(3.6.19). This is particularly convenient, as the Fourier transform of a Voigtian is analytical. In fact, for the pV case we have

$$T_{\rm pV}^{\rm IP}(L) = (1-k)\exp(-\pi^2\sigma^2L^2/\ln 2) + k\exp(-2\pi\sigma L), \tag{3.6.20}$$

where σ = FWHM/2 and where (Langford & Louër, 1982; Scardi & Leoni, 1999)

$$k = \left[1 + (1-\eta)/\left(\eta\sqrt{\pi\ln 2}\right)\right]^{-1}. \tag{3.6.21}$$

Equation (3.6.18) can be found in the literature in a different form and with additional terms accounting, for example, for size effects: besides forcing a symmetry of the profile in 2θ space, these extra terms are a contradiction as they have nothing to do with the instrument itself.

3.6.2.6.4. *Domain size and shape*

In nanostructured materials, the finite size of the scattering domains is usually the dominant source of line-profile broadening. Actually, when dealing with size, we should consider a size and a shape distribution of the domains. In most cases, one or more distributions of similar objects are considered. For an up-to-date description of issues related to size broadening, see Chapter 5.1. The domain shape is not a property of the material and therefore the use of symmetry constraints [*e.g.* spherical harmonics to describe the shape of the scattering object as in the model of Popa (1998) or as a size extension of Stephens' (1999) work] is not justified in the general case (Nye, 1987). Exceptions, however, exist.

The size-broadening contribution in WPPM follows the ideas of Bertaut (1949*a*,*b*, 1950) and of Stokes & Wilson (1942). Bertaut proposed the division of the domains into columns and the analysis of the independent scattering of these columns. The column-length distribution can always be extracted from the data: more complex models involving given shapes or distributions simply modify the way in which the columns are rearranged. Stokes and Wilson introduced the concept of a *ghost* to calculate the Fourier transform for a given shape: the volume common to a domain of shape c and its ghost, *i.e.* a copy of the same domain displaced by a quantity L along the scattering direction hkl, is proportional to the (size) Fourier transform $A^S_{c,hkl}(L, D)$ for the given domain. The calculation has been already carried out analytically for several simple shapes characterized by a single length parameter (Stokes & Wilson, 1942; Lele & Anantharaman, 1966; Wilson, 1969; Langford & Louër, 1982; Vargas *et al.*, 1983; Grebille & Bérar, 1985; Scardi & Leoni, 2001), and can be performed numerically in the general case (Leonardi *et al.*, 2012). It is possible to relate the Fourier coefficients to the size values obtained from traditional methods. In particular, the area-weighted average size $\langle L\rangle_S$ (Warren–Averbach method) and the volume-weighted average size $\langle L\rangle_V$ (Williamson–Hall method) are obtained as

$$\langle L\rangle_S = -\left[dA_c^S(L,D)/dL\big|_{L=0}\right]^{-1} = D/K_k = -D/H_1, \tag{3.6.22}$$

$$\langle L\rangle_V = [\beta(s)]^{-1} = 2\int_0^{D/K} A_c^S(L,D)\,{\rm d}L = D/K_\beta, \tag{3.6.23}$$

where $\beta(s)$ is the integral breadth and K_k and K_β are the initial slope and integral breadth Scherrer constants, respectively (Langford & Wilson, 1978; Scardi & Leoni, 2001).

The average size might have little physical significance in real cases: the size (and shape) distribution can in fact play a key role in determining both the properties and the diffraction line-profile shapes of the powder under analysis. Fortunately, the Fourier coefficients for the polydisperse case can be easily calculated for any given distribution: the log-normal and the gamma distributions are the most common (and the most flexible). The equations and the corresponding moments are

$$g_l(D) = \frac{1}{D\sigma_l\sqrt{2\pi}}\exp\left[-\frac{(\ln D-\mu_l)^2}{2\sigma_l^2}\right],$$
$$M_{l,n} = \exp\left(n\mu_l + \frac{n^2}{2}\sigma_l^2\right), \tag{3.6.24}$$

$$g_g(D) = \frac{\sigma_p}{\mu_g\Gamma(\sigma_g)}\left(\frac{\sigma_g D}{\mu_g}\right)^{\sigma_g-1}\exp\left(-\frac{\sigma_g D}{\mu_g}\right),$$
$$M_{g,n} = \left(\frac{\mu_g}{\sigma_g}\right)^n\frac{\Gamma(n+\sigma_g)}{\Gamma(\sigma_g)}. \tag{3.6.25}$$

The scattered intensity for the given distribution g_i, and the given shape c, is

$$\begin{aligned} I_{c,hkl}(s) &\propto \frac{\int_0^\infty\left[\int_{L=0}^{D/K_{hkl}} A^S_{c,hkl}(L,D)\exp(2\pi iLs)\,{\rm d}L\right]w(D)\,{\rm d}D}{\int_0^\infty w(D)\,{\rm d}D} \\ &\propto \int_{L=0}^\infty\left[\frac{\int_{D=LK_{hkl}}^\infty A^S_{c,hkl}(L,D)w(D)\,{\rm d}D}{\int_0^\infty w(D)\,{\rm d}D}\right]\exp(2\pi iLs)\,{\rm d}L \\ &\propto \int_{L=0}^\infty A^S_{hkl}(L)\exp(2\pi iLs)\,{\rm d}L, \end{aligned} \tag{3.6.26}$$

where $w(D) = g_i(D)V_c(D)$ and where

$$A^S_{hkl}(L) = \frac{\int_{D=LK_{hkl}}^\infty A^S_{c,hkl}(L,D)w(D)\,{\rm d}D}{\int_0^\infty w(D)\,{\rm d}D}. \tag{3.6.27}$$

With a suitable definition of the Fourier coefficients, the polydisperse case therefore becomes analogous to the monodisperse case. Analytic expressions can be obtained in particular cases. For instance, the Fourier coefficients for the log-normal and gamma distributions (Scardi & Leoni, 2001) are

$$A_l^S(L) = \sum_{n=0}^3 {\rm erfc}\left[\frac{\ln(LK_c)-\mu_l-(3-n)\sigma_l^2}{\sigma_l\sqrt{2}}\right]\frac{M_{l,3-n}}{2M_{l,3}}H_n^cL^n \tag{3.6.28}$$

and

$$A_g^S(L) = \sum_{n=0}^3\left(\frac{\sigma_g}{M_{g,1}}\right)^n\frac{\Gamma[\sigma_g+(3-n),K_cL\sigma_g/M_{g,1}]}{\Gamma(\sigma_g+3)}H_n^cL^n, \tag{3.6.29}$$

respectively, where

$$\Gamma(x,a) = \int_a^\infty y^{x-1}\exp(-y)\,{\rm d}y,$$
$$\Gamma(x) = \Gamma(x,0),$$
$${\rm erfc}(x) = 2\pi^{-1/2}\int_x^\infty\exp(-y^2)\,{\rm d}y,$$

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*):