ICANS-XI International Collaboration on Advanced Neutron Sources
KEK, Tsukuba, October 22-26, 1990

RECENT IMPROVEMENTS OF THE PARAMETERIZATION OF BRAGG PEAK PROFILE FUNCTIONS

John M. Carpenter, William C. Dimm[a], and Frank J. Rotella
Intense Pulsed Neutron Source
Argonne National Laboratory
9700 S. Cass Avenue, Argonne, IL 60439

[a]Present Address: Department of Physics, Cornell University, Ithaca, NY

ABSTRACT

The "Jorgensen" profile function conventionally used to describe the shape of observed Bragg peaks in time-of-flight powder neutron diffraction fits individual peaks very well. However, the wavelength or plane spacing variation of the parameters of the components of this function, as they are conventionally represented in Rietveld analysis, is inappropriate for fitting data extending over a wide range of plane spacings, d. We have developed a new representation of the d-dependence of the profile parameters which are generalizations of Pade' approximants, have built-in physically realistic large- and small-d limiting behavior, and provide better fits to parameters derived from individual peak fits than the conventional forms. We report the results of tests of the new parameterization of the profile functions.

I. Introduction

Figure 1 illustrates the Jorgensen profile function[1], which is the sum of truncated rising and falling exponentials normalized to the same value at t=0, convoluted with a Gaussian function. α is the coefficient of the rising exponential, β is the coefficient of the falling exponential, and t_o is the centroid and σ the standard deviation of the Gaussian. All parameters are functions of d, the plane spacing of the reflection presumed to produce the reflection. For detectors at a given scattering angle 2θ, d variation is equivalent to λ variation, since $\lambda = 2d\sin\theta$. We discuss the profile function as a function of time-of-flight, t, the observed variable, with parameters fixed according to the corresponding d (or λ) and θ. Even though the function is of very simple form, experience reveals that it is capable of reproducing the shape of Bragg peaks to quite acceptable accuracy, with only a small systematic deviation near the maximum which is just noticeable in data having better-than-average statistical precision.

The goal of the present work is to develop generally applicable mathematical forms containing wavelength (d spacing) independent parameters specific to instrument and scattering angle, which represent the wavelength (d spacing) dependence of the parameters of the Jorgensen profile function.

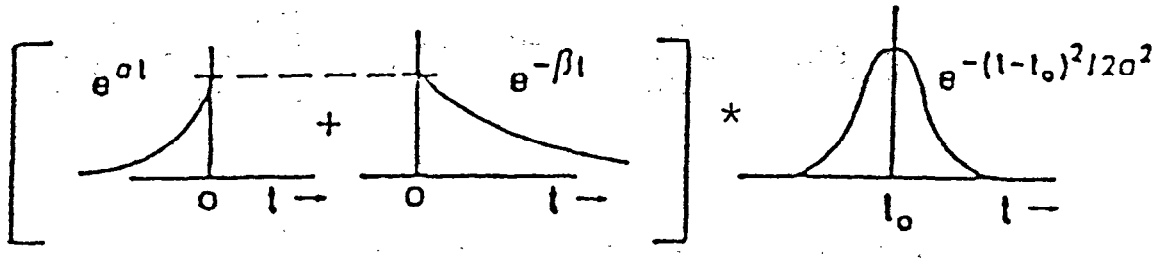

Figure 1. The Jorgensen profile function.

II. Pade' Approximants

Pade' approximants[2] are ratios of polynomials

$$f(x) = x^p \frac{\sum_{i=0}^{i=N_N} a_i x^i}{\sum_{i=0}^{i=N_D} b_i x^i} = x^p \frac{P_N(x)}{P_D(x)} \qquad (1)$$

where a_0 , b_0 , a_{N_N} and b_{N_D} are all different from zero.

The leading terms of a Taylor expansion of (1) are related to the leading terms of a Taylor expansion of f(x) in a simple way.

$$f(x) = \sum_{n=0}^{\infty} f_n x^n \qquad (2)$$

$$a_n = \sum_{k=0}^{n+p} b_{n+p-k} f_k \ , \quad (0 \leq n N_N) . \qquad (3)$$

Similarly, if in a Taylor expansion in y = 1/x,

$$g(y) = \sum_{n=0}^{\infty} g_n y^n \qquad (4)$$

the same polynomials can represent g(y)

$$g(y) = y^q \frac{P_N(1/y)}{P_D(1/y)} \qquad (5)$$

if

$$a_n = \sum_{k=0}^{q+N_D-n} b_{n-q+k} g_k \ , \quad (0 \leq n \leq N_N) . \qquad (6)$$

Equations (3) and (6) can be used to place conditions on the limiting behavior of the function.

The lowest order terms in the Taylor expansions for large and small x are

$$\lim_{x\to\infty} f(x) = \frac{a_{N_N}}{b_{N_D}} x^{(p+N_N-N_D)} \left[1 + \left(\frac{a_{N_N-1}}{a_{N_N}} - \frac{b_{N_D-1}}{b_{N_D}}\right)\frac{1}{x}\right] \tag{7}$$

and

$$\lim_{x\to 0} f(x) = \frac{a_0}{b_0} x^p \left[1 + \left(\frac{a_1}{a_0} - \frac{b_1}{b_0}\right) x\right]. \tag{8}$$

These properties of Pade' approximants, namely the natural way in which limiting behavior required by physical constraints can be built in, led us to choose them for the present purposes. To limit the number of parameters in the functions, we have chosen particular forms of Pade' approximants, namely ones in which most of the disposable a_i's and b_i's are equal to zero. Further, we allow N_N and N_D to have non-integer values, so that in this sense our functions are not properly called Pade' approximants. A necessary constraint on functions in the present context is that the denominator polynomial may have no zeros for real, positive d. When positive-definite quantities appear, we represent them as squares of fitting parameters, respecting the fact that our computer codes operate in the field of real numbers, while the nonlinear least squares routines used for fitting require smooth behavior of the functions with respect to the fitted parameters.

III. Diamond Powder Calibrant

To provide well resolved peaks at the smallest possible wavelengths (d spacings), we use a diamond powder sample with grain size of about 150 μm. (The diamond lattice constant is about 2/3 that of the frequently used silicon powder calibrant.) The grains are purposely large to avoid grain size broadening effects in the measurements, but their large size leads to significant primary extinction effects. The extinction affects the peak intensities, but does not alter the shapes of individual Bragg peaks.

IV. The Coefficient of the Falling Exponential, β

The principal motivation for including a falling exponential in the profile function is to represent the decay of the fundamental eigenfunction in the flux distribution in the moderator. Since the fundamental eigenfunction dominates the energy distribution at long wavelengths, β is expected to approach a constant in the limit of long wavelengths. Experience shows that β approaches the long wavelength limit from shorter wavelengths as (constant)/λ^q, where $q \simeq 4$. On these grounds the present Rietveld codes parameterize the d-variation of β in the form (9). This form cannot describe

$$\beta = \beta_0 + \beta_1/d^4. \tag{9}$$

the behavior of $\beta(d)$ for small d, where (9) diverges non-physically.
Typically, the profile parameters exhibit several inflection points, because of the complicated wavelength dependence of the moderator pulse shape, so a more complicated form is required.
Noting that the decaying exponential must describe the short wavelength behavior of the moderator pulse, which is of the form

$$\phi(\lambda,t) \propto t^2 e^{-a(\lambda)t} \tag{10}$$

where at short wavelengths, $a(\lambda) \rightarrow (\text{constant})/\lambda$, β must be inversely proportional to λ for short wavelengths,

$$\lim_{\lambda \to 0} \beta(\lambda) = (\text{constant})/\lambda. \tag{11}$$

To the extent that β describes geometric effects, β must also tend to the small-λ limit as $1/\lambda$ $(1/d)$. Thus, the form representing β must be modified from (9) at short wavelengths (small d) in some smooth way. We propose the form

$$\beta(d) = (\beta_o/d)\frac{1 + bd^n}{1 + K^2 d^{n-1}} \tag{12}$$

which has the limiting behavior

$$\lim_{d \to 0} \beta(d) = \beta_o/d \tag{13}$$

and (not quite correctly, but simply)

$$\lim_{d \to \infty} \beta(d) = \beta_o (b/K^2)(1 + 1/bd^n - 1/K^2 d^{n-1}) \tag{14}$$

Figure 2 shows the results of fitting (12) to data from the 150° bank of detectors in the SEPD[1], using the diamond powder sample. The experimental values for β were derived from separate fits to the observed, resolvable peaks.

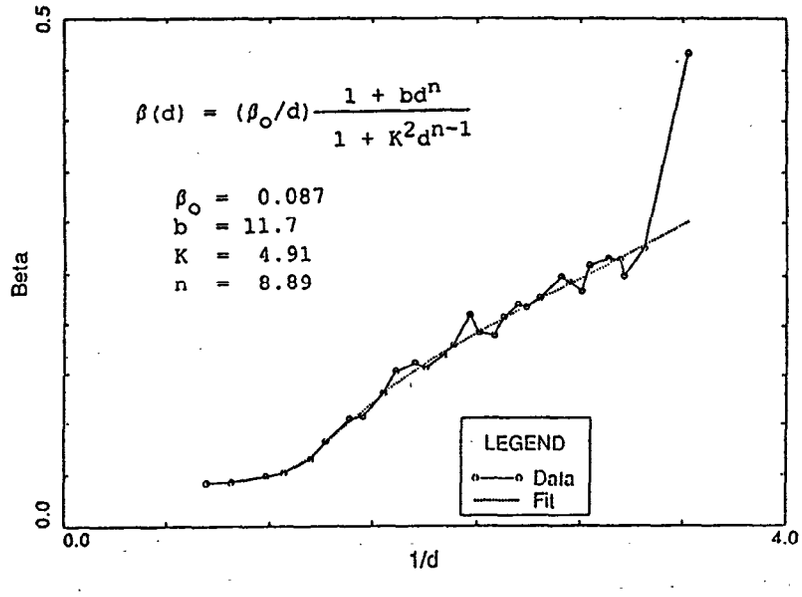

Figure 2. Data and fitted curve, equation (12) for the β parameter describing Bragg peaks measured at 2θ = 150° in the SEPD. The unit of β is μsec^{-1}; the unit of d is Å.

V. The Gaussian Width Parameter

The width of the Gaussian function $\sigma(d)$, must describe the composite of many geometric effects, including the many contributions to the angular distribution of diffracted neutrons, and also must describe the shape of the moderator pulse. Certain sample scattering effects also appear in the Gaussian width function. All these effects add as squares in their contributions to σ^2; this justifies their description as a Gaussian function, according to the central limit theorem. The geometric contributions are strictly proportional to d (or λ). Moderator effects have very complex wavelength dependence, but in the limit of small wavelength, these must contribute to σ as a term proportional to wavelength. It is found empirically that σ behaves as a + bd at long wavelengths, where the constant b is not the same as the slope of σ at small wavelengths.

We have chosen to represent $\sigma(d)$ as

$$\sigma(d) = d \frac{\sigma_o^2 + \sigma_1 d^{n-1} + \sigma_2^2 d^n}{d^n + K^2} \qquad (15)$$

Figure 3 shows the resulting fit to data from the 150° bank of detectors in the SEPD, using the diamond powder sample.

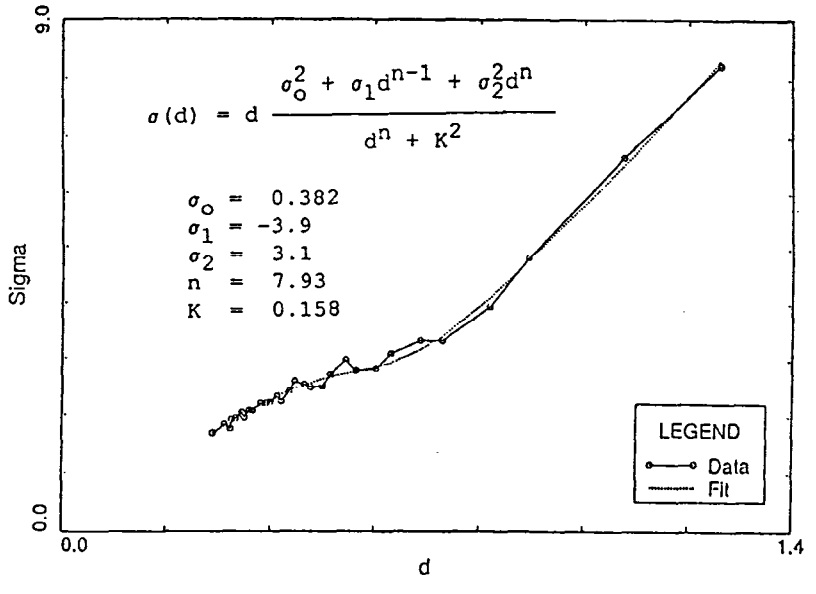

Figure 3. Data and fitted curve, equation (15), for the σ parameter describing Bragg peaks measured at $2\theta = 150°$ in SEPD. The unit of σ is µsec; the unit of d is Å.

VI. The Gaussian Center Time, t_o

The Gaussian center time, t_o, is dominated by the contribution from the total flight path which is proportional to d (or λ), and contains a constant contribution that can be identified with the electronic time delay in the time origin pulse. t_o is not the mean time associated with the Bragg peak, since the rising and falling exponential functions do not in general represent a symmetric function. Furthermore, t_o depends on the shape of the moderator pulse in a complex way. We have chosen to represent $t_o(d)$ as

$$t_o(d) = t_1 + d\,\frac{t_2^2 + t_3 d^{n-1} + t_4^2 d^n}{d^n + K^2}. \quad (16)$$

Figure 4 shows the results of fitting data from the 150° bank of detectors in the SEPD, using the diamond powder sample.

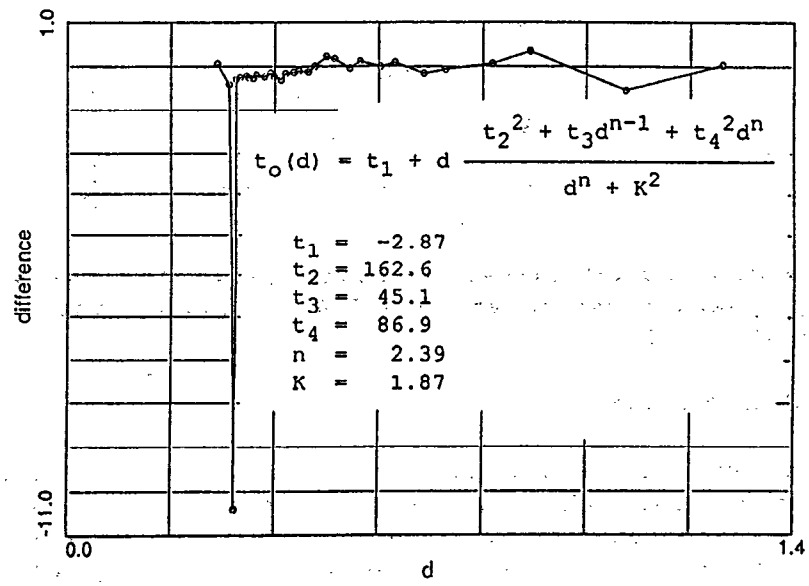

Figure 4. The difference between the data and the fitted curve, equation(16) for the t_o parameter describing Bragg peaks measured at 2θ = 150° in SEPD. The unit of t_o is μsec; the unit of d is Å.

VII. The Coefficient of the Rising Exponential, α

The coefficient of the rising exponential, $\alpha(d)$, represents mostly the effect of detector height (at least at backscattering angles). As such, it describes strictly a geometric effect, and is expected to be simply inversely proportional to λ (or d). Although α is a necessary parameter, the profile functions are not highly sensitive to the value of α, therefore data tend to be poor, but the need for accurate values is correspondingly small. We choose to represent

$$\alpha(d) = \alpha_o/d. \quad (17)$$

Figure 5 shows the results of fitting 150° SEPD data to diamond powder data, using equation (17).

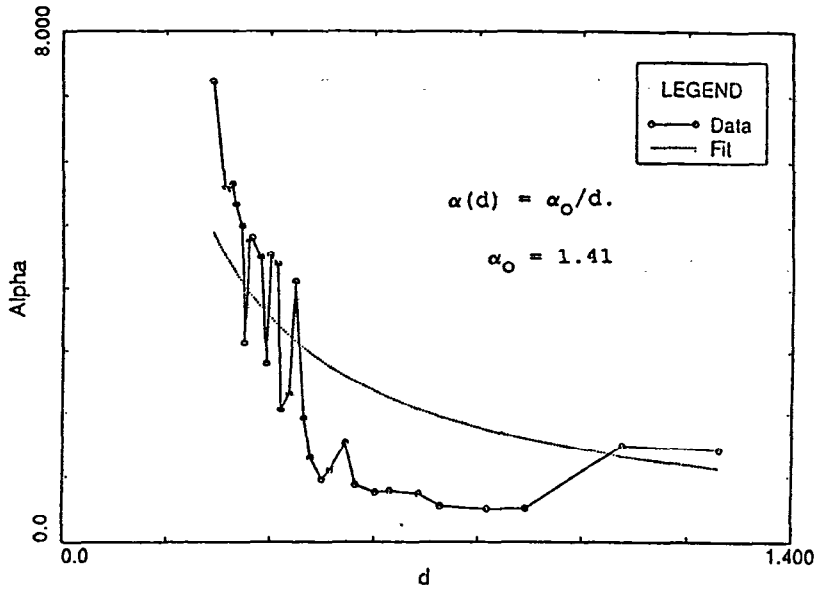

Figure 5. Data and fitted curve, equation (17), for the α parameter describing Bragg peaks measured at 2θ = 150° in SEPD. The unit of α is μsec^{-1}; the unit of d is Å.

VIII. Status and Conclusions

We have conceived and tested a new set of functions having the form of Pade' approximants, to describe the wavelength (d-spacing) variation of the parameters of the Jorgensen profile function. Tests on parameters derived from individual peak fits to data taken from diamond powder at large scattering angles indicate that functions of this form are capable of describing the complicated variation of these parameters, with good accuracy and without requiring an excessively large number of wavelength-independent parameters. This work is really not complete, inasmuch as we have not fully exploited the capabilities of the Pade' approximant forms. Neither have we correctly imposed all the limiting behavior of the profile parameters in the fitting forms, nor been able to recognize which wavelength-independent parameters are related.

Testing of the new functions using the IPNS Rietveld analysis software has begun, addressing questions of refinability, independence of parameters, and the accuracy of Rietveld structure refinement.

We have been able to draw some preliminary conclusions from Rietveld analysis of the 150° SEPD data from the diamond sample in the range $0.2 \leq d \leq 1.3$ Å and from our standard silicon sample in the range $0.3 \leq d \leq 3.3$ Å. The profile fit improves significantly when $\beta(d)$ from the Padé approximant formalism in (12) replaces that described in (9) - e.g., the weighted profile R-factor (R_{wP})[1] reduced from 11.73% to 10.67% in the diamond data analysis. However, virtually no improvement is observed in the fit when the description

for the Gaussian width parameter $\sigma(d)$ in (15) replaces that which is being used at present. We emphasize that these results are preliminary, and in assessing the effects of these functional forms on the accuracy and precision of structural parameters derived from Rietveld analysis, more work on a wider range of standard samples will be required.

Acknowledgements

We express our thanks to J. W. Richardson, R. L. Hitterman, J. D. Jorgensen and K. J. Volin for data collection on GPPD & SEPD. This work was performed under the auspices of the U.S. Department of Energy, Division of Materials Sciences, Office of Basic Energy Sciences, under Contract W-31-109-ENG-38.

References

1. J. D. Jorgensen, J. Faber Jr., J.M. Carpenter, R. K. Crawford, J. R. Haumann, R. L. Hitterman, R. Kleb, G. E. Ostrowski,, F. J. Rotella and T. G. Worlton, J. Appl. Cryst. 22 (1989), 321-333.

2. See for example D. C. Hanscomb, "Methods of Numerical Approximation", Pergamon Press Ltd., Oxford, 1966, p. 99-130.
Messages for figures

3. F. J. Rotella, "User Manual for Rietveld Analysis of Time-of-Flight Neutron Powder Diffraction Data at IPNS", (1988). Argonne National Laboratory, Argonne, IL, USA