An efficient method for calculating asymmetric diffraction peak profiles

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An efficient method for evaluating asymmetric diffraction peak profile functions based on the convolution of the Lorentzian or Gaussian function with any asymmetric window function is proposed. When this method is applied to approximate the convolution with the Howard's window function [J. Appl. Crystallogr. **15**, 615 (1982)], only a few terms of numerical integration give satisfactory results, even if the asymmetry is very strong. © *1998 American Institute of Physics.* [S0034-6748(98)00611-X]

The peak profiles in angular dispersive powder diffractometry generally become asymmetric, which is mainly caused by the effect of vertical (axial) divergence.[1] The asymmetric profile function can be expressed by the following standard formula of convolution:

$$P(y)=\int f(y-z)w(z)dz, \tag{1}$$

where y is the deviation of the horizontal angle of the receiving slit from the diffraction angle, $f(x)$ is a symmetric profile function, and $w(z)$ is an asymmetric window function. The Voigt,[2] pseudo-Voigt,[3,4] or Pearson VII (Ref. 5) function has been used as $f(x)$, and some formulas for $w(z)$ have also been proposed.[1,6,7] Although the convolution can be evaluated by any numerical integration, a rapid method with a fixed formula is strongly desired for application to refinement programs.

In Howard's model[1] the asymmetric window function is expressed by

$$w_H(z)=\frac{|z|^{-1/2}}{2\sqrt{|z_{\min}|}} \quad \text{for} \quad z_{\min}<z<0, \tag{2}$$

and $w_H(z)=0$, elsewhere. Here, $z_{\min}$ is the parameter which specifies the degree of asymmetry. The main feature of the window function proposed by van Laar and Yelon[6] is similar to this model.

Howard has proposed a removal of the singularity from the integrand in Eq. (1) by the substitution

$$z\equiv -u^2, \tag{3}$$

which gives the following formula:

$$P_H(y)=\frac{1}{\sqrt{|z_{\min}|}}\int_0^{\sqrt{|z_{\min}|}} f(y+u^2)du, \tag{4}$$

and utilizing Simpson's rule to evaluate the integral, while van Laar and Yelon and Finger *et al.* have suggested direct application of Gauss–Legendre quadrature procedure to Eq. (1).[6,8] However, it seems difficult to achieve good approximation with those formulas, when the asymmetry is strong and $f(x)$ has a narrow profile. This note is intended to propose useful formulas to approximate asymmetrized Lorentzian and Gaussian profile functions.

First, let us examine the case where $f(x)$ is expressed by the following Lorentzian function:

$$f_L(x)=\frac{1}{\pi\gamma_L}\left[1+\left(\frac{x}{\gamma_L}\right)^2\right]^{-1}, \tag{5}$$

where γ_L specifies the width of the peak. Instead of Eq. (3), the author proposes utilizing the following substitution of the variable:

$$z\equiv y+\gamma_L\tan\left(-\xi^m-\arctan\frac{y}{\gamma_L}\right)$$
$$\Leftrightarrow \xi\equiv\left(\arctan\frac{y-z}{\gamma_L}-\arctan\frac{y}{\gamma_L}\right)^{1/m}, \tag{6}$$

in order to reduce the peak-like behavior of the integrand near $z\sim y$, as well as to remove the singularity at $z\to 0$. The parameter m should be chosen in correspondence with the degree of the singularity of $w(z)$ at $z\to 0$, for example, $m=2$ will be appropriate for $w_H(z)$ given by Eq. (2). The convolution of $f_L(x)$ with any window function $w(x)$ is given by

$$P_L(y)=\int_a^b f_L(y-z)w(z)dz$$
$$=\int_{\alpha_L}^{\beta_L}\frac{m\xi^{m-1}}{\pi}w\left[y+\gamma_L\tan\left(-\xi^m-\arctan\frac{y}{\gamma_L}\right)\right]d\xi, \tag{7}$$

where

$$\alpha_L\equiv\left(\arctan\frac{y-b}{\gamma_L}-\arctan\frac{y}{\gamma_L}\right)^{1/m}, \tag{8}$$

$$\beta_L\equiv\left(\arctan\frac{y-a}{\gamma_L}-\arctan\frac{y}{\gamma_L}\right)^{1/m}. \tag{9}$$

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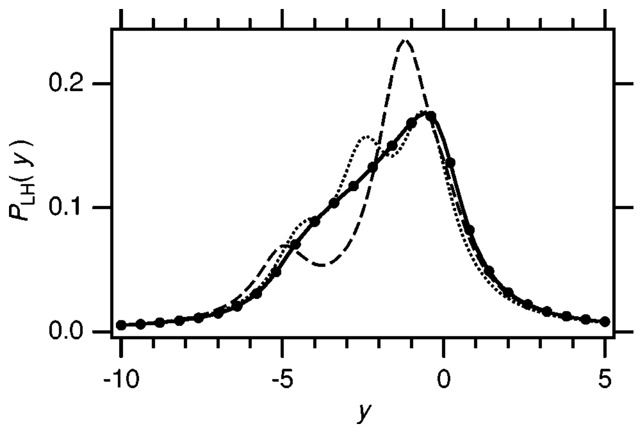

FIG. 1. Approximation of the convolution of the Lorentzian function $f_L(x)$ with the Howard's window function $w_H(x)$ for the case $z_{\min}=-5$ and $\gamma_L=1$. Solid circles are the exact values calculated by Eq. (11), and the lines are the approximations by three-term numerical integrations. Solid line is calculated by Eqs. (7)–(10), while dashed and dotted lines are calculated by the methods of Howard and Finger *et al.*, respectively.

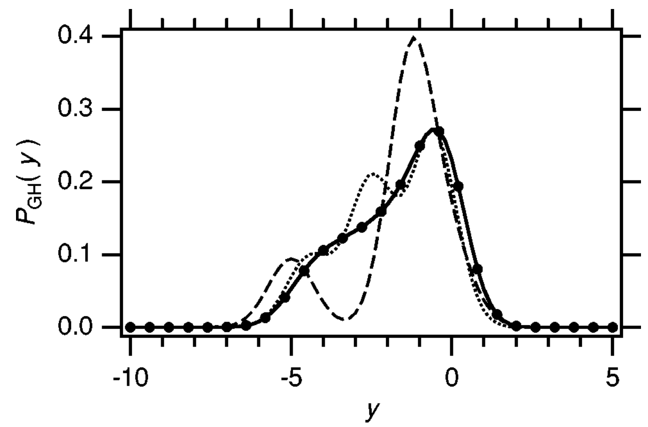

FIG. 2. Approximation of the convolution of the Gaussian function $f_G(x)$ with the Howard's window function $w_H(x)$ for the case $z_{\min}=-5$ and $\gamma_G=1$. Solid circles are the exact values obtained by increasing the terms of the numerical integration, and the lines are the approximations by three-term numerical integrations. Solid line is calculated by Eqs. (15)–(17) and (10), while dashed and dotted lines are calculated by the methods of Howard and Finger *et al.*, respectively.

When we define the integrand of the second equation of Eq. (7) as $g(\xi)$, the approximated formula is given by

$$\int_\alpha^\beta g(\xi)d\xi \sim (\beta-\alpha)\sum_{i=1}^{N} c_i g(\alpha+(\beta-\alpha)x_i), \tag{10}$$

where c_i and x_i are the Gauss–Legendre weights and abscissa associated with the ith point.[9]

Now, the convolution of the Lorentzian function $f_L(x)$ given by Eq. (5) with the Howard's window function $w_H(x)$ given by Eq. (2) is examined. Although Howard has suggested applying numerical integration for evaluating the convolution,[1] the analytical solution of the convolution is certainly available in this case, which is given by

$$P_{LH}(y)=\frac{\sqrt{v+u}}{4\sqrt{2}\pi\gamma_L\zeta v}\left[\ln\frac{\zeta^2+\sqrt{2}\sqrt{v-u}\zeta+v}{\zeta^2-\sqrt{2}\sqrt{v-u}\zeta+v} + \frac{2}{v+u}\left(\arctan\frac{\zeta^2-v}{\sqrt{2}\sqrt{v+u}\zeta}+\frac{\pi}{2}\right)\right], \tag{11}$$

where $\zeta\equiv\sqrt{|z_{\min}|/\gamma_L}$, $u\equiv y/\gamma_L$, and $v\equiv\sqrt{1+u^2}$. Figure 1 compares the exact solution with the approximate functions based on Eqs. (7)–(10) and the methods of Howard[1] and Finger *et al.*,[8] for the case $z_{\min}=-5$ and $\gamma_L=1$. Here, the number of terms of numerical integration is set to be $N=3$ to clarify the difference. The approximation by Eqs. (7)–(10) is almost indistinguishable from the exact solution with only three terms, while the methods by Howard and Finger *et al.* give rather poor results with vibrational structures, which is particularly unfavorable for application to fitting experimental data.

Next, let us examine the case where $f(x)$ has the following form of a Gaussian function:

$$f_G(x)=\frac{1}{\sqrt{\pi}\gamma_G}\exp\left[-\left(\frac{x}{\gamma_G}\right)^2\right]. \tag{12}$$

In this case, we can apply the following substitution:

$$z\equiv y+\gamma_G\,\mathrm{erf}^{-1}\left[-\eta^m-\mathrm{erf}\left(\frac{y}{\gamma_G}\right)\right]$$

$$\Leftrightarrow \eta\equiv\left[\mathrm{erf}\left(\frac{y-z}{\gamma_G}\right)-\mathrm{erf}\left(\frac{y}{\gamma_G}\right)\right]^{1/m}, \tag{13}$$

where erf(x) is the error function defined by

$$\mathrm{erf}(x)\equiv\frac{2}{\sqrt{\pi}}\int_0^x \exp[-t^2]dt, \tag{14}$$

and erf^{-1}(x) is the inverse function of erf(x). The asymmetrized profile function is given by

$$P_G(y)=\int_a^b f_G(y-z)w(z)dz$$
$$=\int_{\alpha_G}^{\beta_G}\frac{m\eta^{m-1}}{2} \times w\left\{y+\gamma_G\,\mathrm{erf}^{-1}\left[-\eta^m-\mathrm{erf}\left(\frac{y}{\gamma_L}\right)\right]\right\}d\eta, \tag{15}$$

where

$$\alpha_G\equiv\left[\mathrm{erf}\left(\frac{y-b}{\gamma_G}\right)-\mathrm{erf}\left(\frac{y}{\gamma_G}\right)\right]^{1/m}, \tag{16}$$

$$\beta_G\equiv\left[\mathrm{erf}\left(\frac{y-a}{\gamma_G}\right)-\mathrm{erf}\left(\frac{y}{\gamma_G}\right)\right]^{1/m}. \tag{17}$$

The approximated formula is given by Eq. (10), again.

The results of various methods for evaluating the convolution of $f_G(x)$ with $w_H(x)$ for the case $z_{\min}=-5$ and $\gamma_G=1$ are shown in Fig. 2. Since the analytical formula of the convolution is not available, the exact solution is evaluated by increasing the terms of the numerical integral. As is shown in Fig. 2, the approximation based on the formulas given by Eqs. (15)–(17) is clearly better than the methods by Howard and Finger *et al.*, again.

Since the pseudo-Voigt function is a sum of Lorentzian and Gaussian functions,[3,4] the asymmetrized pseudo-Voigt function is simply given by the sum of the asymmetrized Lorentzian and Gaussian functions. Furthermore, it will be easy to construct the formula of the substitution like Eq. (6) or Eq. (13) for any $f(x)$, when the primitive function $F(x) \equiv \int f(x) dx$ and its inverse function $F^{-1}(x)$ are both available. Even if $F(x)$ or $F^{-1}(x)$ is not available, it is worth trying the substitution given by Eq. (6) or Eq. (13), when $f(x)$ is approximated by a Lorentzian or Gaussian function.

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