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Expected Values and Variances of Bragg Peak Intensities Measured in a Nanocrystalline Powder Diffraction Experiment

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Synopsis A rigorous analysis of sampling and intensity statistics for a powder diffraction experiment over a range of nanocrystallite sizes is presented.

Abstract We present a rigorous study of sampling and intensity statistics applicable for a powder diffraction experiment as a function of crystallite size. This analysis yields approximate equations for the expected value, variance and standard deviations for both the number of diffracting grains and the corresponding diffracted intensity for a given Bragg peak. The classical formalism published in 1948 by Alexander, Klug and Kummer (Alexander *et al.*, 1948) appears as a special case, limited to large crystallite sizes, in our analysis. We observe that both the Lorenz probability expression and the statistics equations used in the classical formalism are inapplicable for nanocrystalline powder samples.

Keywords: X-ray diffraction; nanocrystals; powder diffraction; sampling and intensity statistics; Lorentz factor

1. Introduction

Bragg peak intensities recorded during a powder diffraction experiment are an important part of the input for subsequent structural analysis (Parrish & Langford, 2004; Etter & Dinnebier, 2014). In both single peak and full-pattern analysis formalisms, peak intensities from different phases of a multi-phase aggregate are used to calculate their relative abundance (Klug & Alexander, 1974) (Toraya, 2016). For single phase materials the diffracted intensities can be linked to the total volume or number of powder grains (crystallites) which are in the diffraction condition (Alexander *et al.*, 1948; Klug & Alexander,

1974). The errors associated with reported phase fractions, diffracting volumes or number of grains can be obtained by propagating the uncertainties of measured diffracted peak intensities (Leon-Reina *et al.*, 2016; Ida, 2016). Most analysis programs which report peak intensity values also report the associated error values. However, in most cases, these errors are based on the minimization of the residual between measured and modelled intensities. Such an approach usually yields a lower bound of error of the relevant diffracted intensity value since not all terms which contribute to the systematic uncertainty are taken into account (Cline *et al.*, 2015; Gagin & Levin, 2016).

Two independent terms contribute to the uncertainty associated with the diffracted intensity measured from a crystalline powder aggregate. The first is the uncertainty of the information volume from which the diffracted intensity originates. This term arises due to random variations in the diffracting grain population, which is caused by size, shape, perfection and orientation distributions of the illuminated crystallites. It can be quantified using “sampling statistics”. The second source is the uncertainty of the measured intensity at a given scattering angle due to the statistical variations in the photon flux arriving at the detector; photon counting (Poisson) statistics are used for the evaluation of this factor. Both terms must be properly evaluated to quantify the uncertainty budget. A sharp, well resolved Bragg peak, with high peak and low background intensities, may not be representative of the powder sample under analysis if it originates only from two or three large crystallites (Noyan & Kaldor 2004).

In diffraction literature the majority of publications which treat measurement uncertainty concentrate on intensity statistics and instrumental aberrations (Daymond *et al.*, 2002) (Rebmann *et al.*, 1998; Madsen & Hill, 1994; Cheary *et al.*, 2004). In these articles diffraction from a representative number of grains is implicitly assumed. There are very few articles which examine correlations between the statistical variations in the number of diffracting grains and the resulting variations in the measured intensity. The seminal work on this subject was published in 1948 by Alexander, Klug and Kummer (Alexander *et al.*, 1948). This formalism (henceforth referred to as the AKK analysis) combined the Lorenz equation for predicting the fraction of grains favourably oriented to diffract for a given reflection with a very basic statistical analysis to formulate equations predicting the expected value and variance in diffracted intensities. These equations were originally tested with experimental intensity data from quartz powder samples with particle sizes between 5 to 50 micrometers. For this size range, the measured and computed uncertainties showed good agreement.

In two recent publications we examined the applicability of the AKK formulation to nanocrystalline powder samples through modelling. In our first study we investigated only sampling statistics and showed that, in this size range, a large fraction of the grains contributed multiple Laue spots to the diffraction profile. Under these conditions, the Lorenz equation is, by definition, inapplicable for computing the

number of grains contributing to the diffraction peak (Öztürk *et al.*, 2014), and we postulated that the relative uncertainties in the number of grains could not be directly correlated to the corresponding variations in diffracted intensities. In our second article we extended our modelling to compute the intensity contributed by each diffracting crystallite to the relevant Bragg peak, and compared the relative uncertainty in the number of diffracting particles to the variation in total integrated intensities (Öztürk *et al.*, 2014, 2015). We observed that these variations were not equal and could not be predicted through the AKK formalism. However, since we did not analytically formulate predictive equations linking expected values of diffracting grains to the expected diffracted intensities, we could not identify all causes contributing to the observed discrepancies.

In this, our third study on sampling and intensity statistics in a powder diffraction experiment, we present a simple analytical treatment, verified by numerical modelling, linking diffracting grain populations to Bragg peak intensities over a range of crystallite sizes. We observe that the AKK formalism appears as a special case, limited to large crystallite sizes. For powders consisting of nanocrystallites, both the Lorenz formulation and the statistics equations used in the classical analysis are invalid.

2. Theory

2.1. The AKK Formalism

For the basic AKK formalism Alexander and co-workers treated a non-textured powder sample comprising of N_g identical crystallites, illuminated with a plane parallel monochromatic x-ray beam of wavelength λ . The crystallite size, D , was assumed to be small enough so that: i- the particles scattered x-rays in the kinematical regime, ii- both secondary extinction and x-ray absorption could be neglected. Under these conditions, for a given sample, they provided the following equations to calculate the expected number, $E[N_{hkl}]$, and variance, $V[N_{hkl}]$, of particles in the diffracting condition:

$$E[N_{hkl}] = N_g p_{hkl} \quad (1-a)$$

$$V[N_{hkl}] = N_g p_{hkl} q_{hkl} \quad (1-b)$$

The term, p_{hkl} , in these equations is the ideal fraction of crystallites properly oriented to satisfy the diffraction condition and q_{hkl} is the complementary fraction; $q_{hkl} = 1 - p_{hkl}$. The relative standard deviation in the number of diffracting particles, $u[N_{hkl}]$, is, then, computed from:

$$u[N_{hkl}] = \frac{\sqrt{V[N_{hkl}]}}{E[N_{hkl}]} = \left(\frac{q_{hkl}}{N_g p_{hkl}} \right)^{\frac{1}{2}} \quad (2)$$

For the x-ray experiment described, p_{hkl} was computed from the classical Lorenz equation:

$$p_{hkl} = \frac{1}{2} m_{hkl} \cos \theta_B \Delta \theta_{1/2} \quad (3)$$

where m_{hkl} is the multiplicity of the hkl planes, θ_B is the Bragg angle for the hkl reflection and $\Delta \theta_{1/2}$ is the acceptance angle of the powder crystals of size D for this experiment.

At this point the AKK analysis posits that the relative standard deviation of the diffracting particle population, $u[N_{hkl}]$, is identical to the relative standard deviation of the diffracted intensity of the Bragg peak, $u[I_{hkl}]$:

$$u[I_{hkl}] = \left(\frac{q_{hkl}}{N_g p_{hkl}} \right)^{1/2} \quad (4)$$

Predictions based on Eq. (4) match most experimental observations: if the denominator, $N_g p_{hkl}$, is large, the relative standard deviation of the intensity, $u[I_{hkl}]$, will be small and intensity measurements from successive powder samples are expected to be in good agreement. For small $N_g p_{hkl}$ values, larger scatter of the intensity values among identical powder samples is predicted. In addition to these predictions, the AKK study reported that $u[I_{hkl}]$ values experimentally determined from powder samples with grain sizes over 5 μm agreed with the corresponding $u[N_{hkl}]$ values for these samples. On the other hand, our simulations (Öztürk *et al.*, 2014) (Öztürk *et al.*, 2015) on much smaller grain sizes did not yield good agreement. We ascribed this disagreement partly to the inapplicability of the Lorentz probability equation (Eq. 3) for this size range. A further review of the statistics used in the AKK analysis showed that a second possible reason for the discrepancy was the assumption, implicit in Eq. 4, that discrete Bernoulli statistics¹ (Forbes *et al.*, 2010) could be used for describing the uncertainty associated with diffracted intensities. In what follows, we investigate this point by performing a more thorough statistical analysis.

2.2. Extended Statistical Analysis

In this analysis we consider an ideal ensemble of perfect single crystals, all of which are identical in shape, size, composition and crystal symmetry. We assume that the population of this ensemble is

¹ Equations 1-a, b strictly apply only to a Bernoulli distribution, which is a discrete distribution with only two possible outcomes. This point is not presented or discussed in the AKK formalism.

infinite, and that the constituent crystals are completely randomly oriented in real-space; there is no correlation between the orientations of individual crystallites. Our goal is to investigate the x-ray intensity diffracted kinematically into a particular hkl reflection when a randomly-populated subset of this ensemble, which contains N_g crystals, is illuminated by a plane-wave of x-rays of wavelength, λ .

Specifically, we will derive equations to predict the following:

1. The expected population of crystals, $E[N_{hkl}]$, oriented properly for diffraction into the hkl reflection
2. The expected intensity values associated with the Bragg peak for this reflection, in particular:
 - a. The expected maximum intensity, $E[I_{\max}]$
 - b. The expected total intensity, $E[I_{\text{total}}]$
 - c. The expected integrated intensity, $E[I_{\text{int}}]$
3. The absolute and relative standard deviation values associated with these parameters.

We consider now a thought experiment based on the diffraction system shown in Figure 1. Here the incoming (x-ray) plane wave, with wavelength λ , propagates along the (unit) vector, $\vec{k}_0$. This wave impinges on a single (randomly selected) crystal at point O , the diffractometer center. If the (hkl) planes of the crystal, with spacing d_{hkl} , satisfy Bragg's law,

$$\lambda = 2d_{hkl} \sin \theta_{B,hkl} \quad (5)$$

a diffracted beam along vector, $\vec{k}_s$, making the angle $2\theta_B$ with the transmitted beam vector, $\vec{k}_t$, will form. The normal to the diffracting planes, $[hkl]$, bisects the angle between the vectors $-\vec{k}_0$ and $\vec{k}_s$;

$[hkl]$ makes the angle, $\Gamma_B = \frac{\pi}{2} - \theta_B$, with $-\vec{k}_0$. During an experiment the 2θ angle takes on values between zero (direct transmission) and π (full back reflection), while the corresponding Γ angle varies between $\frac{\pi}{2}$ and zero.

Rotating the system in Figure 1 to an arbitrary angle ϕ around the incident beam vector, $\vec{k}_0$, does not change any angular relationships between the vectors defining the diffraction geometry. By rotating the system from $\phi = 0$ to $\phi = 2\pi$ while tracing the position of the tips of the relevant vectors, and adding a

unit sphere centered at point O , the three-dimensional construct in Figure 2 is obtained. In this figure the reflection and Debye-Scherrer (D-S) circles are traced by the rotation of the unit vectors, $[hkl]$, and $\vec{k}_s$ respectively. We define two spherical zones centered about these circles:

1. The detection band, also termed the “Debye-Scherrer Halo”, is centered on the D-S circle, with angular width 4β , where β is the full-width-at-half-maximum (FWHM) breadth of the relevant diffraction peak².

The orientations of rays with $\vec{k}_s$ vectors intersecting the sphere surface within the D-S halo will be in the interval, $2\theta_B \pm 2\beta$. The deviation of these vectors from the exact Bragg condition will, thus, be in the range $-2\beta \leq \Delta 2\theta \leq 2\beta$. The orientation of a given $\vec{k}_s$ vector determines its diffracted intensity; this intensity decays continuously and symmetrically with deviation, $\Delta 2\theta$, from the Bragg condition, and tends to zero for $\Delta 2\theta \geq |2\beta|$. Thus, only those diffracted rays intersecting the sphere surface within the D-S halo will have finite intensity. These intersections are called the “diffraction spots”.

2. The “reflection band”, with angular width 2β , is centred on the reflection circle. All $[hkl]$ vectors originating at O , with orientation angles $\Gamma_i \in (\Gamma_B \pm \beta)$ will intersect the unit sphere within the reflection band. These intersection points are termed the “poles” of the corresponding $[hkl]$ vectors. The circumferential angular separation of any i -th pole from the reflection circle is $\Delta\Gamma_i = \Gamma_B - \Gamma_i$. This term, $\Delta\Gamma_i$, defines the mis-orientation of a given set of (hkl) planes from the exact diffraction condition.

Each diffraction spot, with angular position $\Delta 2\theta_i$ will originate from a unique set of (hkl) planes which has its hkl pole at the angular position $\Delta\Gamma_i = (-\Delta 2\theta_i / 2)$ within the reflection band. These poles, falling within the reflection band, are termed the “activated” poles. We assume for the time being that each crystal can have only one activated pole.

The FWHM, β , which is used to define the widths of the D-S halo and the reflection band is obtained from the Scherrer equation:

$$\beta = \frac{K_s \lambda}{D \cos \theta_B} \quad (6)$$

² The angular width of a diffraction peak can be described by different parameters. Most common terms are the full-width-at-half-maximum (FWHM) used here and the integral breadth (IB). The FWHM is also termed half-width and, less commonly, breadth in general usage.

Here D is the size of the crystal along the $[hkl]$ direction and K_s is the Scherrer constant which depends only on the shape of the crystal (Patterson, 1939b). Eq. 6 shows that the FWHM drops rapidly with increasing D .

During our thought experiment, one picks up a subset of crystals sequentially, with $i = 1, N_g$, from the (infinite) ensemble of ideal crystals and tests each one individually for diffracting finite intensity into the D-S halo of the hkl reflection: first the crystal is placed at the origin, O , and the angular position of its $[hkl]$ pole on the unit-sphere surface is determined through vector algebra. Since the orientation of the crystal lattice with respect to the incoming beam is completely random, this hkl pole can fall on any position on the reference sphere surface with equal probability. If the pole falls within the reflection band, a ray with finite intensity will be diffracted from this crystal and a (detectable) diffraction spot will form on the surface of the D-S halo. We classify such a crystal as a diffracting crystal.

The results of each such test can be described by two variables, X and I , where X is a discrete variable which represents whether a crystal is diffracting ($x=1$) or not ($x=0$). I is the diffracted intensity, which can change continuously between zero and its maximum value. Since the types of these variables, X , I , are different, the statistics associated with these variables are also different.

2.2.1. Particle Selection Statistics

The expected value of X , $E[X]$, and its variance $V[X]$ can be computed from standard statistics formulations (Forbes *et al.*, 2010):

$$E[X] = \sum_{j=1}^2 p_j x_j = p_{hkl} \quad (7-a)$$

$$V[X] = E[X^2] - (E[X])^2 = p_{hkl} - p_{hkl}^2 = p_{hkl}(1 - p_{hkl}) = p_{hkl}q_{hkl} \quad (7-b)$$

The probability, p_{hkl} , that the pole of the particular crystal will fall within the reflection band, is equal to the fractional area of the reflection band; this is given by the modified Lorenz formula (Öztürk *et al.*, 2014) (Öztürk *et al.*, 2015):

$$p_{hkl} = \cos \theta_b \sin \beta \quad (8-a)$$

The expected number of diffracting crystals, $E[N_{hkl}]$, and its variance, $V[N_{hkl}]$, when N_g crystals are tested in this manner will be given by:

$$\begin{aligned}
 E[N_{hkl}] &= N_g E[X] = N_g p_{hkl} \\
 V[N_{hkl}] &= N_g V[X] = N_g p_{hkl} q_{hkl}
 \end{aligned}
 \tag{8-b}$$

These equations are identical to those used by the AKK formalism (Eq. 1-a,b) and show that: 1-the diffracting and non-diffracting crystal sets obey the discrete Bernoulli distribution and, 2- the testing of the constituent crystals of a random ensemble for diffraction is a Bernoulli trial, where the Bernoulli set is sampled N_g times.

The relative standard deviation, $u[N_{hkl}]$, of the expected number of diffracting particles, $E[N_{hkl}]$, is given by Eq. 2. Substituting for the probability, p_{hkl} , from Eq. 8-a and expressing the FWHM, β , in terms of experimental parameters using the Scherrer equation (Eq. 6), we obtain:

$$u[N_{hkl}] = \left(\frac{1 - \cos \theta_B \sin \beta}{N_g \cos \theta_B \sin \beta} \right)^{1/2} = \left(\frac{1 - \cos \theta_B \sin \left(\frac{K_s \lambda}{D \cos \theta_B} \right)}{N_g \cos \theta_B \sin \left(\frac{K_s \lambda}{D \cos \theta_B} \right)} \right)^{1/2}
 \tag{9-a}$$

For typical diffraction experiments the particle size, D , is one to three orders of magnitude larger than the wavelength, λ , while the Scherrer constant, K_s , is in the range of 0.85 -1.17 (Patterson, 1939a).

Consequently, the negative term in the numerator can be neglected. Then, utilizing the small angle approximation for the sine term in the denominator, we see that the relative standard deviation of the number of diffracting particles, $u[N_{hkl}]$, does not depend on the reflection indices, hkl :

$$u[N_{hkl}] \approx \left(\frac{D}{\lambda K_s N_g} \right)^{1/2}
 \tag{9-b}$$

Equation 9-b predicts that powder samples consisting of a large number of small crystals will have small relative standard deviations, $u[N_{hkl}]$, associated with the expected number of diffracting particles, $E[N_{hkl}]$. If the powder sample consists of larger crystals, a larger population should be sampled to obtain an acceptable $u[N_{hkl}]$.

2.2.2. Diffracted Intensity Statistics

In contrast to separating crystallites into diffracting and non-diffracting groups where only two outcomes are possible, the (normalized) intensity, I_i , of a given diffraction spot, S_i , within the Debye-Scherrer halo

is a continuous variable which is solely a function of the angular distance, $\Delta 2\theta_i$, of the diffraction spot from the exact Bragg condition. Various functions can be used to depict the form of the diffraction peak. In the approach published by Patterson (Patterson, 1939a) the intensities scattered by all unit cells in a crystal from an incoming plane wave are summed up in the kinematical limit by means of Fourier transforms to compute the variation of intensity with angular deviation, $\Delta 2\theta$. For spherical particles of diameter, D , this approach yields:

$$I(\Delta 2\theta_i) = A^2 \left[3 \frac{-\varsigma \cos \varsigma + \sin \varsigma}{\varsigma^3} \right]^2 \quad (10)$$

where $\varsigma = \frac{\pi}{\lambda} D \cos \theta_B \Delta 2\theta$, and A is a constant proportional to the structure factor of the reflection and the number of unit cells in the crystal³. Eq. 10 predicts that, when the diameter, D , of the spherical crystallite approaches infinity the diffracted intensity will be zero at all $\Delta 2\theta$ except $\Delta 2\theta = 0$. For a particle with finite D , the predicted diffraction pattern consists of a primary peak with its maximum intensity at $\Delta 2\theta = 0$, which is bracketed by subsidiary peaks (thickness fringes) of diminishing intensity with increasing $|\Delta 2\theta|$. Both the zeroes of the subsidiary peaks and the half-width of the primary peak can be used to obtain the diameter, D , of the diffracting particle: Numerically solving Eq.10 for the FWHM of the peak will yield the Scherrer equation (Eq.6), with the Scherrer constant, $K_s = 1.17$ (Patterson, 1939a) (Patterson, 1939b; Yan, 2006) (Ying, 2009).

In addition to physics-based equations, empirical functions which are “good fits” to intensity vs. $\Delta 2\theta$ data are also used for representing diffraction peaks. A popular choice is the Gaussian function⁴:

$$I(\Delta 2\theta_i) = \exp \left[\frac{-\Delta 2\theta_i^2}{2c^2} \right] \quad (11)$$

This equation describes a symmetric peak, with maximum intensity equal to 1, centred at $\Delta 2\theta = 0$. The width parameter “ c ” is related to the full width at half maximum (FWHM), β , of the peak through (Hagen *et al.*, 2007):

³ For the purposes of this paper, we assume, without loss of generality, that $A=1$.

⁴ Using a Gaussian function in this manner does not imply that the diffracted intensity has a normal probability distribution.

$$c = \frac{\beta}{2\sqrt{2\ln 2}} \cong 0.425\beta \quad (12)$$

In diffraction experiments the FWHM, β , is determined from the Scherrer Equation (Eq. 6) for the particular experiment.

Figure 3 shows the peak profiles for a 5 nm spherical particle computed from Equations 10 and 11. It is seen that the Gaussian approximation maintains reasonable fidelity with the actual profile in the main peak, and the primary parameters we are interested in; the maximum intensity, $I_{\max}$, the total intensity, I_{total} , the integrated intensity, I_{int} , as well as the FWHM, β , are very close for both representations. However the Gaussian representation cannot capture the very low intensity subsidiary maxima (thickness fringes) described by Eq. 10. In our analysis we neglect the contribution of these fringes to the peak intensity parameters.

To compute the expected diffracted intensity and its variance, $E[I_s]$, $V[I_s]$, measured from a single crystal placed at the origin of Figure 2, the system used to detect the spot intensities must also be taken into account. Consider Figures 4-a, b where the relevant regions of Figure 2 have been transformed into equivalent representations in one-dimensional angular coordinates, with sub-bands drawn inside the (transformed) reflection and detection bands. In an experiment the detection sub-bands would correspond to pixels of a linear detector, each with approximately constant angular acceptance width, $\Delta 2\theta_{\text{PIX}}$. In such a detector each pixel records the total intensity of all diffraction spots which might fall within its angular range; the angular deviation of the pixel center, $\Delta 2\theta_j$, from the exact Bragg angle, $\Delta 2\theta_j = 2\theta_j - 2\theta_B$, determines the position of the pixel on the diffraction profile. To capture the full Bragg peak of the hkl reflection, detector coverage over four times the FWHM, β , centered at the peak position is required. Thus, the minimum number of active pixels in the detector is given by:

$$N_{\text{PIX}} \cong \frac{4\beta}{\Delta 2\theta_{\text{PIX}}} \quad (13)$$

The reflection sub-bands are the loci of poles belonging to planes which cause diffraction spots in the corresponding detector pixels. These sub-bands are also of constant angular width, $\Delta\Gamma_{\text{SB}}$, where

$\Delta\Gamma_{\text{SB}} = (\Delta 2\theta_{\text{PIX}})/2 = \Delta\theta_{\text{SB}}$. The $1/2$ factor arises due to the geometric requirements of a radial scan.

Consequently, the number of reflection sub-bands is equal to the number of detector pixels, N_{PIX} . Recasting the problem in this form does not change the expected number or variance of diffracting crystals:

the total fractional area where pole activation is possible is the same for Figures 2 and 4-a; Eqs.1 and 9 are still valid in this configuration.

For a given hkl reflection, the expected intensity, $E[I_s]$, and its variance, $V[I_s]$, for one random crystal placed at the centre of the diffractometer can be computed from the sum of the expected intensity values of the diffracting and non-diffracting angular regions of the diffraction system:

$$E[I_s] = E[I_s]_{Non-diffracting} + E[I_s]_{Diffracting} \quad (14-a)$$

The non-diffracting region of the diffractometer encompasses an angular range equal to $2\pi - 4\beta$, and the expected intensity from this non-diffracting region is identically equal to zero. Thus, the expected intensity can be written simply as a sum over the detector pixels which span the Bragg diffraction range:

$$E[I_s] = \sum_{j=1}^{N_{PIX}} p_j I_j \quad (14-b)$$

Using similar reasoning, the equation for the variance of the intensity, $V[I_s]$, becomes:

$$\begin{aligned} V[I_s] &= E[I_s^2] - (E[I_s])^2 \\ &= \sum_{j=1}^{N_{PIX}} p_j I_j^2 - \left(\sum_{j=1}^{N_{PIX}} p_j I_j \right)^2 \end{aligned} \quad (14-c)$$

The term, p_j , is the probability that there will be an activated pole in the j^{th} sub-band, and a corresponding spot, of intensity, I_j , in the j^{th} pixel. For each pixel in the detector, the probability, p_j , is equal to the fractional area of the corresponding reflection sub-band on the sphere. This term is computed using an approach similar to the modified Lorenz equation (Eq. 8-a).

The expected total intensity diffracted into the detector, $E[I_{total}]$, and its variance, $V[I_{total}]$, when N_g crystals are tested are given by:

$$\begin{aligned} E[I_{total}] &= N_g E[I_s] \\ V[I_{total}] &= N_g V[I_s] \end{aligned} \quad (14-d)$$

Thus, the relative standard deviation of the total intensity, $u[I_{total}]$, is given by:

$$u[I_{total}] = \frac{\sqrt{N_g \left[\sum_{j=1}^{N_{PIX}} p_j I_j^2 - \left(\sum_{j=1}^{N_{PIX}} p_j I_j \right)^2 \right]}}{N_g \sum_{j=1}^{N_{PIX}} p_j I_j} \quad (14-e)$$

Comparing Equations 1 and 14a-e we observe that, in general, diffracted intensities from constituents of a randomly oriented ensemble of N_g crystals would not be expected to satisfy the Bernoulli distribution.

Consequently, the relative standard deviation for the expected number of diffracting particles, $u[N_{hkl}]$, and the relative standard deviation of the total intensity that these diffract into a detector, $u[I_{total}]$, might not be equal for all crystal sizes and detector configurations as dictated by Equation 4. In the following analysis we derive the equations for computing relative standard deviation values of diffracted intensity for several cases.

We first consider the special case where the powder sample consists of very large crystals. When the size, D , of the crystals in the ensemble tends to very large values, the corresponding peak FWHM, β , tends to zero (Eq. 6). Consequently, the diffraction peaks of these large particles oriented properly for diffraction become Dirac δ functions, all falling on $\Delta 2\theta = 0$ (Eqs.10, 11). In such cases all diffracting particles will have spots with the same intensity in just the central pixel, and the reflection sub-band corresponding to the central pixel in Figure 4-a will be the entire reflection band. Thus, the summations in Equations 14-a,b will be over two regions, and the expected value and variance for the total diffracted intensity will be identical to the expected value and variance computed for the total number of diffracting crystals using Equations 1-a,b. Under these conditions the diffracted intensities will possess the (discrete) Bernoulli distribution by definition, and $u[N_{hkl}] \equiv u[I_{total}]$.

For the general case, where the crystals making up the powder sample have sizes which result in diffraction peaks of finite breadth, numerical analysis must be employed to compare the relative standard deviations, $u[N_{hkl}]$, $u[I_{total}]$. However, it is possible to obtain a simple analytical comparison by assuming that: 1-the diffracted intensity is represented by the Gaussian equation (Eq.11), and 2- the probability, p_j , of all sub-bands in the reflection band, $j \in [1, N_{PIX}]$, is constant⁵. For convenience we assume that this constant probability, p_{SB} , corresponds to the probability of the (central) sub-band which corresponds to the central pixel in the detector. This probability, p_{SB} , is given by:

⁵ This is a reasonable approximation for relatively sharp Bragg peaks with maxima at low θ_B values.

$$p_{SB} = \cos \theta_B \sin \left(\frac{\Delta \theta_{SB}}{2} \right) \quad (15)$$

Using Equations 11 and 14-b, the expected intensity in the detector when one crystal is tested is expressed as:

$$E[I_s] = p_{SB} \sum_{j=1}^{N_{PIX}} I_j \cong \frac{p_{SB}}{\Delta 2\theta_{PIX}} \int_{-\infty}^{\infty} \exp \left[-\frac{(\Delta 2\theta)^2}{2c^2} \right] d(\Delta 2\theta) = \frac{p_{SB} c \sqrt{2\pi}}{\Delta 2\theta_{PIX}} \quad (16-a)$$

The normalization term, $1/\Delta 2\theta_{PIX}$, transforms the integrated area to the total intensity value. It can be shown numerically that the convergent improper integral used in the evaluation is almost identical to the summation term it replaces when the detector coverage is $\geq 4\beta$.

Substituting for the terms, p_{SB}, c , using Equations 12 and 15, and utilizing the sine small angle approximation :

$$E[I_s] = \frac{p_{SB} c \sqrt{2\pi}}{\Delta 2\theta_{PIX}} \cong 0.266 \beta \cos \theta_B \quad (16-b)$$

Thus, the expected intensity for a Gaussian diffraction peak is proportional to the product of the FWHM of the peak and the cosine of the Bragg angle. Substituting for β from the Scherrer equation (Eq. 6):

$$E[I_s] \approx \frac{0.266 K_s \lambda}{D} \quad (16-c)$$

Thus, when a single crystal is tested in the diffractometer, the expected intensity in the detector is inversely proportional to the crystal diameter.

The variance of the diffracted intensity associated with one crystal, $V[I_s]$, is obtained using a similar procedure:

$$\begin{aligned} V[I_s] &= p_{SB} \sum_{j=1}^{N_{PIX}} E[I_j^2] - (E[I])^2 \cong \frac{p_{SB}}{\Delta 2\theta_{PIX}} \int_{-\infty}^{\infty} \left\{ \exp \left[-\frac{(\Delta 2\theta)^2}{c^2} \right] \right\}^2 d(\Delta 2\theta) - \left(\frac{p_{SB} c \sqrt{2\pi}}{\Delta 2\theta_{PIX}} \right)^2 \\ &= \frac{p_{SB} c \sqrt{\pi}}{\Delta 2\theta_{PIX}} \left(1 - \frac{2 p_{SB} c \sqrt{\pi}}{\Delta 2\theta_{PIX}} \right) \end{aligned} \quad (17-a)$$

Substituting for the p_{SB}, c terms, we obtain:

$$V[I_s] \cong 0.188\beta \cos\theta_B (1 - 0.377\beta \cos\theta_B) \quad (17-b)$$

Since the FWHM, β , of the Bragg peak in radians is much smaller than one, the negative term in the parentheses can be neglected. Thus, we see that the variance of the diffracted intensity increases with increasing peak-breadth and decreasing Bragg angle.

To express the variance, $V[I_s]$, of the single particle in terms of experimental parameters, the Scherrer Equation (Eq. 6) is utilized:

$$V[I_s] \approx \frac{0.188K_s\lambda}{D} \left(1 - \frac{0.377K_s\lambda}{D} \right) \quad (17-c)$$

It is seen that the variance of the expected diffracted intensity also decreases with increasing particle size; since the negative term in the parentheses can be neglected, and given the range of magnitudes possible for K_s and λ , we see that the crystal diameter is the primary variable influencing the variance of the diffracted intensity from one crystallite.

After N_g crystals have been tested, the total expected intensity in the detector and its variance is obtained from Equations 16-c and 17-c:

$$\begin{aligned} E[I_{total}] &= N_g E[I_s] \approx \frac{0.266N_g K_s \lambda}{D} \\ V[I_{total}] &= N_g V[I_s] \approx \frac{0.188N_g K_s \lambda}{D} \end{aligned} \quad (18)$$

The relative standard deviation of the total diffracted intensity, $u[I_{total}]$, is given by:

$$u[I_{total}] = \frac{\sqrt{V[I_{total}]}}{E[I_{total}]} = \left(\frac{2.65(1 - 0.377\beta \cos\theta_B)}{N_g \beta \cos\theta_B} \right)^{1/2} \quad (19-a)$$

Equation 19-a intimates that the relative standard deviation of the total diffracted intensity, $u[I_{total}]$, is identically equal to zero for all N_g , if the difference term in the numerator, $(1 - 0.377\beta \cos\theta_B)$, is zero.

For our experimental conditions, this would correspond to a 111 Au peak with FWHM of approximately 152° ; such a peak breadth would result from a crystal smaller than the diameter of a single atom.

Consequently, this is an unphysical solution.

If, in Equation 19-a, we substitute for β from the Scherrer equation, we can express the relative standard deviation of the total diffracted intensity in terms of experimental parameters:

$$u[I_{total}] \cong \left(\frac{2.65D}{N_g K_s \lambda} \right)^{1/2} \quad (19-b)$$

We can now obtain the ratio of the relative standard deviations of diffracting particles and diffracted intensities from Equations 9-b and 19-b:

$$\frac{u[I_{total}]}{u[N_{hkl}]} \cong \frac{\left(\frac{2.65D}{\lambda K_s N_g} \right)^{1/2}}{\left(\frac{D}{\lambda K_s N_g} \right)^{1/2}} \cong 1.63 \quad (20)$$

Thus, in the most ideal case, the ratio, $u[I_{total}]/u[N_{hkl}]$, is a constant, independent of all experimental parameters. In such a case, for all reflections, the relative standard deviation of the total diffracted intensity is expected to be approximately 1.6 times greater than the relative standard deviation of the number of diffracting particles when the sample size of illuminated particles, N_g , is sufficiently large.

2.2.3. Expected Value and Variance Parameters for Maximum and Integrated Intensities

The analysis described above is applicable to the total diffracted intensity, which is obtained by summing the recorded intensities in all pixels of the active detector. Experiments which record total intensity with wide-open scintillation or proportional counters can also be treated by this formalism. In general practice, however, one usually reports either the maximum, I_{max} , and/or the integrated intensities, I_{int} , associated with the diffraction peak⁶. In what follows we extend our analysis to these parameters.

Expected Value and Variance Values for the Maximum Diffracted Peak Intensity:

We define the maximum peak intensity, I_{max} , as the total intensity in the central pixel which is recorded at $\Delta 2\theta = 0$. We note that for both intensity representations (Eqs. 10, 11), the normalized diffracted intensity from particles properly aligned to scatter into the central pixel is unity, $I_{CP} \equiv 1$. Consequently, if a single particle is placed at the diffractometer origin, the expected value and variance values of the intensity for this pixel are given by:

$$\begin{aligned} E[I_{CP,s}] &= p_{SB} I_{CP,s} = p_{SB} \\ V[I_{CP,s}] &= p_{SB} (1 - p_{SB}) \end{aligned} \quad (21-a)$$

⁶ I_{int} is preferred due to the difficulty in precisely determining I_{max} .

The corresponding values after testing N_g crystals are obtained by substituting $E[I_{CP,s}]$, $V[I_{CP,s}]$ in

Equation 14-d:

$$\begin{aligned} E[I_{\max}] &= N_g p_{SB} \\ V[I_{\max}] &= N_g p_{SB} (1 - p_{SB}) \end{aligned} \quad (21-b)$$

Equations 21-b have the same form as the corresponding values for diffracting particles given by Equations 1-a, b. Consequently, the relative standard deviation of the maximum intensity of the diffraction peak, $u[I_{\max}]$, is expected to be identical to the relative standard deviation of diffracting crystals, $u[N_{hkl}]$. However, since, in general, the sub-band probability is much smaller than the reflection band probability, $p_{SB} \ll p_{hkl}$, the number of crystals tested, N_g , must be quite large to ensure that a statistically sufficient number of particles have their poles within the central reflection sub-band. Otherwise random statistical variations in the number of particles diffracting into the central pixel, which directly affect the maximum intensity observed in the central pixel, might obscure the expected equivalency.

Expected Value and Variance of the Integrated Diffracted Intensity:

Here we define the integrated intensity of the diffraction peak, I_{Int} , as:

$$I_{Int} = \int_{-2\beta}^{2\beta} I(\Delta 2\theta) d\Delta 2\theta \quad (22-a)$$

This quantity corresponds to the area under the diffraction peak (Figure 3). For the geometry shown in Figure 4-b, this integral can be expressed as a Riemann sum:

$$I_{Int} = \sum_{j=1}^{N_{PIX}} \Delta 2\theta_{PIX} I_j \quad (22-b)$$

where $\Delta 2\theta_{PIX}$ is the (constant) pixel width.

The expected value of the integrated intensity for a single illuminated crystal will be:

$$E[I_{Int,s}] = \Delta 2\theta_{PIX} p_{SB} \sum_{j=1}^{N_{PIX}} I_j \quad (23-a)$$

The corresponding value when N_g randomly oriented crystals are tested is given by:

$$E[I_{Int}] = N_g \Delta 2\theta_{PLX} p_{SB} \sum_{j=1}^{N_{PLX}} I_j \quad (23-b)$$

Comparing this equation with Equation 14-d, we see that, when $p_j = p_{SB}$ for all j ,

$$E[I_{Int}] = \Delta 2\theta_{PLX} E[I_{total}] \quad (23-c)$$

Thus, the expected integrated intensity computed using the Riemann sum will be smaller than the expected total intensity evaluated from Equations 14-b, d, due to the multiplier term $\Delta 2\theta_{PLX}$.

The variance in integrated intensity, $V[I_{Int,s}]$, for a single crystal placed in the diffractometer, is obtained from:

$$V[I_{Int,s}] = E[I_{Int,s}^2] - (E[I_{Int,s}])^2 \quad (24-a)$$

Here the $E[I_{Int,s}^2]$ term is given by:

$$E[I_{Int,s}^2] = \sum_{j=1}^{N_{PLX}} p_j (\Delta 2\theta I_j)^2 = p_{SB} (\Delta 2\theta)^2 \sum_{j=1}^{N_{PLX}} I_j^2$$

Thus,

$$V[I_{Int,s}] = p_{SB} (\Delta 2\theta)^2 \left[\sum_{j=1}^{N_{PLX}} I_j^2 - \left(p_{SB} \sum_{j=1}^{N_{PLX}} I_j \right)^2 \right] \quad (24-b)$$

The variance of the integrated intensity when N_g randomly oriented crystals are tested is:

$$\begin{aligned} V[I_{Int}] &= N_g (\Delta 2\theta_{PLX})^2 V[I_{Int,s}] \\ &= (\Delta 2\theta_{PLX})^2 V[I_{total}] \end{aligned} \quad (24-c)$$

Consequently, the relative standard deviation of the integrated intensity becomes:

$$u[I_{Int}] = \frac{\sqrt{V[I_{total}]}}{E[I_{total}]} = u[I_{total}] \quad (25)$$

The relative standard deviation of the integrated intensity, $u[I_{Int}]$, will be equal to the relative standard deviation of the total intensity $u[I_{total}]$. Hence, the relative standard deviation of the integrated intensity

would be approximately 1.6 times greater than the relative standard deviation of the number of diffracting particles.

3. Numerical Modelling

We used two types of numerical modelling to test the formulations described above. In the first case, the simulation was based on the simple, 1-D geometry depicted in Figures 1 and 4, with all of the attendant assumptions. In the second case, we used a full 3-D simulation which relaxed most assumptions; for example, in this model a grain could diffract into the detector with multiple poles. The results of these modelling efforts and their comparison to analytically predicted values will be described next.

3.1. 1-D Modelling

The 1-D diffraction geometry used in this system is shown in Figure 4-a, b. In this figure the angular positions of any hkl pole (Fig. 4-a), and its corresponding diffraction spot (Fig. 4-b) are represented by their projections on the diffractometer axis. To enable the computation of random particle selection, the full length of the diffractometer axis is partitioned into segments, of constant length, which represent the detector pixels and their corresponding reflection sub-bands. In reflection space, where the diffractometer axis spans the full Γ range from $\Gamma = 0$ to $\Gamma = \pi/2$, the segment length is taken as the projection of the arc subtended by the central sub-band of breadth, $\Delta 2\theta_{PIX}/2$. The reflection band, which is the locus of all hkl poles resulting in finite diffracted intensity in the detection band, contains those line segments which are within (projected) angular limits of $\mp \beta$, around angle, Γ_B . This construction places the center of the central sub-band at Γ_B , with the centers of the sub-bands bracketing this central sub-band at angles $\Gamma_{\pm j} = \Gamma_B \pm j(\Delta\theta_{PIX}/2)$. Because of the finite width of the sub-bands, this approach yields reflection band breadths which can be slightly larger than the targeted width, 2β ; this deviation increases with increasing pixel width. We note that this construction is approximately angle-true only for the sub-bands very close to the angle, Γ_B . However, while the individual segments outside the reflection band are not angle-true, the total angular breadth of the diffractometer line not contained in the reflection sub-band corresponds exactly to the angular breadth of the non-diffracting region.

A simple subroutine, based on the integer pseudo-random number generator of the Mathematica (Wolfram Research, 2004) program was used to simulate the poles falling within the sub-bands of the reflection band. This **particle/pole-identification subroutine (PPIS)** generated a set of points which were distributed randomly over all sub-bands on the diffractometer axis. The points which ended up within the sub-bands of the reflection band were designated as active poles. A second sub-routine, the

diffracted-intensity subroutine (DIS), computed the diffracted intensity in each detector pixel by totalling all points within the sub-band corresponding to the particular pixel and multiplying this value by the ideal intensity corresponding to the angular position, $\Delta 2\theta_j$, of the centre of this pixel (Figure 4-b). In this calculation the ideal intensity was computed from Equation 11. By further processing the output from the diffracted-intensity subroutine we could obtain the total, integrated and maximum peak intensities of the reflection being simulated.

In the simulations we modelled the 111 reflection from an ensemble of 100,000, 5 nm diameter, perfectly crystalline, spherical gold particles, illuminated by x-rays of wavelength 1 Å. We assumed a lattice parameter of 4.0800 Å for the FCC Au lattice. We term this construct the “**ideal powder experiment (IPE)**” in the following sections. In this ideal experiment the Bragg angle of the 111 reflection, θ_B , and the [111] orientation angle, Γ_B , correspond to 12.255 and 77.745 deg. respectively (Figure 5), and the FWHM of the 111 peak, computed from Eq.(6) using $K_S = 1.17$, is 1.37 degrees.

3.1.1. Statistics of Number of Diffracting Particles for the Ideal Powder Experiment

Table 1 summarizes the particle statistics results obtained from the PPIS subroutine when the ideal powder experiment described above was simulated, as well as the analytically predicted results for this case. The upper section of Table 1 lists the expected number of particles diffracting into the 111 Bragg reflection, $E[N_{111}]$, its expected standard deviation, $\sqrt{V[N_{111}]}$, and relative standard deviation, $u[N_{111}]$, computed using Equations 8-a,b, for an ensemble containing 100,000 ideal Au spheres. For these computations the ideal breadth of the reflection band, 2β , was used. The lower section of Table 1 contains our simulation results for a pixelated detector; the half pixel-sizes listed in the first column correspond to the angular coverage of the corresponding sub-bands. Column 2 lists the number of sub-bands which cover the entire reflection band. Due to the necessity of using an integer number of pixels, the effective reflection band breadths are broader than the ideal case (see column 3). As expected the deviation from ideal coverage increases with increasing pixel size. Column 4 lists the total numbers of diffracting particles in the effective reflection bands; these values were obtained by summing the particle populations in all reflection sub-bands after 100,000 ideal particles were randomly distributed over the 1-D diffractometer. For each sub-band breadth, the reported values correspond to averages from 10 trials of 100,000 particles each. The associated standard deviations, $\sigma[N_{111}]$, (column 5) were obtained from the dispersion of the N_{111} results within these 10 trials and these were constant, at about 2% for all cases. We note that $\sigma[N_{111}]$ does not reflect the systematic increase of the average number of diffracting particles

vs. their expected value with increasing pixel size; this increase, an instrumental artefact, is caused by the broadening of effective reflection-band breadth with increasing pixel size.

Column 6 of Table 1 lists the relative standard deviations of the number of diffracting particles, $u[N_{hkl}]$, for each pixel size. The average of these values shown in the last row (1.8 ± 0.3 %) is close to the result obtained from the analytical formulation (2%), confirming the validity of the Bernoulli distribution for describing the sampling statistics for diffracting particles within a powder sample of ideal nano-particles.

Table 1 Predicted and simulated statistics for the number of diffracting particles contributing to the 111 reflection of the IPE. The upper section lists the expected number of diffracting particles, $E[N_{111}]$, expected standard deviation, $\sqrt{V[N_{111}]}$, and relative standard deviation, $u[N_{111}]$. The lower section contains the corresponding values from numerical simulations.

Analytical Computation					
		Ideal reflection band breadth (x β)	$E[N_{111}]$	$\sqrt{V[N_{111}]}$	$u[N_{111}]=\frac{\sqrt{V[N_{111}]}{E[N_{111}]}$ (%)
		2	2340	48	2.0
Simulation					
$\frac{1}{2}$ pixel size (deg.)	N_{SB}	Effective reflection band breadth (x β)	N_{111}	$\sigma[N_{111}]$	$u[N_{111}]$ (%)
0.2	15	2.21	2561	56	2.2
0.1	29	2.14	2468	33	1.4
0.04	70	2.06	2426	41	1.7
0.02	139	2.05	2374	42	1.8
0.01	277	2.04	2354	43	1.8
Average					1.8±0.3

3.1.2. Statistics of Total Peak Intensities for the Ideal Powder Experiment

The statistical variations in the total peak intensities for the 111 Au peak (obtained from DIS) are summarized in Table 2. The simulated total intensities, I_{total} , are quite close to the expected intensity value, $E[I_{total}]$, and the systematic bias in the number of diffracting particles caused by finite pixel size is not observed since particles at the edges of the reflection band do not contribute intensity to the peak.

Using the intensity and diffracting particle relative standard deviations, $u[I_{total}]$, $u[N_{111}]$, in Tables 1 and 2, their ratio, $u[I_{total}]/u[N_{hkl}]$, for all cases were calculated. These values are listed in the last column of Table 2. The average value for $u[I_{total}]/u[N_{hkl}]$ obtained from the simulations (1.75 ± 0.15), is in reasonable agreement with the value obtained from the ratio of the analytical computations (1.62), and the prediction of the simplified, reflection-independent form given by Equation 20 (1.63).

Table 2 Predicted and simulated statistical variations in the total intensity of the 111 Bragg peak caused by stochastic diffracting particle selection for the ideal powder experiment.

Analytical Computation				
	$E[I_{total}]$ (A.U.)	$\sqrt{V[I_{total}]}$ (A.U.)	$u[I_{total}]$ (%)	$\frac{u[I_{total}]}{u[N_{hkl}]}$
	623	21	3.4	1.62
Simulation				
Pixel size (deg.)	I_{total} (A.U.)	$\sigma[I_{total}]$ (A.U.)	$u[I_{total}]$ (%)	$\frac{u[I_{total}]}{u[N_{hkl}]}$
0.4	626	23	3.7	1.7
0.2	614	16	2.6	1.9
0.08	613	19	3.1	1.8
0.04	628	17	2.7	1.5
0.02	629	21	3.3	1.8

Average	3.1±0.4	1.75±0.5 ⁷
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3.1.3. Statistics of Integrated Peak Intensities for the Ideal Powder Experiment

One can use either numerical integration or peak-fitting to determine integrated peak intensities and their uncertainties from simulated I_j vs. $\Delta 2\theta_j$ data obtained from the DIS. In our analysis, we fitted each data set using the Gaussian Eq. 11, and tabulated the integrated and maximum intensities obtained from the fitting program. In Figure 5 the average simulated I_j vs. $\Delta 2\theta_j$ data for the Au 111 reflection, obtained from 10 sets of 100,000 gold spheres, are plotted for five pixel sizes. The fitted Gaussian peaks are also shown. In these figures the total intensity for each peak, I_{total} , is constant (Table 2), while the integrated intensity, I_{int} , decreases with decreasing pixel size as predicted by Equation 22-b.

The results of our analysis of integrated intensities are shown in Table 3. We observe good agreement between the computed $E[I_{int}]$, $\sqrt{V[I_{int}]}$ values and their counterparts from the simulation runs, I_{int} , $\sigma[I_{int}]$, for all pixel sizes. The integrated and total intensity ratios, $E[I_{int}]/E[I_{total}]$, I_{int}/I_{total} , in Table 3 satisfy Equation 22-b and yield the pixel size of the detector assumed in the corresponding computation. Furthermore, we observe reasonable agreement between the values listed in columns 4 and 5 and the corresponding columns of Table 2, in agreement with the predictions of Equations 23-25.

3.1.4. Statistics of Maximum Peak Intensities for the Ideal Powder Experiment

In the theoretical analysis section (Eqs. 21-a, b) we showed that, since the ideal normalized intensity diffracted by each particle into the central pixel at $\Delta 2\theta_j = 0$ is one, we expect both the particle and the intensity statistics to obey the Bernoulli distribution, with $E[N_{111,SB}] = E[I_{Max}]$ and $\sqrt{V[N_{111,SB}]} = \sqrt{V[I_{Max}]}$. For such a case the relative mean uncertainties, $u[N_{111,SB}]$, $u[I_{Max}]$, are equal by definition and their ratio, $u[I_{Max}]/u[N_{hkl}]$, is identically equal to unity. Table 4 summarizes our analytical computations and simulation results for this case for a range of pixel sizes. Analytical formulations show that a single pixel collects diffracted intensity from significantly fewer particles and,

⁷ The standard deviation in this case was obtained by propagating the errors associated with $u[I_{total}]$, $u[N_{hkl}]$, in quadrature.

thus, they predict a dramatic increase in the relative mean uncertainties, $u[N_{111,SB}]$, $u[I_{Max}]$, with decreasing pixel size. The simulation results confirm the same trends. However, due to statistics of small numbers, the agreement between predicted values and simulation results is not very good, particularly at the smallest pixel size. Better agreement can be achieved by increasing the number of illuminated crystals; if we used 10,000,000 particles in our simulations, the expected number of particles diffracting into the central pixel would be 853 ± 29 , which would correspond to a relative mean uncertainty of 3.4%.

Table 3 Predicted and simulated statistical variations in the integrated intensity of the 111 Bragg peak caused by stochastic diffracting particle selection for the ideal powder experiment. The results for I_{Int} and $\sigma[I_{Int}]$ are from ten independent least-squares Gaussian fits for each pixel size.

Analytical Computation					
Pixel size (deg.)	$E[I_{Int}]$ (A.U.)	$\sqrt{V[I_{Int}]}$ (A.U.)	$u[I_{Int}]_A$ (%)	$\frac{u[I_{total}]_A}{u[N_{hkl}]_A}$	$\frac{E[I_{Int}]}{E[I_{total}]}$
0.4	249	9	3.73	1.82	0.4
0.2	125	4.2	3.36	1.64	0.2
0.08	50	1.7	3.36	1.64	0.08
0.04	24.9	0.84	3.36	1.64	0.04
0.02	12.54	0.42	3.35	1.64	0.02
Simulation					
Pixel size (deg.)	I_{Int} (A.U.)	$\sigma[I_{Int}]$ (A.U.)	$u[I_{Int}]$ (%)	$\frac{u[I_{total}]}{u[N_{hkl}]}$	$\frac{I_{Int}}{I_{total}}$
0.4	249	10	4.0	1.8	0.40
0.2	125	6	4.5	2.6	0.20
0.08	49	1	2.7	1.6	0.08
0.04	25	1	3.1	1.7	0.04
0.02	13	0.4	3.4	1.9	0.02
Average			3.5±0.6	1.9±0.4	

Table 4 Predicted and simulated statistical variations in the maximum intensity of the 111 Bragg peak caused by stochastic diffracting particle selection for the ideal powder experiment. The simulation results are from ten independent trials for each pixel size. Here the maximum intensity is defined as the intensity in the central pixel located at $\Delta 2\theta_j = 0$, averaged over ten trials.

Analytical Computation-Maximum Intensity			
Pixel size (deg.)	$E[N_{111,SB}]; E[I_{Max}]$ #, (A.U.)	$\sqrt{V}[N_{111,SB}]; \sqrt{V}[I_{Max}]$ #, (A.U.)	$u[N_{111,SB}]; u[I_{Max}]$ (%)
0.4	171	13	8
0.2	85	9	11
0.08	34	6	18
0.04	17	4	24
0.02	9	3	33
Simulation-Central pixel values			
Pixel size (deg.)	$N_{111,SB}, I_{max}$ (A.U.)	$\sigma[N_{111,SB}], \sigma[I_{max}]$ (A.U.)	$u[N_{111,SB}], u[I_{Max}]$ (%)
0.4	174	11	6
0.2	89.7	14	15
0.08	31	5	16
0.04	19	4	19
0.02	10	2	23

3.1.5. Summary for the 1-D simulation of the Ideal Powder Experiment

Our simple 1-D simulation of an ideal powder diffraction experiment shows that, while statistical formulations based on the (binomial) Bernoulli distribution are valid for predicting the uncertainty associated with the number of diffracting particles, these formulations cannot be used to describe the uncertainty in the total or integrated intensities of a Bragg peak when the peak-breadth is finite. However, these (Bernoulli) formulations can be used to link the maximum intensity in the central pixel to the number of particles scattering into this pixel when the pixel width is much smaller than the FWHM of the

peak: In this case all particles diffract the same intensity at the exact Bragg angle, thus satisfying the Bernoulli assumption. We observe that, since the probability of a randomly oriented particle diffracting into this particular pixel is quite small, much larger numbers of crystals should be illuminated to avoid errors associated with small number statistics.

3.2. 3-D Modelling

To check if our 1-D modelling results, with their attendant assumptions, were valid, we modelled the Au 111 reflection in the full 3-D geometry depicted in Figure 2. In keeping with the 1-D modelling, 10 sets of 100,000 identical, randomly oriented, spherical gold crystals, each 5 nm in diameter, were tested for diffraction into the 111 Bragg reflection when illuminated with a plane-wave of x-rays with 1 Å wavelength. The angular breadths of the reflection and detection bands are 2β and 4β , respectively. We assumed that the detection band was instrumented with 0.02° wide pixels. The main difference from the 1-D case was the inclusion of multiplicity in the simulation: in the 3-D model the full symmetry of the cubic lattice was taken into account, i.e., for a given crystal, if any of its eight, symmetrically equivalent $\langle 111 \rangle$ directions intercepted the reflection band, a diffracted beam into the detection band was generated⁸. In addition, if the random orientation of a given crystal was favourable, multiple diffracted spots from this crystal were permitted. The intensities of all diffracted beams were computed from the more exact Patterson Equation (Eq. 10).

The inclusion of all lattice directions related by symmetry necessitated modifying the equations used for predicting expected diffracting particle and diffracted intensity values and their variances. The simplest way to get approximate solutions for these parameters is to multiply the sub-band probability, p_{SB} , defined by Equation 15 by the multiplicity, m_{hkl} , of the particular reflection:

$$p_{SB}^* = m_{hkl} \cos \theta_B \sin \left(\frac{\Delta \theta_{SB}}{2} \right) \quad (26)$$

This modification implicitly assumes that the diffraction probabilities of individual $\langle 111 \rangle$ directions are uncorrelated. For small particle sizes, $D < 10 \text{ nm}$, this is a weak assumption (Öztürk *et al.*, 2014) (Öztürk *et al.*, 2015).

⁸ In the 1-D case we assumed a multiplicity of one; the computed particle and intensity values referred to only a specific [111] direction.

From Equations (26) and (8), the expected number of diffracting poles, $E[P_{hkl}^*]$, its variance, $V[P_{hkl}^*]$ and its relative standard deviation, $u[P_{hkl}^*]$, when N_g crystals are tested in the full 3-D simulation can be computed as⁹:

$$\begin{aligned} E[P_{hkl}^*] &= N_g E[X^*] = m_{hkl} E[N_{hkl}] \\ V[P_{hkl}^*] &= N_g V[X^*] = m_{hkl} V[N_{hkl}] \\ u[P_{hkl}^*] &= \frac{u[N_{hkl}]}{\sqrt{m_{hkl}}} \approx \left(\frac{D}{m_{hkl} \lambda K_s N_g} \right)^{1/2} \end{aligned} \quad (27-a)$$

Here, $E[N_{hkl}]$, $V[N_{hkl}]$ and $u[N_{hkl}]$ refer to the expected number of the particles oriented for diffracting finite intensity into the hkl reflection, its variance and relative standard deviation for the case treated by Equation 8, where plane multiplicity was not taken into account. For this case a single grain could only have a specific member of the m_{hkl} equivalent poles activated in the reflection band to produce a single spot in the diffraction band.

The corresponding intensity parameters, $E[I_{total}^*]$, $V[I_{total}^*]$, and $u[I_{total}^*]$, when N_g crystals are tested in the 3-D model are given by:

$$\begin{aligned} E[I_{total}^*] &= N_g E[I_s^*] \approx m_{hkl} \left[\frac{0.266 N_g K_s \lambda}{D} \right] \\ V[I_{total}^*] &= N_g V[I_s^*] \approx m_{hkl} \left[\frac{0.188 N_g K_s \lambda}{D} \right] \\ u[I_{total}^*] &= \frac{\sqrt{V[I_{total}^*]}}{E[I_{total}^*]} \approx \frac{1}{\sqrt{m_{hkl}}} \left[\frac{2.648}{N_g \beta \cos \theta_B} \right]^{1/2} \end{aligned} \quad (27-b)$$

In these equations, the terms in brackets refer to the corresponding values for 1-D case, where the multiplicity was not taken into account.

By inspection of Equations 27-a, b, we observe that the ratio of the relative standard deviation of the expected total intensity to that of the expected number of activated poles for the 3-D case will be approximately equal to the corresponding ratio for the 1-D case. We note that it is not possible to predict

⁹ In Equation (26), as well as in the following equations, asterisk (*) refers to (1) parameters associated with the modified model where the effects of finite multiplicity are taken into account (assuming uncorrelated poles) and (2) parameters obtained from the 3-D simulation.

the expected number of diffracting grains when the multiplicity is taken into account due to the angular correlations between the orientations of the $\langle hkl \rangle$ directions. Because of this correlation, the probability of any one pole becoming activated cannot be treated as an independent Binomial event.

The results of the full 3-D simulation and the predictions of Equations 27-a, b for 100,000 tested particles are tabulated in Table 5. Acceptable agreement is observed between the predicted and simulated activated pole numbers. However, the number of diffracting grains is ~6% smaller than both the predicted and simulated activated pole populations. This difference is expected (Öztürk *et al.*, 2014), and occurs due to the angular correlation between the $\langle 111 \rangle$ directions: at small crystal sizes the acceptance angle of the crystal increases significantly and some grains contribute more than one activated pole to the reflection band.

Table 5 Simulated statistical variations in the number of activated poles and grains when ten sets of 100,000 ideal Au spheres, each 5 nm in diameter, are tested for diffraction into the 111 Bragg peak in the 3-D geometry when illuminated with monochromatic x-rays ($\lambda=1\text{\AA}$). The analytical computations provide only the activated pole parameters. Both activated pole and diffracting grain populations were obtained in the 3-D simulations where, for all illuminated grains, all eight crystal directions belonging to the $\langle 111 \rangle$ family were tested for diffraction.

Analytical Computation (Eq. 27-a)						
			Ideal reflection band breadth (x β)	$E[P_{111}^*]$	$\sqrt{V[P_{111}^*]}$	$u[P_{111}^*] = \frac{\sqrt{V[P_{111}^*]}}{E[P_{111}^*]}$ (%)
			2	18720	136	0.73
Simulation (3D)						
	$\frac{1}{2}$ pixel size (deg.)	N_{SB}	Effective reflection band breadth (x β)	$P_{111}^*,$ N_{111}^*	$\sigma[P_{111}^*],$ $\sigma[N_{111}^*]$	$u[P_{111}^*],$ $u[N_{111}^*]$ (%)
Act. Poles	0.01	277	2	18616	85	0.46
Grains	0.01	277	2	17696	64	0.36

When we compute the intensity profiles corresponding to the angular distribution of the diffracted spots around the 111 Bragg angle we notice similar trends: as seen in Table 6 the average total diffracted intensity from 10 independent trials (bottom half) is 5% lower than the predictions obtained from the modified analytical model which takes the multiplicity effect into account but not the correlation between poles (upper half). Similar to the results presented in Table 5, the standard deviations and corresponding relative uncertainties from the analytical equations and the 3-D simulations do not match perfectly. The uncertainty in the total diffraction intensities with respect to the relative uncertainty in the corresponding diffracted spot populations seems to be much more pronounced in the realistic 3-D simulation. This is also a direct result of the presence of correlated activated poles which results in correlated diffraction spots in the detector.

Table 6 Predicted and simulated statistical variations in the total intensity of the 111 Bragg peak caused by stochastic diffracting particle selection within the powder samples described in Table 5.

Analytical Computation (Eq. 27-b)					
	$E\left[I_{total}^*\right]$ (A.U.)	$\sqrt{V\left[I_{total}^*\right]}$ (A.U.)	$u\left[I_{total}^*\right]$ (%)	$\frac{u\left[I_{total}^*\right]}{u\left[P_{hkl}^*\right]}$	
	4980	59	1.19	1.64	
Simulation (3D)					
Pixel size (deg.)	I_{total}^* (A.U.)	$\sigma\left[I_{total}^*\right]$ (A.U.)	$u\left[I_{total}^*\right]$ (%)	$\frac{u\left[I_{total}^*\right]}{u\left[P_{hkl}^*\right]}$	$\frac{u\left[I_{total}^*\right]}{u\left[N_{hkl}^*\right]}$
0.02	4700	49	1.04	2.28	2.88

3.3. Extended 3-D Modelling

The 3-D simulation parameters used to obtain the results shown in Tables 6 and 7 were designed to satisfy most of the assumptions used in deriving Equations 26, 27. In particular, the Bragg angle of the 111 reflection and its breadth justified using a single probability, p_{SB} , defined by Equation 15, for the entire reflection band. To investigate the validity of our equations for the general case, where this assumption might not be justifiable, we performed a second set of 3-D simulations based on the geometry shown in Figure 2. In these second-set of simulations, the ideal powder experiment was modified by shrinking the diameter of the spherical gold particles to 2.9 nm, and increasing the x-ray wavelength to

2.29 Å. Both of these changes resulted in significantly broader peaks for the first four Au reflections: 111, 200, 220 and 311. To compensate for the increase in FWHM and the attendant simulation time, the detector pixel size was increased to 0.03°.

In Figure 6 the variation of the actual to ideal probability ratio, $\frac{p_i}{p_{SB}} \cong \frac{\cos \theta_i}{\cos \theta_B}$, is plotted for the 111, 200, 220 and 311 gold reflections over the width of the corresponding reflection bands. Here, the term p_i is the actual probability for the i -th sub-band, centred around the angle $\Gamma_i = \frac{\pi}{2} - \theta_i$ within the reflection band: $p_i = \cos \theta_i \sin\left(\frac{\Delta \theta_{SBi}}{2}\right)$. The ideal probability for the central sub-band, p_{SB} , is given by Equation 15. The angular variables for the ordinate are expressed as fractions of the corresponding FWHM of the Bragg peaks, $\frac{\Delta \theta}{\beta}$. We observe that, for all reflections studied, $\frac{p_i}{p_{SB}}$ changes quasi-linearly, with finite slope, over the reflection band. The slope of the line increases with increasing Bragg angle and peak breadth; for the 311 reflection, p_i of the limiting sub-bands is 1.6x and 0.33x, respectively, of the central band. In comparison, the slope of the $\frac{p_i}{p_{SB}}$ trace for the 111 reflection used in the first set of simulations is approximately zero (black symbols/solid line in Fig. 6); there is less than 1% difference in the p_i values over the entire reflection band. Thus, while using a constant probability, p_{SB} , for all sub-bands within the reflection band is valid for the first set of simulations, it is not expected to be valid for the second (modified) set.

In the modified ideal powder experiment simulation, ten powder ensembles, each consisting of 100,000, spherical gold particles were generated. Then, assuming that a plane wave of x-rays with wavelength 2.29 Å was used, we determined, for the first four Au reflections, the number of activated poles, the number of diffracting particles and the corresponding intensities scattered into a 2-D detector with 0.03° pixel size. Table 7 lists the relevant geometric parameters for this set of simulations.

Table 7 Geometric parameters of the 3-D simulation of sampling and intensity statistics from ideal powder samples consisting of 2.9 nm diameter, spherical gold particles. For these simulations, the wavelength of the incident plane wave was taken to be 2.29 Å. The angular parameters are defined in Figure 1.

Reflection	Multiplicity m_{hkl}	Interplanar spacing, d_{hkl} (Å)	Bragg Angle, θ_B (degree)	FWHM, β (degree)
111	8	2.3556	29.08	6.06
200	6	2.0400	34.14	6.40
220	12	1.4425	52.54	8.70
311	24	1.2302	68.55	14.48

The results of analytical computations and 3-D simulations for the activated poles within the reflection bands of the four reflections for the 2.9 nm diameter particle case are summarized in Table 8. The expected number of activated poles, $E[P_{hkl}^*]$, computed from Equation 27-a, showed excellent agreement with the mean value of activated poles, P_{hkl}^* , obtained from the 3-D simulation of ten ensembles. The agreement between the computed square root of the variance, $\sqrt{V[P_{hkl}^*]}$, and the corresponding standard deviation, $\sigma[P_{hkl}^*]$, from the simulations, was worse: the analytical formulations predicted almost 1.5x greater uncertainty for the 111 and 311 reflections than the simulation results. Consequently, the predicted and simulated relative standard deviation values for these reflections also showed significant differences.

Table 8 Statistics of the number of activated poles when ten sets of 100,000 ideal Au spheres, each 2.9 nm in diameter, are tested for diffraction into the first 4 Bragg reflections in the 3-D geometry. For each grain, all m_{hkl} crystal directions of the $\langle hkl \rangle$ family were tested for diffraction. For the analytical computations, the angular correlations between the orientations of these directions imposed by crystal symmetry were neglected.

Analytical computation (Eq. 27-a)			
Reflection	$E[P_{hkl}^*]$	$\sqrt{V[P_{hkl}^*]}$	$u[P_{hkl}^*] = \frac{\sqrt{V[P_{hkl}^*]}}{E[P_{hkl}^*]}$ (%)
111	74906	261	0.35
200	56167	226	0.40
220	112080	319	0.28
311	222710	450	0.20
3-D Simulation			
Reflection	P_{hkl}^*	$\sigma[P_{hkl}^*]$	$u[P_{hkl}^*]$ (%)
111	74925	183	0.24
200	56175	222	0.40
220	112110	300	0.27
311	222770	297	0.13

The average value, N_{hkl}^* , standard deviation, $\sigma[N_{hkl}^*]$, and relative standard deviation, $u[N_{hkl}^*]$, of the number of diffracting grains for the four reflections obtained from the 3-D simulation¹⁰ are listed in Table 9. As expected (Öztürk *et al.*, 2014) a large fraction of the irradiated grains satisfied the diffraction condition for all reflections. This fraction increased with increasing peak-breadth and multiplicity; for the

¹⁰ There is no expected value for diffracting grains in this table since the angular correlations between the activated poles from a given grain do not permit random sampling statistics to be used in predicting such values.

311 reflection almost 99% of the grains within a given ensemble were in the diffraction condition with one or more activated poles. For the first three reflections, the simulations yielded $u[N_{hkl}^*]$ values which were comparable to $u[P_{hkl}^*]$ for activated poles. For the 311 reflection, however, we obtained a very low $u[N_{hkl}^*]$ value, 0.03%, which indicated a very tight distribution of N_{hkl}^* values for this reflection.

Table 9 The average numbers of diffracting grains, N_{hkl}^* , and their standard deviations, $\sigma[N_{hkl}^*]$, $u[N_{hkl}^*]$, obtained from 3-D simulations when ten sets of 100,000 ideal Au spheres, each 2.9 nm in diameter, are tested for diffraction into the first four Bragg reflections in the 3-D geometry.

3-D Simulation			
Reflection	N_{hkl}^*	$\sigma[N_{hkl}^*]$	$u[N_{hkl}^*]$ (%)
111	52106	148	0.28
200	47595	113	0.24
220	74011	145	0.20
311	98677	25	0.03

Finally, the statistical uncertainty parameters associated with the total diffracted intensity for the powder samples described by Tables 8 and 9 are listed in Table 10. For all reflections the expected total intensity values, $E[I_{total}^*]$, are approximately ~4% greater than the average intensities, I_{total}^* , obtained from the 3-D simulation. The differences between analytical and simulation values, $E[I_{total}^*] - I_{total}^*$, are greater than the dispersions predicted by the corresponding $\sqrt{V[I_{total}^*]}$, $\sigma[I_{total}^*]$ values. The systematic differences between the expected and simulated total intensity values are due to the different intensity equations, i.e. Gaussian vs. Patterson functions, respectively, which diverge appreciably with decreasing particle size due to the increasing thickness fringe amplitudes. We note that, even for this very small particle diameter, the differences in computed and simulated “activated pole” numbers, $E[P_{hkl}^*] - P_{hkl}^*$, were within the predicted (and simulated) dispersion range, $\pm \sqrt{V[P_{hkl}^*]}$ ($\pm \sigma[P_{hkl}^*]$), indicating that the Bernoulli approach is adequate for quantifying the statistics of activated poles.

Table 10 Predicted and simulated total diffracted intensity statistics for the first four Bragg peaks of gold powder samples described in Tables 9 & 10.

Analytical Computation (Eq. 27-b)					
	$E\left[I_{total}^*\right]$ (A.U.)	$\sqrt{V\left[I_{total}^*\right]}$ (A.U.)	$u\left[I_{total}^*\right]$ (%)	$\frac{u\left[I_{total}^*\right]}{u\left[P_{hkl}^*\right]}$	
111	19963	119	0.60	1.71	
200	14973	103	0.69	1.73	
220	29945	145	0.49	1.75	
311	59890	206	0.34	1.70	
Simulation (3D)					
	I_{total}^* (A.U.)	$\sigma\left[I_{total}^*\right]$ (A.U.)	$u\left[I_{total}^*\right]$ (%)	$\frac{u\left[I_{total}^*\right]}{u\left[P_{hkl}^*\right]}$	$\frac{u\left[I_{total}^*\right]}{u\left[N_{hkl}^*\right]}$
111	19218	91	0.47	1.96	1.68
200	14358	120	0.83	2.08	3.46
220	28772	165	0.57	2.11	2.85
311	57229	149	0.26	2.00	8.67

The relative standard deviation ratios between diffracted intensities and activated poles, $\frac{u[I_{total}^*]}{u[P_{hkl}^*]}$ obtained from the analytical formalism and the simulation, as well as that between diffracted intensities and

diffracting grains, $\frac{u[I_{total}^*]}{u[N_{hkl}^*]}$, obtained from the simulation are also listed in Table 10 for all reflections. As

expected, neither $\frac{u[I_{total}^*]}{u[P_{hkl}^*]}$, nor $\frac{u[I_{total}^*]}{u[N_{hkl}^*]}$ equals unity for any case. Thus, the AKK assumption,

$u[I_{total}^*] = u[N_{hkl}^*]$, is inapplicable for all cases. For the 311 reflection, which has the highest multiplicity and the broadest Bragg peak, this assumption fails spectacularly, with $u[I_{total}^*] \approx 9u[N_{hkl}^*]$.

4. Summary and Conclusions

In this article we investigated the relationship between the number of grains satisfying the diffraction condition in a powder diffraction experiment and the corresponding intensity recorded in the detection system for a given reflection¹¹. For this purpose we developed a simple analytical framework that can be used to estimate the statistical uncertainty in these quantities and validated this framework through numerical modelling. We showed that the statistical uncertainty associated with the diffracted intensities and the corresponding population of grains satisfying the diffraction condition depend on both sample and instrumental parameters; in particular on the acceptance angle of the powder grains and on the pixel (slit) size of the detection system. We showed that the relative standard deviation of the diffracted (integrated or total) intensity of a given reflection will be equal to that of the diffracting grains only when all diffraction spots from the powder crystals have the same intensity and fall within a single pixel for that reflection. When these conditions are met, the statistics of the diffracted intensities can be described by the Bernoulli formulation. This special case exactly satisfies the implicit assumptions in the classical work on this subject, published by Alexander, Klug and Kummer in 1948.

When the diffracting particles have dimensions in the nanometer range, such that the size-dependent peak broadening results in a finite number of detector pixels to register the relevant range ($2\theta_B \pm 2\beta$) of the diffracted intensity profile, the expected intensity from a diffracting particle can no longer be predicted by the Bernoulli distribution. In such a case, a more general statistical analysis, using the probabilities of grains diffracting into different pixels with different intensities, must be used. We showed that, in such a case, the statistical uncertainty in the diffracted intensity profile is approximately 1.6 times greater than the statistical uncertainty in the number of diffracting grains. In these cases, the classical AKK formulation is inapplicable.

In diffraction experiments where the size of the diffracting particles is below 10 nm, an additional complication arises. In this size range, the excessive broadening of the acceptance angle of such particles makes it possible for one diffracting particle to contribute more than one diffracted spot to the detector pixels. Consequently, the number of diffraction spots falling on the detector can no longer be considered equal to the number of diffracting grains. In addition, since the diffraction spots belonging to the same grain are angularly correlated through crystal symmetry, their occurrence cannot be treated as discrete

¹¹ The analysis presented discusses the correlated statistical variations in the number of diffracting grains, activated poles and diffracted intensity of a single reflection from a perfectly crystalline material. If full-pattern techniques which utilize multiple reflections (including pair-distribution function analysis) are used, extended statistical formulations which consider the scattering profile over the full angular range must be used. Radial distribution function analysis from an amorphous sample has further challenges Toby, B. H. & Egami, T. (1992). *Acta Crystallographica Section A* **48**, 336-346. Toby, B. H. & Billinge, S. J. L. (2004). *Ibid.* **60**, 315-317. These formulations are beyond the scope of this paper and will be reported in a later article.

random events. This effect results in further enhancement of the relative uncertainties in the diffracted intensities with respect to the corresponding values of the diffracted spot and diffracting grain populations. Our 3-D simulations demonstrate that the correlation between the diffracted spots from a given grain increases the statistical relative uncertainty in the diffracted intensity value to approximately twice that of the statistical relative uncertainty in the number of diffraction spots in the detector. Our results also show that, when correlated spots from single grains appear in the detector, it is not possible to compute the number of diffracting grains and their dispersion analytically using random distribution statistics. Finally we observe, in this regime, that the statistical uncertainty of the diffracted intensities can be much larger than the statistical uncertainty in the number of diffracting grains within the powder sample.

In summary, our past articles and current work show that the seminal Alexander, Klug and Kummer analysis linking diffracted intensity and diffracting particle statistics is a special case, valid only for cases where the particle size is large enough to ensure: 1- the applicability of the Bernoulli statistics to both of these terms, and 2-to limit each grain to contributing a single diffracted spot to the detector. When these assumptions are no longer valid, more general formulations or modelling must be used. The analytical formulations we present in this article can be used to quantitatively link the statistical relative uncertainty in the diffracted intensity value to the statistical relative uncertainty in the number of diffraction spots in the detector within an absolute error of a few percent. This lower error limit occurs due to the correlation of the angular positions of diffracted spots from a single grain while the statistics equations used in our formulations assume that the occurrence of each spot is independent of all others. In addition, for grain sizes below 10 nm or so, rigorous 3-D modelling is needed to link the statistical relative uncertainty in the diffracted intensity value to the statistical relative uncertainty in the number of diffracting grains.

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Figure 1 Ideal geometry for a cubic single crystal oriented for diffraction from the set of (hkl) planes with plane spacing d_{hkl} . The crystal vector $[hkl]$ bisects the angle between incident and diffracted beam vectors, $\vec{k}_0, \vec{k}_S$ respectively.

Figure 3 Expected intensity profile for the 111 rocking curve of a 5nm diameter spherical gold particle illuminated with 1 Å wavelength plane x-ray beam computed via the exact Patterson equation (Eq. 10) and the Gaussian approximation (Eq. 11).

Figure 4 a) One-dimensional representation of the pole distribution within the reflection band partitioned into seven sub-bands of constant width, $\Delta\theta_{SB}$. Due to the random distribution of the hkl poles, approximately the same number of poles is expected in each sub-band, modified only by the term, $\cos\theta$, of Eq. 3. In Figure 4 b), where the detection band has been partitioned into seven sub-bands of width, $\Delta 2\theta_{PIX} = 2 * \Delta\theta_{SB}$, the diffracted intensity corresponding to each sub-band is also plotted.

Figure 5 Simulated 111 Bragg peaks for five pixel sizes. For each pixel size the average intensity of 10 sets of I_j vs. $\Delta 2\theta_j$ values, each set corresponding to the simulation of scattering from 100,000 randomly-oriented gold spheres in the 1-D diffractometer, are shown. The Gaussian peaks fitted to the average values for each pixel size are also included (solid lines). For each pixel size the error bars correspond to the standard deviations of the intensities computed in each detector pixel over 10 trials.

Figure 6 The variation of the actual to ideal diffraction probability ratio, p_i / p_{SB} , over the width of the corresponding reflection bands for the 111, 200, 220 and 311 reflections for 2.9 nm diameter Au particles illuminated with plane x-rays of wavelength 2.29Å. The solid black line shows the same ratio for the 111 Au reflection of 5 nm diameter spheres illuminated with plane x-rays of wavelength 1Å. In this case the p_i / p_{SB} ratio is constant across the reflection band.

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