1998; Scardi & Leoni, 2001):

$$\langle L\rangle_S = \frac{1}{K_k}\frac{M_{i,3}}{M_{i,2}}, \quad \langle L\rangle_V = \frac{1}{K_\beta}\frac{M_{i,4}}{M_{i,3}}. \tag{3.6.30}$$

Here, it is clear that diffraction does not provide the first moment of the distribution directly: ratios between high-order moments are involved.

Using an analytical expression for the description of a size distribution can help in stabilizing the results (as the size distribution curve is forced to be zero at very small and very large size values). Some doubts can, however, arise as to the physical validity of this forcing. An example is the case of a multimodal system. The traditional LPA techniques are unable to directly deal with multimodal size distributions. In cases where the multimodal character is clear and the various distribution are well behaved (*i.e.* when they can be modelled with analytical functions), the pattern can be usually modelled by considering the material as made of different fractions, each of them characterized by a different size distribution.

A possible alternative has been proposed in the literature: replacing the analytical distribution with a histogram. The ability of this model to fit the experimental data has been demonstrated (Leoni & Scardi, 2004; Matěj *et al.*, 2011); a regularization might be necessary to stabilize the shape and/or smoothness of the size distribution. The quality of the measurement and the availability of models describing all contributions to the peak broadening are in most cases the limiting factors for extensive use of the histogram model: correlations of small sizes with the background and with features such as thermal diffuse scattering (Beyerlein *et al.*, 2012) can in fact occur. So far, this is the only available method for exploring cases where the analytical models are unable to correctly describe the observed broadening.

3.6.2.6.5. *Strain broadening (lattice distortions)*

A local variation of the lattice spacing (due, for example, to the presence of a defect) leads to an average phase term that, in general, is a complex quantity:

$$\begin{aligned}\langle\exp[2\pi i\psi_{hkl}(L)]\rangle &= \langle\cos[(2\pi L d^*_{\{hkl\}}\varepsilon_{\{hkl\}}(L)]\rangle \\ &\quad + i\langle\sin[2\pi L d^*_{\{hkl\}}\varepsilon_{\{hkl\}}(L)]\rangle \\ &= A^D_{\{hkl\}}(L) + iB^D_{\{hkl\}}(L).\end{aligned} \tag{3.6.31}$$

The strain $\varepsilon_{\{hkl\}}(L)$ represents the relative displacement of atoms at a (coherence) distance L along the scattering vector hkl. Knowledge of the actual source of distortion allows the explicit calculation of the various terms (van Berkum, 1994). It is quite customary to assume that the strain is the same for symmetry-equivalent reflections [$\varepsilon_{hkl}(L) = \varepsilon_{\{hkl\}}(L)$]: this is a reasonable hypothesis for a powder, where we assume that any configuration is equally probable.

Traditional LPA methods such as the Warren–Averbach method (Warren & Averbach, 1950, 1952; Warren, 1990) take a first-order MacLaurin expansion of equation (3.6.31) to extract the microstrain contribution from the measured data:

$$A^D_{\{hkl\}}(L) \cong 1 - 2\pi^2 L^2 d^{*2}_{\{hkl\}}\langle\varepsilon^2_{\{hkl\}}(L)\rangle, \tag{3.6.32}$$

$$B^D_{\{hkl\}}(L) \cong -\frac{4}{3}\pi^3 L^3 d^{*3}_{\{hkl\}}\langle\varepsilon^3_{\{hkl\}}(L)\rangle. \tag{3.6.33}$$

The term in equation (3.6.33) would cause peak asymmetry. However, we usually consider only the second-order moment of the strain distribution (*root-mean strain* or *microstrain*) and thus symmetric peaks. Owing to the anisotropy of the elastic properties, the broadening described by equation (3.6.32) is in general anisotropic: an extensive discussion of strain anisotropy and of the order dependence of strain broadening can be found, for example, in Leineweber & Mittemeijer (2010) and Leineweber (2011). It should be stressed that in their original form, traditional line-profile methods are unable to deal with this anisotropy (corrections have been proposed for particular cases, for example, in the so-called modified Williamson–Hall (MWH) and modified Warren–Averbach (MWA) analyses; Ungár & Borbély, 1996).

3.6.2.6.6. *Dislocations*

Dislocations are often the main source of strain broadening. The magnitude of this broadening depends not only on the elastic anisotropy of the material, but also on the relative orientation of the Burgers and diffraction vectors with respect to the dislocation line (Wilkens, 1970*a*,*b*). This problem was analysed in the 1960s by Krivoglaz and Ryaboshapka (Krivoglaz & Ryaboshapka, 1963; Krivoglaz, 1969) and then subsequently reprised and completed by Wilkens (1970*a*,*b*). Further elements have been added to put it into the present form (see, for example, Krivoglaz *et al.*, 1983; Groma *et al.*, 1988; Klimanek & Kuzel, 1988; van Berkum, 1994; Kamminga & Delhez, 2000). For the purpose of WPPM, the distortion Fourier coefficients caused by dislocations can be written as

$$A^D_{\{hkl\}}(L) = \exp[-\tfrac{1}{2}\pi b^2\overline{C}_{\{hkl\}}\rho d^{*^2}_{\{hkl\}}L^2 f(L/R'_e)], \tag{3.6.34}$$

where b is the modulus of the Burgers vector, $\overline{C}_{\{hkl\}}$ is the so-called average contrast factor of the dislocations, ρ is the density of the dislocations and R'_e is an effective outer cutoff radius. Only the low-L trend of equation (3.6.34) is well reproduced by Wilkens' theory: a decaying function $f(L/R'_e)$ has thus been introduced to guarantee a proper convergence to zero of the Fourier coefficients for increasing L. Actually, the function $f^*(\eta)$ is mostly quoted in place of (L/R'_e), where $\eta = (e^{-1/4}/2)L/R'_e$: the multiplicative term can however be dropped, considering that the cutoff radius is an effective value [some discussion of the meaning of the f and f^* functions and of the effective cutoff radius can be found in Scardi & Leoni (2004), Armstrong *et al.* (2006) and Kaganer & Sabelfeld, 2010)].

The most complete definition of $f^*(\eta)$ is from Wilkens (1970*a*,*b*):

$$f^*(\eta) = -\ln\eta + \frac{7}{4} - \ln 2 + \frac{256}{45\pi\eta} + \frac{2}{\pi}\left(1 - \frac{1}{4\eta^2}\right)\int_0^\eta \frac{\arcsin y}{y}\,\mathrm{d}y - \frac{1}{\pi}\left(\frac{769}{180\eta} + \frac{41}{90}\eta + \frac{\eta^3}{45}\right)(1-\eta^2)^{1/2} - \frac{1}{\pi}\left(\frac{11}{12\eta^2} + \frac{7}{2} + \frac{\eta^2}{3}\right)\arcsin\eta + \frac{\eta^2}{6}, \qquad \eta \le 1, \tag{3.6.35}$$

$$f^*(\eta) = \frac{256}{45\pi\eta} - \left(\frac{11}{24} + \frac{1}{4}\ln 2\eta\right)\frac{1}{\eta^2}, \qquad \eta \ge 1. \tag{3.6.36}$$

For $\eta < 1$, the integral in (3.6.35) can be calculated in terms of special functions as

$$\begin{aligned}\int_0^\eta \frac{\arcsin y}{y}\,\mathrm{d}y &= \frac{i}{12}\left\{\pi^2 - 6\arcsin^2\eta - 12i\ln\left[2\eta\left(\eta - i\sqrt{1-\eta^2}\right)\right]\arcsin\eta - 6\mathrm{Li}_2\left(1 - 2\eta^2 + 2i\eta\sqrt{1-\eta^2}\right)\right\}\\ &= \ln(2\eta)\arcsin\eta + \frac{1}{2}\mathrm{Im}\left[\mathrm{Li}_2\left(1 - 2\eta^2 + 2i\eta\sqrt{1-\eta^2}\right)\right]\\ &= \ln(2\eta)\arcsin\eta + \frac{1}{2}\mathrm{Cl}_2(2\arcsin\eta),\end{aligned} \tag{3.6.37}$$

where $\mathrm{Li}_2(z)$ and $\mathrm{Cl}_2(z)$ are the dilogarithm function (Spence's function) and the Clausen integral, respectively:

$$\mathrm{Li}_2(z) = \sum_{k=1}^{\infty} z^k/k^2, \tag{3.6.38}$$

$$\mathrm{Cl}_2(z) = \sum_{k=1}^{\infty} \sin(kz)/z^2 = -\int_0^x \ln[2\sin(t/2)]\,\mathrm{d}t. \tag{3.6.39}$$

The approximation proposed by van Berkum (1994) for (3.6.35) and (3.6.36),

$$f^*(\eta) = \begin{cases} -\ln\eta + \dfrac{7}{4} - \ln 2 + \dfrac{\eta^2}{6} - \dfrac{32\eta^3}{225\pi}, & \eta \le 1 \\ \dfrac{256}{45\pi\eta} - \left(\dfrac{11}{24} + \dfrac{1}{4}\ln 2\eta\right)\dfrac{1}{\eta^2}, & \eta \ge 1, \end{cases} \tag{3.6.40}$$

should not be employed, as the derivative is discontinuous at $\eta = 1$. A simpler approximation, valid over the whole η range, was provided by Kaganer & Sabelfeld (2010):

$$f^*(\eta) = -\ln\left(\frac{\eta}{\eta_0 + \eta}\right). \tag{3.6.41}$$

With $\eta_0 = 2.2$, the results of equation (3.6.41) are similar to those of (3.6.35) and (3.6.36).

Together with dislocation density and outer cutoff radius, a parameter traditionally quoted for the dislocations ensemble is Wilkens' dislocation arrangement parameter $M = R_e\sqrt{\rho}$ (Wilkens, 1970*a*). By combining the information on dislocation screening and dislocation distance, it gives an idea of the interaction of dislocations (strength of the dipole character; Ungár, 2001). A value close to or below unity indicates highly interacting dislocations (for example, dipole configurations or dislocation walls), whereas a large value is typical of a system with randomly dispersed dislocations (weak dipole character).

The anisotropic broadening caused by the presence of dislocations is mainly taken into account by the contrast (or orientation) factor C_{hkl}. The contrast factor depends on the strain field of the dislocation and therefore on the elastic anisotropy and orientation of the scattering vector with respect to the slip system considered. The average of the contrast factor over all equivalent slip systems, $\overline{C}_{hkl}$, is often used in the analysis of powders. The averaging is usually performed under the assumption that all equivalent slip systems are equally populated. The calculation of the contrast factor can be lengthy: full details can be found in the literature (Wilkens, 1970*a*,*b*, 1987; Krivoglaz *et al.*, 1983; Kamminga & Delhez, 2000; Groma *et al.*, 1988; Klimanek & Kuzel, 1988; Kuzel & Klimanek, 1989) for the cubic and hexagonal cases. For a generalization, the reader is referred to the recent work of Martinez-Garcia *et al.* (2007, 2008, 2009). It is possible to show that the contrast factor of a given material has the same functional form as the fourth-order invariant of the Laue class (Popa, 1998; Leoni *et al.*, 2007):

$$\begin{aligned}d^4_{\{hkl\}}C_{\{hkl\}} &= E_1h^4 + E_2k^4 + E_3l^4 + 2(E_4h^2k^2 + E_5k^2l^2 + E_6h^2l^2)\\ &\quad + 4(E_7h^3k + E_8h^3l + E_9k^3h + E_{10}k^3l + E_{11}l^3h + E_{12}l^3k)\\ &\quad + 4(E_{13}h^2kl + E_{14}k^2hl + E_{15}l^2hk).\end{aligned} \tag{3.6.42}$$

In the general case, 15 coefficients are thus needed to describe the strain anisotropy effects. Symmetry reduces the number of independent coefficients: for instance, two coefficients survive in the cubic case, and the average contrast factor is (Stokes & Wilson, 1944; Popa, 1998; Scardi & Leoni, 1999)

$$\overline{C}_{\{hkl\}} = (A + BH) = A + B\frac{h^2k^2 + h^2l^2 + k^2l^2}{(h^2 + k^2 + l^2)^2}. \tag{3.6.43}$$

The values of A and B can be calculated from the elastic constants and slip system according to the literature (Klimanek & Kuzel, 1988; Kuzel & Klimanek, 1989; Martinez-Garcia *et al.*, 2007, 2008, 2009). Excluding the case of $\overline{C}_{\{h00\}} = 0$, the parameterization $\overline{C}_{\{hkl\}} = \overline{C}_{\{h00\}}(1 + qH)$ proposed by Ungár & Tichy (1999) can also be used. Some calculated values for cubic and hexagonal materials can be found in Ungár *et al.* (1999) and Dragomir & Ungár (2002), respectively.

As the calculation of the contrast factor for a dislocation of general character is not trivial, it is customary to evaluate it for the screw and edge case and to refine an effective dislocation character φ (Ungár *et al.*, 1999),

$$\begin{aligned}\overline{C}_{\{hkl\}} &= [\varphi\overline{C}_{E,\{hkl\}} + (1-\varphi)\overline{C}_{S,\{hkl\}}]\\ &= [\varphi A_E + (1-\varphi)A_S] + [\varphi B_E + (1-\varphi)B_S]H,\end{aligned} \tag{3.6.44}$$

where the geometric term H is the same as in equation (3.6.43). Although not completely correct, the approach proposed in equation (3.6.44) allows the case where a mixture of dislocations of varying character are acting on equivalent slip systems to be dealt with. For a proper refinement, however, the active slip systems as well as the contrast factors of the edge and screw dislocations should be known.

It is worth mentioning that the invariant form proposed by Popa (1998) has been reprised by Stephens (1999) to describe the strain-broadening anisotropy, for example, within the Rietveld method: the formula correctly accounts for the relative broadening (*i.e.* for the anisotropy), but it does not give any information on the actual shape of the profiles. This is the major reason

why the Stephens model can be considered as only phenomenological (it captures the trend but not the details): when the source of microstrain broadening is known, we can obtain the functional form of the profile (as proposed, for example, here for dislocations) and the model can become exact.

3.6.2.6.7. *Twin and deformation faults*

Planar defects, *i.e.* a mismatch in the regular stacking of crystallographic planes, are quite frequent in a vast family of technologically important materials and, in some cases, are responsible for their macroscopic properties. In the general case, the analysis of faulting using a Bragg-type method is troublesome. The local change in the structure causes the appearance of diffuse scattering (*i.e.* extra intensity) between the Bragg spots. This can be handled in the single-crystal case (Welberry, 2004), but can be challenging in a powder, where the reciprocal space is rotationally averaged and the (weak) diffuse scattering is lost in the background. The handling of diffuse phenomena is the main difference between the Rietveld (1969) and the pair distribution function (PDF) (Billinge, 2008) methods.

A simple description of the broadening effects of faulting, useful for WPPM, is available only for a restricted class of systems, namely face-centred cubic (f.c.c.) ($Fm\bar{3}m$), body-centred cubic (b.c.c.) ($Im\bar{3}m$) and hexagonal close packed (h.c.p.) ($P6_3/mmc$) lattices. Monatomic metals with f.c.c. (*e.g.* Cu, Ni and Au), h.c.p. (*e.g.* Ti, Co and Zr) and b.c.c. (*e.g.* W and Mo) structures fall into this list. Faulting in the wurtzite structure ($P6_3mc$) leading to a local transformation into sphalerite ($F\bar{4}3m$) can be handled with rules completely analogous to those for the h.c.p./f.c.c. case. The main types of faults in all of these systems are the so-called deformation and twin faults: looking at the planes on the two sides of the faulting, a deformation fault appears as a shear, whereas twinning causes a mirroring of the atomic positions. The effect of these defects can be modelled using recurrence equations for the stacking. Initially proposed for the h.c.p. case by Wilson (Edwards & Lipson, 1942; Wilson, 1942), this idea was then extended to the f.c.c. case (Paterson, 1952; Gevers, 1954*a*,*b*; Warren, 1959, 1963). More recently, Estevez-Rams *et al.* (2003, 2008) improved the accuracy and extended the validity range by including all terms in the stacking probability formulae, whereas Velterop *et al.* (2000) corrected the formalism to properly take the various *hkl* components of a peak into account.

In an f.c.c. system, reliable information can be obtained up to a few per cent of faults on the {111} plane. The trick is to describe the lattice with hexagonal axes, effectively transforming the problem into that of ⟨001⟩ stacking on the {111} plane. Under these hypotheses, the average phase term due to faulting can be written as

$$\left\langle \exp\left[2\pi i\varphi(L; d^*_{\{hkl\}}, L_0/h_0^2)\right]\right\rangle = A^F_{hkl}(L) + iB^F_{hkl}(L), \qquad (3.6.45)$$

where $L_0 = h + k + l$ and $h_0^2 = h^2 + k^2 + l^2$. The lattice symmetry influences the definitions of these two parameters. Faulting is one of the typical cases where a complex (sine) term is present, as peak shift and asymmetry in the profiles is expected (unless twin faults are absent). Following the treatment of Warren (see, for example, Warren, 1963), a set of recurrence equations can be written for the probability of the occurrence of faulting. The solution of the recurrence equations is used to generate the Fourier coefficients for faulting. In particular, if the probabilities of deformation and twin fault are α and β, respectively, then

$$S^2 = 3 - 12\alpha - 6\beta + 12\alpha^2 - \beta^2 + 24\alpha\beta(1-\alpha),$$
$$Z = \sqrt{(1-\beta^2) + S^2}/2 \qquad (3.6.46)$$

and, introducing the sign function,

$$\sigma_{L_0} = \begin{cases} +1 & \text{for } L_0 = 3N+1 \\ 0 & \text{for } L_0 = 3N \\ -1 & \text{for } L_0 = 3N-1 \end{cases} \qquad N = 0, \pm1, \pm2, \ldots, \qquad (3.6.47)$$

the Fourier coefficients can be obtained as

$$A^F_{hkl}(L) = \exp\left[\tfrac{1}{2}\ln(Z)|Ld^*_{\{hkl\}}\sigma_{L_0}L_0/h_0^2|\right], \qquad (3.6.48)$$

$$B^F_{hkl}(L) = -\sigma_{L_0}\frac{L}{|L|}\frac{L_0}{|L_0|}\frac{\beta}{S}A^F_{hkl}(L). \qquad (3.6.49)$$

Besides being asymmetric, each profile subcomponent can also be shifted with respect to the average Bragg position. For the subcomponent *hkl* the shift is

$$\delta_{hkl} = -\left[\frac{1}{2\pi}\arctan\left(\frac{s}{1-\beta}\right) - \frac{1}{6}\right]d^*_{\{hkl\}}\frac{L_0}{h_0^2}\sigma_{L_0}. \qquad (3.6.50)$$

In a given reflection family {*hkl*}, reflections affected and unaffected by faulting coexist, leading to peculiar shapes of the corresponding peak profiles.

Analogous formulae can be obtained for the b.c.c. and h.c.p. cases. In the former, the selection rule becomes $L_0 = -h - k + 2l$, whereas for the latter $L_0 = l$ and the condition for faulting is based on $h - k = 3N \pm 1$. Implementation requires the application of the proper formula to the particular reflection *hkl* considered in the analysis.

Analysing faults by observing just the peak shift, as in the original treatment of Warren (1959, 1963) or within the Warren–Averbach method (Warren & Averbach, 1950, 1952), would be erroneous, as it does not take the fine details of the broadening into account.

An alternative to the adoption of Warren's formalism was proposed by Balogh *et al.* (2006). Instead of performing the calculation explicitly, the authors parameterized the profiles obtained from the *DIFFaX* software (Treacy *et al.*, 1991) calculated for increasing quantities of faulting. The *DIFFaX* software is based on a recursive description of the stacking: the intensity is calculated along rods in reciprocal space using the tangent cylinder approximation. The parameterization, which is performed in terms of a sum of Lorentzian curves, is then employed for the evaluation of the fault-broadening profile at any angle. The modelling should be performed on a profile that contains a faulting-only contribution: note that for high faulting probabilities, it becomes arbitrary whether to assign the diffuse scattering part to one or another Bragg reflection. This introduces some arbitrariness in the subsequent (directional) convolution of the faulting profile with the other broadening effects. When applicable, however, this parameterization has several advantages: it takes the actual shape of the reciprocal-space rods into account (in an effective way), it does not necessitate any *hkl* selection rule and an analytical treatment can be employed, as the Lorentzian has an analytical transform. With the above caveats, it is in principle not even necessary to decompose the *DIFFaX*-generated profile if a numerical convolution is employed. This would also correspond to an extension of WPPM to the *DIFFaX*+ idea (Leoni, Gualtieri & Roveri, 2004; Leoni, 2008), or *vice versa*, where *DIFFaX*+ uses a corrected and improved version of the recursive approach of *DIFFaX* to