

COMPUTATIONAL ANALYSIS OF
DIFFRACTION IN IDEAL
NANOCRYSTALLINE POWDERS

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ABSTRACT

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Quantifying the statistical uncertainty in diffracted intensities was first investigated by Alexander, Klug and Kummer in 1948, who developed a formulation that estimated the relative uncertainty in the diffracted intensities from the relative uncertainty in the populations of diffracting particles within an irradiated powder. In this thesis, we show that this formulation becomes inapplicable for powder ensembles with particle sizes below 1 micron. In this size regime, the probability of diffraction cannot be formulated based on simple area ratios, and the classical multiplicity, m_{hkl} should be replaced by effective multiplicities. To properly relate the diffracted intensities collected by the detector to the grains participating in diffraction, we develop a modeling methodology which isolates the sampling and intensity spaces and links each diffracting particle to its own diffracted spot. The independent investigation of diffracted intensities and diffracting particle populations reveals that the uncertainties in the diffracted intensities are almost always greater than those in the diffracting particle populations. The only special case, where the two uncertainties are equal, occurs for 'large' particle sizes, where the full angular width of the particle's characteristic rocking curve is smaller than the angular resolution of the detector pixel. Our modeling results also show that the population of particles required to reach the ultimate average diffracted intensities predicted by the Debye equation depends on the size and crystallinity of the irradiated particles. Finally, the direct link between diffracting grains and diffracted intensities is not preserved in the formulation of the Debye scattering equation, and therefore the analysis and refinement of experimental diffraction data against the Debye model are shown to result in ambiguous structural parameters.

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Chapter 1

Motivation

Current Status of the Characterization of Nanocrystalline Powders with Diffraction Techniques

X-ray diffraction is a non-destructive characterization technique, originally developed to study the structure of crystalline materials. With the increasing interest in nanomaterials in science and industry, the use of X-ray diffraction has been extended and is now focused heavily on studies of nanocrystalline powders. The current literature investigating the characterization of nanocrystalline powders by X-rays reports mostly the effort focused on processing the diffraction data, obtained either experimentally or by computer simulations, by using appropriate fitting routines and developing a plausible structural model for the atomic positions inside the nanomaterial. In that respect the data analysis efforts can be classified in two categories depending on what is implied in the analytical models that the diffraction data are optimized for: 1) the Debye scattering equation, which starts with an amorphous body as the scattering volume and 2) Rietveld refinement, which assumes infinite periodicity of the atoms within the scattering volume.

Researchers who belong to the first category are strong supporters of the direct optimizing and fitting of the whole analytical diffraction spectra generated by the Debye equation against experimentally obtained diffraction data and assigning physical meanings to the deviation from the Debye predicted intensities. For instance, Cervellino *et al.* [13] developed

an algorithm to fit the theoretical diffraction spectra of gold nanoparticles in the size range of 2-4 nm to their experimental spectra collected with synchrotron source and refined for the ensemble parameters such as particle size distribution and structure model. Chiche *et al.* [15] followed a similar fitting and refinement procedure with a simulated analytical pattern from the Debye equation and experimental diffraction data obtained by a laboratory source and also included a comparison between the diffraction based refined parameters against TEM characterization results, pointing out the differences between the information volumes of direct space (TEM) and reciprocal space (XRD) characterization techniques. Kumpf *et al.* [38] extended the same procedure to other particle systems and fitted analytically obtained diffraction spectra from ZnO, CdS and ZnS nanocrystalline powders with sizes below 5 nm against their experimental diffraction profiles, including an additional comparison between the Debye equation based whole pattern fitting and the standard Rietveld fitting algorithm.

Some researchers claimed that Rietveld-based refinement methods could not be used to model the diffraction signal from nanocrystalline powders due to the characteristic shell structure that has been shown to differ from the bulk lattice and the resulting lack of 3-D periodicity in these samples [44; 38]. But they also did not choose to optimize and fit the whole diffraction spectra from the Debye equation and instead combined the least squares error reduction algorithm behind the Rietveld method with the Debye equation based descriptions of diffraction spectra. Among them, Hall *et al.* [26] attempted to obtain the particle size distribution from an ensemble of gold nanoparticles with diameters below 5 nm by Fourier transforming the experimentally obtained diffraction spectra. This method relied on the argument that the Fourier transform of the Debye scattering equation yielded the average interatomic spacing distribution and that the maximum interatomic spacing from the distribution could reveal information about the size of the particle. This method was, however, of limited use since it did not reveal any information about the shape of the coherently diffracting volume, although it provided some advantage to the data analysis procedure by not assuming a 3-D periodicity of the atomic stacking inside the diffracting particles. Later, this method has been extended to what is known as the Pair Distribution Function (PDF) analysis, and its use on fitting the diffraction spectra from nanocrystalline

powders and refining crystallographic parameters from these fits have almost become a standard procedure [8; 40; 41; 23].

Despite the numerous criticism stated by the former group of researchers, some groups still used the Rietveld refinement analysis on the diffraction profiles of nanocrystalline powders: Rietveld refinement is based on generating diffraction profiles assuming a particular shape function for the intensity profiles and structural models with uninterrupted, long range order for the atomic stacking, which determine the position of these profiles [53]. The method was initially developed to analyze diffraction profiles of bulk materials and its application with nanocrystalline powders is based on implementing size-dependent features of such samples on their analytical diffraction spectra. Chen *et al.* recently published an article where the stress-induced texture effects were investigated by the X-ray diffraction profiles from 3, 20 and 500 nm Ni nanocrystalline powders [14]. Alayoglu *et al.* [2] did an extensive study with Pt-Ru core-shell nanoparticles combining different imaging capabilities of a number of techniques such as XRD, Debye equation fitting, PDF fitting and TEM. To analyze the diffraction data, they used the Rietveld refinement, PDF refinement and Debye function simulation and tried to incorporate the findings of all these techniques to obtain a plausible structural model.

Importance of Statistical Variations in Powder Diffraction Experiments

Although there is an immense amount of literature concentrating on different methods of analyzing experimentally collected or simulated diffraction spectra from nanocrystalline powders, there is currently no general agreement on how to process these data accurately and interpret the results. Furthermore, there is little or no understanding of how the diffracted signal originates from nanocrystalline powders and to what extent the results obtained from analyzing the diffraction data make physical sense. One of the reasons why there is no consensus on these topics is that direct imaging techniques, such as TEM measurements, are, most of the time, unable to validate independently the accuracy of the structural parameters obtained from processing the diffraction spectra: The structural parameters

obtained from analyzing diffraction patterns are volume weighted averages over the whole diffracting particle population whereas, those that are recovered from TEM measurements are local properties belonging only to the particles that are being imaged. In most cases there is no feasible way to image every single particle within the powder sample and obtain the structural parameters for the whole powder. Secondly, one does not have many options to choose from to validate the diffraction results, since most characterization techniques are destructive and/or there is incompatibility between the information and measurement volumes of different techniques [42]. As a result of these challenges, many mistakes in the characterization procedure can go unnoticed, leaving the results from current data analysis methods open to misinterpretation and contradiction.

In addition to the lack of independent justification by complementary characterization techniques, another factor that increases the ambiguity in the current diffraction analysis procedures is the complete disregard of the statistical aspect of powder diffraction experiments. Powder diffraction is inherently based on statistical orientation selection, through which a subset of particles that satisfy the diffraction condition from a larger batch are selected by the X-ray beam and allowed to contribute to the diffracted signal. When the powder is untextured and consists of identical particles, the selection process becomes identical to a random sampling event. Hence, there is always a statistical uncertainty in how many particles are selected from the larger batch and contribute to the diffraction event. In other words, even when the same experiment is repeated under fixed conditions with a number of powder samples consisting of identical particles with the exact same populations, the collected data will differ slightly from each other, due to random variations in the orientations of particles satisfying the Bragg's Law (the diffraction condition) for various reflections. This type of uncertainty is different from the uncertainty associated with the photon counting process and therefore cannot be easily estimated from the diffracted signal [19]. When the analytical diffraction spectra are modeled by the Debye equation or by assuming a structural model based on ideal 3-D periodicity in the atomic positions, as in all of the current analysis routines, there is no allowance made for these statistical fluctuations. In such cases, comparing or refining real diffraction data against ideal analytical spectra and assigning physical meanings to the deviations from such data may compromise

the accuracy of the information collected from the sample.

The literature investigating the sampling statistical aspect of the powder diffraction method is disproportionately scarce; however, one major work stands out and has been treated as the general solution to the problem of sampling statistics to date. This work was published in 1948 by Alexander, Klug and Kummer (AKK) [3], and has been the textbook reference on the topic [36; 35]. Confirmed by experimental data from bulk quartz powders [3], the AKK analysis is based on the Lorentz analysis [11] combined with the assumption that the statistical convergence behavior of the measured intensities can be directly related to the statistics of the population of particles contributing to the diffracted intensities, and there is a proportionality between the statistical uncertainties between the population of diffracting particles and the measured intensities.

Apart from Alexander, Klug and Kummer themselves, there are a few other examples in the literature where the direct application of the AKK analysis on experimental data was presented. Elton and Salt[19] published a comprehensive work in which the magnitudes of intensity uncertainty due to counting and particle sampling statistics were compared for experimental diffraction data from quartz powders with sizes between 3-9 μm . They showed that when the individual particle size was close to the upper limit, the uncertainty from particle sampling statistics could be an order of magnitude larger than the uncertainty from counting statistics. Smith [56] focused on quantifying the effect of sampling statistics in whole pattern fitting analyses of diffracted intensities and suggested an upper limit of 1 μm particle size for powder samples below which one could measure diffracted intensities that would result in repeatable refinements. Ida *et al.* [32], later confirmed for quartz and silicon powders of size 7-23 μm and 5 μm respectively that the relative uncertainties due to particle sampling statistics in diffracted intensities collected with a spinner-scan method were inversely proportional to the multiplicity of the reflections. By this finding, they suggested that the proportionality between the multiplicities and the uncertainties in the diffracted intensities could be used as a way of detecting texture in the tested powder samples.

The works of these researchers confirmed the proportionality between the intensity and particle sampling statistics predicted by the AKK analysis with experimentally obtained

diffraction data from bulk powder samples, where the individual particle size was on the order of a few microns. However, the equality between the magnitudes of relative uncertainty in the diffracting particle populations and their corresponding intensities has never been demonstrated experimentally. For some of the previously mentioned studies, the dynamic effects in the diffraction event due to large crystallite sizes were designated as the source of inequality between the uncertainties of the intensities and particle population[3]. The lack of completely controlled, monodispersed powder samples and finely tuned, high resolution experimental setups hindered further checks and confirmation of the AKK analysis with experimental data. We note that, even if these requirements were met, conducting such an experiment would be a non-trivial undertaking.

The original derivation of the AKK analysis does not specify a particle size for the statistics formulation to be applicable, hence it has been thought to be applicable globally for all random powder ensembles, irrespective of the particle size. However, this idea is unjustified: In the original derivation of the AKK analysis, the authors assumed that all diffracted intensities were concentrated at the exact Bragg angles or in their close vicinity. For bulk powders, as the past literature confirmed, this assumption is mostly satisfied; whereas, for nanocrystalline powders, the rocking curve of the particles or the angular range where the particles can diffract appreciable intensity can be as much as an order of magnitude larger than their bulk counterparts. This means that a given particle that does not satisfy the diffraction condition exactly, may still diffract a considerable amount of energy within a large angular extent. The immediate consequence of this would be higher than expected intensity measurements from small amounts of irradiated powders than the diffraction probability term predicts. The distribution of the diffracted intensities over a larger angular extent, then, may cause the measured intensities to converge to their expected values much faster than the conventional AKK formulation predicts. This discrepancy between the theoretical convergence rates and actual convergence rates of diffracted intensities has recently been observed and discussed by Fewster [21]. In this work, the author collected the diffraction profile from 300 LaB_6 crystals with sizes within 2 to 5 microns irradiated by Cu $K\alpha$ X-rays (1.54 Å) and observed the presence of clear, well separated peaks. This work suggests that for nanocrystalline powders, the failure of the AKK analysis in predicting the

intensity uncertainties due to particle sampling may be more severe. Hence, a validation of the applicability of the AKK analysis on nanocrystalline powder ensembles is required.

Structure of the Thesis

In this thesis, a new approach has been introduced to elucidate the physics behind powder diffraction experiments, focusing specifically on their application to nanocrystalline powders. This has been achieved by dividing the diffraction space into two half-spaces: A sample half-space which consists of elements accessed via real space coordinate vectors, such as the particles making up the powder sample and their corresponding pole vectors; and a diffraction half-space which consists of the diffracted spots accessed by reciprocal space coordinates. Treating these half-spaces independently, a pathway has been developed for the first time, connecting individual particles directly to their diffraction spots in the intensity space. These direct connections between the powder samples and their diffracted intensity profiles are crucial for understanding how the diffracted signal is formed and how to relate its statistical behavior mathematically to the statistics of the irradiated powder ensemble.

The analyses presented throughout the thesis have been developed by computational efforts, directly modeling the sample and its diffraction signature. In each chapter, one aspect of the new statistical formulation for nanocrystalline powder ensembles has been detailed. In **Chapter 2**, the mathematical foundations of the kinematical diffraction theory have been outlined and the process of generating ideal powder diffraction data has been detailed. In **Chapter 3**, the two half-spaces representing the diffraction event have been introduced and the parameters belonging to these half spaces (particles, poles, diffraction spots) have been described. Then, the statistical formulations developed by Alexander, Klug and Kummer [3] have been rederived for ideal gold nanocrystalline ensembles and their applicability on the statistics of the sample half-space parameters has been discussed with the help of a counting algorithm. The results from this algorithm have been used to show that the statistics of the diffracting grains and their activated poles converged to the bulk mean values at different rates. In **Chapter 4**, the different processes behind the

selection of grains and poles from a random nanoparticle ensemble have been established and the statistical analyses of the activated poles and diffracting grains have been extended to the statistics of intensity half-space parameters, namely integrated intensities and peak intensities. These computations have revealed that not only is there a difference between the statistical convergence behaviors of diffracting grain populations and activated poles from these grains, but there is also an enhancement in the statistical uncertainties of the diffracted intensities relative to the respective activated pole populations. In **Chapter 5** the mathematical foundations of the uncertainty enhancement in the integrated intensities, relative to those of the activated pole populations from ideal random nanocrystalline powders have been presented. This analysis has been followed by an investigation of the special case of powder diffraction experiments in which the assumptions of the AKK analysis were satisfied and its predictions were confirmed. In **Chapter 6** the Debye scattering equation has been analyzed and its applicability in modeling the diffraction spectra of amorphous and crystalline nanoparticle ensembles has been discussed. Lastly, in **Chapter 7** a complete summary of the new analysis has been presented and its implications on the analysis of data from diffraction experiments with nanocrystalline powder samples have been discussed.

Chapter 2

Theoretical Background

2.1 Introduction

X-ray diffraction is a commonly used, non-destructive characterization technique for analyzing the atomic structures of a wide range of materials including crystalline and amorphous materials. For the last couple of decades, it is also being increasingly used to study nanocrystalline systems. The theory of X-ray diffraction has been developed for two regimes, according to the type of interaction the incoming X-rays have with the irradiated material. These are kinematic and dynamic regimes. In kinematic diffraction, the incoming X-ray beam travels through the sample and gets scattered by the electrons across its path only once. There is no interaction between the incoming and the diffracted beams, hence the resulting diffracted intensities are due to the interaction between the X-ray beam and the material. In dynamic diffraction, this situation is completely different: In this case, there is strong interaction between the irradiated material and the X-ray beam, therefore multiple scattering within the material is observed. In addition, the diffracted beam interacts with the incoming beam, causing the extinction phenomenon, which may completely dominate the resulting intensity spectra [62; 4].

The question of which theoretical model best describes a particular diffraction event can be answered from the type of the irradiated sample: Dynamic diffraction theory provides a complete and accurate description of the underlying processes of diffraction for materials

with large coherent volumes, such as single crystalline materials above a certain size and with small to negligible defect concentrations. For samples consisting of many grains with different orientations or for nanocrystalline materials with very small coherent volumes, kinematic diffraction is a better model. Therefore, it is the purpose of this chapter to explain the basics of kinematic diffraction along with the mathematical tools we use throughout the thesis. As we explain the theory, the reasoning behind the choice of kinematic diffraction in our studies with nanocrystalline powder samples will become clear to the reader.

2.2 Kinematic Scattering From a Finite Sized Particle

In this section, the kinematic scattering formulation will be described for a finite sized particle. For such systems irradiated with X-rays, the underlying phenomenon behind the measured intensity spectrum is the interference between individually scattered waves from all scattering centers. Depending on the phase relationship between the scattered waves at a certain point, constructive or destructive interference may take place, which, then, leads to the minima and the maxima observed within an intensity spectrum, respectively, and determines the characteristic shape of the spectrum.

The kinematic scattering from a single particle can be formulated by two approaches: A local approach, in which the total diffracted beam is constructed from individually scattered waves from all atoms within the particle, is preferred in systems with low symmetry and periodicity. Materials consisting of amorphous particles, where atoms are distributed randomly within the particle volume are suitable candidates for the local approach. If the material possesses high symmetry and the stacking of atoms can be expressed in terms of simple periodic density functions, a global approach that treats the whole system with a single set of general parameters can be advantageous. Crystalline materials with negligible defects and imperfections are good candidates for this formalism.

2.2.1 Kinematic Sum over Atoms

Here we introduce the local approach where the total scattering amplitude of a given particle will be constructed from the individual contributions of each atom making up the particle.

Consistent with the procedure followed, the formulation is called the kinematic sum.

Scattering from a single atom

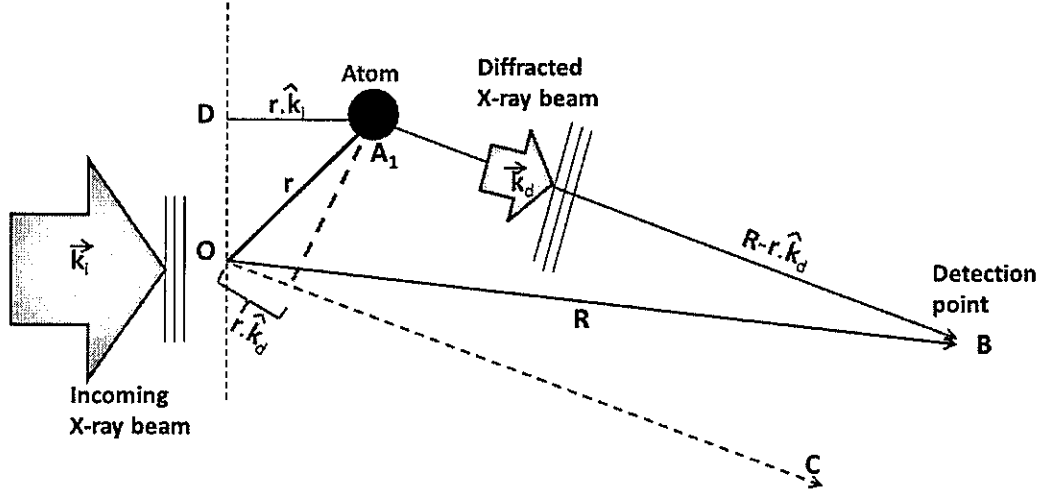


Figure 2.1: Schematic of scattering from a single atom. The notation used here distinguishes between the vector with full magnitude ($\vec{k}$) and the unit vector ($\hat{k}$) pointing in the direction of the original vector, i.e., $\vec{k} = |\vec{k}|\hat{k}$.

Figure 2.1 depicts the scattering geometry for an atom positioned at point A_1 . Here, point O is the origin of the coordinate system and point B is where the diffracted signals are to be detected. The wavevector $\vec{k}_i$ shows the propagation direction of the incoming X-ray beam which is monochromatic and planar with an amplitude $A = A_0 \exp(-2i\pi\vec{k}_i \cdot \vec{x})$ and wavelength λ , where $|\vec{k}_i| = \frac{1}{\lambda}$ (The transient component $\exp(2\pi i\omega t)$ of the wavefronts are ignored for convenience). The diffracted waves have a wavevector of $\vec{k}_d$ and they propagate from point A_1 to B . The vector $\vec{r}$ from point O to A_1 is the position vector of the atom and R is the distance from point O to B where the diffracted beams are collected.

When the X-ray beam travels from the origin to point A_1 , the electric field of the beam excites the bound electrons of the atom at A_1 , causing them to accelerate. From classical theory of electromagnetism [16; 25; 60], accelerated electrons radiate X-ray photons of the same wavelength, λ , as the wavelength of the incoming radiation, with a phase shift of π . Therefore, the scattered photons from the electrons of the atom have a def-

inite phase relationship with the incoming X-ray beam and are coherent with it. This coherency property of the scattered waves from all electrons of the atom forms the basis of the diffraction process. During the scattering process we assume that there is no energy exchange between the electrons and the incoming photon, but only a momentum exchange. Therefore, the wavelength of the radiated photons is the same as the wavelength of the incoming X-rays. This type of scattering is called elastic scattering [60; 16; 25]. Note that, for the X-ray beam-electron interaction to be an elastic process, the energy of the incoming X-ray beam has to be below the characteristic absorption energies of the atom. Otherwise, the loosely bound electrons of the atom couple strongly with the incoming beam. This causes the electrons to be excited to higher energy levels and scatter photons of lower energy, which contribute incoherently to the scattered signal [16].

In order to compute the amplitude of the coherently scattered X-ray beam by the electrons of the atom, we need to know the scattering power of the atom per unit irradiation and the phase of the diffracted waves at point B. Among these, the scattering power of an atom can be derived based on formulations that explain the interaction of the electric field of the X-rays with the electrons of the atom and solving the Schrödinger equation for the electrons [4]. These will not be included here as they are outside of our scope, but for the purposes of this text we introduce the atomic scattering factor 'f' which is an angle dependent term that is characteristic for each element and is a relative measure of the scattering amplitude of a particular atom with respect to the scattering amplitude of a single electron [60]. Its numerical value can be estimated from empirical expressions [30] or obtained from various databases [55].

To calculate the phase of the diffracted waves, we need to follow the trace of the incoming X-ray field and relate its phase change to the phase of the diffracted X-rays. For a propagating wave, the distance traveled in the direction of the wavevector can be related to the phase shift via $\phi = \frac{d2\pi}{\lambda}$, where 'd' is the distance covered. As seen in Figure 2.1, the phase of the incoming beam propagates to the detection point in three steps. In the first step, the incoming wave travels from the origin to point A_1 and covers a distance equal to $|\mathbf{DA}_1| = \vec{r} \cdot \hat{k}_i$ where $\hat{k}_i$ is the unit vector in the direction of $\vec{k}_i$. In the second step, this phase at point A_1 is transferred to the diffracted beam via the interaction between

the incoming beam and the electrons with an additional shift of π . Finally in the third step, the diffracted X-ray photons travel a distance equal to $|\mathbf{A}_1\mathbf{B}|$. In a setup where the distance from the origin to the detector is much larger than the distance from the origin to the scattering center, we can approximate the line segments $|\mathbf{A}_1\mathbf{B}|$ and $|\mathbf{OB}|$ to be parallel, $|\mathbf{A}_1\mathbf{B}| \parallel |\mathbf{OB}|$ (when in fact $|\mathbf{A}_1\mathbf{B}| \parallel |\mathbf{OC}|$). This condition is known as the far field or plane wave approximation [4] and when $R \gg |\mathbf{OA}_1|$ is applicable, $|\mathbf{A}_1\mathbf{B}| \cong R - \vec{r} \cdot \hat{k}_d$. Therefore the phase of the diffracted beams at point $\mathbf{B}$ relative to the phase of the incoming beam at origin, $\phi_{\mathbf{O}-\mathbf{B}}$ can be calculated as:

$$\phi_{\mathbf{O}-\mathbf{B}} = \frac{2\pi(\vec{r} \cdot \hat{k}_i + R - \vec{r} \cdot \hat{k}_d)}{\lambda} + \pi$$

Finally, omitting the last term which is a constant shift for all electrons that participate in scattering, the complex amplitude of the X-ray beams that are scattered by the atom at $\mathbf{A}_1$ and travel to point $\mathbf{B}$ can be written as [60]:

$$A_{atom} = f \exp(i\phi_{\mathbf{O}-\mathbf{B}}) = f \exp\left[\frac{2\pi i R}{\lambda}\right] \exp\left[-2\pi i \vec{r} \cdot (\vec{k}_d - \vec{k}_i)\right] \quad (2.1)$$

where 'f' is the atomic scattering factor. The first exponential term in Eq. 2.1 is a constant for all scattering electrons and depends only on the detector position, and therefore can be absorbed into the remaining constants. In that case, we see that the interference phenomenon is governed solely by two terms: The position of the scattering center $\vec{r}$ and the difference between the wavevectors of the incoming and diffracted X-ray beams, $\vec{k}_d - \vec{k}_i$. The second term is also known as the momentum transfer vector, denoted by $\vec{q}$.

A commonly used visual representation of the diffraction event in the kinematic and elastic regime is known as the Ewald sphere construct shown in Figure 2.2. In constructing the Ewald sphere, the incoming and diffracted wavevectors are positioned at the center of the sphere preserving their relative orientation. Hence the difference vector $\vec{q}$ starts at the tip of $\vec{k}_i$ and ends at the tip of $\vec{k}_d$. The orientation of the incoming wavevector is arbitrary, but aligning it horizontally makes the mathematical identities stand out more easily. As mentioned previously, the magnitudes of both $\vec{k}_i$ and $\vec{k}_d$ are equal to $\frac{1}{\lambda}$ and therefore the radius of the Ewald sphere is $\frac{1}{\lambda}$ as well. By convention, the angle between the incoming and the diffracted waves is denoted by 2θ and called the scattering angle. From this, the

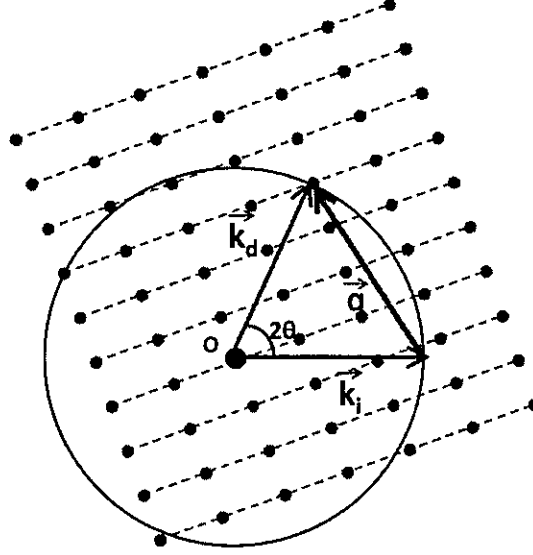


Figure 2.2: Ewald sphere construction

magnitude of the difference vector, that is the momentum transfer vector can be derived as $\frac{2 \sin \theta}{\lambda}$, where θ is half the scattering angle. The periodic points in the background of the sphere are the reciprocal lattice points.

Scattering from Many Atoms

For a given particle that consists of many atoms with known coordinate vectors, the total scattering amplitude at a point can be computed by adding up the contributions from all atoms. Since we assume a perfectly monochromatic and planar beam, the phase and amplitude of the electric field each atom interacts with are the same and therefore, the scattered waves from these atoms given by 2.1 can be summed up coherently, resulting in:

$$A_{particle}(\vec{q}) = \sum_{m=1}^N f_m \exp[-2\pi i(\vec{q} \cdot \vec{r}_m)] \quad (2.2)$$

Here N is the total number of atoms inside the particle. To calculate the total intensity, the amplitude expression must be multiplied by its complex conjugate:

$$I_{particle}(\vec{q}) = \sum_{m=1}^N \sum_{n=1}^N f_m f_n \exp[-2\pi i(\vec{q} \cdot \vec{r}_{mn})] \quad (2.3)$$

where $\vec{r}_{mn} = \vec{r}_m - \vec{r}_n$ is called the interatomic distance vector.

As seen, Equation 2.3 does not assume any symmetry operators for the position of the atoms inside the particle. Hence, it is completely general and can be used to calculate the diffracted intensity for both amorphous and crystalline particles.

2.2.2 Kinematic Sum over Unit Cells

If the scattering particle is crystalline, the atoms inside the particle are stacked periodically and thus related to each other via certain translation and rotation rules. In this case, a repeating symmetry member called a unit cell, which consists of a finite number of atoms, can be defined to represent the general atomic configuration inside a particle. Therefore, for such particles, the total scattering amplitude can be computed by summing up the scattering amplitude from individual unit cells, instead of the atoms. The scattering amplitude of a single unit cell relative to the scattering amplitude of a single electron is called the structure factor and is given by:

$$F(\vec{q}) = \sum_{m=1}^{N_c} f_m \exp[-2\pi i(\vec{q} \cdot \vec{r}_m)] \quad (2.4)$$

As seen, Equation 2.4 has the same form as Equation 2.2. The only difference between the two is in the upper limits of the summations: In the former expression, the summation is taken over all atoms in the particle whereas in the latter, it is performed over the total number of atoms within one unit cell. The value of N_c depends on the crystallographic symmetry of the particle: As an example, N_c equals to 2 for BCC materials (e.g. iron) and 4 for FCC materials (e.g. gold).

For a diffracting particle that consists of identical unit cells, we can write the atomic coordinates with respect to an arbitrary origin in terms of the distance of these atoms from the center positions of the unit cells and the positions of these unit cells relative to the origin. As a simple example, Figure 2.3 shows a cubic crystalline particle with cubic unit cells aligned parallel to the edges of the particle. For this particle, the total scattering amplitude takes the following form:

$$A_{particle}(\vec{q}) = \sum_{t_1=1}^{T_1} \sum_{t_2=1}^{T_2} \sum_{t_3=1}^{T_3} \sum_{m=1}^{N_c} f_m \exp \left[-2\pi i \vec{q} \cdot \left(\vec{r}_m + \vec{R}_{t_1, t_2, t_3} \right) \right]$$

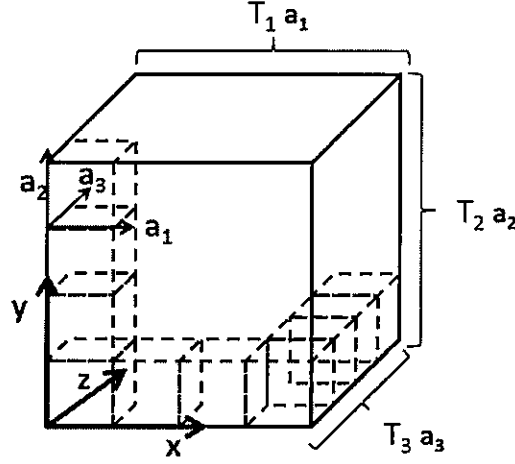


Figure 2.3: Cubic crystalline particle with cubic unit cells stacked parallel to the coordinate axes (xyz) of the particle. $\vec{a}_i, i = 1, 2, 3$ refer to the coordinate axes of the unit cells

In the above expression, T_i ($i = 1, 2, 3$) refer to the number of unit cells along the three coordinate axes of the particle, $\vec{R}(t_1, t_2, t_3)$ with $0 \leq t_i \leq T_i$ is the position vector of the unit cell center that is an orthogonal distance of $|t_i \vec{a}_i|$ from the origin in the direction of the $\vec{a}_i$ vector and $\vec{r}_m$ is the position vector of atom 'm' from the origin of the reference unit cell. Assuming that all unit cells are identical, the number of atoms in each unit cell N_c is the same and m satisfies $0 < m \leq N_c$. Expanding of the above expression and recognizing the definition of the structure factor given in Eq. 2.4) we obtain

$$\begin{aligned}
 A_{particle}(\vec{q}) &= \sum_{t_1=0}^{T_1-1} \sum_{t_2=0}^{T_2-1} \sum_{t_3=0}^{T_3-1} F(\vec{q}) \exp \left[-2\pi i \vec{q} \cdot \vec{R}_{t_1, t_2, t_3} \right] \\
 &= \sum_{t_1=0}^{T_1-1} F(\vec{q}) \exp \left[-2\pi i t_1 (\vec{q} \cdot \vec{a}_1) \right] \sum_{t_2=0}^{T_2-1} \exp \left[-2\pi i t_2 (\vec{q} \cdot \vec{a}_2) \right] \sum_{t_3=0}^{T_3-1} \exp \left[-2\pi i t_3 (\vec{q} \cdot \vec{a}_3) \right]
 \end{aligned}$$

The three summation operations have the form of a geometric series and can be evaluated by the following identity [60]:

$$\sum_{n=0}^N r^n = 1 + r + r^2 + r^3 + \dots + r^N = \frac{r^{N+1} - 1}{r - 1}$$

Simplifying further and using the definition of intensity, $I(\vec{q}) = A(\vec{q})A(\vec{q})^*$, we get the final form of the total diffracted intensity from the crystalline particle [60]. This is called the

Laue summation equation:

$$I_{particle}(\vec{q}) = F(\vec{q})^2 \left(\frac{\sin[\pi T_1 \vec{q} \cdot \vec{a}_1]}{\sin[\pi \vec{q} \cdot \vec{a}_1]} \right)^2 \left(\frac{\sin[\pi T_2 \vec{q} \cdot \vec{a}_2]}{\sin[\pi \vec{q} \cdot \vec{a}_2]} \right)^2 \left(\frac{\sin[\pi T_3 \vec{q} \cdot \vec{a}_3]}{\sin[\pi \vec{q} \cdot \vec{a}_3]} \right)^2 \quad (2.5)$$

As seen, the Laue summation equation has three multipliers of the form $\left(\frac{\sin Nx}{\sin x} \right)^2$. These terms define substantially sharp peaks since in one dimension we have:

$$\lim_{x \rightarrow n\pi} \left(\frac{\sin Nx}{\sin x} \right)^2 \rightarrow N^2 \quad (n \in \mathbb{Z})$$

where $N = T_i$ and $x = \pi \vec{q} \cdot \vec{a}_i$. In three dimensions the diffracted intensity becomes proportional to N^6 . Therefore, we can see that Eq.2.5 predicts almost zero intensity everywhere except when $x \approx n\pi$ for particles including many unit cells, $N \gg 1$. From this, the condition for diffracting maximum intensity from a crystalline particle can be written as

$$\pi \vec{q} \cdot \vec{a}_1 = h\pi \quad (2.6a)$$

$$\pi \vec{q} \cdot \vec{a}_2 = k\pi \quad (2.6b)$$

$$\pi \vec{q} \cdot \vec{a}_3 = l\pi \quad (2.6c)$$

The Equations 2.6 are known as the Laue equations [60] and $h, k, l \in \mathbb{Z}$ are the Miller indices. We note that Equations 2.6 are an alternative statement of the Bragg's law.

Describing Diffraction via Fourier Transforms

The mathematical expressions derived until now for calculating the scattering amplitudes were based on summations over the number of discrete scattering units, atoms or unit cells within the irradiated material. There is, however, an alternative way to represent a crystalline structure [20; 60] using continuous electron density functions. In this case, the scattering centers appear as concentrated peaks inside the volume of the material.

Defining an electron density function of $\rho(\vec{r})$, Eq. 2.2 can be written as [20; 60]:

$$A(\vec{q}) = \int_0^\infty \rho(\vec{r}) \exp[-2\pi i (\vec{q} \cdot \vec{r})] d\vec{r} \quad (2.7)$$

Here $\vec{r}$ is the radial distance from the origin of the scattering material and the integral is taken over all space. The volume of the space where $\rho(\vec{r})$ takes nonzero values is defined by

the boundaries of the scattering material. Using the definition of the Fourier transforms, the transform of the electron density can be written in the following form:

$$\mathfrak{F}[\rho(\vec{r})] = \int_0^\infty \rho(\vec{r}) \exp[-2\pi i(\vec{q} \cdot \vec{r})] d\vec{r}$$

Comparing the form of $\mathfrak{F}(\rho(\vec{r}))$ with Eq. 2.7 we see that the far-field scattering amplitude of a continuous electron density irradiated by a plane monochromatic beam is analogous to the Fourier transform of the charge density. The Fourier variable in the transform corresponds to the momentum transfer vector $\vec{q}$ in Eq. 2.7 which has the units of inverse length. This is also consistent with the Ewald sphere construct shown in Figure 2.2 where $|\vec{q}| = \frac{2 \sin \theta}{\lambda}$. By similarity, we can also state that the structure factor $F(\vec{q})$ defined by Eq. 2.4 is equivalent to the Fourier transform of the charge distribution inside a unit cell.

2.2.3 Patterson Function

The relationship between the Fourier transform of a continuous charge density and its far-field scattering amplitude allows us to use a global approach for calculating the scattering intensity from an irradiated material. In this case, we first construct an infinitely periodic charge density in three dimensional space and then define the boundaries of the particle within this space. The charge density confined by these boundaries makes up the irradiated particle. Mathematically, this operation can be represented by a product of the shape function $y(\vec{r})$ of the particle with the infinitely periodic and three dimensional electron density ρ_∞ , i.e., $\rho(\vec{r}) = y(\vec{r})\rho_\infty(\vec{r})$. Inserting this definition of the electron density, Eq. 2.7 takes a new form:

$$A_{particle}^{Pat}(\vec{q}) = \int_0^\infty y(\vec{r})\rho_\infty(\vec{r}) \exp[-2\pi i(\vec{q} \cdot \vec{r})] d\vec{r} \quad (2.8)$$

Now, if we write the momentum transfer vector inside the structure factor $F(\vec{q})$ in terms of its reciprocal space vector components $\vec{a}_i^*$, $i = 1, 2, 3$, as depicted in Figure 2.2, we obtain an alternative form:

$$F_{hkl} = \int_{cell} \rho_\infty(\vec{r}) \exp(-2\pi i \vec{H} \cdot \vec{r}) d\vec{r} \quad (2.9)$$

In Eq.2.9, $\vec{H} = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*$ is a 'special' momentum transfer vector at the exact Bragg condition with integer multiples $[h, k, l]$ of the reciprocal space vectors. (The reason why

we differentiate between $\vec{q}$ and $\vec{H}$ will become clear as the derivation continues.) Since F_{hkl} is the Fourier transform of the electron density $\rho_{\infty}(\vec{r})$ at the lattice point $[h, k, l]$, we can expand $\rho_{\infty}(\vec{r})$ in terms of the Fourier series expansion of the structure factor [60; 62]:

$$\rho_{\infty}(\vec{r}) = \frac{1}{\nu_{cell}} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F_{hkl} \exp(2\pi i \vec{H} \cdot \vec{r}) \quad (2.10)$$

Inserting the Fourier series expansion of $\rho_{\infty}(\vec{r})$ (Eq. 2.10) into Eq. 2.8, we obtain

$$A_{particle}^{Pat}(\vec{q} - \vec{H}) = \frac{1}{\nu_{cell}} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F_{hkl} \int_0^{\infty} y(\vec{r}) \exp[-2\pi i (\vec{q} - \vec{H}) \cdot \vec{r}] d\vec{r}$$

where $(\vec{q} - \vec{H})$ is the deviation of the momentum transfer vector $\vec{q}$ from the special momentum transfer vector $\vec{H}$ at the exact hkl lattice point. Now notice that the integral on the right is just the Fourier transform of the shape function $y(\vec{r})$. Hence, the amplitude expression can be further simplified:

$$A_{particle}^{Pat}(\vec{q} - \vec{H}) = \frac{1}{\nu_{cell}} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F_{hkl} Y(\vec{q} - \vec{H}) \quad (2.11)$$

where $Y(\vec{q} - \vec{H}) = \mathfrak{F}[y(\vec{r})]$. As seen in Eq. 2.11 the complex scattering amplitude around a Bragg reflection is a combination of scattering amplitudes at an infinite number of lattice points, i.e. $-\infty < (h, k, l) < \infty$. However in real diffraction experiments with crystalline particles, only a finite number of these components dominate the diffracted amplitude and usually these are the closest lattice vectors to the momentum transfer vector, i.e. $\vec{q} - \vec{H} \approx 0$. This condition corresponds to the case where each diffraction peak is well resolved and far from the other diffraction peaks within a spectrum. Assuming that $\vec{H}$ satisfies these conditions, the amplitude expression reduces to a multiplication of the Fourier transform of the shape function with the structure factor corresponding to the closest lattice vector.

$$A_{particle}^{Pat}(\vec{q} - \vec{H}) \approx \frac{1}{\nu_{cell}} F_{hkl} Y(\vec{q} - \vec{H}) \quad (2.12)$$

In conclusion, the use of Fourier transforms simplifies the computation of the scattering amplitude from a crystalline particle substantially, since it only requires the Fourier transform of the shape function and the structure factor of the particle. However, this method is only applicable when the distribution of the atoms within a particle is perfectly periodic

so that a single structure factor accurately represents the general stacking of the atoms in the material, and the shape of the particle is regular so that simple analytical functions are capable of defining the shape. This set of conditions is hard to satisfy in most experiments, especially for crystalline particles with dimensions in the nanometer range. However, for our purposes we will limit our treatment to ideal crystalline particles that have regular shapes.

Crystalline Particles with Spherical Shapes

For a spherical particle with radius $R_s = \frac{D}{2}$, the shape function $y_{sph}(\vec{r})$ is given as follows:

$$y_{sph}(\vec{r}) = \begin{cases} 1 & : |\vec{r}| \leq R_s \\ 0 & : |\vec{r}| > R_s \end{cases}$$

Hence, the Fourier transform of the shape function can be computed from:

$$Y_{sph}(\vec{q} - \vec{H}) = \int_{r=0}^{R_s} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \exp[-2\pi i \vec{r} \cdot (\vec{q} - \vec{H})] r \sin \theta d\theta r d\phi dr$$

Making a change of variables, $\vec{q} - \vec{H} = \Delta\vec{q}$, and expanding the inner product inside the exponential as $\vec{r} \cdot \Delta\vec{q} = |\vec{r}| |\Delta\vec{q}| \cos \phi$, the above integral can be simplified and analytically evaluated [62]:

$$Y_{sph}(\Delta\vec{q}) = \frac{-2\pi |\Delta\vec{q}| R_s \cos(2\pi |\Delta\vec{q}| R_s) + \sin(2\pi |\Delta\vec{q}| R_s)}{2\pi^2 |\Delta\vec{q}|^3} \quad (2.13)$$

Now, at the exact Bragg condition, $\Delta\vec{q} = 0$, the integral given for $Y_{sph}(\vec{q} - \vec{H})$ reduces to the volume integral of $y_{sph}(\vec{r})$ since the exponential term becomes unity. However, by definition the volume integral of the shape function yields the volume 'V' of the particle. Therefore we can write:

$$\lim_{|\Delta\vec{q}| \rightarrow 0} Y_{sph}(|\Delta\vec{q}|) = \frac{4\pi R_s^3}{3}.$$

(The value of this limit can be obtained by repeated (triple) application of the L'Hospital's rule on Eq. 2.13.) From this limit it can be shown that the maximum intensity at the exact Bragg angle corresponding to the hkl lattice point (or reflection) becomes equal to $F_{hkl}^2 V_{sph}^2$, where V_{sph} is the volume of the spherical crystallite and F_{hkl} is the structure factor of the material.

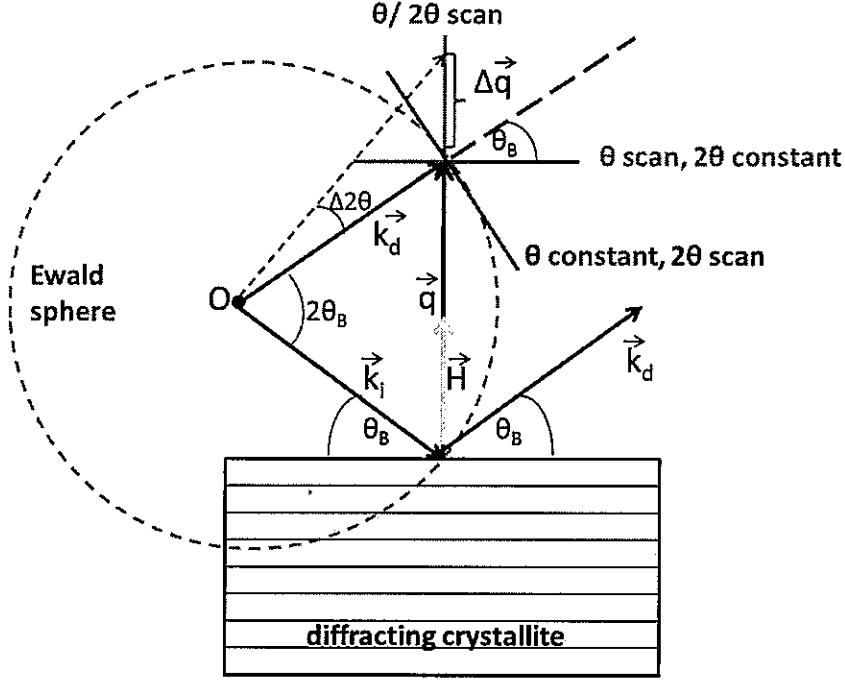


Figure 2.4: Common scan types used in diffraction experiments. Here, point O is the center of the Ewald sphere and the momentum transfer vector $\vec{q}$ is aligned normal to the surface of the diffracting crystallite, also parallel to the lattice vector $\vec{H}$. Therefore, the exact Bragg condition is satisfied and the angle between the incoming and diffracted wavevectors is $2\theta_B$. In radial scan, a.k.a. ($\theta/2\theta$ scan), both $\vec{k}_i$ and $\vec{k}_d$ rotate in such a way that $\vec{q}$ moves along the direction of the lattice vector. For small rotation angles, the trace followed by $\vec{q}$ can be approximated to a straight line, as shown in green. (Sketch adapted from [62])

In diffraction experiments, a commonly used scan type is radial scan ($\theta/2\theta$), where the incoming and the diffracted wave vectors are rotated in such a way that the momentum transfer vector moves along the lattice vector $\vec{H}$ [62]. At radial scan mode, $|\Delta\vec{q}|$ can be obtained from the geometry seen in Figure 2.4 as $|\Delta\vec{q}| = \frac{\Delta 2\theta \cos \theta_B}{\lambda}$ and from that the scattering intensity of a spherical particle can be written as:

$$I_{sph}^{Pat}(\xi) = N_c^2 |F_{hkl}|^2 \left[3 \frac{-\xi \cos \xi + \sin \xi}{\xi^3} \right]^2 \quad (2.14)$$

where $\xi = 2\pi R_s |\Delta\vec{q}|$. Here N_c is the number of unit cells within the particle volume. As

an example, Figure 2.5 shows the profile of the (200) peak intensity predicted by Eq.2.14 with respect to the scattering angle, 2θ , for a spherical gold particle along with a cubic gold particle having an equal linear size of 2.86 nm. To obtain these profiles, the X-ray wavelength was assumed to be 1 Å and therefore the peaks were centered at $2\theta = 28.37^\circ$.

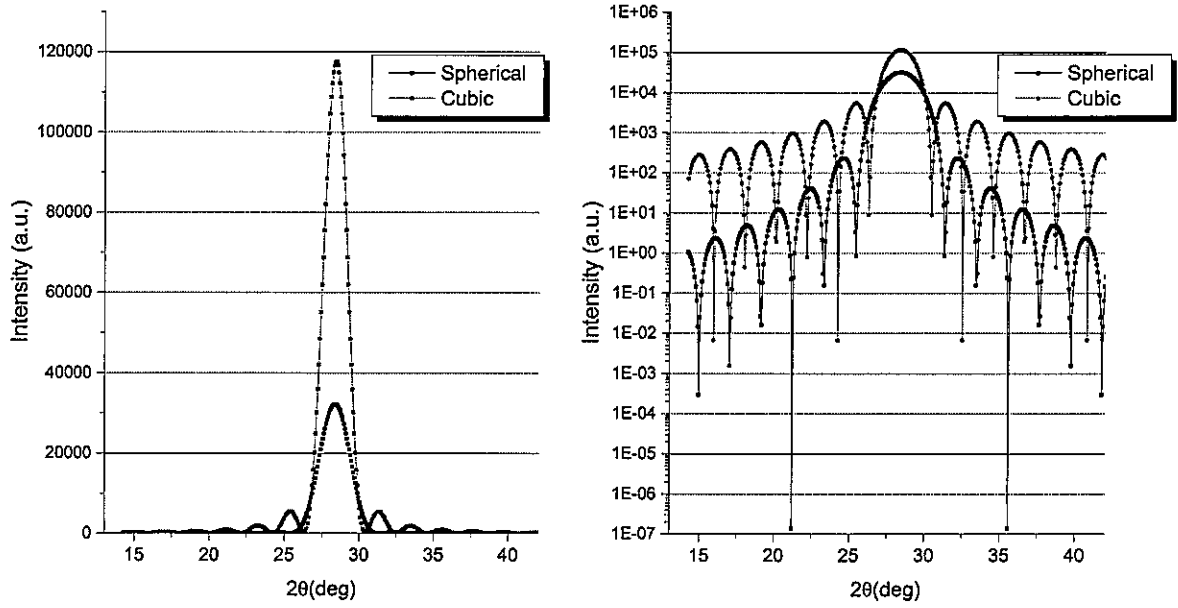


Figure 2.5: Diffracted intensity profiles predicted by the Patterson function around the 200 reflection for a spherical and a cubic gold crystallite with diameter and side length equal to 2.86 nm. The constant term F_{hkl} was excluded from the calculations for simplicity. (Left: Linear scale. Right: Logarithmic scale. $\lambda = 1$ Å.)

Crystalline Particles with Cubic Shapes

Using similar arguments as in the previous case, the diffracted intensity from a cubic particle can be analytically obtained. Assuming that the cube has a side length of t , the Fourier transform of the shape function for such a particle, centered at an arbitrary origin can be written as follows:

$$Y_{cube}(\Delta\vec{q}) = \int_{-\frac{t}{2}}^{\frac{t}{2}} \int_{-\frac{t}{2}}^{\frac{t}{2}} \int_{-\frac{t}{2}}^{\frac{t}{2}} \exp[-2\pi i(\Delta\vec{q} \cdot \vec{r})] dx dy dz$$

Here x, y, z are the Cartesian coordinate axes of the particle and $\vec{r} = \vec{r}(x, y, z)$. For the simplest case where the scanning vector $\Delta\vec{q}$ is parallel to the cube coordinate axis z , the above expression simplifies to:

$$Y_{cube}(\Delta\vec{q}) = t_x t_y t_z \frac{\sin(\pi t |\Delta\vec{q}_z|)}{\pi t |\Delta\vec{q}_z|}$$

where $|\Delta\vec{q}_z|$ is the z component of $\Delta\vec{q}$. Substituting $\frac{\cos \theta_B \Delta 2\theta}{\lambda}$ for $|\Delta\vec{q}_z|$ in the above expression yields the diffracted intensity from a cubic crystallite predicted by the Patterson formulation:

$$I_{cube}^{Pat}(\Delta 2\theta) = |F_{hkl}|^2 [Y(\Delta\vec{q})]^2 = |F_{hkl}|^2 (t_x t_y t_z)^2 \left[\frac{\sin \zeta_z}{\zeta_z} \right]^2 \quad (2.15)$$

where $\zeta_z = \frac{\pi t \cos \theta_B \Delta 2\theta}{\lambda}$. Since $t_x t_y t_z = V_{cube}$ where V_{cube} is the volume of the particle, the maximum diffracted intensity becomes

$$I_{cube}(\Delta 2\theta \rightarrow 0) = I_{cube}(\Delta\vec{q} \rightarrow 0) \cong |F_{hkl}|^2 V_{cube}^2$$

Comparison Between the Patterson Functions for Spherical and Cubic Particles

Looking at Eqs. 2.14 and 2.15 we notice that for the same structure factor F_{hkl} , the maximum intensities predicted by the Patterson formulation only depend on the volume of the irradiated particles. The shape of the particles do not affect the maximum values. This is shown in Figure 2.5 where the (200) intensity profiles computed by the respective Patterson functions of the cubic and the spherical particles of size 2.86 nm are seen. The irradiation wavelength used in the calculations is 1 Å and the particles are assumed to be gold with FCC lattice structure. As seen in both the linear (left) and the logarithmic (right) scales, the maximum diffracted intensity from the cubic particle is much larger than the spherical particle, since the total volume of the cubic particle is larger than that of the spherical particle with the same linear dimension. Similar arguments hold for the integrated intensities as well: the total area under the Patterson function of the cubic particle is larger than that of the spherical particle. In addition, the primary (central) peak of the Patterson function of the cubic particle is narrower than that of the spherical particle, whereas it takes a much larger angular deviation for the cubic Patterson function to decay to the background level compared to the spherical Patterson function. The positioning of the peak minima and

maxima are also different: Except for the primary peak, the positions of the secondary maxima and minima do not match, but maintain a constant phase difference instead.

2.2.4 Evaluation of the Discrete Summation (Atomistic sum and Laue equations) and Patterson Formulations for Computing the Diffracted Intensity for an Isolated Cubic Particle

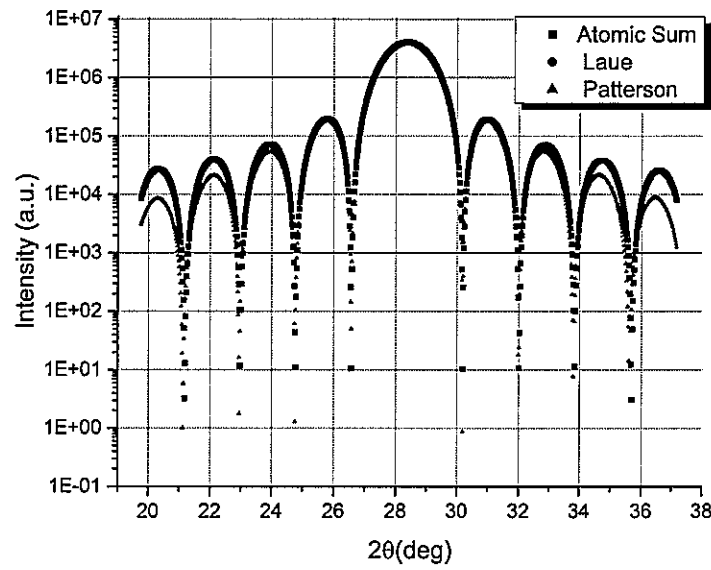


Figure 2.6: Intensity profile of a single cubic gold crystallite irradiated by planar X-rays of 1 Angstrom wavelength. The peak corresponds to the 200 reflection and the side length of the cube is 1.63 nm

A comparison between the intensity profiles computed by the atomistic summation (Eq.2.3), Laue equation (Eq. 2.5) and the Patterson function (Eq.2.15) is shown in Figure 2.6 for a single, cubic gold particle. As seen, the intensities computed by the summation methods, match perfectly at all scattering angles considered. On the other hand, the Patterson intensities fall short compared to the intensities from the other methods in the secondary peak regime; although there is very good agreement in the primary peak range. The main source of the substantial disagreement in the secondary peak regime between the two formulations lies in the difference between the two terms $\frac{\sin(Nx)}{\sin(x)}$ and $\frac{N \sin(Nx)}{Nx}$. Al-

though these two functions yield almost the same values in the vicinity of the central peak, they start to diverge from the first minimum of the peak profile. The reason for this is the small angle approximation inherent in the $|\Delta\vec{q}|$ term, which is accurate only in the close vicinity of the Bragg angle. (For larger deviations from the Bragg angle, the $|\Delta\vec{q}|$ term can not be approximated to a line in the radial scan mode and therefore the Fourier integral can not be reduced to a sinc type function.) Another contributing factor to the disagreement is the assumption of a single dominant Fourier component in the Patterson function, which fails when there are overlapping peaks in the intensity spectrum. For the case considered here, the difference contributed by the second factor was computed to be no larger than a few percent and the first factor was the dominant source of deviation.

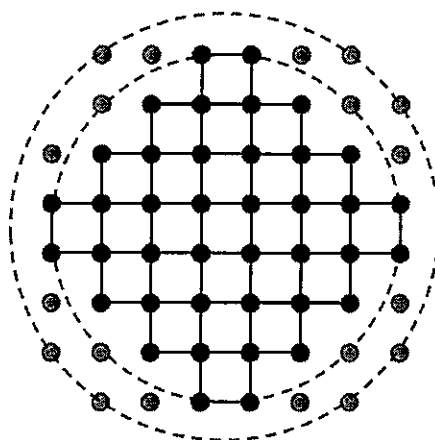


Figure 2.7: Spherical crystalline particle consisting of identical cubic unit cells. Blue dots represent the atoms placed inside unbroken unit cells and green dots represent the atoms that are outside the particle boundary.

Repeating the same analysis with a spherical particle is more challenging than the cubic particle. In this case, creating the shape of an ideal sphere using cubic unit cells is not possible, especially when the particle diameter is small. As seen from Figure 2.7 many of the unit cells on the surface of the particle are broken and have missing atoms (shown in green) that are outside the sphere boundary. Therefore, these unit cells do not have the same scattering power, as they do not include the same number of atoms as the unit cells in the inner regions of the particle. In order for the Laue equation to be applicable, the broken

unit cells on the particle boundary need to be assigned a modified structure factor and the summation must be performed over whole unit cells and broken unit cells separately. The presence of broken unit cells complicates the evaluation of the Patterson function as well: although the 'intended' particle shape is a sphere, the actual shape obtained from stacking cubic cells is a castellated sphere, which has a more complex shape function than an ideal sphere. The most convenient method for formulating the diffracted intensity profiles from such particle systems, then, becomes the atomistic sum approach. For these reasons the above mathematical comparison between the analytical formulations of diffracted intensities will not be included for the spherical particle.

2.3 The Scherrer Equation

In the previous section, we introduced three formulations that can be used to compute the diffracted intensity from a given particle illuminated by plane monochromatic X-rays in the far field regime. These formulations yield the distribution of diffracted intensity over a finite angular range around a particular Bragg angle and link the number of atoms or, alternatively, the number of unit cells, to the diffracted intensity. The width or 'breadth' of an intensity profile is another highly utilized parameter that yields information about the coherently diffracting regions.

The importance of the peak breadth of an intensity profile was first pointed out by Scherrer in 1918 [54; 46]. Scherrer showed that the broadening of an intensity profile from a particle illuminated by plane monochromatic X-rays was inversely proportional to the size of the particle. Assuming that the intensity profile approximates to a Gaussian function, he proposed the following expression to relate the amount of peak broadening to the particle size:

$$\beta_{hkl}(2\theta) = \frac{C\lambda}{t \cos \theta_{B,hkl}} \quad (2.16)$$

In Eq. 2.16 $\beta_{hkl}(2\theta)$ is the full-width-at-half-maximum of the peak profile in the 2θ axis, C is the Scherrer constant and t is the coherent domain size of the irradiated sample along the direction of the momentum transfer vector. Based on the Gaussian profile approximation, the numerical value of the Scherrer constant was found to be 0.93.

As seen from its derivation, this initial form of the Scherrer constant is independent of the particle size and shape and is also constant over the angular range of the diffraction spectrum. Its applicability is conditional on the Gaussian peak assumption; however, current literature still includes many examples [5; 28; 61; 68; 50] where this numerical value (or unity as a commonly used approximation) is still in use, even when the intensity profiles are far from having Gaussian shapes¹. A comprehensive work by Langford and Wilson [39] summarizes the sources of confusion and resulting discussions over the numerical values and the physical meanings of the various forms of the Scherrer constant.

Later in 1939, Patterson published his classical papers in which he computed the intensity profiles from crystalline particles with regular shapes by Fourier transforming the shape function [47] and derived the appropriate Scherrer constants considering not only the Bragg angle but also the particle shape [46]. Throughout this thesis, we will rely on Patterson functions as analytical descriptions of the intensity profiles, rather than an approximate Gaussian profile, and utilize the correct Scherrer constants pertaining to the Patterson formulation. These will be briefly reviewed for spherical and cubic crystallites.

For a perfect spherical crystallite, the analytical expression for the intensity profile is given in Eq.2.14. This function reaches its maximum at $\Delta 2\theta = 0$ and hits $|F_{hkl}|^2 V_{sph}^2$ at the exact Bragg angle. Equating the intensity to half of the maximum value and solving for ξ we obtain:

$$\begin{aligned} \xi \left(I_{sph}(\xi) = \frac{|F_{hkl}|^2 V_{sph}^2}{2} \right) &\rightarrow 1.8148 \\ \beta_{hkl} = 2 \times \left[\Delta 2\theta \Big|_{I=\frac{I_{max}}{2}} \right] &= \frac{\xi \lambda}{2\pi R_s \cos \theta_B} \\ \therefore C_{sph} &\approx 1.16 \end{aligned} \tag{2.17}$$

Due to the inherent symmetry of the spherical crystallite, the Scherrer constant is independent of the direction of the momentum transfer vector and hence the Bragg peak.

In the case of cubic crystallites however, the Scherrer constant changes according to the direction of the momentum transfer vector. Using similar arguments as in the case of

¹In most cases, the intensity profiles do have non-Gaussian shapes; in fact, Gaussian peak intensities are empirical constructs for robust data processing and have no analytical basis.

spherical crystallite, for the 100 reflection we obtain for the cubic crystallite:

$$\begin{aligned} \frac{|F_{hkl}|^2 V_{cube}^2}{2} &= |F_{hkl}|^2 V_{cube}^2 \left[\frac{\sin(\pi t \cos \theta_B \Delta 2\theta / \lambda)}{\pi t \cos \theta_B \Delta 2\theta / \lambda} \right]^2 \\ \frac{\pi t \cos \theta_B \Delta 2\theta}{\lambda} &\approx 1.39156 \\ \therefore C_{cube}^{100} &\approx 0.886 \end{aligned} \quad (2.18)$$

Similarly for the 110 reflection

$$\begin{aligned} \frac{|F_{hkl}|^2 V_{cube}^2}{2} &= |F_{hkl}|^2 V_{cube}^2 \left[\frac{\sin(\pi t \cos \theta_B \Delta 2\theta / \sqrt{2} \lambda)}{\pi t \cos \theta_B \Delta 2\theta / \sqrt{2} \lambda} \right]^4 \\ \frac{\pi t \cos \theta_B \Delta 2\theta}{\lambda} &\approx 1.41691 \\ \therefore C_c^{110} &\approx 0.902 \end{aligned} \quad (2.19)$$

Finally, for the 111 reflection

$$\begin{aligned} \frac{|F_{hkl}|^2 V_{cube}^2}{2} &= |F_{hkl}|^2 V_{cube}^2 \left[\frac{\sin(\pi t \cos \theta_B \Delta 2\theta / \sqrt{3} \lambda)}{\pi t \cos \theta_B \Delta 2\theta / \sqrt{3} \lambda} \right]^6 \\ \frac{\pi t \cos \theta_B \Delta 2\theta}{\lambda} &\approx 1.42531 \\ \therefore C_c^{111} &\approx 0.907 \end{aligned} \quad (2.20)$$

As seen, the Scherrer constants based on the Patterson functions of cubic and spherical crystalline particles are slightly different from each other, even for particles with identical linear dimension and around the same Bragg reflection. These differences are consistent with our previous observations about the primary peak width in Figure 2.5. In fact, a simple Gaussian peak function fitted to these intensity profiles reveals $\beta_{cube} = 1.74^\circ$ and $\beta_{sph} = 2.31^\circ$ for the full-width-at-half-maxima of the cubic and the spherical particles, respectively. These values are within $\pm 5\%$ of the predictions from Eqs. 2.17(1.83°) and 2.18(2.43°). If the alternative expression with $C=0.93$ was used, the estimated breadth would be 2.12° for both particles, irrespective of their different shapes. This is a problem overlooked in many textbooks and it results in the wrong application of the Scherrer equation.

2.4 Scattering from an Ideal Powder Ensemble

At this point, we have the required tools to compute the scattering intensity of isolated particles. As the next step, the formulation for computing the diffracted intensity from a

collection of crystalline particles will be outlined. Throughout this thesis the terms 'particle', 'crystallite' and 'grain' will be used interchangeably, and all will refer to a domain of charge density from which the diffracted waves that originate are coherent with each other.

The primary difference between a collection of atoms and a collection of particles lies in the phase relationship between the scattered photons from individual scattering units: When a group of periodically stacked atoms are irradiated by a monochromatic, planar X-ray beam in the far field regime, the scattered photons from these atoms are in phase; hence, their total effect is obtained by a coherent (amplitude) sum over all atoms. For a crystalline powder ensemble, on the other hand, the contribution to the total diffracted X-rays by individual particles can be out of phase, depending on the mode of the experiment or the coherency of the beam. Therefore, their combined effect is calculated by an incoherent (intensity) sum over all particles. We note that, even when a fully coherent, plane X-ray beam is used to irradiate the particles one at a time while continuously summing their contributions to the diffracted beam, the combined pattern will still be the sum of the intensities, representing an incoherent scattering experiment over particles. This is because the powder ensembles we consider throughout this thesis will have the following properties:

1. The orientation of any one particle within the ensemble is independent of the orientation of the remaining particles
2. The cumulative orientation distribution for the ensemble is such that the orientation vectors belonging to the particles cover the surface of a unit sphere with uniform probability. Therefore, there is no favorable orientation for a given particle. Such samples are also called 'ideal' or 'untextured' powders.

The mathematical expression that yields the scattering intensity from an ideal powder can be derived in several ways depending on how the scattering intensity from a single particle is calculated. However, it is greatly simplified if, in addition, the particles are monodispersed in size and shape. For such an ideal powder sample including P particles, the total diffracted intensity, based on kinematic summation over the atoms within a particle, can be computed by:

$$I_{tot}^{KS}(\vec{q}) = \sum_{p=1}^P I_p(\vec{q}) = \sum_{p=1}^P \left[\sum_{m=1}^N \sum_{n=1}^N f_{p,m} f_{p,n} \exp[-2\pi i \vec{q} \cdot \vec{r}_{p,mn}] \right] \quad (2.21)$$

In Eq.2.21 'p' is the index of the particle within the powder ensemble where $I_p(\vec{q})$ is the intensity from this particle, whereas 'm' and 'n' are the indices of the atoms inside particle p. Consequently, $\vec{r}_{p,mn}$ is the interatomic spacing vector between the m'th and n'th atoms of the p'th particle. This is the most general form of the intensity expression for the scattering of a powder ensemble. For Eq.2.21 to be applicable, the orientation distribution of all particles as well as the atomic coordinates within each particle must be known. If the particles within the ensemble are not monodispersed, then appropriate changes are needed in the upper indices of the double sum.

In a similar logic, an alternative formula can be derived for the total intensity from an ideal powder sample, based on Patterson functions:

$$I_{tot}^{Pat}(\vec{q}) = \sum_{p=1}^P N_c^2 |F_{hkl}(\vec{q})|^2 \left[3 \frac{-\xi \cos \xi + \sin \xi}{\xi^3} \right]^2 \quad (2.22)$$

Here the variable ξ can be obtained from $\xi = 2\pi R_s |\Delta \vec{q}|$ based on a radial scan setting and the powder ensemble is assumed to contain spherical crystalline particles. A similar expression can be derived for a cubic particle ensemble.

Finally, we can use the venerable Debye scattering equation² [18]:

$$I_{avr}^{Debye}(\vec{q}) = \sum_{m=1}^N \sum_{n=1}^N \frac{\sin(4\pi |\vec{q}| |\vec{r}_{mn}|)}{4\pi |\vec{q}| |\vec{r}_{mn}|}$$

In the above expression, I_{avr} refers to the average intensity of a single particle including N atoms over all possible orientations of the particle. Therefore for a number of P particles within a powder ensemble, the total diffracted intensity can be written as:

$$I_{tot}^{Debye}(\vec{q}) = \sum_{p=1}^P \left[\sum_{m=1}^N \sum_{n=1}^N \frac{\sin(4\pi |\vec{q}| |\vec{r}_{mn}|)}{4\pi |\vec{q}| |\vec{r}_{mn}|} \right] \quad (2.23)$$

Comparing Equations 2.21, 2.22 and 2.23 we see that the only difference between the first two and the third expressions comes from how the orientation averaging is achieved: In the first two equations the intensity of each particle is computed first at their (single) original

²A detailed analysis of the Debye equation will be presented in Chapter 6.

orientation and then these intensities are added up incoherently, whereas in the Debye based approach, the average intensities from individual particles are added up. Therefore, depending on the value of P (number of particles inside the ensemble), the summation based equations may or may not converge to Eq.2.23 (Further discussions on this topic will be delayed until Chapter 6.).

2.5 Summary and Conclusions

In this chapter, we have reviewed the foundations of the kinematic scattering theory and introduced its main mathematical tools that can be used to obtain simulated diffraction data from an ideal powder ensemble. Here, we will focus on justifying how this theory is a representative physical model for our case of ideal nanocrystalline powders and will conclude by introducing our choice of modeling methodology with its pros and cons in application.

2.5.1 Assessment of the Basic Assumptions

1. Plane wave approximation

This condition is the foundation of the atomic scattering formulation given in Eq. 2.1. In order for the plane wave approximation to be applicable, both the distance between the X-ray source and the irradiated sample and that between the sample and the detector must be much greater than the linear sample dimension. The plane wave approximation, once satisfied, guarantees that the wavefront of the incoming X-ray beam is planar within the region where it interacts with the sample, so that each atom receives the same phase shift from the electric field at a given instant in time. When the sample to detector distance is long enough, the scattered X-rays from the atoms have approximately planar wavefront around the detector region and can be assumed to travel along parallel trajectories [4].

For the nanocrystalline powder samples we will study via simulated powder diffraction experiments, the source to sample and sample to detector distances will be chosen in order to satisfy the plane wave approximation. There are, however, certain types of diffraction experiments where a non-planar wavefront for the incoming beam is desirable, such as coherent diffraction experiments with focused beams. In these cases, the spatial variation

of the phase shift over the projected area of the wavefront of the incoming beam onto the irradiated sample must be taken care of separately [63; 66].

2. Multiple scattering of the X-rays within the irradiated sample volume can be neglected.

In order for the kinematic regime to be a realistic description of the mode of scattering, each X-ray beam must scatter once within the sample volume. This condition needs to be satisfied in order to exclude the extinction effect within the sample, that is a result of multiple scattering. For nanocrystalline particles, the small coherent volume is the driving force for the kinematic scattering to be the dominant mode. In this case, there is simply not enough scattering centers for the incoming X-rays to interact with and therefore the possibility of multiple scattering is nonexistent.

3. The interaction between the incoming and the diffracted X-rays can be omitted.

When there is strong interaction between the incoming X-ray beam and the diffracted beams, the scattering mode falls into the dynamic scattering regime. The strength of interaction between these two beams, however, depends on their relative intensities. For an isolated crystalline particle, we show in Equations 2.1, 2.2, 2.5 and 2.8 that the scattering amplitude is proportional to number of scattering units, be it a unit cell or an atom. Therefore, the intensity of the diffracted wave becomes proportional to the square of the amount of scattering material. For our case of small, crystalline nanoparticles, the diffracted intensity is negligible compared to the incoming X-ray beam intensity due to few scattering centers. When the crystalline particles are not stacked periodically but dispersed randomly in a volume, as in an ideal powder, such an enhancement in the diffracted beam becomes even less, almost negligible. Therefore, nanocrystalline powder samples are good candidates of scattering materials that satisfy the conditions for kinematic scattering regime.

4. The interaction between the incoming X-ray beam and the irradiated material is an energy-conserving process.

All of the equations derived to calculate the diffracted intensity rely on the assumption that the wavelength (or energy) is kept constant during the interaction between the X-rays and the scattering material. (Otherwise, there would be no coherence between the individually scattered waves from different atoms.) This type of scattering, however, is not the only interaction mode between an X-ray beam and a scattering material, as there are other possible modes depending on the irradiation wavelength, such as fluorescence or Compton scattering. Although, the coherent scattering intensity makes up only a very small portion of the incoming X-ray intensity [4], these inelastic and incoherent components to the diffracted intensity do not usually dominate over the coherent portion, since in most experimental setups they can be properly eliminated.

Compton scattering occurs when the interaction between the X-ray beam and the electron is so strong that the electron is knocked out by gaining energy from the incoming photon [4; 25]. As a result, the X-ray photon loses its initial energy and its wavelength becomes longer. Compton scattering is likely to be a dominant source of background scattering in diffraction experiments with high X-ray beam energies [20; 34]. There are also various databases with information about the cross sections of numerous types of scattering modes for a list of materials [55] that one can check to avoid any wavelength of radiation beyond the threshold value.

Fluorescence is another type of inelastic and incoherent interaction mode of the material with incoming X-ray beams. In this case the incoming photon, with an energy close to the characteristic absorption edges of the atom, excites the interacting electron and causes it to shift to a higher energy band, while leaving the atom in an unstable electronic configuration [16]. Once the electron shifts back to the original energy level to reestablish the stable configuration, it ejects the energy difference between the electronic levels in the form of X-ray photons. The scattered photons, in this case, have fixed energies equal to the energy difference of the electron levels, so the resulting fluorescent intensity is coherently enhanced as more electrons are involved in the process. However, the wavelength of fluorescent scattering is larger than that of the incoming and the diffracted X-ray beams,

and therefore fluorescent scattering degrades the quality of coherent and elastic scattering intensity greatly, unless properly eliminated. This can be achieved by choosing X-rays with energies away from the absorption edges of the scattering material.

Apart from these incoherent modes of diffraction, there is also the *linear absorption* of the X-ray photons inside the material, as the photons travel through the sample volume. However, due to the very small sizes of nanocrystalline particles, we can safely assume that the decay due to absorption is negligible.

2.6 Choosing a Suitable Computational Methodology

In previous sections, we introduced three methods to compute the diffracted intensity from a single particle. Among these, **the kinematic sum** over all atoms (Eq. 2.3) of the particle is the most general formulation that can be chosen. In this formula, the existence of the particle is only 'implied', i.e., there is no emphasis on the particle volume, shape or crystallinity. This can be very beneficial in performing computations especially when the atoms inside the particle are dispersed randomly inside the particle volume or when the boundary of the particle is not regular but jagged (as in Figure 2.7). A familiar example of such structures are nanoparticles: These structures have been experimentally reported to contain high concentrations of stacking faults and defects [38; 50]. There is also an extensive amount of literature reporting the differences in atomic stacking within the surface layers and the bulk regions of a nanoparticle and a possible existence of a core-shell structure for such systems [33; 44; 45]. To deal with the difficulties imposed by the positioning of the atoms inside the particle, kinematic sum is the most feasible and robust methodology to generate the theoretical diffraction intensity. The only downside of the use of Eq. 2.3 is the large number of terms to evaluate inside the double sum. As expected, the computation time scales with the square of the number of atoms inside the particle, which can be prohibitively long for mid to large sized nanoparticles (≈ 10 nm and above).

One way to overcome the limiting computation times for mid- to large size nanoparticles is to take advantage of ideal, periodic stacking of atoms inside the particle. If the particle has crystalline structure, a unit cell can be defined and the electron distribution can be written

in terms of periodic functions. This condition allows the use of the **Laue summation** (Eq. 2.5) as well as the Fourier transform based **Patterson formulation** (Eq. 2.8) both of which require a single unit cell to be the repetitive unit of the atomic distribution inside the particle. In that respect, the above mentioned surface effects or stacking faults or defects commonly observed in real nanoparticles cannot be accommodated in the computations when formulations relying on a single unit cell are preferred.

When it comes to computing the diffracted intensity from a representative amount of particles from a nanocrystalline powder ensemble, however, the previously mentioned shortcomings of the Patterson functions are outweighed by the advantage of preserving and including the particle construct as a computational parameter. This enables us to study the effect of increasing particle sampling on the statistical variations of the intensity data. The emphasis on the particle construct is the biggest advantage of using Eq. 2.22 over the **Debye equation** as well, since in the latter, the computation of the ultimate statistical limit of diffracted intensity is the main goal, without any consideration of the amount of irradiated powder sample or whether that amount is statistically representative of the total powder ensemble.

In conclusion, we find **the kinematic scattering formulation based on Patterson functions** to be the most convenient methodology in computing the diffracted intensities from nanocrystalline powder ensembles of known quantities. In the upcoming chapters, the problem of statistical convergence of the diffracted intensities will be introduced and discussed in detail from various perspectives.

Chapter 3

Sampling Statistics of Diffraction for Nanocrystalline Powder Aggregates

3.1 Introduction

In powder diffraction experiments, there are two main sources of statistical uncertainty that contribute to the measured intensities at any given angle: The first one is 'photon counting statistics', which is generally well-approximated by the Poisson distribution for photon counting detectors, and hence introduces an uncertainty proportional to the square root of the measured data [43; 51; 49]. The second source of uncertainty is due to the variations in the population of grains that are selected from a larger ensemble of irradiated grains by the diffraction event. This type of uncertainty is termed particle sampling statistics.

Powder diffraction inherently involves a selection process. Within the diffracted intensity spectrum, each intensity peak represents a subgroup of particles having a specific orientation with respect to the incoming X-ray beam. When a number of ideal powder ensembles with identical populations of grains are irradiated by a planar X-ray beam, the slight differences in the orientation distributions of these powder ensembles cause statistical variation between the population of subgroups of particles that are selected for diffraction

at a given orientation. Diffraction experiments with these powder samples, performed under identical instrumental conditions will, therefore, result in a finite variation in the diffracted intensities corresponding to these particle subgroups.

Quantifying and accounting for the intensity variation due to sampling statistics is crucial in the proper analysis of diffraction data. As an example, the diffracted photon counts from nanocrystalline samples are in general much lower than their bulk counterparts, due to their characteristically small, coherently scattering volumes. In this case, even the slightest variation in the photon counts within their diffraction spectra may alter the results from the refinement of such data. There are examples in the literature that intend to estimate the uncertainty in the measured intensities due to photon counting statistics or due to correlation between neighboring detection points (pixels) on a detector [59; 64]. In most cases, this type of counting uncertainty can be lessened by appropriate experimental procedures such as increasing the coherently scattered photon counts or proper treatment of the measured data. However, because it is an integral part of the diffraction process, particle sampling statistics can not be eliminated by following these recipes.

Currently, there are no data analysis and refinement software packages available that quantify and properly treat the intensity uncertainty due to the particle sampling statistics. Hence, significant uncertainty is transferred from the diffraction data to the refinement results by such software when bulk powders of relatively small particle sizes are investigated [56]. Even greater uncertainties are expected to be transferred to the refinements of the diffraction spectra from nanocrystalline materials. In that respect, it is quite disappointing that most of the current publications are ignorant of this fact, considering that there was an attempt to address the uncertainty problem more than half a century ago: it is still the only reference in the literature that focuses on quantification of uncertainty in the diffraction data due to particle sampling statistics and it was published in 1948 by Klug, Alexander and Kummer [3]. The literature also includes some example works reporting the application of the treatment by Klug *et al.* on experimental data from bulk powder samples [32], but no such work exists concerning the diffraction data from nanomaterials.

In this chapter, we will address the particle sampling statistics from the point of view of ideal nanocrystalline powders. To do this, we will first survey the original reference [3]

critically and adapt its formulation to ideal, random nanocrystalline powder samples. Then, these new formulations will be tested for applicability on simulated diffracted spectra from ideal nanocrystalline powders.

3.2 The Classical Formulation for Estimating the Uncertainty in Diffraction Intensities

In powder diffraction experiments where an X-ray beam illuminates a population of crystalline particles with different orientations, there is a finite subset of particles for each reflection that satisfies the diffraction condition. The population of this subset depends on the orientation distribution of the particles with respect to the X-ray beam, crystallite perfection, beam size and divergence properties, as well as the geometrical arrangement of the experimental setup [3]. For monodispersed particle ensembles where absorption can be neglected, the probability of diffraction has a constant and finite value; hence the expected population of the diffracting particles is finite. However, according to probability theory, there is always a deviation in the actual number of diffracting particles from the expected value due to random fluctuations in the number of particles oriented properly for diffraction, i.e. satisfying Bragg's law. This deviation introduces uncertainty in the diffracting particle population, which propagates directly to the measured intensity values. Given a total of N particles that are irradiated by a plane monochromatic X-ray beam, the actual population of grains n_f that satisfies the diffraction condition at a specific Bragg reflection can, then, be written as [3]:

$$n_f = Np + u \quad (3.1)$$

Here, Np is the expected number of diffracting particles where p stands for probability of diffraction for a single particle and u is the deviation from the expected number. Laplace's general probability theorem states that the probability distribution of the deviation with respect to its magnitude u can be analytically calculated by the following expression:

$$P(u) = \frac{\exp(-u^2/Npq)}{\sqrt{2\pi Npq}} \quad (3.2)$$

where q is the probability of a particle to not diffract, $q = 1 - p$. Eq. 3.2 is applicable when the magnitude of deviation u is much smaller than both the expected value of the diffracting particles, $u \ll Np$, and the population of the non-diffracting particles, $u \ll Nq$. When these conditions are not satisfied, Eq. 3.2 must be suitably modified. When it is applicable, the variance in the population of diffracting particles n_f among N particles is given by

$$\sigma^2 = Np(p - 1) = Npq$$

from which the relative standard deviation or relative uncertainty can be calculated as

$$U = \frac{\sqrt{\sigma^2(u)}}{Np} = \sqrt{\frac{q}{Np}} \quad (3.3)$$

Using Eq.3.3 it is possible to estimate the uncertainty due to sampling statistics in the oriented particle population from a single measurement, if the total number of irradiated particles N and the diffraction probability p are both known. Additionally, since the total diffracted intensity is proportional to the number of diffracting particles at that reflection, the uncertainty (due to particle sampling statistics) in the measured intensity must be directly equal to the uncertainty in the diffracting particle population. Therefore, assuming we have knowledge of N , the only quantity that we need to obtain is the diffraction probability term 'p'.

3.3 Calculation of the Diffraction Probability

Following the original reference [3], the probability of diffraction for a single crystallite can be derived based on the classical diffraction geometry. Here, a slight modification needs to be incorporated into the classical derivation when adapting it to nanocrystalline samples: in the reference work [3] a finite 'X-ray source width' in addition to the crystallite rocking angle was included in the computation to account for the particle sampling process based on finite acceptance angles. In the current work, a plane monochromatic X-ray beam with zero divergence is assumed for simplicity and the particle selection probability will, therefore, be solely a result of the acceptance angle of an individual crystallite. This is a reasonable model for current powder diffraction experiments with nanoparticle ensembles, since the

particle size introduces a large broadening to the measured profiles, and for this particle size regime, instrumental broadening is relatively negligible [65].

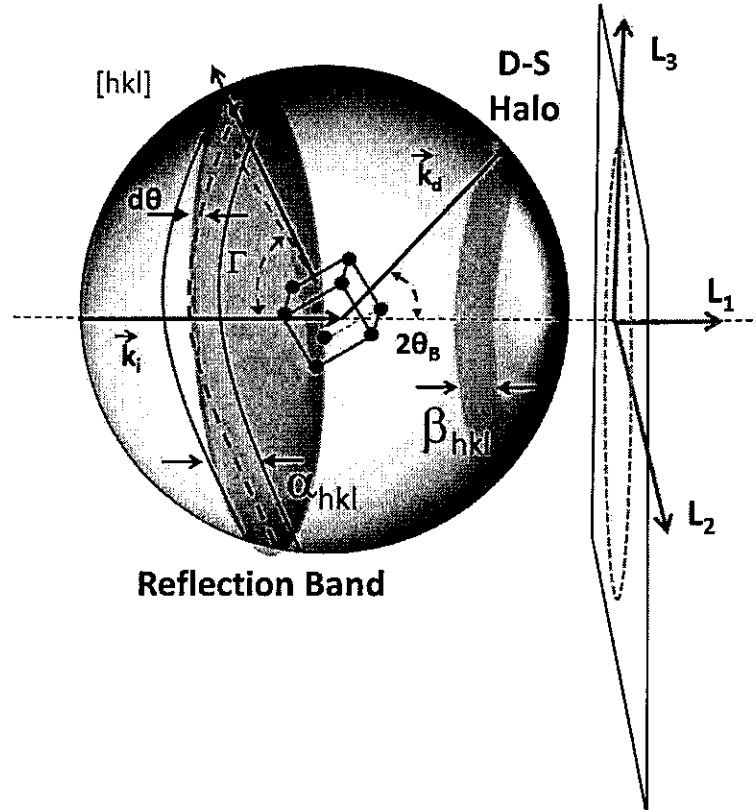


Figure 3.1: Single crystalline particle satisfying the exact Bragg diffraction

Figure 3.1 shows an isolated cubic crystallite at the center of a reference sphere. The axes $\vec{L}_i$ depict the reference sphere (laboratory) coordinate system. It is assumed that $\vec{L}_i$ share the same origin with the unit cell axes, $\vec{a}_i$, and the origin is placed at the center of the reference sphere. $\vec{k}_i$ is the incoming X-ray beam that is monochromatic and planar, whereas $\vec{k}_d$ is the diffracted X-ray beam travelling towards the detector. The angle between the incoming and the diffracted X-ray beam is shown as $2\theta_B$ and the vector that is normal to the diffracting planes is shown by $[hkl]$. The intersection of the $[hkl]$ normal vector with the surface of the sphere is called the 'hkl pole'¹.

¹In this thesis we reserve (hkl) to denote a particular set of planes with h, k, l Miller indices; $\{hkl\}$

If only a single crystallite is considered, the total number of hkl poles on the surface of the sphere will be equal to the corresponding multiplicity, m_{hkl} , of the particular family of hkl planes, $\{hkl\}$. For example, for the $\{100\}$ family in a cubic crystal, there would be six poles on the surface of the reference sphere, each corresponding to the intersection of a specific member of the family of directions with the reference sphere surface. When the diffraction condition is satisfied for a particular hkl reflection, any one of the $[hkl]$ normal vectors is 'activated' by aligning itself as the bisector of the angle that is supplementary to $2\theta_B$; in other words $\Gamma = \frac{\pi - 2\theta_B}{2}$. Here θ_B is the Bragg angle, which can be calculated from Bragg's formula, $2d_{hkl} \sin \theta_B = \lambda$.

When the normal vectors do not satisfy the Bragg condition exactly but are aligned slightly off from the Bragg angle, there may still be finite intensity diffracted from the corresponding crystallite. The amount of diffracted intensity, in this case, depends on the deviation from the Bragg angle. This angular range is called the crystallite acceptance angle and is shown by α_{hkl} in Figure 3.1. In the reference work [3], an acceptance angle on the order of a couple of arc-seconds (this was attributed to the imperfections within the coherent scattering domain of the particle) combined with the X-ray source divergence was used, as mentioned in the beginning. For nanoparticles, the acceptance angle for which (non-negligible) finite intensity is diffracted can be as large as several degrees and can be analytically related to the size-dependent peak broadening term given by the Scherrer equation [54; 46]:

$$\beta(2\theta) = \frac{C\lambda}{D \cos \theta_B} \quad (3.4)$$

In Eq. 3.4, C is a numerical constant determined by the shape of the coherently diffracting volume and D is the size of this volume in the direction of the momentum transfer vector $\vec{q} = \vec{k}_d - \vec{k}_i$. Using the above geometry, it can be seen that any rotation in 2θ axis (detector rotation) must be reciprocated by a rotation that is half of this value in θ axis (sample rotation), yielding $\alpha_{hkl} = \frac{\beta_{hkl}}{2}$.

When a number of randomly oriented, identical crystallites are placed at the center of the reference sphere, those with normal vectors satisfying the diffraction condition exactly

indicates the family of planes which are equivalent due to crystal symmetry; $[hkl]$ and $\langle hkl \rangle$ denote specific and symmetrically equivalent directions respectively.

will start to populate the surface of the reference sphere and the red ring shown in dashed lines will emerge. This ring is called the reflection ring and the corresponding pattern on a two dimensional detector is called the Debye ring. The normal vectors corresponding to the crystallites which are slightly off from the Bragg condition, however, will populate the surrounding yellow band centered at the reflection circle. This band is called the reflection band and its thickness is denoted by α_{hkl} on the figure. Corresponding to the finite range of the acceptance angle is the peak breadth, β_{hkl} .

At this point, each particle is assumed to be mapped to a single pole on the reference sphere. Those poles that are within the area of the reflection band are activated and contribute to the diffracted intensity with finite intensities, whereas the rest are not activated and do not participate in diffraction. Therefore the probability of diffraction for a randomly oriented particle can be reduced to finding the ratio of the area of the reflection band to the total surface area of the reference sphere [3]. This yields

$$\frac{A_{band}}{A_{sphere}} = \frac{\int_{\Gamma - \frac{\alpha_{hkl}}{2}}^{\Gamma + \frac{\alpha_{hkl}}{2}} 2\pi \sin \Gamma' d\Gamma'}{4\pi} = \frac{\alpha_{hkl} \cos(\theta_{B,hkl})}{2} \quad (3.5)$$

Since for a given crystallite, there are as many normal vectors as the multiplicity m_{hkl} of the hkl reflection, the likelihood of a randomly oriented grain to be in diffraction condition must be linearly scaled by the multiplicity. Replacing α_{hkl} by half the Scherrer broadening term and including m_{hkl} , the 'modified' probability equation of diffraction for an irradiated particle based on the reference work [3] becomes

$$p_{G,AKK} = m_{hkl} \frac{C\lambda}{2D \cos \theta_B} \frac{\cos \theta_B}{2} = \frac{m_{hkl} C\lambda}{4D} \quad (3.6)$$

3.3.1 Extended Analysis of the AKK Formulation of Diffraction Probability

Equation 3.6 indicates that, for a random powder sample illuminated by a plane monochromatic X-ray beam, the fraction of the grains satisfying the diffraction condition for the complete Debye-Scherrer ring with finite thickness is independent of the Bragg angle. In addition, since the probabilities are now related to the particle size and that the numerical value of $p_{G,AKK}$ must be within the closed interval of [0,1], Eq. 3.6 predicts a lower limit

for the particle size, D_{min} , below which the fraction of diffracting grains, $p_{G,AKK}$, is greater than unity regardless of their orientation (i.e., all grains contribute diffracted rays into the particular Bragg peak):

$$D_{min} = \frac{C\lambda m_{hkl}}{4} \quad (3.7)$$

Although a numerical value that is larger than unity is unphysical for $p_{G,AKK}$, the conditions required for approaching such a value are not extreme: For example, if Cr K_α radiation ($\lambda = 2.29 \text{ \AA}$) is used to irradiate a monodispersed powder sample of spherical grains ($C \cong 1.17$) of an FCC material, all particles would be expected to diffract into the 311 Debye ring ($m_{hkl} = 24$) if the particle diameter is equal to or less than 1.6 nm. For crystallites with cubic unit cells, $p_{G,AKK} \geq 1$ will be satisfied for any reflection with $m_{hkl} = 48$ if the irradiated particle population consists of spheres with diameters equal to or less than 3.2 nm. If monochromatic, 12.4 keV X-rays $\lambda \cong 1 \text{ \AA}$ are used, the corresponding values are 0.7 nm and 1.4 nm for any two reflections with multiplicities 24 and 48.

Finally, when Eq.3.3 is evaluated with the current form of $p_{G,AKK}$, it predicts zero relative mean deviation for powder samples where the particles have diameters equal to D_{min} , whereas for particle sizes smaller than D_{min} , Eq. 3.3 yields complex numerical values and is obviously not applicable. These observations indicate that the classical formalism for the diffraction probability for a randomly oriented particle is questionable, and that there may be a certain particle size range for which the formalism is applicable, although such an assumption is not explicit in the original reference. This issue will be addressed next.

3.3.2 Alternative Derivation of the Diffraction Probability

In the previous section we stated that the large wavelength to particle diameter ratio combined with the high multiplicity of certain reflections invalidated the use of the probability expression (Eq. 3.6) that was derived on the basis of grain acceptance angles. In this section an alternative formulation will be given by treating the grain-pole construct as two independent parameters and focusing on the distribution of pole vectors on the surface of the reference sphere.

Consider Figure 3.1 again, where a single cubic crystallite is shown with one of its $[hkl]$ pole vectors satisfying the diffraction condition exactly. When N_G similar crystallites with

random orientations are placed at the center of the reference sphere and irradiated one by one, the total number of hkl poles on the surface of the sphere becomes $N_P = N_G m_{hkl}$. Among these N_P poles, those that are within the reflection band area will be activated and will contribute to the diffracted intensity around the hkl reflection.

If the distribution of all of these N_P poles on the surface of the reference sphere is assumed to be uniform, then the areal density ρ of the poles on the surface will be a constant that is equal to $\rho = \frac{N_G m_{hkl}}{4\pi}$. Based on this, the fraction of poles $p_{P^*,hkl}$ that are activated for the hkl reflection can be obtained by computing the ratio of the area bounded by the reflection band to the total area of the sphere:

$$p_{P^*,hkl} = \frac{N_{P^*,hkl}}{N_P} = \frac{\int_{\theta_{B,hkl}-\frac{\alpha_{hkl}}{2}}^{\theta_{B,hkl}+\frac{\alpha_{hkl}}{2}} \cos \theta d\theta \int_0^{2\pi} d\phi}{4\pi}$$

$$= \cos \theta_{B,hkl} \sin \left(\frac{\alpha_{hkl}}{2} \right) = \cos \theta_B \sin \left(\frac{s\beta_{hkl}}{4} \right)$$

For small $\frac{s\beta}{4}$ values, where s is a range multiplier, $\left(\frac{s\beta}{4} < \approx 0.3 \text{ rad}, s \in \mathbb{Z} \right)$, the above expression simplifies to:

$$p_{P^*,hkl} = \frac{N_{P^*,hkl}}{N_P} = \frac{s\beta_{hkl} \cos \theta_{B,hkl}}{4} \quad (3.9)$$

Finally, substituting the Scherrer equation for the β_{hkl} term

$$p_{P^*,hkl} = \frac{sC\lambda}{4D} \quad (3.10)$$

From Eq. 3.10, the fraction of poles that would result in diffracted beams within one full-width at half-maximum of the diffraction angle (i.e. within the angular range $2\theta_B \mp s\beta_{hkl}/2$ where s=1) is obtained as

$$p_{P^*,hkl} = \frac{C\lambda}{4D}$$

Comparing the expression for the activated pole probability with that for the diffracting grain probability (Eq. 3.6), we see that the derivation based on pole distributions does not include the multiplicity factor. Consequently, the minimum particle size D_{min} that would result in 100% diffraction probability, when calculated by the pole based probability expression, turns out to be smaller than the X-ray wavelength for most cases: since the

Scherrer constant takes values around $C \approx 1 - 1.2$, setting the left side of Eq. 3.10 and the numerical value of s to unity yield $D_{min} = \frac{C}{4}\lambda < \lambda$. For this (λ, D_{min}) pair, it is questionable even to call the scattering phenomenon 'diffraction' since there is barely more than a single layer of atoms for the common irradiation wavelengths. Based on this analysis we conclude that the probability expression derived based on pole distribution, does not predict 100% diffraction probability, unlike the grain based formulation, even for nanocrystalline particles with large acceptance angles.

3.3.3 Comparison Between the Pole and Grain Based Probability Formulations

At this point, there appears to be an inconsistency in the form and predictions of the two probability formulations Eqs. 3.6 and 3.10. In the formulation by Alexander, Klug and Kummer [3], the probability of a randomly oriented grain to satisfy the diffraction condition was found to be proportional to the multiplicity of the diffracting plane, whereas the pole distribution based derivation led to a form that excluded the multiplicity factor. Essentially, these two formulations rely on the same construct by Lorentz, and both assume that the pole distributions are truly random over the surface of the reference sphere, including the reflection band area. However, three conditions must be met in order to guarantee their agreement:

1. The irradiated grains must be of identical size and shape.
2. The grain orientations must be perfectly random.
3. Each diffracting grain must have one and only one of its pole vectors (belonging to the hkl reflection) within the reflection band area.

Under these conditions, the populations of diffracting grains $N_{G^*,hkl}$ and activated poles $N_{P^*,hkl}$ must be equal by definition. However, the lattice vectors belonging to an $\langle hkl \rangle$ family of a particular grain are related through the symmetry operators of the unit cell and therefore cannot be considered uncorrelated. This means that, when a population of randomly oriented grains is irradiated, there are in fact $N_{G,hkl}$ randomly distributed 'groups of poles' with each group having m_{hkl} members. Among these groups of poles, none, one

or maybe more than one pole may fall within the area of the reflection band. Under these circumstances and for large reflection band areas, one grain may have more than one pole inside the reflection band, which are perfectly correlated by crystal symmetry. In that case, the number of activated poles and the number of grains contributing these poles may differ. This explains the apparent inconsistency between the pole and grain based probability expressions and their predictions. In the next section, we will test this hypothesis by direct modeling and simulation.

3.4 AKK Analysis Applied on Powder Diffraction Simulations with Nanocrystalline Particle Aggregates

The simulation of powder diffraction experiments in our analysis is based on irradiating all particles from a powder ensemble individually by a plane monochromatic X-ray beam and testing if the normal vectors of these particles satisfy the diffraction condition or not. During the computations, the direction of the incoming X-ray beam is fixed and assumed to be towards the L_1 axis of the laboratory coordinate system, as illustrated in Figure 3.1.

3.4.1 Simulating Ideal, Monodispersed Powder Ensembles

The ideal powder ensembles are generated by assuming a number of perfectly spherical, gold crystallites with FCC unit cells and a lattice parameter of $4.08 \text{ \AA}$. In the beginning, the initial coordinates of all plane normal vectors for the first four reflections, namely $\langle 111 \rangle$, $\langle 200 \rangle$, $\langle 220 \rangle$ and $\langle 311 \rangle$ families, are collected in the local coordinate system of each particle. The final orientation distribution of the crystallites is generated by setting the local $\vec{a}_3$ axis of each particle as 'the initial orientation vector' and then randomizing this vector in such a way that all of its intersections with the surface of the reference sphere are uniformly distributed over the area of the reference sphere. As expected, this operation also determines the orientation distribution of the plane normal vectors.

The randomization operator is constructed from three single rotation matrices around the individual Euler angles of the particle using a published algorithm from past literature [37] (The details of the process is included in the Appendix). This randomization matrix

is then operated on the coordinate matrix of the plane normals for each particle, and the final coordinates of the normal vectors are obtained keeping the interplanar angles and the length of the normal vectors constant.

3.4.2 Testing the Particles in an Ideal Powder Ensemble for Diffraction

Based on the formulations introduced in the previous parts, we developed an algorithm that tests for diffraction all m_{hkl} normal vectors of all grains from a randomly oriented crystalline nanoparticle ensemble. A given normal vector $[hkl]$ contributes a diffracted spot if the following condition is satisfied:

$$\frac{1}{2} \left[\pi - \left(2\theta_B + \frac{s\beta_{hkl}}{2} \right) \right] < \Gamma < \frac{1}{2} \left[\pi - \left(2\theta_B - \frac{s\beta_{hkl}}{2} \right) \right]$$

where s is the (integer) range multiplier; otherwise it is counted as not contributing. If any one grain has at least one activated pole within the hkl reflection band area, it is recorded as a diffracting grain. By this procedure, we are able to obtain the total number of activated poles and diffracting grains independently.

Once the activated pole and diffracting grain populations are obtained, we use a simple expression as a measure of the *enhancement* of the diffracted spots per grain, which is given below:

$$N_{P^*,hkl} = N_{G^*,hkl} H_{hkl} \quad (3.11)$$

In Eq. 3.11 the term H_{hkl} is called the pole enhancement factor, which is a scalar that relates the two populations, namely diffracting grains and contributed poles to the reflection band.

3.4.3 Simulation Results

Case 1: $D=1.63$ nm $\lambda = 2.29$ Å

Numerical results from a single run of simulation with an ensemble of 10^4 randomly oriented spherical gold crystallites that are 1.63 nm in diameter and illuminated by monochromatic, 5.41 keV X-rays (2.29 Å) are listed in Table 1 for the (111), (200), (220) and (311) reflections with Bragg angles at 29.09°, 34.16°, 52.57° and 68.61°, respectively. In this simulation, the

acceptance angle of the crystallites was set to $\frac{\beta_{hkl}}{2}$, which means that the poles that fell within the reflection band area contributed finite and non-negligible intensity over the area of the respective Debye ring with thickness of one full breadth. Due to the very small crystallite diameter and large wavelength, these FWHM values were large, starting from 10.77° degrees for the (111) peak and rising up to 25.80° degrees for the (311) peak.

Reflection	$N_{G^*,p=1}$	$N_{G^*,p=2}$	$N_{G^*,p=3}$	$N_{G^*,p=4}$	$N_{G^*,tot}$	$N_{P^*,tot}$	H_{hkl}
111(8)	2473	417	0	0	2890	3307	1.14
200(6)	2166	126	29	0	2321	2505	1.08
220(12)	3515	646	35	0	4196	4912	1.17
311(24)	4789	2201	150	35	7175	9781	1.36

Table 3.1: Computation results for 10^4 randomly oriented spherical gold nanocrystals with diameter 1.63 nm. The irradiation wavelength is 2.29 Å and $s=1$. The multiplicity of each reflection is given in parantheses to the right of the reflection.

In Table 3.1, $N_{G^*,p=i}$ represents the population of particles among 10^4 which have i of their hkl plane normal vectors (or poles) satisfying the diffraction condition. $N_{G^*,tot} = \sum_{j=1}^6 N_{G^*,p=j}$ represents the total population of particles diffracting at the hkl condition, whereas $N_{P^*,tot} = \sum_{j=1}^6 j \times N_{G^*,p=j}$ stands for the total number of poles contributed by these diffracting particles. $H_{hkl} = \frac{N_{P^*,tot}}{N_{G^*,tot}}$ is the pole enhancement factor, as introduced previously. Based on this data, we can list the following observations:

1. For all of the reflections considered, the total number of activated poles exceeds the total number of diffracting particles contributing to the intensity profile within one FWHM of the diffraction angle, $2\theta_B$. In other words, the area of the reflection band is large enough to accommodate, on average, more than one of the m_{hkl} plane normals per diffracting particle. As the multiplicity of the reflection increases, this enhancement effect is larger, as reflected in the increasing numerical value of the H_{hkl} terms.

2. 72% of the 1.63 nm diameter crystallites from the ensemble containing 10^4 particles have poles within the 311 reflection band. The expected proportion of diffracting grains based on the classical analysis, i.e. Eq. 3.6, however, is 99% for this reflection since the corresponding D_{min} is 1.63 nm.
3. The total number of particles participating in diffraction, obtained by summing up the diffracting particle populations for the four reflections, is 16582. This is approximately 1.7 times the population of the total irradiated particles, demonstrating that some of these particles satisfy the diffraction condition for more than one reflection.

Case 2: $D=1.63$ nm $\lambda = 1.0$ Å

Reflection	$N_{G^*,p=1}$	$N_{G^*,p=2}$	$N_{G^*,p=3}$	$N_{G^*,tot}$	$N_{P^*,tot}$	H_{hkl}
111(8)	1312	48	0	1360	1408	1.03
200(6)	1013	22	0	1035	1057	1.02
220(12)	1737	153	0	1890	2043	1.08
311(24)	2633	722	57	3412	4248	1.24

Table 3.2: Computation results for 10^4 randomly oriented spherical gold nanocrystals with diameter 1.63 nm. The irradiation wavelength is 1 Å and $s=1$. The multiplicity of each reflection is given in parantheses to the right of the reflection.

If the energy of the incident radiation is increased to 12.4 keV ($\lambda = 1.0$ Å), the Bragg angles and FWHM values computed for the 1.63 nm diameter gold crystallites decrease significantly. For this case, the numerical values of the (θ_B, β_{hkl}) pairs for the 111, 200, 220 and 311 reflections are $(12.25^\circ, 4.20^\circ)$, $(14.19^\circ, 4.24^\circ)$, $(20.28^\circ, 4.38^\circ)$ and $(23.98^\circ, 4.50^\circ)$ degrees, respectively. Pole and particle counts that participate in diffraction for the same ensemble (10^4 particles with 1.63 nm diameter) considered in Case 1 and obtained from numerical simulation are shown in Table 3.2. As seen, all activated pole and diffracting particle populations dropped significantly, compared to the previous case. For the lower multiplicity, i.e. 111 and 200 reflections, the pole and particle populations are quite close, and the corresponding H_{hkl} are within 5% of their ideal value, that is unity. For these

reflections, some particles contribute two poles but there are no particles which contribute three or more poles, unlike Case 1. For the highest multiplicity reflection, 311, there are still particles which contribute up to three poles to the reflection band but the fraction of these particles contributing more than two poles is below 1% of the total ensemble population.

Case 3: $D=2.86$ nm $\lambda = 1.0$ Å

Reflection	$N_{G^*,p=1}$	$N_{G^*,p=2}$	$N_{G^*,p=3}$	$N_{G^*,tot}$	$N_{P^*,tot}$	H_{hkl}
111(8)	780	15	0	795	810	1.02
200(6)	587	10	0	597	607	1.02
220(12)	1114	53	0	1167	1220	1.05
311(24)	1842	280	6	2128	2420	1.14

Table 3.3: Computation results for 10^4 randomly oriented spherical gold nanocrystals with diameter 2.86 nm. The irradiation wavelength is 1 Å and $s=1$. The multiplicity of each reflection is given in parantheses to the right of the reflection.

In this third set of simulations, the X-ray energy was maintained at 12.4 keV ($\lambda = 1$ Å) but the crystallite diameter was increased to 2.86 nm. Consequently, the FWHM values for all reflections dropped even more to approximately 2.5° ($\beta_{111} = 2.40^\circ$, $\beta_{311} = 2.57^\circ$) while the Bragg angles remained unchanged from the previous case. The results of these computations are shown in Table 3.3. According to the table, the further decrease in the FWHM eliminated most of the grains that contribute more than two poles to the highest multiplicity reflection circle, 311. $N_{G^*,p=3}$ is still finite for the 311 reflection but the fraction of grains contributing three poles is below 0.1%. The fractions of diffracting grains contributing two poles to the 111 and 200 reflections are below 0.2%. For the highest multiplicity 311 reflection, this fraction is still reasonably high ($\approx 2.8\%$).

Case 4: Grains Simultaneously Diffracting at More Than One Reflection

As we saw from the analysis of the simulation data presented in Case 1, for some (D, λ) pairs, the total number of grains that are diffracting at a finite number of reflections may

be larger than the total number of irradiated grains. This points to the fact that one grain may well be satisfying the diffraction condition for more than one reflection, simultaneously. In addition to the large acceptance angles of individual crystallites, this type of a multiple Bragg diffraction is caused by the 'combined' high multiplicities of certain pairs of reflections. Table 3.4 reports the population of such grains among 10^4 illuminated grains, that contribute intensity to two different reflections. The particle size for this simulation is 2.86 nm as in the previous case, and the X-ray beam wavelength is 1 Å. As we see, the percentage of grains participating in multiple Bragg diffractions among the total diffracting grain populations may be as high as $\approx 5\%$ (220 - 311 pair) when both reflections have high multiplicities. This high multiplicity effect also explains the mechanism that makes it possible for even two Bragg peaks that are apart from each other on the angular axis, such as 111 and 311 reflections, to still have a finite number of 'shared grains' satisfying the diffraction condition simultaneously.

		Reflection Pairs		
Parameter	$111 \cap 200$	$111 \cap 220$	$111 \cap 311$	$220 \cap 311$
$N_{\cap}$	35	120	127	206
$N_{\cap}/N_G(\%)$	0.75	2.6	2.7	4.4

Table 3.4: The number of grains, $N_{\cap}$, that contribute diffraction spots to Debye rings of two independent reflections ($\alpha_{hkl} = \beta_{hkl}/2$ for each band) when 10^4 randomly oriented spherical gold crystallites, 2.86 nm in diameter, are irradiated with 1 Å wavelength X-rays. The last row reports these populations as a percentage of the total number of diffracting grains or $N_{\cap}/N_G$.

3.4.4 Comparison of the Pole and Grain Counts with Predictions from Analytical Equations

Until here, our simulation results showed that for particle ensembles consisting of nanocrystallites, the large acceptance angle of the particles causes the total populations of activated poles to outnumber the populations of diffracting grains. As a result, the probabilities of

diffraction, obtained from activated pole (Eq. 3.10) and diffracting grain populations (Eq. 3.6) do differ. In this part, we try to answer the question of whether one probability formulation is a better description of the sampling statistics of nanocrystalline powder ensembles than the other.

Reflection (m_{hkl})	$\frac{ \Delta p_{G_{sim}}^* }{p_{G_{AKK}}^*}$ (%)	$\frac{ \Delta p_{P_{sim}}^* }{p_{P^*}}$ (%)	H_{hkl} (s=1)	H_{hkl} (s=2)	H_{hkl} (s=4)
200 (6)	2.85	1.22	1.02	1.03	1.05
111 (8)	2.97	1.14	1.02	1.05	1.10
220 (12)	5.04	0.73	1.05	1.10	1.21
311 (24)	13.42	1.55	1.14	1.30	1.64

Table 3.5: Fractional differences in grain and pole counting probabilities (%) obtained from the simulated data and from the analytical expressions (Eqs. 3.6 and 3.10). The ensemble population is 10^4 particles, individual crystallite diameter is 2.86 nm and X-ray beam has 1 Å wavelength. In the last three columns, the pole enhancement factor is tabulated for different (s=1,2,3) reflection bandwidths.

Table 3.5 reports the percent deviation between the diffracting grain and activated pole populations calculated from the analytical expressions (Eqs. 3.6 and 3.10) and obtained directly from numerical simulations presented in Case 1, 2 and 3, previously. Here, the probabilities from numerical simulation were computed by $p_{G_{sim}}^* = N_{G_{sim}}^*/N_G$ and $p_{P_{sim}}^* = N_{P_{sim}}^*/(N_G m_{hkl})$. The first three columns list the results from simulations with reflection bandwidth set to $\frac{\beta_{hkl}}{2}$ whereas in the last two columns the bandwidth is increased. From these results, the following can be inferred:

1. The fractional error for the probability of diffracting grains (Column 2), computed from Eq. 3.6 increases with increasing multiplicity and is non-negligible for the higher multiplicity reflections.
2. The fractional error for the probability of poles falling inside the area of a reflection band (Column 3) computed from Eq.3.6 is less than 2% for all reflections. There is

no apparent trend in these values related to the multiplicity of the reflection.

3. For all reflections, the pole enhancement factor is greater than one. As the breadth of the intensity profile or the width of the reflection band increases, the enhancement effect becomes more prominent. This shows that the random distribution of poles on the reference sphere surface assumed in the derivation of Eqs.3.6 and 3.10 is not rigorously correct for the D and λ values used in the simulation.

Based on this analysis, we conclude that the probability of diffraction expression, Eq.3.6, based on the AKK analysis does not accurately predict the true population counts of diffracting grains for the nanocrystalline particle ensembles we considered. Moreover, the deviation between the true and the predicted particle populations increases as the pole enhancement factor diverges from unity (Table 3.5). As a result, the uncertainty expressions derived based on these probabilities, Eq. 3.3, must be used with caution when estimating the relative uncertainties in the diffracting particle populations especially for experimental setups where the pole enhancement effect is substantial.

For practical purposes, the effect of H_{hkl} on the statistical sampling uncertainty in grain populations can be calculated by relating it to the uncertainty terms for the pole and grain populations. Denoting $u_{P^*,hkl}$ and $u_{G^*,hkl}$ as the relative uncertainties for the activated pole and diffracting grain populations at an hkl reflection based on Eq. 3.3 and combining Equations 3.3, 3.6, 3.10 and 3.11 we obtain:

$$\frac{u_{G^*}}{u_{P^*}} = (H_{hkl})^{\frac{1}{2}} \left[\frac{m_{hkl} (1 - p_{G^*,hkl})}{m_{hkl} - H_{hkl} p_{G^*,hkl}} \right]^{\frac{1}{2}} \quad (3.12)$$

For typical experiments, it is justifiable to simplify the denominator by $m_{hkl} - H_{hkl} p_{G^*,hkl} \approx m_{hkl}$, and the numerator by $1 - p_{G^*,hkl} \approx 1$, since the proportion of the properly oriented grains, $p_{G^*,hkl}$, is usually small. Therefore, $\frac{u_{G^*,hkl}}{u_{P^*,hkl}} \approx (H_{hkl})^{\frac{1}{2}}$ holds. For the cases considered in this study, typical values would correspond to a ~ 1.5 fold increase in $u_{P^*,hkl}$ with respect to $u_{G^*,hkl}$.

3.4.5 Variation of the Pole Enhancement Factor

Based on the previous discussions, we state that the pole enhancement factor is a statistical parameter that increases with the acceptance angle of the individual crystallite and the

multiplicity of the reflection. Since the acceptance angle of a crystallite is related to the coherent size of the crystallite by the Scherrer equation, we must be able to tune the pole enhancement effect by varying the particle size. To test this, we collected simulated data from a set of ensembles consisting of 10^4 spherical gold nanoparticles with different diameters. The results of this computation are shown in Figure 3.2:

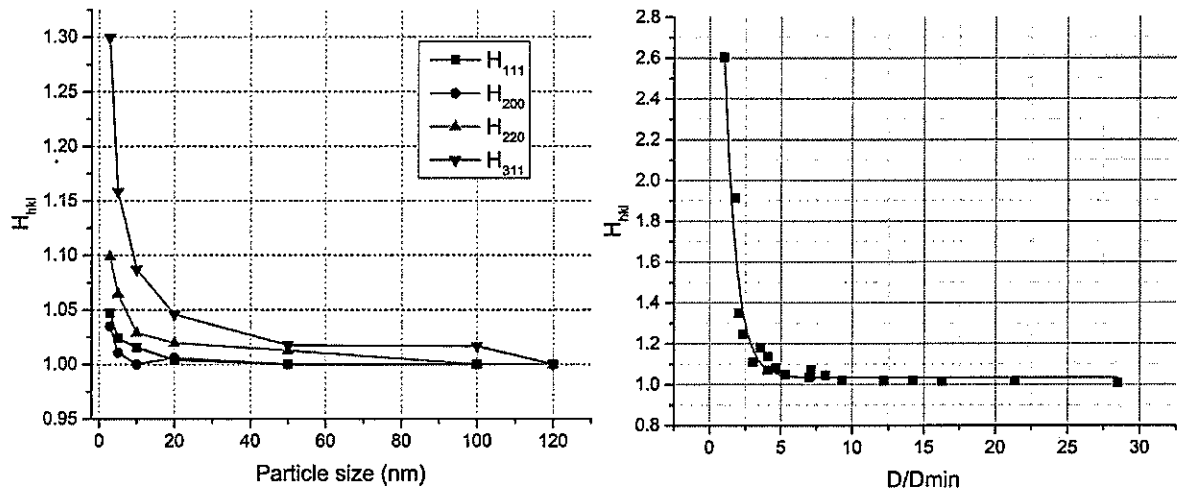


Figure 3.2: Left: Pole enhancement factor vs particle size for the first 4 reflections of an ideal powder sample consisting of spherical, gold nanoparticles. The irradiated particle population is 10^4 , $s = 1$ and $\lambda = 1 \text{ \AA}$. Right: Variation of the pole enhancement factor with respect to the dimensionless size parameter D/D_{min} . The red curve shows the best fitting exponential decay function to the raw data.

As seen in Figure 3.2 on the left, the largest pole enhancement effect is observed for particle sizes below 10 nm and around the 311 reflection with the highest multiplicity. As the multiplicity of the reflection decreases, the pole enhancement factor also decreases for all particle sizes. Due to this variation in the H_{hkl} parameter with the reflection, the ratios of the activated pole populations from two reflections with similar bandwidths will not be equal to the ratios of their respective multiplicities, $\frac{N_{P^*,hkl_1}}{N_{P^*,hkl_2}} \neq \frac{m_{hkl_1}}{m_{hkl_2}}$. Secondly, the pole enhancement effect decays as the particle size increases for a particular reflection as a direct consequence of the decreasing acceptance angle. H_{hkl} vanishes completely beyond a particle diameter of 100 nm for all tested reflections (but perhaps not for higher order

reflections with higher multiplicities). The decay in H_{hkl} with particle size approximates to an exponential decay function, as shown in Figure 3.2 on the right, but with different decay rates for different reflections.

Further analysis of Equations 3.6 and 3.10 indicates that, for nanoparticles with sizes D similar in magnitude to the multiplicity, the magnitudes of the Scherrer constant, C , and the X-ray wavelength λ , may have non-negligible effects on the number of grains or poles contributing to the reflection band of angular width $\alpha_{hkl} = \frac{\beta_{hkl}}{2}$. For example, C is 0.886 for a cubic crystal and 1.17 for a spherical one, which would change the activated pole probability pp^* by 1.13x just by changing the particle shape from cubic to spherical. In a similar manner, increasing the X-ray energy from 5 to 20 keV would decrease this term to one quarter of its initial value. To investigate the combined effect of C , λ , m_{hkl} and D on the pole enhancement factor, we defined a dimensionless size parameter D/D_{min} , where D_{min} was given by Eq. 3.7, and performed more tests to study the variation of H_{hkl} with D/D_{min} . The right side of Figure 3.2 shows the results for these simulations where $N_G = 10^4$ and $\alpha_{hkl} = \frac{s\beta_{hkl}}{2}$. As seen, H_{hkl} shows a power-law dependency (the red trace in the figure) and tends to unity beyond $D/D_{min} \approx 10$. Similar results were observed when different parameter sets were used in the simulations.

Based on these analyses, we conclude that it is safe to use the AKK analysis to estimate the statistical sampling uncertainty in randomly oriented grain populations when the particle sizes within the random ensembles are an order of magnitude or more larger than D_{min} . For smaller particle sizes, i.e., for $D < D_{min}$, this analysis should not be employed since for this regime the pole enhancement effect is non-negligible, $H_{hkl} > 1$.

3.5 Summary and Conclusions

The discussions presented in this chapter show that the formalism proposed by Alexander, Klug and Kummer for modeling the statistical behavior of the diffracting particles in an ideal powder ensemble cannot be rigorously justified when the sample consists of nanocrystalline particles. In particular, the implicit assumptions in this reference, that each grain satisfying the diffraction condition contributes only one pole to the reflection circle, and

that the activated poles are completely uncorrelated and randomly distributed on the reference sphere surface, are only applicable for particle aggregates with sizes D , such that the dimensionless size ratio, D/D_{min} is greater than 10. Here the denominator, D_{min} is a deterministic parameter which depends only the Scherrer shape constant, C , of the irradiated particles, the multiplicity of the reflection and the wavelength of the X-rays used in the experiment.

For powder aggregates where $D/D_{min} < 4$, the probability that some grains may contribute multiple poles to the reflection band becomes significant, and thus, the number of poles within the reflection band area is greater than the number of diffracting grains. In addition, since the positions of the poles originating from a single grain and belonging to the same family of reflection are related through crystal symmetry, the assumption of a completely random (uncorrelated) distribution of poles on the surface of the reference sphere becomes unjustified. Consequently, when numerical analysis is used to determine the number of poles within a particular reflection band area and the number of grains contributing these poles at the corresponding reflection, the estimates for an acceptable relative mean deviation in these parameters can be different than those predicted by the classical AKK approach, which assumes that only one pole per grain falls into the reflection band. The deviations between the predictions of the AKK formulation and the results from the counting algorithm increase with decreasing particle size and increasing multiplicity. We note that our analysis is limited to the sampling statistics of the diffraction process. Thus, it may not, by itself, be sufficient to predict the statistical errors of the diffracted intensity profiles. In particular, the validity of assuming the same formulation for sampling and intensity statistics for monosized nanoparticle aggregates must be validated through further analysis. This problem will be addressed in the upcoming chapters.

Chapter 4

Correlating Particle Sampling Statistics with Intensity Statistics for Powder Diffraction Experiments with Nanoparticles

4.1 Introduction

In the previous chapter, we showed that the classical analysis formulated by Alexander, Klug and Kummer in 1948 to estimate the uncertainty in the measured X-ray intensities due to particle sampling statistics was not applicable when the irradiated powder sample consisted of nanocrystalline particles. The reason behind the incompatibility between the classical formulation and the nanocrystalline particle ensembles stemmed from the two implicit assumptions in the original derivation: First of all, in the original formulation, each diffracting particle was assumed to have a single pole vector activated in the reflection circle. This assumption guaranteed the uniformity of the activated poles within the area of the reflection circle, thereby enabling an analytical, area based derivation of a probability expression for pole activation. Secondly, since one grain was allowed to have one and only one activated pole, the same expression derived for the pole activation probability applied to

calculations of diffraction probability for a randomly oriented grain within an ideal powder ensemble.

These two assumptions are not justified for nanocrystalline powder ensembles. To start with, nanocrystals upon irradiation with X-rays, result in diffraction spectra in which the intensity peaks are almost an order of magnitude more broader than their bulk counterparts. This also means that a single nanocrystalline particle can satisfy the diffraction condition over a wide range of angles in the vicinity of the Bragg angle. This enables one crystallite that satisfies the diffraction condition, to have more than one of its pole vectors activated at a particular reflection band. Hence, the diffracting grain and activated pole counts start to diverge, invalidating the equality between the probability expressions for the activated poles and diffracting grains. Secondly, area based, analytical formulations for activated poles are not rigorous for nanocrystalline particle ensembles, since the distribution of all activated poles from the powder ensemble is not perfectly random. The randomness of the activated pole distribution deteriorates due to the existence of 'sibling poles' that are contributed by the same grain and are members of the same family of planes; these siblings are related by crystal symmetry and cannot be randomly oriented. In other words, not only are the probability expressions for activated poles invalid for estimating the probability of diffracting grains within an ensemble, but also there is no rigorous analytical description of the probability distribution of the activated poles due to the non-randomness of sibling poles.

In this chapter, we will rigorously dissect the diffraction process into its unit components and analyze each step of a powder diffraction experiment tracing the diffracted X-ray beams back to the diffracting grains that they originate from. This type of a direct modeling will allow us to reconstruct the sampling space from its components, i.e. the diffracting grains and activated poles, and link it to the intensity space, which is related to the 'average Fourier transform of the electron density' within the sample in angular domain. First, the probability terms for the pole and grain populations will be rederived to obtain a general expression that holds irrespective of the particle size. This will be achieved by combining the arguments of the classical analysis [3] with the multiple beam diffraction phenomenon that was observed in particles that had large acceptance angles. Then, these expressions will be

extended to predict the relative uncertainties in the pole and grain populations. Following this analysis, we will compute the intensity profiles from the diffracting particle populations and investigate the statistical convergence of the intensity parameters to their expected values. At the end of the complete, independent analyses of the sampling and intensity parameters, we will relate the statistical behaviors of the sampling and the intensity spaces.

4.2 Area Based Probability Equations for Activating Uncorrelated and Correlated Poles from a Single Grain

In this section, the area based probability formulation that set the basis of the classical analysis by Alexander, Klug and Kummer [3] will be revisited. Following their procedure, we will expand this analysis to obtain a generalized probability description that also explains the multiple beam diffraction phenomenon observed in our previous simulations. For this purpose, we provide a new classification of activated poles from a nanocrystalline powder ensemble:

Uncorrelated Poles or Singlets: The population of singlets, P_1^* , includes all activated poles that are contributed by different grains, which are independent of each other in orientation. As a result, none of these poles are siblings, and therefore they are not related to each other by crystal symmetry.

n-fold Correlated Poles: These poles belong to 'n-let' groups ($n \geq 2$), such as doublets, triplets etc., with each group having n members of the poles within the same hkl family of a particular grain. The i'th member ($i \leq n$) of these n-lets will be denoted by $P_{n,i}^*$. Contrary to the singlets, the orientations of n-lets are not independent, since they originate from the same grain and are fixed by the crystal symmetry of the grain.

For large particle sizes, the peak broadening, as well as the crystallite acceptance angle are very small as predicted by the Scherrer equation [54]; therefore, each grain contributes no more than a single activated pole to the reflection band. As the particle size becomes smaller, increasing acceptance angle and peak broadening allow for multiple poles from a single grain to be activated. In this case, the total number of activated poles from the

particle ensemble becomes the sum of all uncorrelated and correlated poles:

$$N_{P^*T,hkl} = N_{P_1^*} + \sum_{n=2}^r n N_{P_{r,n}^*} \quad (4.1)$$

Here r is the largest n -let dimension that can be observed for the particular crystallite in a particular diffraction geometry. For example, $r = 3$ for the 200 reflection of an FCC gold crystallite (The reason why an upper limit exists for 'r' will be clarified later). Using area based probability formulation, the total probability of finding activated poles of any type (either correlated or uncorrelated), $p_{P^*,hkl}$, can be expressed as:

$$\begin{aligned} p_{P^*,hkl} &= \frac{N_{P^*,hkl}}{N_G m_{hkl}} \\ &= \sum_{n=1}^r p_{P_{r,n}^*} \approx s \frac{C\lambda}{4D} \end{aligned} \quad (4.2)$$

where N_G is the total number of irradiated grains. From the above equation we see that the probability of having **any one activated pole** from a particular $\langle hkl \rangle$ family can be predicted by the Lorentz equation. Any form of Lorentz equation or its extensions, on the other hand, are insufficient to estimate the sub-population of singlets or certain n -lets among all activated poles. Doublets and other highly correlated pole probabilities will be investigated in the next part.

4.2.1 Probability of One Grain to Contribute Doublets in the Reflection Band

Figure 4.1 shows the geometrical arrangement required for activating a doublet from a single crystallite placed at the center of the reference sphere. As before, $\vec{k}_i$ denotes the incoming X-ray beam direction. The vertical circle on the surface of the sphere drawn with a solid line is the reflection circle, which consists of the set of all intersection points of the pole vectors that satisfy the exact Bragg condition with the sphere surface. On the other hand, the two circles on both sides of the reflection circle are the boundaries of the reflection band. As seen, the width of the reflection band is $\frac{s\beta}{2}$, where β is the full-width-at-half-maximum of the Bragg peak, and s is the (integer) range multiplier. This case illustrates the condition of activating a doublet from the $\langle h00 \rangle$ family.

Activating a doublet is a two-step geometrical process: In the first step, the pole belonging to any one member of the $\langle hkl \rangle$ family is placed inside the reflection band area. In Figure 4.1 this pole is denoted by P_{C3} . In the second step, a ξ rotation around the $\vec{C}_3$ vector is required to position the second pole P_{C2} inside the reflection band area without moving P_{C3} outside the reflection band. Since $\vec{C}_2 \perp \vec{C}_3$ for the $\langle h00 \rangle$ direction family, the trajectory of the $\vec{C}_2$ vector as a result of the second rotation is a great circle with a radius equal to that of the reference sphere. In Figure 4.1 two great circles, each belonging to one of the two bounding reflection circles positioned at $\Gamma = \frac{\pi}{2} - \theta_B \pm \frac{s\beta}{4}$, are shown with grey solid lines. These circles intersect at two points on the sphere surface. In the figure, point A represents one of the two intersections. The curved tetragon shown as a pale yellow patch on the surface of the sphere is the intersection area of the reflection band with the lune bounded by the circular trajectories of the second activated pole. For this setup, there are two such intersection areas one of which lies on the back of the sphere and was not shown for clarity.

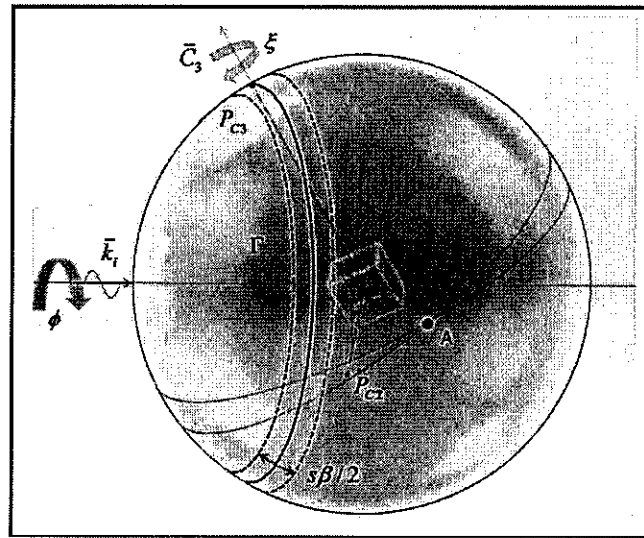


Figure 4.1: Schematic depicting the condition for activating an $\langle h00 \rangle$ type doublet from a single, diffracting crystallite

According to Figure 4.1, once the first member of the doublet is activated, the probability of activating the second member can be calculated by finding the ratio of the area of the

tetragon to the area of the lune:

$$\begin{aligned}
 p_{P^*2,2} \propto \frac{A_{quad}}{A_{lune}} &= \frac{2 \int_{\Gamma=\frac{\pi}{2}-\theta_B+\frac{s\beta}{4}}^{\Gamma=\frac{\pi}{2}-\theta_B+\frac{s\beta}{4}} \int_{\phi=-\frac{s\beta}{4}}^{\phi=\frac{s\beta}{4}} r d\Gamma r \sin \Gamma d\phi}{2 \times 4\pi r^2 \frac{\left(\frac{s\beta}{2}\right)}{2\pi}} = \frac{r^2 s\beta \cos \theta_B \sin \left(\frac{s\beta}{4}\right)}{2r^2 (s\beta)} \quad (4.3) \\
 &= \frac{1}{2} \cos \theta_B \sin \left(\frac{s\beta}{4}\right)
 \end{aligned}$$

Inserting the Scherrer based peak breadth and using small angle approximation, $\sin \left(\frac{s\beta}{4}\right) \rightarrow \frac{s\beta}{4}$, Equation 4.3 simplifies to $p_{P^*2,2} \approx \left(\frac{sC\lambda}{4D}\right)$. Now combining the conjugate probabilities of activating both poles, $p_{P^*2} \propto p_{P^*1,2} \times p_{P^*2,2}$, we obtain

$$p_{P^*2} \propto \left(\frac{sC\lambda}{4D}\right)^2 \quad (4.4)$$

Therefore, the area based probability formulation predicts that for a given crystallite, the probability of activating two $\langle h00 \rangle$ type poles simultaneously is proportional to the square of the ratio of the normalized angular range factor (s) to the particle diameter, $(s/D)^2$. As seen, this formalism is highly simplified: The vectors associated with each pole are mutually orthogonal and the range considered for the acceptance angle is assumed to be small. With the orthogonality requirement, the formalism given here cannot be directly extended to other reflections, since the pole vectors are not necessarily mutually orthogonal in other families of planes. In addition, this formalism excludes the probability that a third pole from the same $\langle h00 \rangle$ family be activated at the same time. The probability of the third pole activation is more complicated than the first two poles: since the position of the third pole is dictated and already determined by the crystal symmetry, its activation probability is not independent of the probabilities of activation for the first two poles and cannot be computed by simple area fractions.

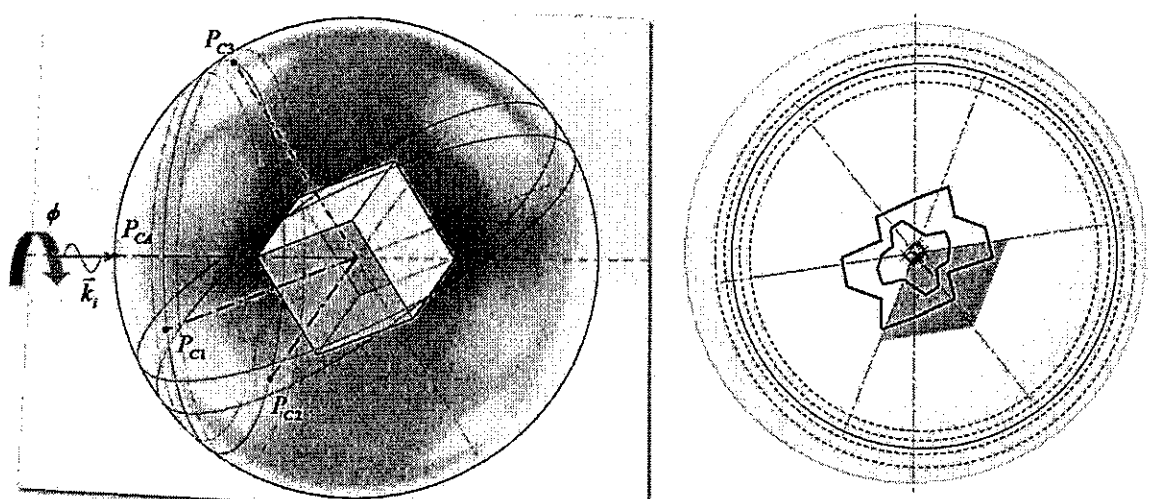


Figure 4.2: Left: Diffraction geometry when three h00 poles belonging to one crystallite with cubic symmetry (an h00 triplet) fall exactly on the reflection circle corresponding to the Bragg angle. This condition is automatically satisfied when a $\langle 111 \rangle$ body diagonal is antiparallel with the incident beam vector. Right: Schematic of the areas swept by the pole vector $\vec{C}_A$ while keeping all three h00 poles within the reflection band. The red and black circles represent the boundaries of the two reflection bands of 5 and 10 degrees angular width, respectively (not-to-scale). Here the viewer is assumed to be looking at the reference sphere along the incident beam vector direction, $\vec{k}_i$. (These figures were created with the assistance of Mr. A. Ellis of IBM Research Division and Ms. Connie Phung of the Department of Mechanical Engineering, Columbia University)

4.2.2 Probability of One Grain to Contribute Triple or Higher Correlated Poles in the Reflection Band

Let us consider a general hkl reflection, as shown in Figure 4.2 on the left, where three poles P_{C1}^* , P_{C2}^* and P_{C3}^* from this family of planes are activated and $\vec{C}_i$ are the corresponding pole vectors with coordinates $[h_i, k_i, l_i]$, ($i = 1, 2, 3$) belonging to the activated poles. In this case, a simultaneous activation of these poles requires the crystal orientation vector $\vec{C}_A = [m, n, p]$ that is anti-parallel to the incident X-ray beam $\vec{k}_i$ to satisfy the following relation:

$$\vec{C}_A \cdot \vec{C}_i = |\vec{C}_A| |\vec{C}_i| \cos \Gamma \Rightarrow \Gamma = \arccos \left[\frac{mh_i + nk_i + pl_i}{\sqrt{m^2 + n^2 + p^2} \sqrt{h_i^2 + k_i^2 + l_i^2}} \right] \quad (4.5)$$

for the three pole vectors. Due to the crystallography of the unit cell, the pole vectors must satisfy additional constraints:

$$\vec{C}_i \cdot \vec{C}_j = |\vec{C}_i| |\vec{C}_j| \cos \gamma_{ij} \Rightarrow \gamma_{ij} = \arccos \left(\frac{h_i h_j + k_i k_j + l_i l_j}{h^2 + k^2 + l^2} \right) \quad (4.6)$$

Here γ_{ij} are the interplanar angles between the planes normal to $\vec{C}_i$ and $\vec{C}_j$ which can be computed easily. These interplanar angles define the angular separation of the vectors corresponding to the activated poles on the reflection circle. For low multiplicity reflections, the sets of equations given above uniquely determine the geometrical condition for the activation of a triplet of correlated poles. Such a limiting case is the $h00$ reflection from cubic crystals where $m_{hkl} = 6$. For this case, only a unique crystal vector $\vec{C}_A$ satisfies the condition for simultaneous activation of three pole vectors from the $\langle h00 \rangle$ family. This condition can be observed by combining Eq.4.5 with the Bragg's law:

$$\lambda = 2d_{hkl} \sin \theta_B \Rightarrow \theta_B = \arcsin \frac{\lambda}{2d_{hkl}} \quad (4.7)$$

$$\frac{\lambda}{2d_{hkl}} = \frac{\vec{C}_A \cdot \vec{C}_i}{|\vec{C}_A| |\vec{C}_i|}$$

Here, d_{hkl} is the interplanar spacing between the planes that diffract at the hkl Bragg reflection. Solving for λ , we can calculate the irradiation wavelength required for three $h00$ poles to be simultaneously activated. We call this particular wavelength 'enhanced-selection wavelength', λ_{E-S} . Simplifying Eq. 4.7 further, we obtain:

$$\lambda_{E-S} = \frac{2d_{h00}}{\sqrt{3}} \quad (4.8)$$

In the case of a gold crystallite with lattice parameter 4.08 Å, Equation 4.8 predicts that 200 type triplets, where all poles are at the exact Bragg condition, would be observed when λ_{E-S} equals 2.36 Å. However, the finite breadth of the reflection band $\frac{s\beta_{hkl}}{2}$, permits the observation of these triplets not at the reflection circle but in its close vicinity over a range of wavelengths, $\lambda_{E-S} + \Delta\lambda$. This range can be determined by substituting $\theta = \frac{\pi}{2} - \Gamma \mp \frac{s\beta}{4}$ into the Bragg's law. For a particle size of 28.56 Å, for example, the lower and upper limits of the irradiation wavelength for enhanced pole selection become 2.03 Å and 2.85 Å. When triplets are activated at these wavelengths other than λ_{E-S} , the crystal orientation vector $\vec{C}_A$ deviates from the exact antiparallel alignment with the incoming X-ray beam. The right side of Figure 4.2 shows the areas swept by the crystal orientation vector $\vec{C}_A$ due to the allowable movement of the activated 200 triplets for two reflection band widths; one within $\alpha_{200} \approx \beta_{200}$ and another with $\alpha_{200} \approx 2\beta_{200}$. Using numerical analysis, the area ratios of these bands to the sphere surface are found to be proportional to

$$p_{P^*3} \propto \left(\cos \theta_B \frac{s\beta}{4} \right)^2 = \left(\frac{sC\lambda}{4D} \right)^2 \quad (4.9)$$

4.2.3 Probability of One Grain to Contribute One and Only One Activated Pole to the Reflection Band

For a single crystallite placed at the origin of the reference sphere, the maximum number of poles that are in the half sphere containing the reflection band is half the multiplicity of the particular reflection, i.e. $m_{hkl}/2$. To treat the case where only a single pole among these poles is activated, the probability formalism must be modified to include a term describing the conjunctive probability of having none of the remaining $\frac{m_{hkl}}{2} - 1$ poles to be activated. Since all the poles within the same family of reflection are correlated according to the particular crystallography of the cell, this probability cannot be computed simply by $\prod_{j=2}^g (1 - p_{P_j^*})$, where $g = \frac{m_{hkl}}{2}$ and $p_{P_j^*}$ being the probability of activation for j sibling poles (e.g., doublets and triplets for the case of h00 reflection). However, using Equation

4.2 it is possible to write:

$$p_{P^*1} \cong p_{P^*} - \sum_{n=2}^g p_{P^*n}$$

Here the summation is over all possible n-lets up to 'g'. For the case of h00 reflection, the above expression can be expanded as:

$$\begin{aligned} p_{P^*1} &\cong p_{P^*} - (p_{P^*2} + p_{P^*3}) \\ p_{P^*1} &\cong \frac{sC\lambda}{4D} - (p_{P^*2} + p_{P^*3}) \end{aligned} \quad (4.10)$$

Since both p_{P^*2} (Eq. 4.4) and p_{P^*3} (Eq. 4.9) are proportional to $\left(\frac{s}{D}\right)^2$, the numerical value of p_{P^*1} should also exhibit a nonlinear variation with $\frac{s}{D}$. Furthermore, since both p_{P^*2} and p_{P^*3} should rapidly decay to zero for large D, Equation 4.10 should tend to the classical probability of 'any one pole being activated' (p_{P^*}). For the extreme case where the particle diameter is small enough to broaden the reflection band over the entire half sphere, the probability of having one and only one independent pole per grain to be activated for diffraction will be identically zero since all poles will have correlated siblings and the sum $p_{P^*2} + p_{P^*3}$ must identically reach p_{P^*} . For more realistic values of β_{hkl} , the probability of having one and only one pole from a particular crystallite will, then, be smaller than the probability values computed using the modified Lorentz equation, $\frac{sC\lambda}{4D}$.

Selection Rules for Higher Multiplicity Reflections

The selection rules derived for the h00 reflection can be extended to reflections with higher multiplicity through geometric analysis. In the general case, many activated triplets within the $\langle hkl \rangle$ family, corresponding to arrays of orientation vectors $\vec{C}_A$ and enhanced selection wavelengths λ_{E-S} , will exist. Similar considerations apply to having simultaneously activated quadruplets, quintuplets or higher order n-lets of poles for higher multiplicity reflections. In such cases, the governing equations that need to be solved for are quite complicated, and therefore they will be investigated through modeling.

4.3 Sampling Statistics of Activated Poles and Diffracting Grains

In the previous section, we derived area based analytical expressions that predict the probability of observing different types of activated poles, accounting for the geometric restrictions due to their correlation orders. For uncorrelated and doubly correlated poles, the probability expressions (Eqs. 4.2, 4.4 and 4.9) included a power of the term $\frac{sC\lambda}{D}$. In higher correlated poles including triplets, the probability of simultaneous activation was further dictated by the crystal symmetry and these poles were observed only at special wavelengths, λ_{E-S} . These results intimate that the activated pole populations from a given ideal powder ensemble can be tuned by modifying s , C , λ and D . However, despite being useful in guiding our expectations, these expressions involve simplifying assumptions. Moreover, those that we derived previously are applicable only for h00 type reflections where all pole vectors are mutually orthogonal. In most cases, the analytical expressions for the probability of correlated pole populations are complicated. As a result, we will use numerical modeling in the upcoming parts to investigate the effect of these experimental parameters (C , s , λ , D) on the activated pole and diffracting grain populations.

4.3.1 Wavelength Dependence of the Activated Pole and Diffracting Populations

The first parameter we investigate is the irradiation wavelength, λ . Figure 4.3 shows a classification of the population of activated n-lets with respect to the irradiation wavelengths as well as the total population of activated poles and diffracting grains. The powder sample considered in this set of simulations consists of 10^4 gold nanoparticles with 2.86 nm diameter size and $s=4$ for all cases. To minimize statistical error over the number of runs, each simulation was repeated 10 times and the data points report the average value over the runs. As seen from the figure, the population of singlets and doublets are continuous, non-monotonic and nonlinearly dependent on the wavelength parameter tested for all reflections. However, the populations of triplets and higher order correlated poles are finite only at certain wavelengths, especially for relatively low multiplicity reflections. In particular for

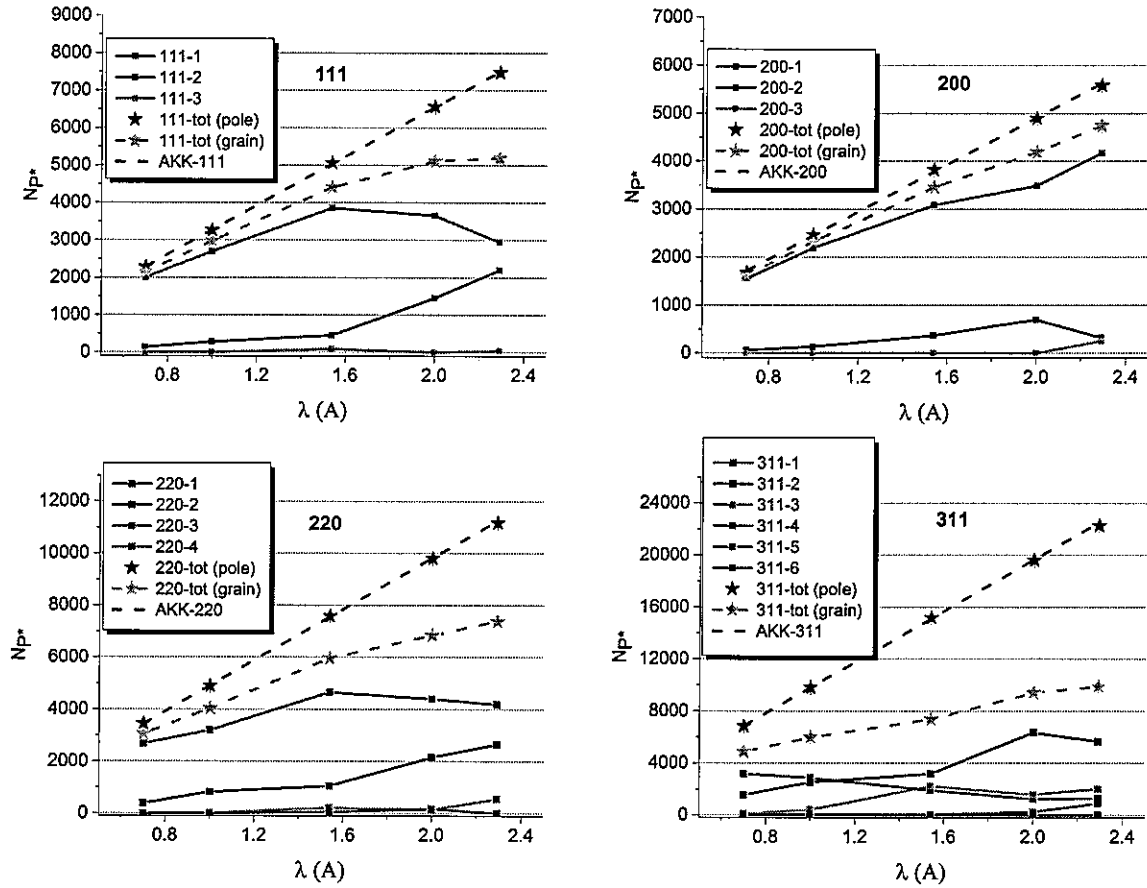


Figure 4.3: The population of activated n -lets in 111, 200, 220 and 311 reflection bands of an ensemble of 10^4 spherical gold nanoparticles with 2.86 nm diameter ($s=4$). The data points report the average populations over 10 runs of simulation and the marker sizes correspond to the error bars which are the standard deviations from the mean values. The plots shown in dashed lines are the total number of activated poles, $\sum_{n=1}^6 n N_{P^*,n}$, and diffracting grains, $\sum_{n=1}^6 N_{G^*,n}$. The lines connecting the data points for the n -lets do not imply trends but are shown just to guide the eye. The dashed lines denoted by AKK- hkl in each reflection represent the activated pole populations predicted by the modified AKK formula (Eq. 4.2)

111 reflection, grains with triplets are observed only at wavelengths of 1.54 and 2.29 Å whereas 200 triplets are observed only at 2.29 Å. In higher multiplicity reflections such as 220, triplets exist at all wavelengths except 0.7 Å and quadruplets start appearing at 1.54 Å and they are the highest correlated pole populations observed over the wavelength range considered. For the 311 reflection, the population of singlet poles shows a decaying trend over the range of wavelengths tested and the decrease in these poles is compensated by doublets, triplets and quadruplets, whose populations increase almost monotonically as the wavelength increases. Fifth and sixth order correlations among 311 poles are observed only at smaller wavelengths, i.e. 0.7 and 1.54 Å.

As far as the total populations of diffracting grains and activated poles are concerned, both quantities are continuous and monotonically increasing over the wavelength range considered. This is not surprising because by the Scherrer equation, we expect the increasing X-ray wavelength to broaden the intensity peak, thereby increasing the acceptance angle of the irradiated crystallites. The variation of the total activated pole populations is linearly dependent on the wavelength as predicted by the modified AKK formulation, $N_{P^*} - AKK = N_G m_{hkl} \frac{sC\lambda}{4D}$, and the deviation of the total pole populations from the analytical formula is within $\pm 2.5\%$ of the simulation results, for all reflections. However, the dependency between populations and irradiation wavelength is nonlinear for the diffracting grains; their populations rise with a diminishing rate with the increase in the X-ray wavelength. The discrepancy between the total number of grains and poles, as a result, escalates as the irradiation wavelength becomes larger and this is consistent with the diminishing validity of the one grain-one pole assumption for systems with large $\frac{\lambda}{D}$ ratios.

4.3.2 The Dependence of the Uncorrelated and Correlated Pole Populations on s/D

In order to test the dependencies predicted by the area based probability expressions for singlets, doublets and higher correlated activated poles on s/D at a constant λ , several simulations were performed, where the particle diameter D and range multiplier s were allowed to take numerical values within the following limits, $2.86 \text{ nm} < D < 20 \text{ nm}$ and $s = 2, 3, 4$. For each (s, D) pair, simulations were run 10 times to minimize the statistical

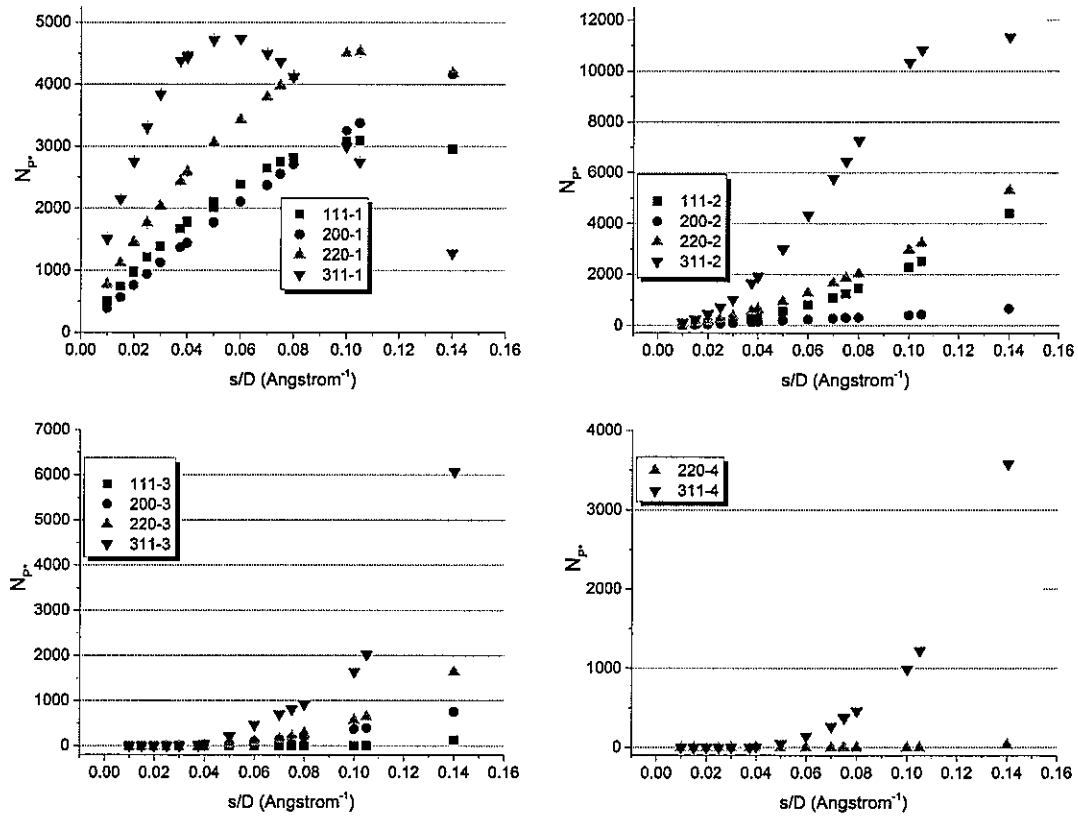


Figure 4.4: The dependence of the correlated pole populations on $\frac{s}{D}$ for the first four reflections of gold particle ensembles at $\lambda = 2.29 \text{\AA}$. The data points represent the mean counts over 10 runs of simulation.

error between individual runs. Since the 200-triplets only appeared at the special X-ray wavelength of $\lambda = 2.29 \text{\AA}$, this wavelength was chosen for the simulations. The results of this study are plotted in Figure 4.4. In each subplot, the population of the observed n -let poles with correlations ($1 < n < 4$) are reported with respect to s/D for the 111, 200, 220 and 311 reflections of gold.

The first observation we can make from Figure 4.4 is that the variations of the correlated pole populations over s/D follow different trends for different direction families even if the correlation order is the same. This is expected since each family of planes requires a

different geometric condition (or λ_{E-S}) to be satisfied for the activation of correlated poles. (Note that Eq. 4.3 was derived for the h00 family where the pole vectors were mutually orthogonal). Secondly, even for the 200 reflection with mutually orthogonal pole vectors, the doublet and triplet probabilities do not follow a quadratic dependence on s/D : as it was mentioned before, Equation 4.3 does not exclude the probability of triplet poles. Moreover, at this X-ray wavelength, the Scherrer broadening becomes much more prominent, hence the small angle approximation used in the derivation of Eq. 4.4 is no longer valid. This proves our hypothesis that the area based probability expressions are not applicable in estimating the individual sub-populations of correlated poles from an ideal powder sample. Some additional observations from Figure 4.4 are as follows:

1. The singlet populations do saturate at particular s/D values, beyond which their relative populations start to decay and are replaced by higher order correlated poles. The saturation values for s/D increase with decreasing multiplicity of the reflection.
2. For higher multiplicity reflections, in which highly correlated n-lets ($n > 3$) are observable, the doublet populations also have saturation points.
3. The sub-population of correlated poles (with correlation degree of second order or higher) does follow some kind of a power law dependence on s/D , albeit not a simple quadratic relation. This is because the quadratic relations resulting from the area ratio based expressions do not exclude the possibility of higher correlated or completely independent singlet type poles being activated alongside.

Even though the individual sub-populations of the uncorrelated and correlated pole counts cannot be accurately estimated by analytical means, the area based probability expression $p_{P^*, hkl}$ for the total activated pole populations may still hold irrespective of the particle size. Figure 4.5 on the left demonstrates the deviations, $\Delta N_{P^*, hkl}$, of the activated pole populations obtained by the counting algorithm from the expected populations calculated by $N_{P^*, hkl} = N_G m_{hkl} p_{P^*, hkl}$ for the first four reflections of the gold nanoparticle system with respect to the parameter (s/D). As seen, the deviation between the activated pole populations $\Delta N_{P^*, hkl}$ systematically increases with the multiplicity of the reflection and also with increasing s/D . This observation intimates that the rising share of the 'corre-

lated' poles among the total activated pole populations is invalidating the assumption of the pole probability being constant over the area of the reference sphere, which is the basis of $p_{P^*} = \frac{sC\lambda}{4D}$. The right side of Figure 4.5 reports these deviations expressed as the percent fraction of the true populations obtained by the simulations. According to this plot, the percent deviations are, on average, below 5% for the whole s/D range at all reflections and below 1% for higher multiplicity reflections beyond $s/D > 0.04$. At the very low s/D values, the large error bars are due to the large propagated statistical errors. In this range, the number of poles activated is much smaller due to the combined effect of small numerical value of s and large particle diameter.

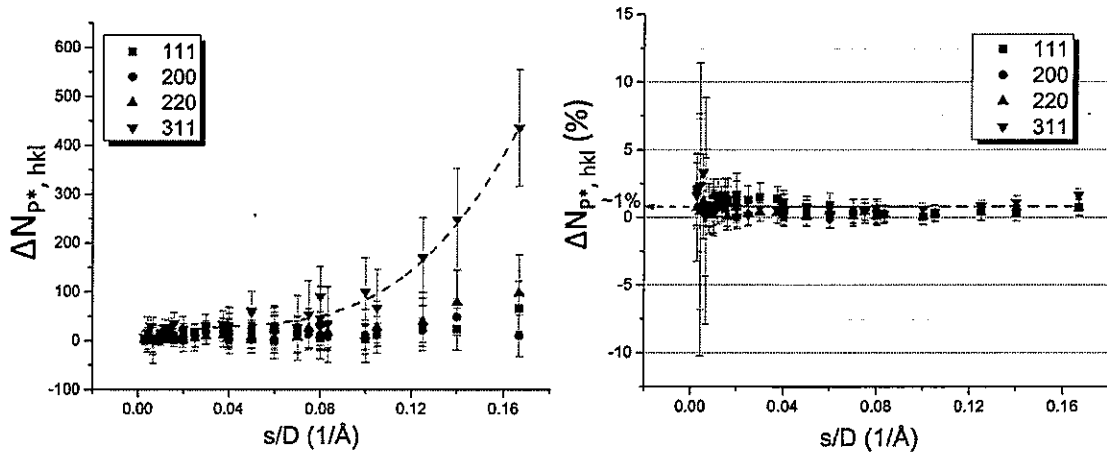


Figure 4.5: Left: The difference between the total number of poles obtained from simulation and by evaluating $(N_G m_{hkl} p_{P^*, hkl})$ with the pole probability estimated from Eq. 4.2 Right: $\Delta N_{P^*, hkl}$ expressed as the percent fraction of the true pole counts obtained by direct simulation. The data markers correspond to the average deviations for 10 independent trials and the error bars are the standard deviations from the mean values. ($\lambda = 2.29 \text{\AA}$)

4.3.3 Population Ratios of Diffracting Grains and Activated Poles at Different Reflections

In the last part, the close agreement between the total number of activated poles obtained from simulations and from the predictions of Eq. 3.10 has been demonstrated for the first

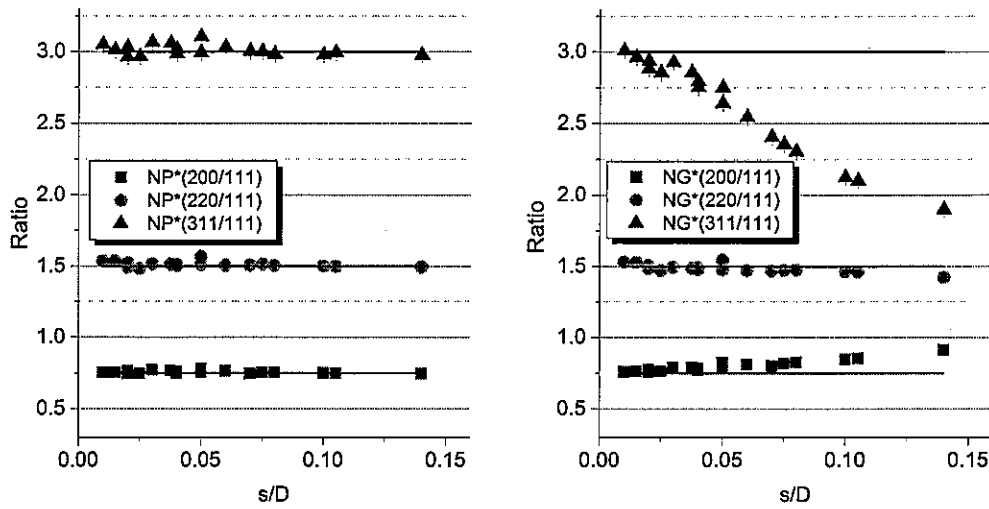


Figure 4.6: The ratio of pole (left) and grain (right) populations for various reflection pairs with respect to s/D . The data points represent the mean counts over 10 runs of simulation and the straight lines are the ratios of the multiplicities of the respective reflections. ($\lambda = 2.29 \text{ \AA}$)

four reflections of the gold nanoparticle system, for a range of values for s and the particle diameter D . Based on these results, we expect the ratios between the total activated pole populations at various reflection pairs to follow the ratios between the multiplicities of these reflection pairs. Figure 4.6 shows these ratios for the total activated pole populations (left) and diffracting grain populations (right) at one of the 200, 220 and 311 reflections to those at the 111 reflection of the gold powder ensemble. For all simulations, the wavelength was kept at $2.29 \text{ \AA}$ and the total number of irradiated particles was 10^4 . Each run was repeated 10 times to incorporate the statistical variation. As seen from the figure, our expectation is largely obeyed, as the ratios of the activated pole populations at all reflections to those at the 111 reflection follow the same ratios as the multiplicities (shown by straight lines) of the respective reflections to the multiplicity of the 111 reflection. On the other hand, the ratios of the diffracting grain populations at the same reflections to those at the 111 reflection diverge from the multiplicity ratios as s/D increases, for all reflection pairs considered. This

is a result of the pole enhancement effect, which becomes more dominant as the particle size becomes smaller and s/D becomes larger. The closest grain population ratio to the multiplicity ratio is observed with the (111, 200) pair, since these families have multiplicities that are close to each other and as a result, the pole enhancement effect is also similar. On the other hand, the largest deviation from the multiplicity ratio is seen with the (111, 311) pair where the multiplicities and the pole enhancement factors are substantially different from each other.

4.3.4 The Distribution of the Activated Pole Populations Around the Bragg Angle

Until here, we investigated the effects of various experimental parameters on the total populations of diffracting grains and activated poles. In this part, we will analyze how these activated poles are distributed over the width of the reflection bands.

For an ideal powder, the orientation distribution of crystallites over the surface of the reference sphere is uniform by definition [25]. This means that if each crystallite from the powder sample has a single pole vector that is normal to a particular atomic plane, the orientation distribution of that vector for the whole ensemble would be uniform, as well. However, due to the high symmetry of crystallites, there are as many as the multiplicity of such pole vectors for a given plane, which are related to each other through crystal symmetry operations. In other words, the orientation of one of the m_{hkl} pole vectors determines the orientation of the remaining pole vectors. As a result, the distribution of m_{hkl} pole vectors from an isolated, single crystallite is not uniform over the reference sphere surface.

When there is a finite number of such high symmetry crystallites, the distribution of all pole vectors may or may not be random, depending on the total population of the ensemble. To test whether it is random or not, we collected the angular distribution data of all activated poles from an ideal, crystalline particle ensemble for a number of simulations and analyzed the data. In Figure 4.7, the results from 10 simulations with ensembles of 10^5 randomly oriented gold nanoparticles, having 2.86 nm diameter and irradiated with 2.29 Å wavelength X-rays are presented. Each subfigure reports all existing n -let populations, N_{P^*n} , and their sum $N_{P^*T,hkl}$ with respect to the reflection bandwidth for the first four

reflections of gold. The horizontal axes range from $-\beta_{hkl}$ to β_{hkl} and the angular range is sampled in 100 equi-spaced points.

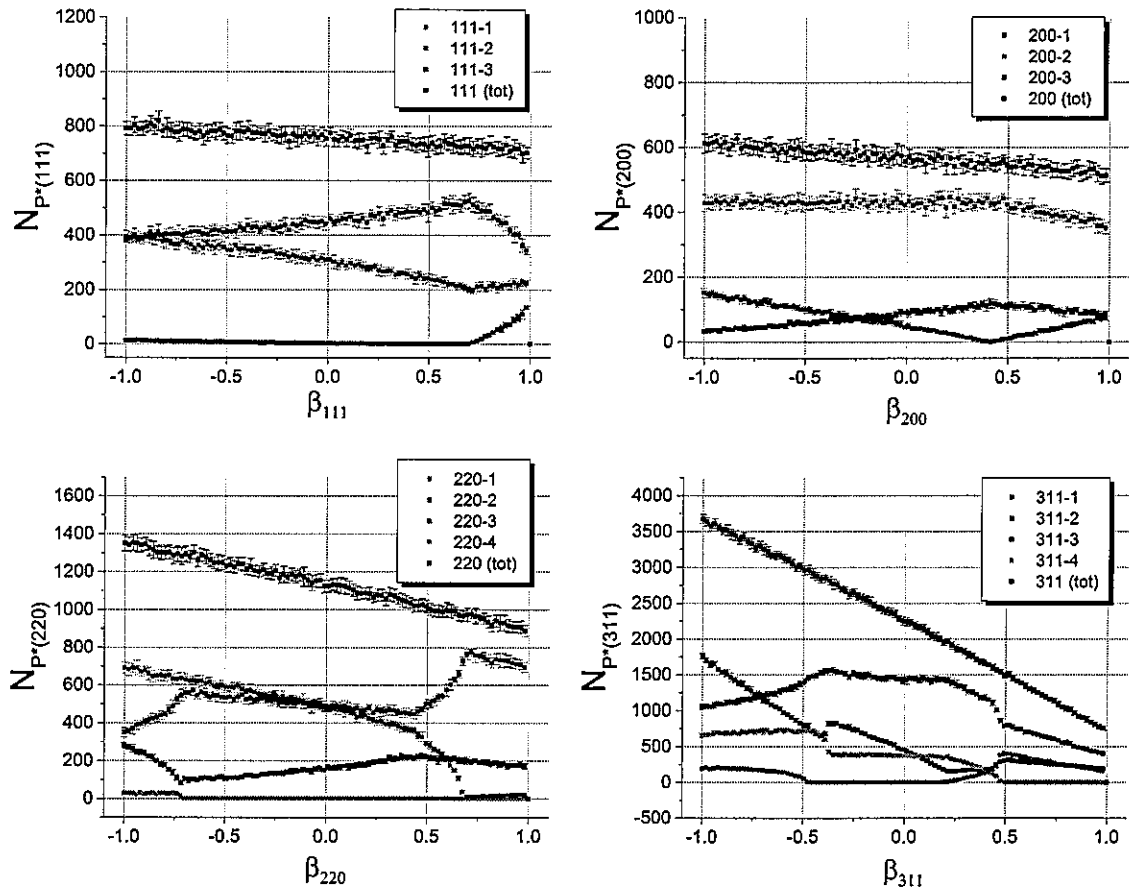


Figure 4.7: The distribution of activated n -let poles in 111, 200, 220 and 311 reflection bands of a 2.86 nm diameter spherical gold nanoparticle. The data points report the average populations over 10 runs and the error bars are the standard deviations from the mean values. The powder sample includes 10^5 particles for each run and $\lambda = 2.29 \text{ \AA}$.

From Figure 4.7 we observe that, in general for all reflections, the distribution of the total activated poles, $N_{P^*T,hkl}$, over the angular width of the reflection band follows a linear trend, whereas all individual n -let populations ($n \geq 1$) have sharp features and discontinuities. The total activated pole populations decay from negative to positive deviation angles, because

the radius of the reflection band changes over the angular range, proportional to $\sin \Gamma$ where $\Gamma = 90^\circ - (\theta_B + \Delta\theta)$. As seen in Figure 4.1, for positive deviation angles, the radius is larger and the probability that a given pole will be inside the reflection band area will be higher due to larger band area. A more detailed discussion and consequences of this geometric artifact will be revisited again in the next section. For the 111 and 200 reflections, the highest correlated pole populations that are observed are triplets; however, for 220 and 311 reflections quadruplets are also detected.

The overall trends of the individual n-let populations suggest that for all reflections, the total activated pole populations can be considered as an approximately conserved quantity over the range of the deviation angle. In particular, for the 111 reflection, the triplets (111-3) start to appear right after the doublets (111-2) hit their maximum and then start to decay. It is also no surprise that the triplet appearance is observed at positive deviation angles for the 111 reflection. Likewise, for the 200 reflection and in the angular range where the singlet poles (200-1) keep constant (up to $\Delta\theta \approx 0.2\beta_{200}$), the trends followed by the doublet and triplet distributions seem to be exactly opposite to each other. Similarly, in 220 reflection, doublets and singlets show antagonistic trends. Due to the existence of quadruplets, the individual trends of n-let populations in the 311 reflection seem to be more complex than the lower multiplicity reflections.

Based on this analysis we conclude that the correlated, activated (n-let) pole populations are definitely not distributed uniformly over the angular width of the reflection band. However, the total pole populations are distributed almost uniformly for all reflections. The negative slope that exists in these distributions is a result of the decreasing radius of the reflection band over the angular width.

4.4 Computation of the Diffracted Intensities from Polycrystalline Ensembles

At this point, we know the distribution of all activated pole populations, as well as sub-populations of correlated poles over the angular width of the reflection band. With this information, it is possible to obtain the corresponding intensity profiles from any given

powder ensemble using Patterson functions. In this section, this procedure will be described and the intensity profiles obtained will be investigated in detail.

In Chapter 2, Patterson function was introduced as the analytical expression of the rocking curve scan of a single crystalline particle with a regular shape. In this context, the rocking curve of a particle can be interpreted as the intensity response of the particle to a monochromatic, plane wave irradiation as a function of the particle's relative orientation with respect to $\vec{k}_i$. Similarly, Patterson function can also be thought of as the collective intensity response from an ensemble of identical particles, where each particle has a fixed orientation (that is slightly different and independent from the remaining particles) with respect to the incoming beam. Accordingly, each point on the angular axis in the vicinity of the Bragg angle is prescribed a definite diffracted intensity value. Therefore, by using the Patterson formula, the intensity response from a monodispersed polycrystalline particle ensemble irradiated by a monochromatic, plane X-ray beam can be decomposed into two components: 1) a deterministic 'response function', that is the Patterson function which assigns a finite diffraction intensity to a diffracting particle, compatible with its orientation deviation from the exact Bragg condition, 2) an angular distribution function of all diffracting particles from the ensemble.

The above description of the intensity response from an ideal powder ensemble relies on the assumption that each diffracting particle has a single diffracted spot captured by the detector. However, as illustrated in the previous sections, the population of diffracted Laue spots from nanocrystalline particle ensembles diverges from that of diffracting particles and cannot be obtained from the information of the latter. As a result, the collective response of all diffracted spots must be obtained from the activated poles rather than the diffracting particles. Using the activated pole distribution information we obtain from numerical modeling, we can write the following expression for the total diffracted intensity:

$$I_{tot}(\Delta 2\theta_j) = \sum_{i=1}^{N_{P^*j}} I_{j,i} = N_c^2 |F_{hkl}(\Delta 2\theta_j)|^2 \sum_{i=1}^{N_{P^*j}} \left[3 \frac{-\xi_{j,i} \cos \xi_{j,i} + \sin \xi_{j,i}}{\xi_{j,i}^3} \right]^2 \quad (4.11)$$

Here, N_{P^*j} specifies the number of diffracted spots that are $\Delta 2\theta_j$ away from the exact Bragg angle, N_c is the total number of unit cells within the particle and F_{hkl} is the structure factor for the unit cell. The term inside the square brackets is the Fourier transform of

the spherical shape function. As seen, Eq.4.11 is simply a multiplication of an angular diffracted spot distribution (the statistical component) with an intensity response function (the deterministic component).

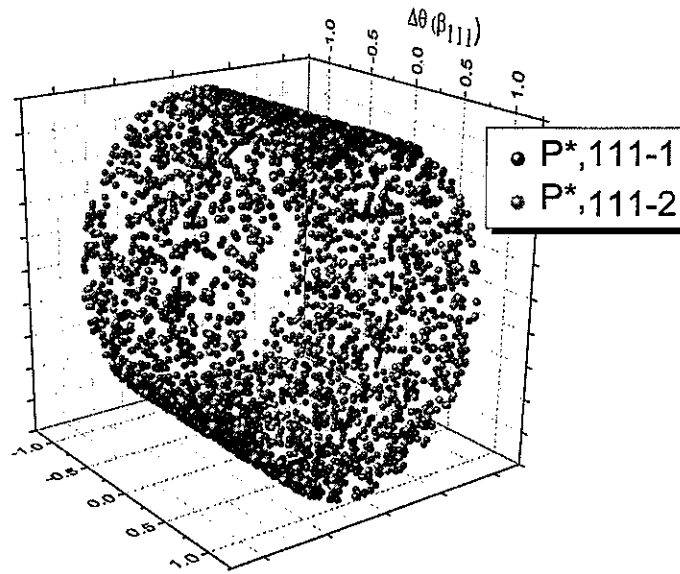


Figure 4.8: 3D distribution of the activated 111 singlets and doublets on the reflection band area. The sample considered for this simulation consists of 10^4 spherical nanoparticles with 2.86 nm diameter. The black dashed lines show the position of the reflection circle. The X-ray wavelength is 1 Å.

For an ideal powder sample of 10^4 gold particles with 2.86 nm diameter, irradiated by 1 Å X-rays, a typical distribution of the activated poles on the reflection band area is shown in Figure 4.8 for the 111 reflection band with thickness $2\beta_{111}$ ($s=4$). Here, the central circle that passes through $\Delta\theta = 0$ is the reflection circle, corresponding to the positions of the activated poles that satisfy the exact Bragg condition. A first look at this distribution intimates that neither the singlets shown in red, $N_{P^*,111-1}$, nor the doublets shown in green, $N_{P^*,111-2}$, seem to be concentrated on certain regions. Such a situation, if present, might alter the diffraction profile significantly, if the bias is along the $\Delta\theta$ axis of the conic area. Since the intensities assigned to the activated poles only depend on the deviation angle measured along the width of the reflection band and not the angular positions of the poles on

the circumference of the band, the 3D distribution of the activated poles can be compressed to a 2D plot and projected to the detector area without modifying the intensities. The 2D diffracted spot distribution corresponding to the 3D pole distribution presented above is shown in Figure 4.9:

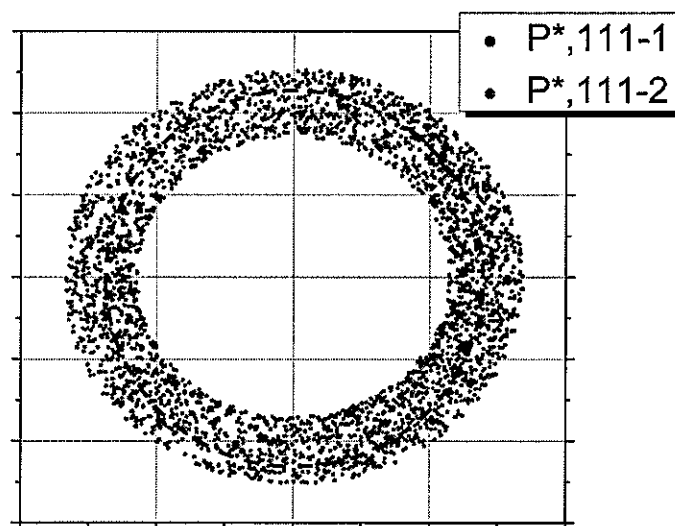


Figure 4.9: 2D distribution of the diffracted 111 spots on the detector area. The circle shown in black dashed lines is the Debye ring indicating the positions of all diffracted spots that satisfy the exact Bragg condition.

In Figure 4.9, the 111 Debye ring, which was obtained by compressing and projecting the 3D activated pole distribution shown in Figure 4.8, is seen where the thickness of the ring indicates the breadth of the respective intensity profile. The center point of this plot shows the position of the zeroth order peak at $2\theta_B = 0^\circ$ and the radial distance from the center to the diffracted spots indicates the diffraction angle, 2θ . Assuming transmission geometry, the diffraction angle of each diffracted spot can be computed by the following equation:

$$\frac{r_s}{L} = \tan 2\theta$$

where r_s is the radial distance of a diffracted spot from the center of the detector and L is the distance from the irradiated powder sample to the detector center. When the

angular distribution of these diffracted spots is inserted into Eq. 4.11, the corresponding intensities can be obtained for each diffracted spot. An azimuthal integration, following the intensity calculations over this Debye ring, then, yields the rocking curve scan or the diffracted intensity profile of the powder ensemble with respect to the angular deviation from the Bragg angle. This procedure is equivalent to evaluating Equation 4.11, and the resulting intensity profiles of two sub-populations of spots from the random powder ensemble considered above are plotted in Figure 4.10.

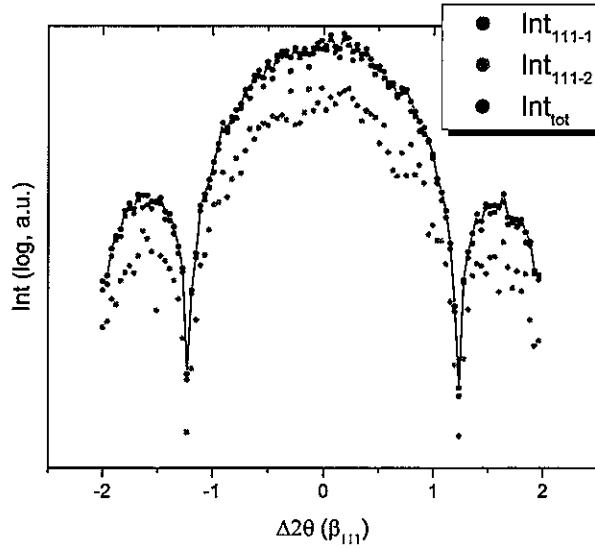


Figure 4.10: The diffracted intensity distribution (in logarithmic scale) at the 111 reflection from the powder sample with 10^4 spherical particles ($\lambda = 1 \text{ \AA}$). The particle diameter is 2.86 nm. and the diffraction angle is given in terms of multiples of the Scherrer broadening, β_{111} . Int_{111-1} and Int_{111-2} are the diffracted intensities contributed by singlet and doublet type poles, respectively and $Int_{tot} = Int_{111-1} + Int_{111-2}$.

4.4.1 Setting the Appropriate Angular Bounds of a Diffraction Peak

The counting algorithm we developed for obtaining the activated pole and diffracting grain distributions requires the boundaries of a given intensity profile as input. In most ex-

perimental cases, the angular range of an individual intensity peak within the diffraction spectrum cannot be set arbitrarily, but instead it is imposed by external factors. Some of these factors are the intensity of background scattering and the resolution of the instruments, as well as the quality of the irradiated sample, etc. As an advantage of computer simulations, our algorithm generates intensity data that are free of any of these complicating factors and therefore, the limits of an isolated intensity peak at any reflection can be assigned as desired. However, these limits must also account for the particle size dependent broadening of the intensity peaks and they must be related to the population of the particles participating in diffraction.

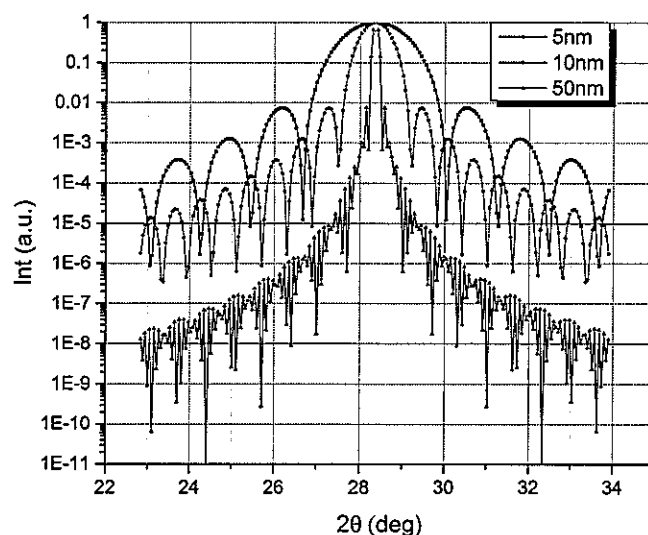


Figure 4.11: Rocking curve scans of three isolated, gold crystalline particles with 5, 10 and 50 nm diameter at the 200 reflection. The wavelength of the X-ray beam used in this calculation is 1 Å.

In Figure 4.11 the rocking curve scans of three spherical, crystalline gold nanoparticles with varying diameters of 5 nm, 10 nm and 50 nm are shown. The intensity data are computed at an irradiation wavelength of 1 Å and all profiles belong to the 200 reflection. From the figure we observe that as the particle size increases, the intensity profile becomes

sharper; in other words, the peak breadth becomes narrower, consistent with the predictions of the Scherrer equation. For this case, setting the limits of all three peak profiles at identical diffraction angles (2θ) will correspond to larger information volume from the irradiated particle populations of the sharper peak than those of the broader peak. This means that a fixed angular deviation from the Bragg angle on the intensity spectrum would map to particles that diffract much lower intensities in the larger particle ensemble, than the ensemble with smaller particles. This is because in the latter case a similar amount of decay in the diffracted intensity relative to the peak value takes much larger angular deviation. In order to avoid the information volume bias due to varying particle size, we use an integral multiple of the Scherrer broadening term to set the limits of the simulated intensity profiles.

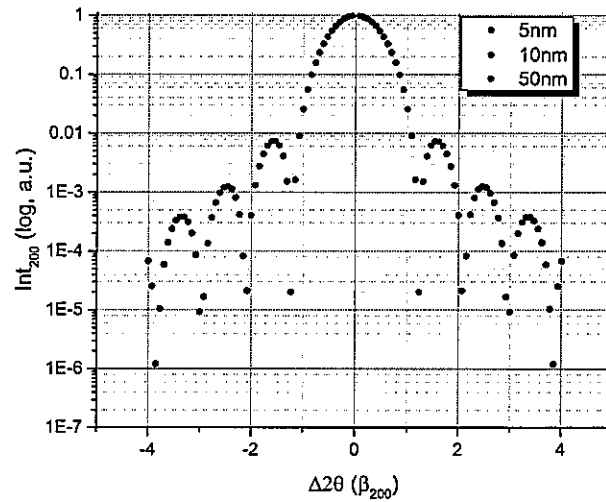


Figure 4.12: Rocking curve scans of three spherical, crystalline gold particles with 5, 10 and 50 nm. diameter around the 200 reflection. (The data sets corresponding to each particle size overlap perfectly well and therefore cannot be visually distinguished.)

As seen in Fig. 4.12, the new dependent variable $s\beta_{200}$ takes care of the information volume bias due to the peak broadening related to the particle size and aligns the positions of all fringe maxima and minima in the angular space for the three profiles. As a next step, a meaningful value must be set for the parameter 's'. Ideally, 's' should be large enough so that it captures only those Laue spots within $\pm s\beta$ of the Bragg angle with finite

intensity contribution. To find this value, we analyzed the change in integrated intensity with respect to increasing angular extent of a given intensity profile. The results of this analysis are presented in Figure 4.13:

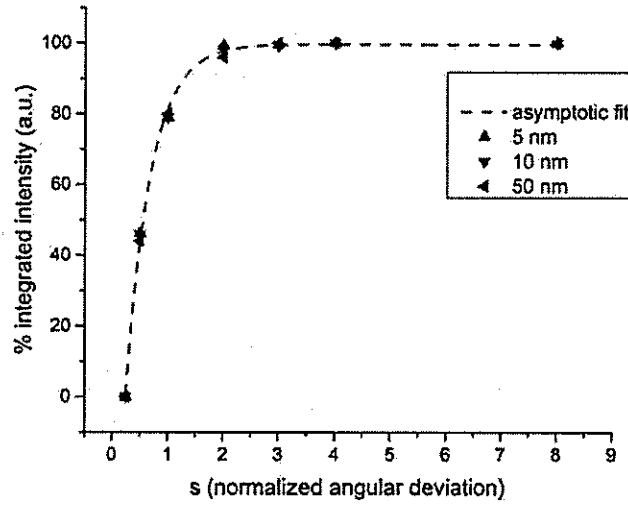


Figure 4.13: Normalized integrated intensity with respect to the extent of the intensity profile in integer multiples of the peak breadth (β).

To obtain the data presented in Figure 4.13, the integrated intensities $\bar{I}$ were computed by evaluating $\bar{I}(s\beta) = \int_{-s\beta/2}^{s\beta/2} I(\Delta 2\theta) d(\Delta 2\theta)$ over the interval of $0 < s \leq 8$. According to Figure 4.13, almost all integrated intensity is contributed by the Laue spots that are located within $\pm 2\beta$ ($s=4$) of the Bragg angle of the peak and there is almost negligible addition from the Laue spots that are farther away. Thus, we conclude that reflection bands of width 2β (which correspond to intensity profiles of width 4β) are wide enough to capture practically all activated poles for any wavelength and crystallite diameter. In other words, setting s equal to 4 and varying only particle size D should be sufficient to compare sampling and intensity statistics for each wavelength. From this point on, all intensity profiles and their corresponding reflection bands will be considered within this range.

4.5 Geometric Correction for the Activated Pole Distributions and the Resulting Intensity profiles

In Fig 4.14 the distribution of the total activated pole populations at the 200 reflection and the corresponding intensity profiles are presented for an ideal powder sample consisting of 10^4 gold particles with 2.86 nm diameter, irradiated with three different wavelengths. On the left, the data points refer to the average activated pole populations at each deviation angle from the position of the reflection circle, whereas the error bars refer to the standard deviations from the mean value for a set of 10 simulation runs. Along with the simulation results are the line fits drawn to visualize the trends followed by the pole population distributions with respect to the deviation angle given in terms of $s\beta_{200}$. Note the advantage of normalizing the deviation angles by multiples of the peak broadening: it makes comparisons between simulation results obtained with different experimental parameter sets fair and easy. Finally, the intensity profiles on the right were computed by Eq. 4.11 with only the mean activated pole populations. The error bars on the vertical axes are not shown for clarity.

Since random orientation distributions of the constituent crystallites were generated for simulations with ideal powder ensembles, we expect statistically equal numbers of activated poles at each deviation angle, resulting in straight lines with zero slopes for all cases. Looking at the left side of Figure 4.14, we observe for all three wavelengths that the distributions of the total number of activated poles obtained from the simulation program indeed follow a linear trend over an interval of $2\beta_{200}$ on the reflection bandwidth. However, these distributions have finite slopes, the magnitudes of which increase with increasing irradiation wavelength: The slopes obtained from the least-squared-error lines fitted to these distributions are -0.96 (0.29), -1.36 (0.36) and -5.47 (0.50) for 1, 1.54, and 2.29 Å wavelengths, respectively (The values in parentheses are fitting errors reported by OriginLab). This indicates that fewer poles were activated at the positive deviation angles ($\Delta\theta > 0$) from the Bragg peak position.

These uneven population distributions of activated poles within the reflection band widths result in peak position shifts towards the direction of higher pole counts in the

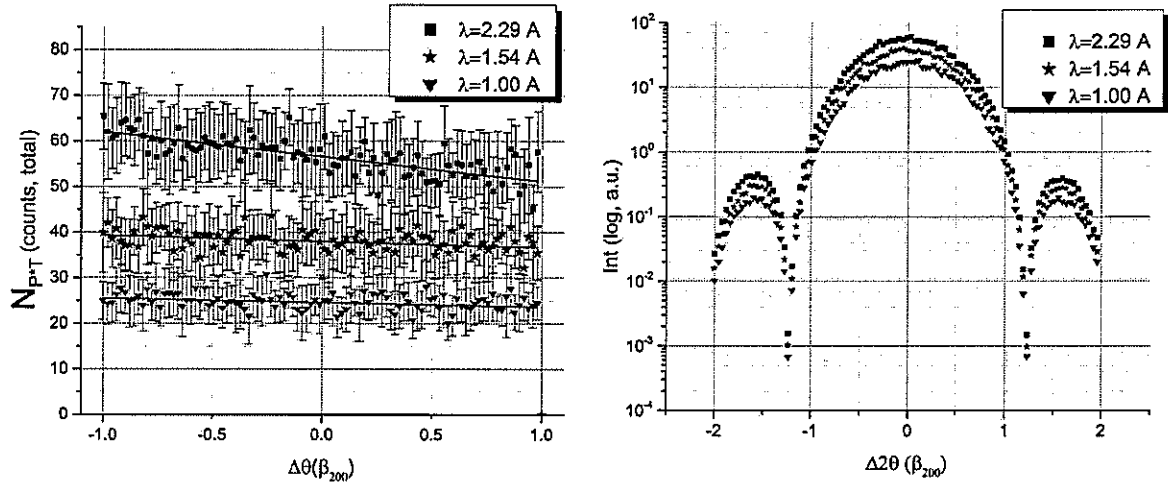


Figure 4.14: Left: The angular distribution of the total activated pole populations over 200 reflection band width from an ensemble of 10^4 spherical gold nanoparticles with 2.86 nm diameter and irradiated by three different wavelengths. Right: The corresponding intensity profiles (in logarithmic scale) computed by the average pole distributions.

corresponding intensity profiles. This can be seen from the intensity profiles presented in Figure 4.14 on the right. Fitting Gaussian functions to these intensity profiles, the peak characteristics can be quantitatively obtained. These are presented in Table 4.1. Here the values in the first two columns were computed from the Bragg's law and Scherrer equation for the listed wavelengths and assuming a lattice parameter of $4.08 \text{ \AA}$, whereas the fourth and the fifth columns report values obtained from the Gaussian function fits to the simulated profiles. The last column of the table reports the apparent microstrains computed by taking the ratio of the variation in the interplanar spacing values resulting from the peak shifts to the theoretical values of the interplanar spacing:

$$\frac{\Delta d}{d}(\mu\epsilon) = \frac{\frac{\lambda}{2 \sin \theta_{B,fit}} - \frac{\lambda}{2 \sin \theta_{B,theo}}}{\frac{\lambda}{2 \sin \theta_{B,theo}}} \times 10^6 \quad (4.12)$$

It is obvious from Table 4.1 that as the wavelength increases, the apparent microstrain due to the peak shift from the theoretical value of the Bragg angle increases. Comparing the peak breadths obtained from the Gaussian function fits, on the other hand, we see

Wavelength Å	θ_B (theory, deg)	β (theory, 2θ , deg)	θ_B (fit, deg)	β (fit, 2θ , deg)	$\frac{\Delta d}{d}$ (fit, $\mu\epsilon$)
1	14.19	2.42	14.19 (0.01)	2.50 (0.06)	207
1.54	22.18	3.90	22.17 (0.01)	3.90 (0.06)	214
2.29	34.14	6.50	34.10 (0.02)	6.48 (0.09)	1082

Table 4.1: Theoretical and fitting based peak parameters and the apparent strains due to peak shift error for the 200 intensity profiles shown in Figure 4.14. The values in parentheses are fitting errors reported from the peak-fitting algorithm included in the Origin software (OriginLab, Northampton, MA.).

no appreciable difference between the theoretical values and those extracted from the fits. The trend observed in the peak shifts with changing wavelength for a fixed particle size and reflection suggests that the amount of shift must increase with larger Bragg angles. This hypothesis is confirmed by additional sets of simulations where the activated pole distributions from four different reflection bands were computed for a fixed particle size of 2.86 nm irradiated by 2.29 Å wavelength X-rays. These distributions are presented in Figure 4.15. For this case, the line fits yield -5.08 (± 0.46), 5.47 (± 0.50), -23.21 (± 0.55) and 149.11 (± 0.88) for the slopes of the pole distributions for the 111, 200, 220 and 311 reflection bands, respectively.

These observations suggest that without proper correction to compensate for the finite slope in the activated pole distributions, the resulting intensity peaks suffer from spurious peak shifts that might lead to erroneous conclusions about microstrain in the irradiated sample. A proper correction procedure will be described in the next section.

4.5.1 Correcting the Uneven Pole Distributions

Correction factors, which are implemented on measured intensity profiles for fair comparison between the diffracted energy at different reflections, have been a topic of intense discussion in the past literature. Currently, there are many different forms of the 'Lorentz factor' suggested, depending on the experimental setup and the type of the diffracting sample. A

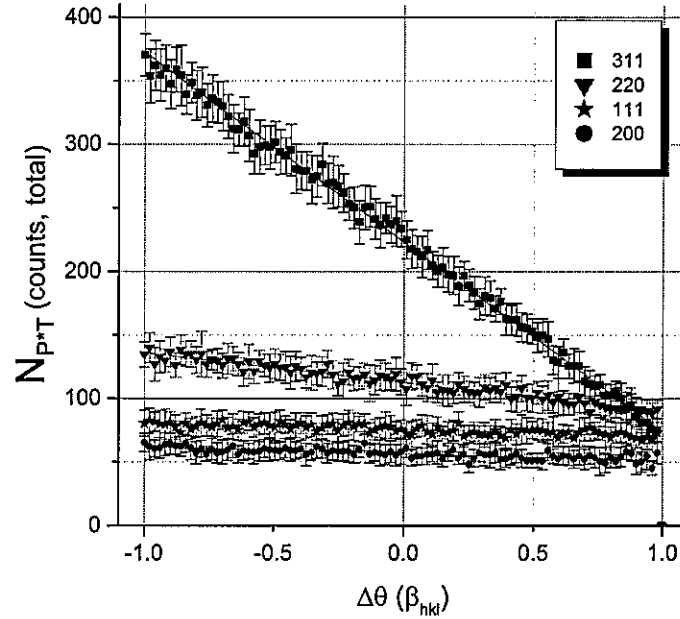


Figure 4.15: Distributions of activated pole populations (for 10 trials) for the first four reflections of gold nanoparticle ensemble consisting of 10^4 particles. λ equals 2.29 Å and the particle diameter is 2.86 nm. ($s=4$)

few prominent examples related to this discussion were included in [11],[16],[52] and [67]. Based on these references, the most common forms of the Lorentz factor for the line profile (or intensity distributions) and the integrated intensity are given as below:

$$L_{LP}(\theta) = \frac{1 + \cos^2 2\theta}{\sin^2 \theta} \quad (4.13a)$$

$$L_{int}(\theta) = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \quad (4.13b)$$

Today most experimentally obtained diffraction data are post-processed automatically by these correction factors without putting in much thought about what is being corrected and why. For our case, none of these factors given in Eq. 4.13 are directly applicable, since we do not intend to correct for the deterministic component of the diffracted intensities (Patterson functions) but only the statistical part contributed by the activated pole dis-

tributions. In order to derive a correction factor for our purposes, we need to revisit the diffraction geometry, which is shown in a simplified version in Figure 4.16:

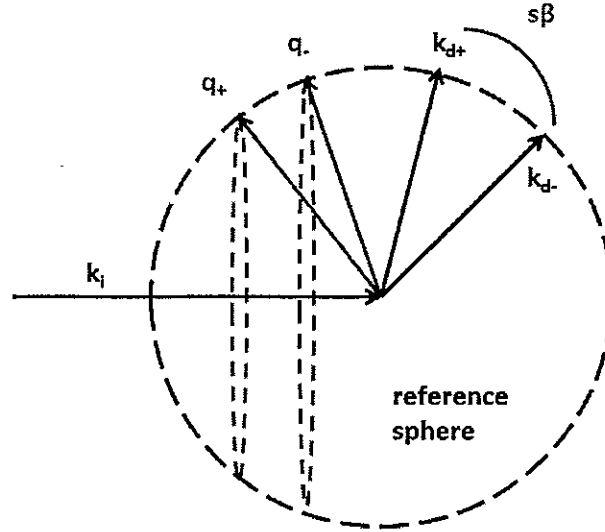


Figure 4.16: As the diffracted beam rotates from $\vec{k}_{d-}$ to $\vec{k}_{d+}$, the momentum transfer vector rotates in the same direction as well from $\vec{q}_-$ to $\vec{q}_+$. As a result, the radius of the reflection band becomes shorter.

Historically, Lorentz was the first person to suggest that the diffraction geometry itself imposed a selection bias among the irradiated particles, and that even ideal powder ensembles were not being sampled with equal probability by the allowed reflections of the crystallite (This information was found in the compilation by Bijvoet [7] and it was attributed to a discussion by P. Debye and P. Scherrer). The variation of the $\cos \theta$ term was given as the source of the sampling bias [16; 7]. Figure 4.16 illustrates this concept: As the momentum transfer vector is rotated from the $\vec{q}_-$ position to $\vec{q}_+$ position, as a result of the rocking curve scan by the detector movement from $\vec{k}_{d-}$ to $\vec{k}_{d+}$, the radii of the corresponding reflection circles drawn at each position of $\vec{q}$ decrease, as seen in the transition from the red circle to the blue one. Therefore, on a given activated pole distribution plot, each population count is negatively biased by the deviation angle it corresponds to. This bias can be easily corrected by scaling the pole counts with the inverse of the radius of the respective reflection circle at the corresponding deviation angle. From Figure 4.16, we find

that this radius equals $\sin \Gamma$, where Γ is the complementary angle to the angle between $\vec{k}_i$ and $\vec{q}$, or equivalently by $\cos \left(\theta_B + \frac{\Delta 2\theta}{2} \right)$.

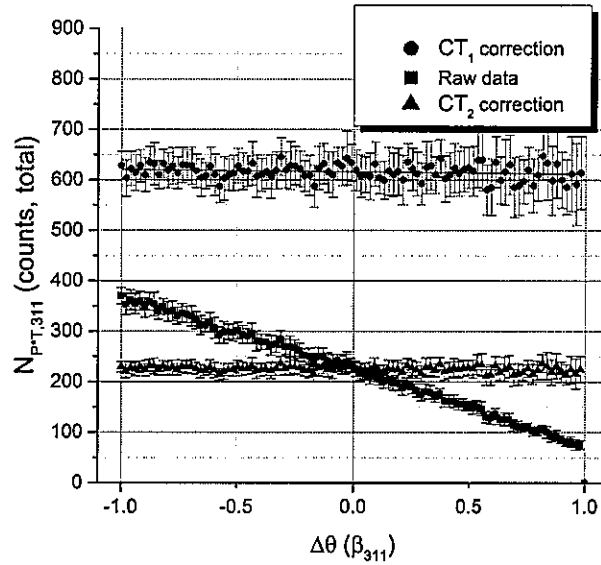


Figure 4.17: Two types of correction factors implemented on the as-simulated 311 pole distribution plot (shown in black) to fix the sampling bias.

Figure 4.17 shows the original (raw data) and corrected pole distributions (CT_1 correction) belonging to the 311 reflection from the powder sample considered previously in Figure 4.15. The corrected counts were obtained by multiplying the initial counts by $\frac{1}{\sin \Gamma} = \frac{1}{\cos(90 - \theta_{311} + \Delta\theta)}$ and $CT_1 = \frac{1}{\sin(\theta_{311} + \Delta\theta)}$. Initially, the slope of the line fitted to the raw data was -149.11. After applying the CT_1 correction, this slope reduces to -4.43 (± 2.54), which is around 4% of the original slope and shows significant improvement. However there is a drawback: The total pole count corresponding to the CT_1 corrected data is artificially enhanced. The total number of 311 poles from the simulation was originally 22308 ± 162 whereas the total count from the CT_1 corrected data is 61002 ± 444 , which is almost three times the true value. To keep fidelity with the pole counts at the exact Bragg angle, we suggest a modified correction factor, that is $CT_2 = \frac{\cos \theta_B}{\cos(90 - \theta_B + \Delta\theta)}$. When CT_2 is implemented on the raw data, we obtain the dataset shown in blue in Figure 4.17. In this case the slope and the total pole count in the corrected distribution (CT_2) are calcu-

lated to be -1.62 ± 0.93 and 22251 ± 149 , respectively. The corrected distributions obtained by implementing the CT_2 correction factor on the as-simulated pole counts presented in Figure 4.15 are also shown in Figure 4.18.

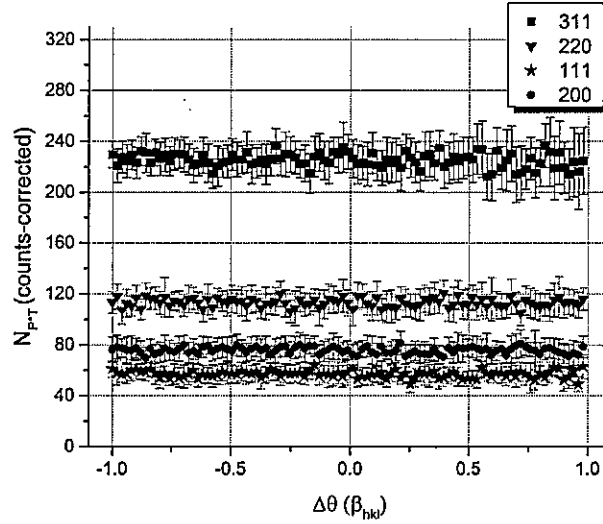


Figure 4.18: The CT_2 corrected pole counts corresponding to the raw simulation data presented in Figure 4.15

In conclusion, the large acceptance angles of nanocrystalline particles result in non-negligible sampling bias on the pole population distributions across the reflection band widths. This bias causes significant peak shifts in the corresponding intensity profiles which, when analyzed by single peak fitting algorithms, yield spurious strains in the irradiated particles. To correct for the bias, we find CT_2 to be a preferable scaling factor that zeroes out the slope in the pole distributions without distorting the true pole population counts. We note that this correction term is not directly applicable in a full-profile fitting algorithm such as Rietveld analysis, since it is strictly derived for the activated pole distributions in the sampling space.

4.6 Comparison of Sampling and Intensity Statistics

Here a comparison will be presented between the statistical characteristics of the sampling and intensity parameters from an irradiated, ideal powder ensemble. To do this, first the statistics formulations given in the original reference [3] will be reviewed.

In the original reference [3], a geometrical analysis was presented to derive a formula to estimate the probability of diffraction, and relevant statistical quantities were obtained from this probability formula based on the Laplace probability theory [3]. In previous discussions, we suggested a modification to the original probability term by defining the crystallite acceptance angle in terms of an integer multiple of the Scherrer broadening term and obtained a modified probability formula for nanocrystalline powder ensembles based on AKK analysis, $p_{G,AKK} = \frac{m_{hkl} s C \lambda}{4D}$. From this, the statistical quantities can be calculated as:

$$\bar{N}_{G^*,AKK} = p_{G^*,AKK} N_G \quad (4.14a)$$

$$u_{N_{G^*,AKK}} = \sqrt{p_{G^*,AKK}(1 - p_{G^*,AKK})} \quad (4.14b)$$

$$\tilde{u}_{N_{G^*,AKK}} = \sqrt{\frac{1 - p_{G^*,AKK}}{N_G p_{G^*,AKK}}} \quad (4.14c)$$

Alternatively, the statistical characteristics of the activated pole and diffracting grain populations obtained from the simulations can be computed directly by the following expressions:

$$\bar{x} = \frac{1}{T} \sum_{i=1}^T x_i \quad (4.15a)$$

$$u_x = \sqrt{\frac{1}{T-1} \sum_{i=1}^T (x_i - \bar{x})^2} \quad (4.15b)$$

$$\tilde{u}_x = \frac{u_x}{\bar{x}} \quad (4.15c)$$

In Equations 4.15, x_i refers to the variable of interest, which, in our case, can be either the sampling parameters, e.g. the population of diffracting particles and activated poles, or intensity parameters, e.g. peak and integrated intensities, for simulation number 'i'. u_x refers to the standard deviation of the quantity x from its mean value, $\bar{x}$, assuming x_i is

normally distributed; and finally $\tilde{u}_x$ is the relative uncertainty within the data where T specifies the number of times a given quantity is simulated.

A direct comparison can be made between the mean values and their standard deviations predicted by the classical statistics formulations (Eq. 4.15) applied on simulated data and by the AKK approach (Eq. 4.14) for particles, poles and intensities. Table 4.2 presents the results of such a comparative analysis for intensity and sampling parameters from a powder sample consisting of 2.86 nm diameter nanocrystallites with varying populations. For this analysis, the X-ray beam wavelength was assumed to be 2.29 Å, and 200 and 311 reflections, which had the lowest and the highest multiplicities among the first four reflections of gold, were considered. For each parameter set (N_G, hkl), activated pole distributions and diffracting grain counts were collected for 10 trials and the corresponding intensity profiles were generated based on Eq. 4.11. The intensity data were then post-processed by fitting ideal Gaussian peak functions, and then the maximum intensities (I_{max}) were extracted from the best fitting model. For the integrated intensities, I_{int} , the raw intensity data were numerically integrated.

N_G	I_{max}	I_{int}	N_{G^*}	N_{P^*}	$N_{G^*,AKK}$
10^4 (200)	57.93 ± 1.2	58.27 ± 0.8	4793 ± 60	5589 ± 65	5629 ± 50
5×10^4 (200)	287.22 ± 2.9	289.53 ± 2.4	23761 ± 120	28038 ± 129	28144 ± 111
10^5 (200)	577 ± 7	579 ± 5	47595 ± 113	56175 ± 222	56290 ± 157
10^4 (311)	234 ± 2	231 ± 2.6	9864 ± 7	22273 ± 113	N/A
5×10^4 (311)	1158 ± 6	1155 ± 5	49331 ± 25	111370 ± 170	N/A
10^5 (311)	2325 ± 11	2316 ± 6	98677 ± 25	222770 ± 297	N/A

Table 4.2: Sampling and intensity statistics of ideal gold particle ensembles with 2.86 nm diameter around 200 and 311 reflections. The irradiation wavelength is 2.29 Å and the errors in parentheses show the standard deviation from the mean values for 10 independent trials.

Table 4.2 suggests that for both 200 and 311 reflections, a particular amount of increase in the number of irradiated particles, N_G , leads to almost the same amount of increase in the

mean or expected values of all sampling (N_{G^*}, N_{P^*}) and intensity parameters (I_{max}, I_{int}) when the remaining experimental parameters are kept constant. This means that the mean values of both the sampling and intensity parameters are linearly correlated with the ensemble size or the total number of irradiated particles. In addition, for both reflections the integrated and maximum intensities are very close, intimating that almost all of the integrated intensity is contributed by the diffracted spots that are closest to the Bragg angle. This necessitates the statistics of I_{max} and I_{int} to be similar, which is confirmed by the data in the table. When we compare the pole statistics with the grain statistics, on the other hand, we see that the number of diffracting grains falls short of the number of activated poles, as the one grain-one pole assumption does not hold in this size regime, and, on average, one grain contributes more than one activated pole to the reflection band. Looking at the last column of the table where the predictions of the modified AKK approach for the mean number of diffracting grains and its uncertainties are given, we see that these numbers agree well with the statistics of the pole counts rather than the grain populations. More importantly, since the probability of diffraction at the 311 reflection is larger than 100% ($p_{G,AKK} = 2.25$), Eq. 4.14c yields complex values which are unphysical for the relative uncertainties. Hence for the 311 reflection, the uncertainties were not estimated by the AKK approach.

In addition, a comparison between the data for the 200 and 311 reflections suggests that maximum and integrated intensities, as well as the pole counts scale linearly with the multiplicities. For all ensemble sizes, $\frac{I_{max,311}}{I_{max,200}}, \frac{I_{int,311}}{I_{int,200}}$ and $\frac{N_{P^*,311}}{N_{P^*,200}}$ are equal to $\frac{m_{311}}{m_{200}} = 4$ within statistical error. This ratio, however, is approximately 2.1 for the grain populations and correlates with none of the quantities considered in this table. The grain ratios are expected to catch up with the pole and intensity ratios only within the regime where the 1 grain 1 pole assumption holds.

As a second example, we focus on a single reflection while changing the irradiation wavelength and study how the intensity and sampling parameters vary as a function of the wavelength for a fixed ensemble population. Repeating the same analysis as in Table 4.2 for the 200 reflection of gold with a powder sample that contains 10^4 particles with 2.86 nm diameter, we obtain Table 4.3 where the mean values and the standard deviations

are reported for the same sampling and intensity parameters. Note that this system was studied previously, and the pole distribution plots and corresponding intensity profiles were presented in Figure 4.14.

$\lambda(\text{\AA})$	$I_{\max}$	I_{int}	N_{G^*}	N_{P^*}
1	25.21(± 1.56)	25.87(± 0.75)	2321(± 41)	2457(± 42)
1.54	38.60(± 1.48)	39.50(± 1.01)	3425(± 34)	3787(± 38)
2.29	57.93(± 1.2)	58.27(± 0.82)	4739(± 60)	5589(± 65)

Table 4.3: The mean values and standard deviations of activated pole and diffracting grain populations as well as the peak and integrated intensities corresponding to these pole populations for the system considered in Figure 4.14. The powder sample contains 10^4 grains with 2.86 nm diameter and 10 sets of data were collected for each parameter set.

Table 4.3 suggests that an increase in the X-ray wavelengths leads to an increase in the mean values of both the intensity parameters and the pole and grain populations that take part in diffraction. This is a result of the increasing acceptance angle of the individual crystallites as λ gets larger. However, the relative increases in the mean grain populations once again lag behind the relative increases in the mean peak and integrated intensities, as well as the activated pole counts.

Now that the trends followed by the mean number of activated poles and diffracting grains, as well as the corresponding intensities are established, we can address whether the core statement in the original reference [3] holds for nanocrystalline powder samples. In other words, are the relative uncertainties in the diffracting grain populations equal to the relative uncertainties in the corresponding intensities? To answer this question, we calculated the relative uncertainties for pole and grain populations and corresponding intensities for the system considered previously and reported in Table 4.2. These are presented in a separate Table 4.4:

Table 4.4 shows that the relative uncertainties of the intensity parameters ($\tilde{u}_{I_{\max}}$ and $\tilde{u}_{I_{\text{int}}}$) are not equal to the relative uncertainties of either the activated pole populations or the diffracting grain populations. The uncertainties predicted by the AKK approach, for the

N_G	$\bar{u}_{I_{\max}}$	$\bar{u}_{I_{\text{int}}}$	$\bar{u}_{N_{G^*}}$	$\bar{u}_{N_{P^*}}$	$p_{G,AKK}$	$\bar{u}_{AKK}$
10^4 (200)	0.0207	0.0137	0.0125	0.0116	0.5629	0.0088
5×10^4 (200)	0.0102	0.0083	0.0051	0.0046	0.5629	0.0039
10^5 (200)	0.0121	0.0086	0.0024	0.0040	0.5629	0.0028
10^4 (311)	0.0085	0.0113	0.0007	0.0051	2.25	N/A
5×10^4 (311)	0.0052	0.0043	0.0005	0.0015	2.25	N/A
10^5 (311)	0.0047	0.0026	0.0003	0.0013	2.25	N/A

Table 4.4: The relative uncertainties in the activated pole and diffracting grain populations as well as the peak and integrated intensities corresponding to the data presented in Table 4.2. The powder sample contains 10^4 grains with 2.86 nm diameter and $\lambda = 2.29 \text{ \AA}$.

200 reflection, are also different from the uncertainties in the intensities and in the sampling parameters. Since in this particle size regime the diffraction probability for the grains cannot be calculated accurately by Eq. 3.6, we do expect to see divergence between the uncertainties calculated based on this equation and those calculated from the direct modeling algorithm. Another reason that explains the presence of deviation in the uncertainties predicted by the two methods (Eq. 4.15 and 4.14) would be the small number of simulation runs ($T=10$) used to generate the statistics for the direct modeling approach¹. Consequently, we prove that the AKK formulation is incapable of estimating or even bounding the limits of uncertainties in either the grain populations or the diffracted intensities.

At this point, the current formulation does not enable us to infer whether the differences between the uncertainties predicted by the two methods for grains, poles and intensities are systematic or just due to statistical fluctuations. A more detailed analysis of the mathematical statements is required to draw conclusions on this topic and this analysis will be presented in the next chapter.

¹In a real experimental setting, it is not standard practice to collect the same data set more than once, so 10 is actually an optimistic number for the independent data sets that one can obtain.

4.7 Summary and Conclusions

The analysis presented in this chapter leads to the following conclusions:

1. The activated poles within the reflection band area can be divided into two subgroups. The independent poles or singlets have no other member of the $\langle hkl \rangle$ family within the band. n-lets, on the other hand, have n perfectly correlated members, all belonging to a particular crystallite. The largest n-let dimension, n_{max} can be half the multiplicity of the particular reflection. The individual fractions of grains which contribute n poles to the reflection band cannot be predicted from simple area fractions due to the dependencies of the probabilities and geometrical requirements dictated by the crystallography. For correlation orders greater than two, crystallographic orientation relationships can limit the formation of n-lets to specific wavelengths, which we term enhanced-selection wavelengths, λ_{E-S} .
2. Unlike the individual sub-populations of correlated poles, the total activated pole populations can be estimated by using the modified AKK formulation (3.10) with approximately 1% accuracy. The deviation between the pole counts obtained by simulation and by Eq. 3.10 increases with multiplicity of the reflection and with increasing (s/D). The reason behind this deviation is the diminishing applicability of the uniform pole distribution approximation over the area of the reference sphere.
3. The relative populations of total activated poles at different reflections are proportional to the relative multiplicities of these reflections. However, the relative populations of the diffracting particles deviate largely from the multiplicity ratios. This is a result of the pole enhancement effect due to large acceptance angles of nanocrystallites.
4. Analysis of the angular distribution of the activated poles over the reflection bandwidth shows that their population decreases with increasing θ . This sampling bias was first predicted by Lorentz [7] and was attributed to the variation of the $\cos\theta$ term over the width of the reflection band. This bias causes the Bragg peak positions obtained from analyzing the corresponding intensity profiles of the pole population

distributions to shift to lower diffraction angles, and appears as spurious strains in the intensity profiles. The sampling bias can be eliminated by multiplying the activated pole counts within the reflection band by the factor, $CT_2 = \cos \theta_B / \cos \theta$. This term removes the sampling bias while maintaining fidelity to the total population of the activated poles over the reflection band area.

5. A simple numerical computation shows that, for an ideal powder ensemble consisting of identical, spherical crystallites, almost all of the activated poles which contribute finite intensity to the diffraction peak appear within the area of a reflection band of width 2β .
6. The classical Lorentz formulation for computing the expected fraction of grains in the Bragg condition within a randomly oriented aggregate of crystallites is valid only for the large particle size regime where each grain is expected to contribute only a single activated pole to the reflection band. The failure of this condition also invalidates the intensity statistics developed by Alexander, Klug and Kummer [3], which links the uncertainty in the integrated and maximum intensities to the statistical variations in the number of properly oriented particles for diffraction. The relative standard deviations in intensity values obtained from simulations with such samples, where the particle sizes are small, are consistently much higher than the relative standard deviations in the number of diffracting grains and activated poles. This finding precludes using the AKK formulation in the nanocrystalline particle regime for estimating the number of particles required in the irradiated volume for obtaining a specified relative standard deviation in the measured intensities.

Chapter 5

Quantification of Intensity Uncertainty due to Particle Sampling Statistics in Ideal Powder Ensembles

5.1 Introduction

In the previous chapter, we showed through modeling that the mean values and the relative uncertainties in the diffracting grain and activated pole populations, as well as the resulting intensities were all different from each other. Information about the statistical behavior of one quantity among the three, i.e. activated poles, diffracting grains and diffracted intensities, did not provide any insight about the behavior of the remaining quantities. Moreover, area based probability expressions from classical formulations [3] were of no help when we attempted to estimate the number of diffracting grains within an ideal powder sample, even though the irradiated sample amount, individual particle size and shape were known with full accuracy. The main reason behind this was found to be the failure of one grain-one pole assumption: incomplete wave cancellation due to small coherent size in nanocrystals resulted in large acceptance angles for diffraction, leading to broad diffraction

peaks and correspondingly wide peak breadths. For such cases, a given crystallite could contribute more than one diffracted beam to a given Bragg peak. This one particle-multiple beam condition, as shown before, complicated the correlation between grain and intensity statistics. Furthermore, the widening of the reflection band, and the attendant broadening of the diffraction peak with decreasing particle size changed the type of statistical formulations that could be used to analyze the uncertainty in the number of diffracting grains. For these reasons, the direct link between the sampling and intensity statistics was lost.

In this chapter, we reformulate the statistics formulations regarding the convergence behavior of diffracted intensities to their expected values based on a priori information about the diffracted spot histograms over the rocking curve range of the intensity peak. Starting from classical definitions and building up from there will allow us to isolate and investigate the contributing sources to the intensity uncertainty and will also help to establish guidelines about how to compare and relate the uncertainties in different statistical quantities, i.e. grains, poles and intensities.

5.2 Discrete and Continuous Random Variables in Powder Diffraction Experiments

In statistics, 'a variable which may take any of the values of a specified set of values and which is associated with a probability distribution is called a **random variable**' [29]. In this context, there are two different categories of random variables: in the first category, the variables can take only a countable number of different values and are called discrete variables. The variables in the second category, however, can take any value within a specified interval of numbers and are called continuous random variables. Different statistical models are applicable to investigate the convergence behavior of these random variables [29].

When modeling powder diffraction experiments with perfectly random (ideal) and monodispersed particle ensembles, each particle is assigned a single orientation vector that defines its angular position with respect to the incoming X-ray wavevector $\vec{k}_i$. Since the orientation of one particle is independent of the orientation of the remaining particles, each particle has two options: it either satisfies the diffraction condition or not. Therefore, the mathematical

statement of whether a given particle satisfies the diffraction condition or not can take only two discrete values; 0 for no diffraction and 1 for diffraction. Similar arguments hold for whether a pole is classified as an activated pole or not. Based on these, the populations of activated poles and diffracting grains can be classified as discrete random variables in a powder diffraction experiment.

When it comes to computing the diffracted intensity from a given population of randomly oriented particles, a totally different picture appears. Assuming an ideal, perfect experimental setup, where there is no noise or background scattering contributing to the measured intensities, no imperfections within the particles (whose sizes are finite) and infinite detector resolution, the diffracted intensity from a single particle can take any value between 0 and the peak maximum. In this case, the intensity value is solely a function of the deviation of the particle orientation from the exact Bragg condition in angular space. An example of such a function is the Patterson formula [47], which was introduced previously, or Gaussian peak function, which is a standard first order description of an experimentally obtained diffracted intensity profile [57]. For this reason, the diffracted intensity from a randomly oriented particle can be classified as a continuous random variable.

Due to the differences between the statistical nature of the sampling parameters and the diffracted intensities, the convergence behaviors regarding pole-grain populations and resulting intensities may not be the same. In the next section, the statistical properties of pole and grain populations will be evaluated by direct modeling and simulation. The results obtained will, then, be compared with classical formulations for discrete random variables. Next, the crystallite size dependency of the statistical behaviors of sampling poles and grains will be investigated, focusing on the implications of the failure of the one grain-one pole assumption.

5.3 Discrete Probability Distributions: Pole and Grain Statistics

Activated poles and diffracting grains are two quantities that are classified as discrete random variables. To analyze the statistics of random variables in this category, Binomial

distribution is the most commonly used model: In this model, the random variables are allowed to take only two different values, and each trial has constant probability, which is independent of the remaining trials.

For 'bulk powders' where one grain-one pole assumption holds due to small acceptance angles of individual crystallites, the activated pole and diffracting grain populations are the same, hence they are expected to follow the same statistical behavior. For nanocrystalline powders, on the other hand, multiple activated poles and diffracted beams can be associated with the same grain. In this case, we expect the statistics of the two quantities to diverge from each other.

5.3.1 Binomial Distribution

Assume that we have a powder sample that contains N_G particles, each with a random orientation with respect to the wavevector of the incoming X-ray beam. If our ensemble is truly random, then the orientation vectors from all of the grains cover the surface of a reference sphere uniformly. This means that the areal grain density is constant and equal to $\rho_G = \frac{N_G}{4\pi}$, regardless of where the area patch is located on the sphere. If we focus on a particular hkl reflection band, the ratio of all grains whose orientation vectors form poles within the area of this band must be proportional to the band area, $N_{G^*} = \rho_G A_{band}$. Therefore, the probability that a randomly oriented grain has its pole within the reflection band area becomes $p = \frac{N_{G^*}}{N_G} = \frac{A_{band}}{4\pi}$. We call the grains whose poles are within the reflection band area as diffracting grains and those that are outside the band as non-diffracting grains. Therefore, the probability that a given particle does not satisfy the diffraction condition is $q = 1 - p$, since there is no other option for this particle. Using the definitions of the first and second order moments for discrete random variables [29], where $p(x = 1) = p$ and $p(x = 0) = q$, we obtain for a single particle:

$$\mu = \sum_{i=1}^2 x_i p(x_i) = 1 \times p + 0 \times q = p \quad (5.1a)$$

$$\sigma^2 = \sum_{i=1}^2 (x_i - \mu)^2 p(x_i) = (1 - p)^2 \times p + (0 - p)^2 \times q = p - p^2 \quad (5.1b)$$

$$u_x = \frac{\sqrt{\sigma^2}}{\mu} \quad (5.1c)$$

These are the expressions for the mean or expected value, variance and coefficient of variation[29] or relative uncertainty[3] of the Binomial distribution, also known as the Bernoulli trial problem. Based on Equations 5.1, for N_G trials, we expect a mean population of pN_G particles satisfying the diffraction condition with a variance of σN_G from the mean.

When one grain-one pole assumption holds, the probability of diffraction can be computed based on area ratios as shown in previous chapters. In that case, each diffracting grain and activated pole is independent and Equations 5.1 are applicable to calculate the statistical characteristics of the population distributions for both the grains and poles. When that assumption fails, on the other hand, poles within a particular family of planes that belong to the same grain will no longer be independent of each other, as the crystallography of the unit cell will determine their relative orientations. Hence, these m_{hkl} poles, which are tested for contributing to the same reflection, cannot be considered as m_{hkl} independent trials. As a result, the formulations derived for the Binomial distribution may not hold, since the independence requirement is not satisfied for all trials. This problem will be addressed in the next section.

5.3.2 Testing for Randomness

Figure 5.1 demonstrates the reference sphere (on the left) and the distribution of poles formed by the intersection of the orientation vectors from 10^5 randomly oriented particles with the surface of this sphere (on the right)¹. The image on the right is a rectangular grid with 720 rows and 360 columns that are uniformly distributed over the angular ranges

¹The spherical surface is stretched out to a 2-dimensional planar surface for ease of viewing.

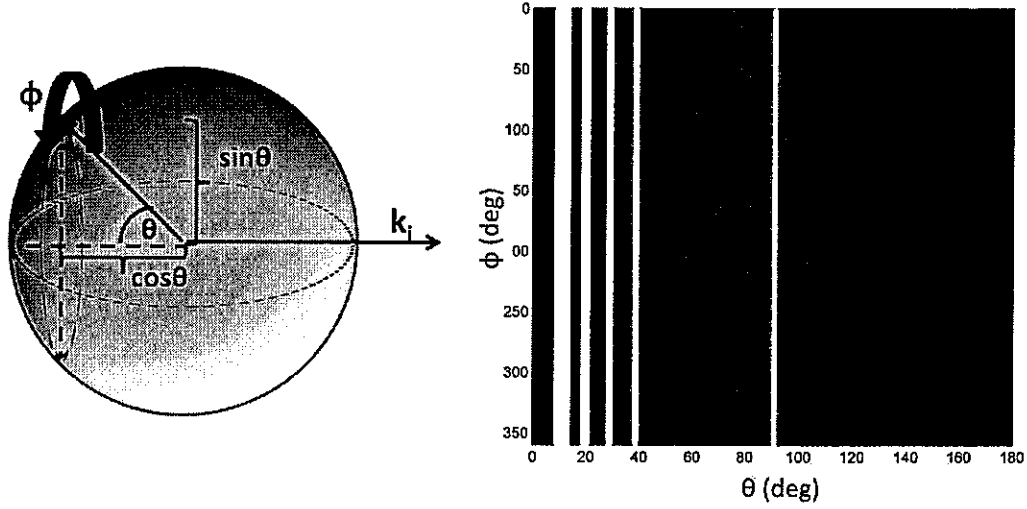


Figure 5.1: Left: Schematic of the reference sphere. $\vec{k}_i$ is the incoming X-ray beam, θ is the angle between the grain orientation vector and $-\vec{k}_i$. ϕ is the polar angle of the grain orientation vector around $-\vec{k}_i$. Right: Distribution of 10^5 randomly oriented poles on the surface of the reference unit sphere. The white colored areas refer to the bands centered at $\theta = 10^\circ, 20^\circ, 30^\circ, 40^\circ$ and 90° , which cover equal surface area.

($0 \leq \phi \leq 2\pi$, $0 \leq \theta \leq \pi$) and each grid element is called a 'bin'. The color coded map shows the number of poles that each bin contains, thus the area integral of this pole distribution plot yields the total number of grains, 10^5 . Since the area of each bin on the unit sphere is $A_{bin} = \sin\theta d\theta d\phi$, there is appreciable bias in the area coverage of individual bins, which is proportional to the sine of the θ coordinate of the bin. As a result, the bins around the central region ($\theta \approx 90^\circ$) cover relatively larger solid angles, which causes a higher concentration of poles in this region. In contrast, the bin areas are unbiased with respect to the ϕ axis.²

Since, an ideal powder sample is represented by randomly distributed poles on the surface of the reference sphere, we first test whether Equations 5.1 are able to capture the

²When the same pole distribution is plotted on an equi-area grid, in which the grids cover equal solid angles but θ and ϕ axes are unevenly sampled, the pole density appears to be constant.

randomness in the data shown in Figure 5.1. This is a necessary condition for Equations 5.1 to be applicable for statistical characterization: it guarantees that the probability of capturing a pole is constant and unbiased over the spherical surface. To do this, we choose five bands on the 2-dimensional grid, which are centered at $\theta = \theta_C = 10^\circ, 20^\circ, 30^\circ, 40^\circ, 90^\circ$ and extend from 0° to 360° on the ϕ axis, and obtain the pole distribution counts within the areas of these bands. To keep the areas of each band and the individual bins (within the bands) constant, we set the angular width $\Delta\theta$ proportional to $1/\sin\theta_C$ for all bands and their corresponding bins. As a result, the bins in the bands which are centered at lower θ values on the horizontal axis are wider than those centered at higher θ values. Once the boundaries are set in both axes for each band and bin, the pole counts per bin are collected. The frequency histograms of these bins with respect to the number of poles they contain are shown in Figure 5.2.

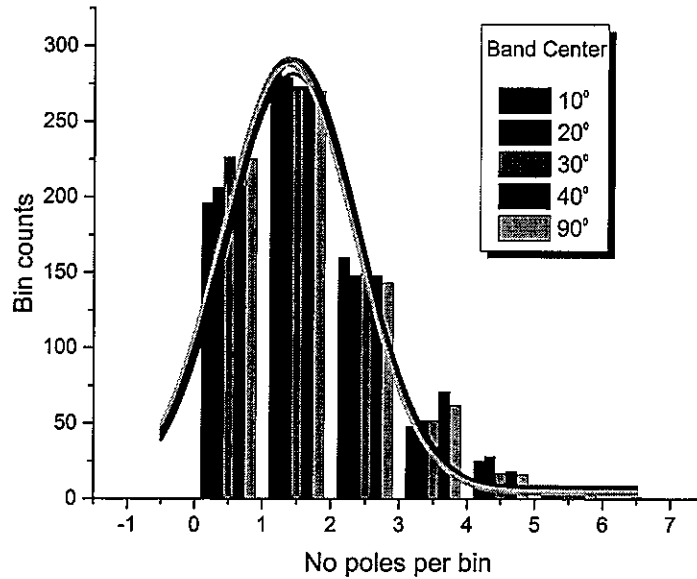


Figure 5.2: Frequency histograms of bins within the area of 5 bands shown on the right side of Figure 5.1 (white color). The total number of randomly oriented grains tested for simulation is 10^5 and each band contains 720 equal-area bins. The curves shown on top of the bar plots are the best fitting Gaussian functions to the raw data sets.

From Figure 5.2 we see that the frequency histograms of the bins with respect to their pole counts are similar in all bands and that the variation between bands is not systematic but due only to the statistical fluctuations in the pole distributions. In other words, there is no bias in the pole densities among different bands and therefore the grain distribution is truly uniform as expected from an ideal powder ensemble. Once this is established, the statistical characteristics (mean and variance) of individual bins within the 5 bands are obtained. This can be achieved in 3 different ways:

1. *Direct computation from the grain counts in all bins.* This was done using the standard definitions of the mean and the variance given below:

$$\mu_{sim} = \frac{\sum_{i=1}^N x_i}{N} \quad (5.2a)$$

$$\sigma_{sim}^2 = \frac{\sum_{i=1}^N (x_i - \mu_{sim})^2}{N - 1} \quad (5.2b)$$

2. *From the center position and width of the best fitting Gaussian (normal distribution) curves to the bin frequency histograms.* In this case, first the frequency histograms of the bins with respect to the number of poles they contained were obtained. Then, the following form of the Gaussian function was optimized to fit to these pole count histograms and model the probability distribution [29]:

$$\phi(x) = \frac{1}{\sigma_{fit}\sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{x - \mu_{fit}}{\sigma_{fit}} \right)^2 \right] \quad (5.3)$$

where μ_{fit} and σ_{fit} are the mean and variance of the distribution. The fitting was achieved by numerical analysis software (Origin).

3. *Binomial distribution.* In this case, Eqs.5.1 were evaluated with the probability term p obtained from the ratio of the band areas to the total area of the reference sphere.

The first method is trivial. The second method, however, needs the fitted model to be representative of the raw data distribution and can be challenging even with good mathematical analysis algorithms. Finally, the third method requires the numerical value of the diffraction probability: since each grain is represented by a single orientation vector, the

diffraction probability on the reference sphere can be calculated based on area fractions. For a band of angular width $\Delta\theta = \theta^+ - \theta^- = \frac{1}{\sin\theta_C}$ on the reference sphere, where θ^+ and θ^- refer to the positive and negative θ limits of the band, the probability that an orientation vector will be inside the band area is proportional to the integral over the circumference of the sub-bands making up the total band area (See Figure 5.3 for the solid angles covered by bands, bins and sub-bands.). From Figure 5.1 the circumference of a sub-band is $A_{sub-band} = 2\pi \sin\theta\Delta\theta$, where $\Delta\theta$ is the infinitesimal thickness of the sub-band. Therefore,

$$p_{band} = \frac{\int_{\theta^-}^{\theta^+} 2\pi \sin\theta d\theta}{4\pi} = \frac{\cos\theta^- - \cos\theta^+}{2} \quad (5.4)$$

Evaluating Eq. 5.4 for the 5 bands shown in Figure 5.1 reveals $p_{band} = 0.0087$ for all bands. Since this probability is distributed evenly over all ϕ angles within a sub-band and the ϕ axis is spanned by 720 bins, the area-based diffraction probability per bin becomes $p_{bin} \approx \frac{p_{band}}{720} = 1.212 \times 10^{-5}$. From the numerical value of p_{bin} , the expected number of grains per bin and its variance can be computed. Table 5.1 presents these values computed by the three methods listed previously:

Band center(°)	Mean (Sim)	Variance (Sim)	Mean (Gauss)	Variance (Gauss)	Mean (Binomial)	Variance (Binomial)
10	1.24	1.10	1.46	0.88	1.21	1.21
20	1.22	1.11	1.40	0.86	1.21	1.21
30	1.13	1.04	1.36	0.92	1.21	1.21
40	1.21	1.07	1.43	0.96	1.21	1.21
90	1.15	1.06	1.36	0.92	1.21	1.21

Table 5.1: Mean number of poles per bin and its variance for the 5 bands considered in 5.2. The total number of grains tested independently is 10^5 .

Table 5.1 confirms that there is no bias in the expected pole counts per bin among different bands if the bin areas are kept constant. Comparing the results from the three methods we see that the mean values predicted from the raw data (Eqs. 5.2) and Binomial formulation (Eqs. 5.1) are close, although the Binomial formula predicts larger variance

than the actual variance computed from the raw data. The Gaussian (normal distribution) fits obviously do not capture the variance for the pole counts, however their predictions for the expected pole counts are within 10% of the true values.

5.3.3 Inapplicability of the Gaussian (Normal) Distribution

One of the reasons why the Gaussian fit does a bad job in modeling the probability distribution of the pole counts per bin is that it is an incompatible model for the raw data: the raw data (number of poles per bin) are bounded on the left side of the histogram peak position since the number of poles per bin cannot be less than zero. This left bound, however, is not balanced by a symmetric bound on the right because the maximum number of poles within a given bin can only be limited by the total number of grains tested; although the probability that one bin captures all of the poles is negligibly small (but nonzero). The existence of a lower bound in the pole counts per bin introduces appreciable skewness to the raw data towards the positive side of the horizontal axis. In contrast, the ideal Gaussian model is unbounded in both the positive and the negative axes and thus has zero skewness[29].

Secondly, approximating a discrete probability distribution to a continuous model is inherently problematic in most cases. For such an approximation to be reasonable, the sample size, N_G , must be above some threshold. There is immense amount of material in the statistics literature discussing this issue and suggesting various criteria for the required sample size for discrete random distributions to approximate to a continuous, normal distribution [1; 10]. As a rule of thumb, it is advised to increase the sample size if possible. On the other hand, there is an interesting discussion on 'lucky' (p, N_G) pairs for discrete populations that converge to continuous distributions, as well as some 'unlucky' pairs [10], where convergence is never established by increasing the sample size. For the purposes of our work, we can conclude that to address both of these problems, increasing the sample size would be a reasonable option since it would: 1) improve the agreement between the Binomial formulation and the Gaussian (normal) distribution fits and also 2) push the mean pole counts per bin to larger values, thereby lessening the effect of the skewness.

5.3.4 Applicability of the Binomial Distribution in Pole and Grain Statistics: 1 Grain - 1 Pole

After we demonstrated that Eqs. 5.2 and the Binomial formulation (5.1) did capture and agree on the statistical characteristics of the frequency histograms of equal area bins, we now focus on the total pole counts within the areas of the 5 bands considered previously and look at the repeatability over a number of trials. For that purpose, we collect data from 10 runs of simulation and replicate the analysis presented earlier. This time, for the Binomial formulation, the area based probability expression for the whole band is used, and the numerical value of the probability term becomes $p_{band} = 0.0087$. Table 5.2 reports these results.

1 Grain 1 Pole	Band 1	Band 2	Band 3	Band 4	Band 5
Mean (sim)	879.9	865.4	868.2	872.9	869
std (sim)	21.9	35.7	33.9	41	28
Rel. Unc. (% , sim)	2.5	4.1	3.9	4.7	3.2
Mean (Binomial)	870	870	870	870	870
std (Binomial)	29.4	29.4	29.4	29.4	29.4
Rel Unc. (% , Binomial)	3.4	3.4	3.4	3.4	3.4

Table 5.2: Mean number of poles per band and its variance for 5 bands. The total number of grains tested is 10^5 and the results from 10 simulations are reported.

In Table 5.2 we compare the mean and variance in the total number of poles obtained by direct simulation and Binomial formula. (For this case we did not include the Gaussian fits to the histogram counts of the poles since the small number (10) of trials caused unstable and non-converging fits for most of the bands.) For the mean or expected number of poles within the bands, the Binomial formula does an acceptable job in predicting the mean values and the standard deviations. The relative uncertainties computed by taking the ratio of the standard deviation (square root of the variance) to the mean, are within %30 of the values obtained from the raw data. Comparing Tables 5.1 and 5.2 we notice that the uncertainties in the individual bin counts are around 90% whereas the uncertainties in the whole band

areas are around 5%. This is expected since each band includes 720 bins and it is much slower for an individual bin than the totality of 720 of such bins to converge to the ultimate limit. In fact, the uncertainties for the bands computed by the Binomial formulation are proportional to $\frac{1}{\sqrt{720}}$ of the uncertainties of the individual bins. In other words, integral quantities converge much faster than their differential counterparts.

Next we look at the first four reflection bands of the gold particle ensemble and repeat the previous analysis. For this set of computations, the angular width of each band was set to $2\beta_{hkl}$ of the corresponding reflection, where β is the full-width at half maximum of the intensity peak estimated by the Scherrer equation and $\approx 100\%$ of the total integrated intensity is contributed by the poles activated within this range of the reflection band. For this set of calculations, the ratios of the reflection band areas to the total area of the unit sphere were 0.0936, 0.0936, 0.0934 and 0.0928 for the first four reflection bands, respectively. As seen from Table 5.3, there is good agreement between the mean and standard deviations of the populations calculated from the raw data and the Binomial formulation for all reflection bands. There is slight decrease in the pole counts from 111 to 311 reflection and an accompanying increase in the relative uncertainties predicted by the Binomial formulation, unlike Table 5.2: this is caused by the progressive decrease in the area ratio of the reflection bands as the Bragg angle increases.

At this point we conclude that the randomization algorithm used to model an ideal powder ensemble generates truly random orientations for grains and their respective poles, provided that each grain has a single pole. Hence, the areal density of the poles over the surface of the reference sphere is constant. The randomness of the grain and pole distributions allows the use of the Binomial formulation in addition to the classical statistics formulae. Although, the randomness of these distributions implies that their statistical characteristics must be captured by normal or Gaussian probability distribution as well, insufficient population of the sample size and small probability values for diffraction introduce asymmetry in the raw distributions, preventing their true characteristics to diverge from those of an ideal normal distribution function.

Since there is no statistical bias among different equal-area bands on the surface of the reference sphere, the above conclusions apply to the first four reflection bands of the gold

1 Grain 1 Pole	$N_{P_{111}^*}$	$N_{P_{200}^*}$	$N_{P_{220}^*}$	$N_{P_{311}^*}$
Mean (sim)	9352	9283	9274	9290
std (sim)	108.5	110.9	86.9	91.5
Rel. Unc. (% , sim)	1.16	1.19	0.94	0.98
Mean (Binomial)	9363	9361	9340	9279
std (Binomial)	92.1	92.1	92.0	91.8
Rel. Unc. (% , Binomial)	0.98	0.98	0.99	0.99

Table 5.3: Mean number of poles per band and the standard deviation for the first 4 reflection bands of the gold nanoparticle ensemble. The nanoparticles are assumed to be spherical with diameter 2.86 nm and the X-ray beam has wavelength 2.29 Å. The total number of grains in the ensemble for each run is 10^5 and 10 independent trials were considered for the statistical analysis.

nanoparticle ensemble, irradiated by a plane monochromatic X-ray beam, as well. For the first four reflection bands of the gold nanoparticle ensemble, the statistical description of the pole distribution in reflection bands by the Binomial formulation converges to that obtained directly from the raw data. However, all these calculations considered a single pole per each grain, and therefore practically, they are applicable only to ensembles consisting of 'bulk' particles.

5.3.5 Applicability of the Binomial Distribution in Pole and Grain Statistics: 1 Grain - m_{hkl} Poles

In this part, the statistical characteristics of pole and grain distributions for the particle ensembles, in which the one grain-one pole assumption fails, will be investigated and the applicability of the Binomial formulation will be tested. To do this, we again focus on the first four reflection bands of the gold particle ensemble. The angular width of the bands is set to $2\beta_{hkl}$. Assuming spherical nanocrystallites with diameter 2.86 nm and an irradiation wavelength of 2.29 Å, we collect the diffracting grain and activated pole counts for 10 trials considering all m_{hkl} pole vectors in the simulations. The statistical properties

of the distributions are then obtained by Equations 5.1 and 5.2 treating each correlated pole vector within a reflection family as an independent trial. For the set of variables selected the ratio of the reflection band area to the total area of the reference sphere using Eq. 5.4 is computed to be $p_{band} = 0.0936$ for all reflection bands. From the value of p_{band} , the variance is calculated to be 0.0848 per trial. The statistical characteristics obtained by following the two formulations are reported in Table 5.4:

1 Grain m_{hkl} Poles	$N_{P_{111}^*}$	$N_{G_{111}^*}$	$N_{P_{200}^*}$	$N_{G_{200}^*}$	$N_{P_{220}^*}$	$N_{G_{220}^*}$	$N_{P_{311}^*}$	$N_{G_{311}^*}$
Mean (sim)	74925	52106	56175	47595	112110	74011	222770	98677
std (sim)	182.75	147.51	222.45	113.13	300.49	145.19	296.93	25.20
Rel.Unc.(%, sim)	0.24	0.28	0.40	0.24	0.27	0.20	0.13	0.03
Mean (Bin.)	74906	9363.3	56160	9360	112080	9340	222710	9280
std (Bin.)	260.52	92.11	225.62	92.11	318.77	92.02	449.50	91.75
Rel.Unc.(%, Bin.)	0.35	0.98	0.40	0.98	0.28	0.99	0.20	0.99

Table 5.4: The mean population and the standard deviation of diffracting grains and activated poles within the first four reflection bands of the gold particle ensemble. The particle diameter is 2.86 nm, $\lambda = 2.29 \text{ \AA}$, the total number of grains tested is 10^5 and 10 runs of simulation is considered. (Bin. stands for Binomial.)

From this table we see that the expected pole counts and their standard deviations computed from the raw data and the Binomial formulation are quite close for all reflections. As a result, the relative uncertainties do also agree. This indicates that the non-uniform orientation distributions of activated sibling poles or n-lets, which disqualify them from being independent trials, do not completely discard the applicability of the Binomial formulation for obtaining the statistical characteristics of the activated and correlated pole counts. For the grain counts, however, both the expected populations and the standard deviations computed by the two methods diverge greatly: this is expected since under the condition where one grain-one pole assumption does not hold, the diffraction probability for a given grain cannot be computed by simple area ratios, and therefore the probability term required for the Binomial formulation is unknown. If we define a 'mean probability' term, p_{mean} based

on the mean population of the diffracting grains obtained from direct simulation, we compute 0.521, 0.476, 0.740 and 0.987 for the probability of diffraction for 111, 200, 220 and 311 reflections respectively. Inserting these into Equations 5.1 yields 0.30, 0.33, 0.19 and 0.04 for the percent relative uncertainties in diffracting grain populations for these four reflections. These values seem to be much closer to the true uncertainties. In other words, if the true probability of diffraction could be obtained for the grain populations, then the Binomial formulation would be an applicable model to estimate the statistical characteristics of diffracting grain populations. In the absence of analytical equations, this probability can only be obtained from direct modeling and simulation.

5.4 Continuous Probability Distribution: Intensity Statistics

In the previous section, the numerical value of the possible outcomes of a diffraction experiment for a randomly oriented grain (or pole) was discrete and either 0 or 1: if at least one pole vector of the grain fell into the reflection band area, this grain would be assigned 1 and if not, it would be assigned 0. If we intend to calculate the expected intensity from a randomly oriented grain, however, the situation is different: if the grain does not satisfy the diffraction condition, its intensity is recorded as 0 but if it does diffract, the expected intensity is not necessarily 1. The intensity from a 'diffracting grain' can take numerous different values depending on the deviation of the grain orientation from the exact Bragg condition. In this case, the possible intensity values for a diffracting grain, within the extent of the Bragg peak, must be linked to the probability of this grain being oriented at a specific angular position in the reciprocal space. This can be achieved by combining the probability expression (Eq. 5.4) with the Patterson formula [47]. Such an analysis yields the expected intensity and the variance per pole or grain as:

$$\mu(\bar{I}) = \int_{-2\beta}^{2\beta} p_{sub-band} \left(\frac{\Delta 2\theta}{2} \right) Pat(\Delta 2\theta) d(\Delta 2\theta) \quad (5.5a)$$

$$\begin{aligned} \sigma^2(\bar{I}) = & \int_{-2\beta}^{2\beta} p_{sub-band} \left(\frac{\Delta 2\theta}{2} \right) Pat^2(\Delta 2\theta) d(\Delta 2\theta) \\ & - \left[\int_{-2\beta}^{2\beta} p_{sub-band} \left(\frac{\Delta 2\theta}{2} \right) Pat(\Delta 2\theta) d(\Delta 2\theta) \right]^2 \end{aligned} \quad (5.5b)$$

In Equations 5.5, $\bar{I}$ stands for the integrated intensity and μ and σ are the mean and variance, as before. As seen, these expressions simply involve the diffracted intensity per grain weighted by the probability of having the activated pole from that grain at a particular deviation angle $\Delta\theta = \frac{\Delta 2\theta}{2}$, which is then integrated over the extent of the peak. Therefore, we will refer to this method as the weighted sum in the upcoming sections. Multiplying the mean and variance per grain (or pole when 1 grain-1 pole assumption holds) by the total number of irradiated grains from the powder sample, we obtain the corresponding expected integrated intensity and its variance from the mean for the whole ensemble.

5.4.1 1 Grain - 1 Pole

To test the applicability of Eq. 5.5 on capturing the statistical characteristics of the diffracted intensities, we first study the case where one grain is allowed to have a single pole. The importance of this case comes from the fact that: 1) it satisfies the one grain - one pole assumption which was implicit in the formulations of the original reference [3], 2) since the irradiated sample is an ideal powder, the diffracting grains and the activated poles are randomly distributed and each pole or grain is independent, hence the Binomial formulation is rigorously applicable on the grain and pole population distributions.

To proceed, the thickness of each reflection band is set to $2\beta_{hkl}$, thereby letting the deviation angles for the diffracted spots vary in the interval $|\Delta 2\theta| \leq 2\beta_{hkl}$ around $2\theta_{B,hkl}$ in the angular space. Only one pole vector from the m_{hkl} family is allowed per grain, and the number of grains that satisfies the diffraction condition in a powder sample of 10^5 grains is obtained for 10 trials, as well as the distribution of the activated poles on the reflection band area. The particles making up the powder are assumed to be spherical as usual, with a diameter of 2.86 nm and the X-ray beam has 2.29 Å wavelength. As in the previous section, the grain and pole statistics are obtained both from the raw counts directly and from the Binomial formulation. Similar procedure is repeated for the intensity statistics: first the corresponding intensity profiles are computed from the angular distribution of the activated poles and the Patterson formula. Then, the raw intensity profiles are integrated numerically and the mean value and variance in the integrated intensities are calculated for 10 trials using Eqs.5.2. The same calculation is also done by Equations 5.5.

1 Grain - 1 Pole	$\bar{I}_{111}$	$N_{P_{111}^*}$	$\bar{I}_{200}$	$N_{P_{200}^*}$	$\bar{I}_{220}$	$N_{P_{220}^*}$	$\bar{I}_{311}$	$N_{P_{311}^*}$
Mean (sim)	2397	9351.5	2402.9	9282.6	2405.2	9274.4	2411.9	9289.7
std (sim)	48.51	108.46	44.98	110.84	53.71	86.89	34.91	91.48
Rel.Unc.(%, sim)	2.02	1.16	1.87	1.19	2.23	0.94	1.45	0.98
Mean (Eq. 5.5)	2400	9363	2400	9361	2400	9340	2400	9278.8
std (Eq. 5.5)	41	92.12	41	92.11	41	92.03	41	91.75
Rel.Unc.(%, Eq. 5.5)	2.44	0.98	2.44	0.98	2.44	0.99	2.44	0.99

Table 5.5: Mean (expected) number of poles within the reflection band and the corresponding mean integrated intensities for the first 4 reflections of the ideal gold powder. The particle diameter is 2.86 nm and the X-ray wavelength is 2.29 Å. The total number of grains tested is 10^5 and 10 runs of simulation are considered to generate the raw data. (The grain counts are the same as pole counts for all reflections.)

Table 5.5 presents the results of these computations along with the relative uncertainties. As seen, both the mean integrated intensities and the standard deviations calculated directly from the integrals of the intensity profiles by Eqs. 5.2 and by the weighted sum (Binomial formulation) agree well for all 4 reflections. Therefore, the weighted sum is an appropriate model to estimate the statistical parameters of the integrated intensities from an ideal powder ensemble when the one grain-one pole condition holds. However, even when this condition is satisfied, as in the case of the original reference [3], the uncertainties in the integrated intensities are systematically larger than those of the corresponding pole or grain populations. This trend is confirmed by the predictions of both formulations, Eqs. 5.5 and 5.2. Since the multiplicity effect is disregarded for this set of computations, the relative uncertainties in the pole populations and the integrated intensities are similar among different reflections, as are the expected values for the two quantities. The slight decrease in the expected pole populations going from 111 to 311 reflections and the small increase in the relative uncertainty predicted by Eq. 5.1 for the 311 pole population are a result of the relative decrease in the 311 reflection band area compared to those of the remaining bands.

5.4.2 Mathematical Basis of the Difference in the Uncertainties of Pole Counts and Corresponding Integrated Intensities

The discrepancy between the uncertainties in the pole populations and the corresponding integrated intensities for a given reflection is a result of the different (discrete vs continuous) nature of the pole (or grain) and intensity parameters, and therefore cannot be eliminated. However, if the angle dependent variation of the expected intensities due to the shape of the rocking curve can be eliminated, the continuous probability distribution of the intensity can reach the discrete regime, which would merge the pole and intensity statistics. There are two ways this can be achieved:

1. If the intensity distribution of the diffracting particle is constant with respect to the deviation angle $\Delta 2\theta$ within the extent of the intensity profile, then each diffracting grain would contribute the same amount to the total diffracted intensity. This would push the intensity statistics to the discrete regime. In that case, Eqs.5.5 yield for the relative uncertainty per grain:

$$\begin{aligned}\mu(\bar{I}) &= \int_{-2\beta}^{2\beta} c p_{sub-band} \left(\frac{\Delta\theta}{2} \right) d(\Delta 2\theta) = c p_{band} \\ \sigma^2(\bar{I}) &= \int_{-2\beta}^{2\beta} c^2 p_{sub-band} \left(\frac{\Delta\theta}{2} \right) d(\Delta 2\theta) - \left[\int_{-2\beta}^{2\beta} c p_{sub-band} \left(\frac{\Delta\theta}{2} \right) d(\Delta 2\theta) \right]^2 \\ &= c^2 (p_{band} - p_{band}^2) \\ u(\bar{I}) &= \frac{\sqrt{\sigma^2}}{\mu(\bar{I})} = \frac{\sqrt{p_{band} - p_{band}^2}}{p_{band}}\end{aligned}$$

where c is the value of the constant diffracted intensity within the whole extent of the peak. From previous discussions we also know that when one grain-one pole assumption holds, the probability of diffraction for a grain and a pole is the same and equal to the area ratio of the reflection band to that of the reference sphere, and the weighted sum approach is applicable. Therefore p_{band} can safely be inserted into Eqs.5.1 yielding the same uncertainty expression per grain. Multiplying $u(N_{G^*}) = u(N_{P^*}) = u(\bar{I})$ by the number of irradiated grains, then, yields the same relative uncertainty for the total diffracting grain populations and the integrated intensities.

2. If the individual crystallite size is above a threshold, then the Scherrer breadth

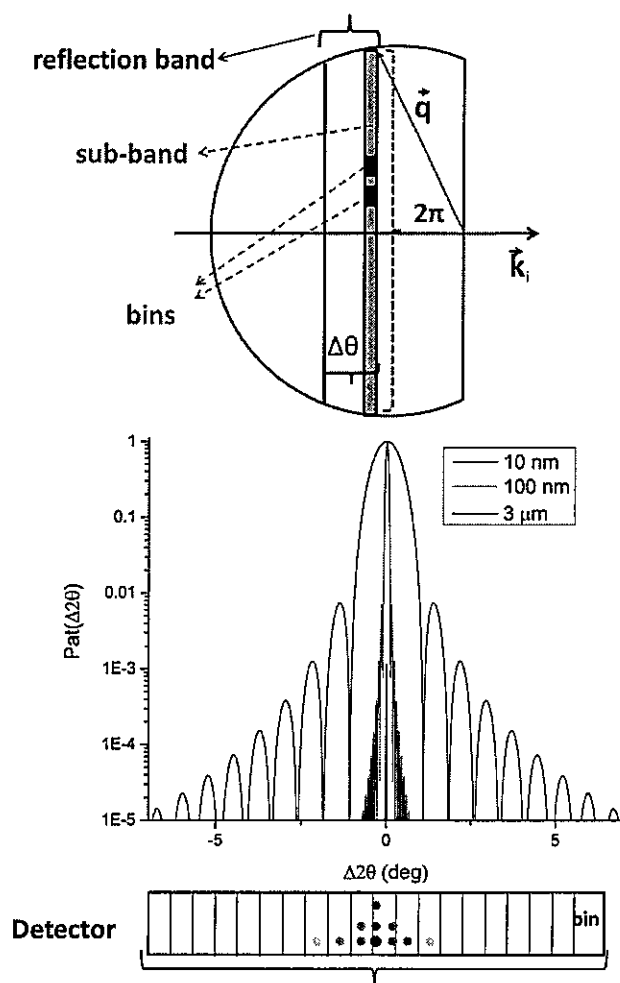


Figure 5.3: Top: The placement of bins and sub-bands inside the reflection band area. The activated poles in each sub-band is projected to the detector coordinate system. Bottom: The continuous rocking curve scans calculated by the Patterson functions of three spherical gold nanoparticles with different diameters. The detector consists of equi-spaced, discrete bins (or pixels) that capture the diffracted spots. The dots shown inside the detector bins represent the diffracted spots recorded from the three profiles. The rocking curves and the corresponding dots were colored similarly for ease of viewing and the fading colors imply decreasing intensity.

of the intensity profile becomes very narrow, reaching zero in the ultimate limit (infinite particle size). In that case:

$$\lim_{D \rightarrow \infty} Pat(\Delta 2\theta) = \lim_{\Delta 2\theta \rightarrow 0} Pat(\Delta 2\theta) \approx \delta(\Delta 2\theta) \quad (5.6)$$

where $\delta(\Delta 2\theta)$ is the Dirac-delta function [62]. However, this condition is never observed in practice: it requires infinite resolving power for the detector pixel [20] to distinguish infinitesimally small angular intervals. In a realistic setup, the pixels are distributed discretely and have a finite angular resolution, Δd , which also determines the maximum possible intensity the Laue spots can diffract by setting the minimum distinguishable value of $\Delta 2\theta$. Hence, the rocking curve does not reduce to an ideal Dirac delta function but to a constant valued function of angular extent Δd . Assuming $\Delta d \geq 4\beta_{hkl}$, all diffracted spots are recorded by the same pixel and are assigned the same diffracted intensity, as seen in the schematic in Figure 5.3. On the sampling side of the diffraction space, this corresponds to the case where there is a single reflection sub-band with angular width $\Delta\theta = \frac{\Delta d}{2}$ containing all activated poles, i.e. $p_{sub-band} = p_{band}$. Therefore, the integrals in Eqs. 5.5 are discarded and the diffracted intensity becomes a discrete, single valued function. Then, we have:

$$\begin{aligned} \mu(\bar{I}) &= p_{sub-band} \left(\Delta\theta = \frac{\Delta d}{2} \right) \times Pat(\Delta 2\theta = \Delta d) \\ \sigma^2(\bar{I}) &= p_{sub-band} \left(\Delta\theta = \frac{\Delta d}{2} \right) \times [Pat(\Delta 2\theta = \Delta d)]^2 \\ &\quad - \left[p_{sub-band} \left(\Delta\theta = \frac{\Delta d}{2} \right) \times Pat(\Delta 2\theta = \Delta d) \right]^2 \\ &= [Pat(\Delta 2\theta = \Delta d)]^2 \left[p_{sub-band} \left(\Delta\theta = \frac{\Delta d}{2} \right) - p_{sub-band}^2 \left(\Delta\theta = \frac{\Delta d}{2} \right) \right] \\ u(\bar{I}) &= \frac{\sqrt{\sigma^2}}{\mu(\bar{I})} = \frac{\sqrt{p_{sub-band} - p_{sub-band}^2}}{p_{sub-band}} \end{aligned}$$

As seen, this is exactly the relative uncertainty estimated by Eq. 5.1 for the pole or grain populations.

To verify these analytical limits by the direct modeling algorithm, we ran a set of simulations varying the particle size while keeping the angular bin size constant and collected

pole population distributions and calculated the corresponding intensity profiles. Then, the relative uncertainties for the activated pole populations, as well as the integrated intensities of the corresponding profiles were calculated assuming one grain had a single pole. Figure 5.4 summarizes the results of these computations.

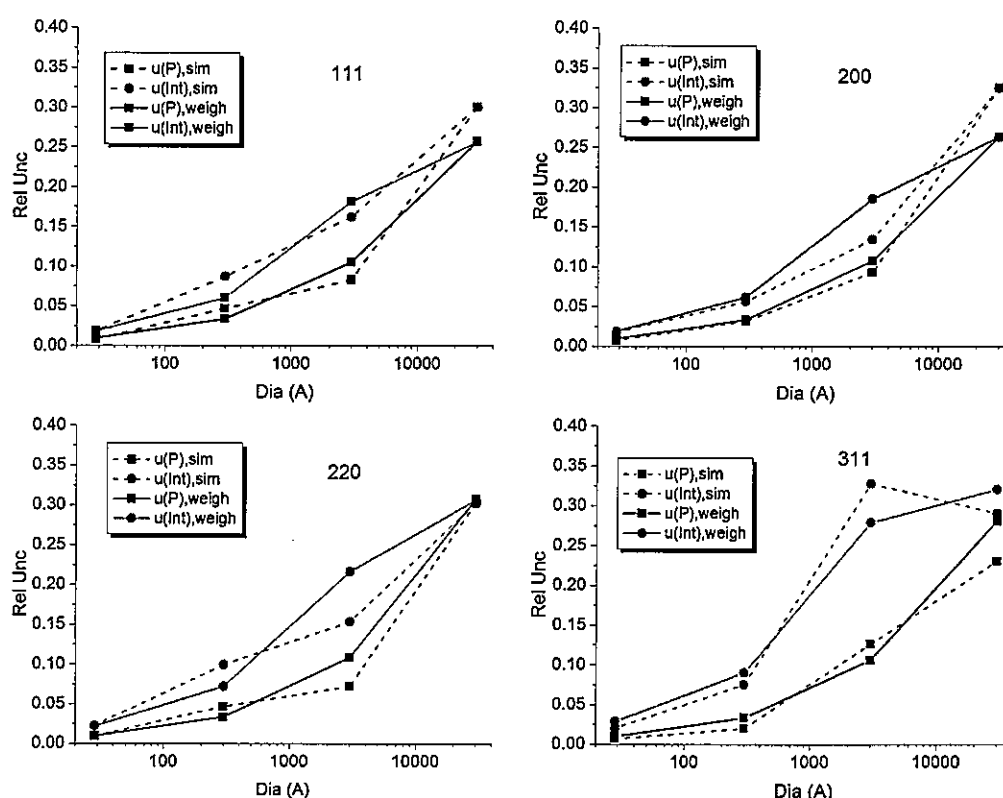


Figure 5.4: Relative uncertainties in the pole populations and the corresponding integrated intensities with respect to particle size for the first four reflections of gold powder sample. The sample consists of 10^5 spherical particles, $\lambda = 2.29 \text{ \AA}$ and each experiment was repeated 10 times.

In Figure 5.4, the solid lines indicate the relative uncertainties computed by evaluating Eq. 5.5 whereas the dashed lines represent the relative uncertainties directly obtained from the simulated pole distributions and respective integrated intensities from 10 independent trials. The pixel resolution is set to $\Delta 2\theta = 0.03^\circ$, which corresponds to the angular cover-

age of a single bin, and the width of the reflection band is 0.015° . As expected, increasing particle size decreases the crystallite acceptance angle and the diffraction probability p_{band} , leading to an increase in the relative uncertainties in both the pole populations and the integrated intensities for all four reflections. For particle sizes up to 3 microns, the uncertainties in the integrated intensities are consistently higher than those of the corresponding pole (or grain) populations.

When the particle diameter reaches around 3 microns, however, the relative uncertainties in the pole populations and in the corresponding integrated intensities merge at the same value for 111, 200 and 220 reflections. At this particle size, the breadth of the first four Bragg peaks are 0.0059° , 0.0062° , 0.0084° and 0.0140° , respectively, and for the first three reflections the crystallite acceptance angle, $\Delta\theta = 2\beta_{hkl} \leq \frac{0.03}{2}$. Hence, all activated poles are captured within the same bin and are assigned a constant intensity value of $Pat\left(\Delta 2\theta = \frac{0.03}{4}\right) \approx 0.99998$. In particular for the 311 reflection, the activated poles are captured by three bins (instead of one) in the vicinity of the Bragg angle, and therefore there is slight difference between the uncertainties in the pole populations and the integrated intensities, as confirmed also by Eq. 5.5.

This analysis confirms that the original reference from 1948 [3] indeed considers the case where each diffracting grain has a single activated pole and all diffracted spots are assigned the same intensity value. This is clearly a special case in the big picture and based on our simulations, it can only be observed when the particle size is larger than ≈ 1 micron. The pixel resolution, irradiation wavelength, as well as any parameter that increases the peak breadth of a given crystallite raises this size threshold. The statistical formulation given in this reference [3] is, as a result, not applicable in the nanocrystalline size regime and in general we expect higher relative uncertainties in the integrated intensities than the corresponding diffracting particle and activated pole populations.

5.4.3 1 Grain - m_{hkl} Poles

Now that the mathematical basis for the inherent difference between the intensity and sampling statistics has been established, we repeat the previous computation, this time including all pole vectors from the hkl plane. Following the same procedure, the corre-

sponding intensities are generated by the Patterson formula and the statistical analyses are done on both the pole populations and the intensities using the simulated data from 10 trials and by Eq. 5.5. These results are presented in Table 5.6 for a powder sample of 10^5 spherical particles with 2.86 nm diameter.

1 Grain m_{hkl} Poles	$\bar{I}_{111}$	$N_{P_{111}^*}$	$\bar{I}_{200}$	$N_{P_{200}^*}$	$\bar{I}_{220}$	$N_{P_{220}^*}$	$\bar{I}_{311}$	$N_{P_{311}^*}$
Mean (sim)	19218	74925	14358	56175	28772	112110	57229	222770
std (sim)	90.92	182.75	119.55	222.45	164.58	300.49	148.67	296.93
Rel.Unc.(%, sim)	0.47	0.24	0.83	0.40	0.57	0.27	0.26	0.13
Mean (Eq. 5.5)	19207	74907	14405	56168	28804	112130	57555	222690
std (Eq. 5.5)	115.97	260.56	100.43	225.63	168.65	318.81	200.80	449.48
Rel.Unc.(%, Eq. 5.5)	0.60	0.35	0.70	0.40	0.59	0.28	0.35	0.20

Table 5.6: Mean number of poles within the reflection band area and the corresponding mean integrated intensities for the first 4 reflections of the gold powder. The particle diameter is 2.86 nm and the X-ray wavelength is 2.29 Å. The total number of grains tested is 10^5 and 10 runs of simulation is considered to generate the raw data.

From Table 5.6 we see that the relative uncertainties in the intensities are once again larger than those of the activated pole populations for all reflections. This trend is observed in both the statistics obtained from the simulated data directly for 10 trials and from the results of evaluating Eq. 5.5. Since the multiplicity effect is considered in this set of calculations, unlike the previous section, the expected pole counts and integrated intensities are different in each reflection and are directly proportional to the multiplicities. Not surprisingly, the relative uncertainties are inversely proportional to the multiplicities. Comparing the absolute value of the uncertainties in the pole counts and the integrated intensities in this table with those from Table 5.5 we notice almost an order of magnitude decrease that accompanies the multiplicity effect. This trend is confirmed by powder ensembles of various particle sizes as shown in Figure 5.5:

As seen in Figure 5.5 the relative uncertainties in both the poles and the integrated intensities are inversely proportional with the multiplicity of the reflection. Also, the relative

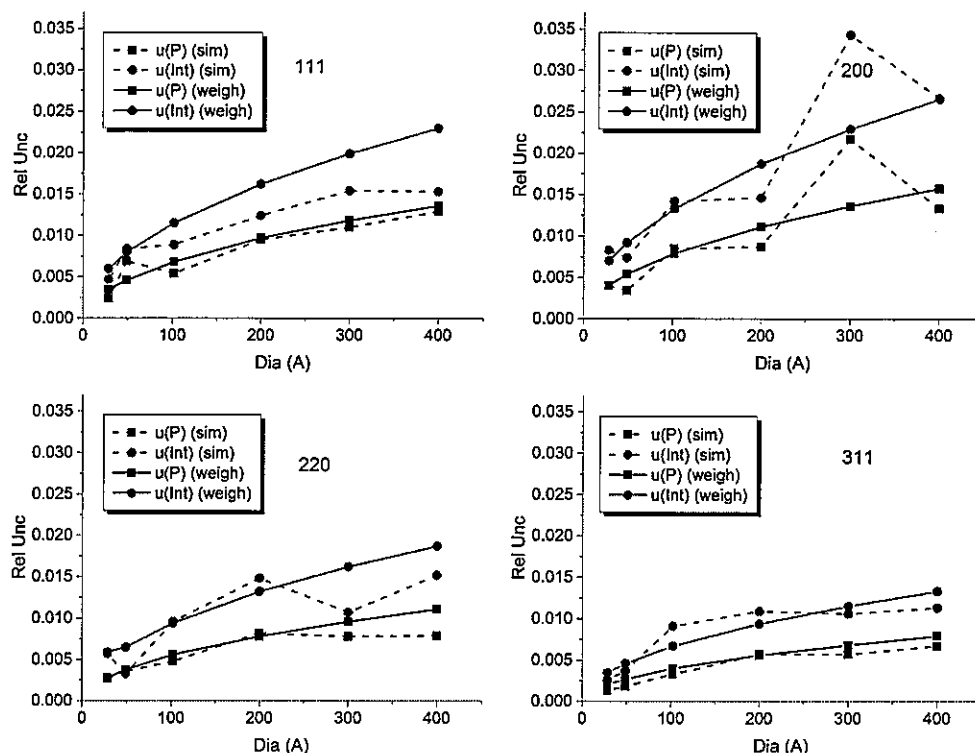


Figure 5.5: Relative uncertainties in the pole populations and the corresponding integrated intensities with respect to varying particle size for the first four reflections of gold powder sample. All samples consist of 10^5 spherical particles, $\lambda = 2.29$ Å and each experiment was repeated 10 times.

uncertainties computed from the raw data for 10 trials seem to follow the predictions of Eqs. 5.5 with visible oscillations. Even though there exists a large number of 'sibling poles' within the activated pole populations, which cannot be considered as independent trials, this does not seem to completely invalidate the applicability of Eqs. 5.5 in estimating the intensity uncertainty, as was the case for the activated pole populations discussed in previous sections.

5.5 Variation of the Statistical Uncertainties in the Sampling and Intensity Parameters with the Ensemble Size

For the sake of completeness of our discussion, one final analysis is included on the statistical uncertainties in the sampling and intensity space with respect to changing ensemble population.

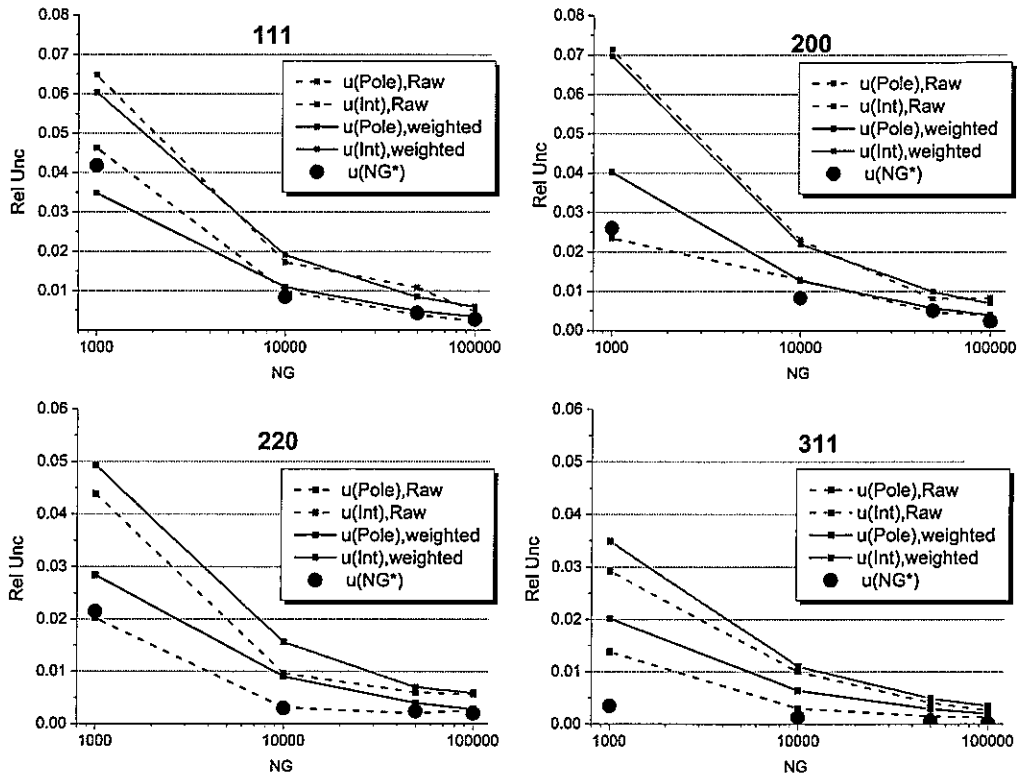


Figure 5.6: Relative uncertainties in the sampling parameters (pole, grain populations) and corresponding integrated intensities with respect to varying ensemble population for the first four reflections of gold powder sample. For all ensembles the particle diameter was set to 2.86 nm, $\lambda = 2.29 \text{ \AA}$ and each experiment was repeated 10 times.

Figure 5.6 shows the statistical uncertainties in the activated pole populations, diffracting grains and corresponding integrated intensities from powder ensembles consisting of

10^3 , 10^4 and 10^5 spherical, gold particles irradiated by 2.29 Å X-rays. For each data point shown on the plot, 10 independent simulations are run and the particle diameter is kept constant at 2.86 nm for all runs. The statistical analyses are performed by two methods as before; namely, weighted sums and Eq. 5.2.

From the figure, we see that for all reflections, the statistical uncertainties obtained for the integrated intensities are larger than those of the activated pole populations. This trend is confirmed by both methodologies used in the calculations and irrespective of the ensemble size. The uncertainties in all sampling (grain, pole populations) and intensity parameters (integrated intensities) are inversely proportional to the multiplicity of the reflection and the ensemble size, N_G . Looking at the grains, we see that the uncertainties in the diffracting grain populations are in general very close to the uncertainties in the activated pole populations.

The results presented in Figure 5.6 indicate that, one needs to accommodate for the uncertainty enhancement in the diffracted intensities as compared to the grains diffracting at a particular reflection, in order to design powder diffraction experiments with ideal monodispersed powders which yield diffraction data with a particular uncertainty limit. Depending on the multiplicity of the reflection, the total number of irradiated particles, particle and pixel size and the irradiation wavelength, the uncertainty difference between the diffracting grain populations and the respective integrated intensities may be as high as 700% (as seen for 1000 grains at 311 reflection). Therefore, to set up experiments in which the irradiated particle population is low, a simple simulation of the physics model, as presented here, may be beneficial in selecting the remaining parameters.

5.6 Summary and Conclusions

In this chapter, the relative uncertainty in the expected integrated intensities from an ideal powder ensemble, irradiated by a plane monochromatic X-ray beam was analyzed through direct modeling and simulation. The results obtained from our simulations demonstrated that the formulations by Alexander, Klug and Kummer [3] which estimated the uncertainty in the measured intensities due to particle sampling were valid only when one grain had a

single pole and the particle diameter was above a certain threshold. This is a special case within the framework of a larger problem and a more comprehensive formulation is required. For the general powder diffraction experiment with nanocrystalline particle ensembles, our results lead to the following conclusions:

1. In powder diffraction experiments, sampling parameters, such as the populations of activated poles and diffracting grains, are discrete random variables, therefore, their statistical behavior can be modeled by the Binomial distribution. Integrated intensities, on the other hand, are continuous random variables and the direct application of the Binomial formulation is not valid in investigating their convergence behaviors.
2. Binomial formulation is applicable under certain circumstances: First, the ensemble for which statistical information is to be obtained must be perfectly random, which guarantees that the selection probability for the parameter of interest is constant and uniform over the entire ensemble. Second, the outcome of each selection from this random ensemble must be an independent event. In a powder diffraction experiment these conditions are rigorously satisfied only when one grain has a single pole that can be activated at a certain reflection band.
3. Based on our simulations, it was shown that the grain and pole statistics from ideal gold nanoparticle ensembles obtained directly from the raw simulation data agreed well with the Binomial formulation when one grain-one pole assumption was enforced in the simulations. When one grain was allowed to have more than one activated pole, however, the statistical parameters of the activated poles, i.e. expected values and relative uncertainties, did still agree well with the predictions of the Binomial formulation. This means that an ensemble size of 10^5 particles is too large for the orientation dependencies of the sibling poles, that are activated within the same reflection band, to have a visible effect on the statistical characteristics of the sampling space. For the diffracting grain populations, the statistical parameters directly calculated from raw data did not agree with the predictions of the Binomial formulation since the area based selection probability for grains was inaccurate when one grain-one pole assumption did not hold.

4. The simulation results also showed that the relative uncertainties in the integrated intensities were systematically larger than those of the corresponding activated pole and diffracting grain populations. This discrepancy was shown to result from the different convergence behaviors of discrete and continuous random variables and therefore could not be eliminated.
5. Although the relative uncertainties in the integrated intensities would theoretically be larger than the uncertainties in the respective activated pole populations, this discrepancy may disappear above some threshold particle size due to the finite angular resolution of the detector pixels. When the particle diameter satisfies $\Delta d \geq 4\beta_{hkl}$ where Δd is the angular coverage of a single pixel, then all diffracted spots are captured by the same pixel and are assigned the same intensity. As a result, the statistical uncertainties of activated pole populations and the corresponding integrated intensities merge at the same values.

Chapter 6

The Debye Scattering Equation

6.1 Introduction

Computation of kinematic X-ray diffraction spectra from crystalline and semi-crystalline nanoparticle powder ensembles using analytical formulations has been reported in the past literature by numerous groups. In most of these studies, the classical Debye scattering equation was chosen to model the diffraction signature analytically and the sensitivity of the diffraction spectra in response to varying structural or experimental parameters was investigated. For instance, Bawendi *et al.* [5] compared experimentally obtained and Debye equation based analytical intensities and analyzed the effect of thermal vibrations of the atoms, stacking faults, surface reconstructions and bond compression phenomena on the diffraction signature for CdSe particles below 4 nm diameter. They concluded that surface reconstruction effect was not apparent in the Debye-predicted diffraction spectra. Beyerlein *et al.* [6] used the Debye equation to generate the diffraction spectra of monodisperse and polydisperse crystalline particle ensembles and investigated the variation of inter-particle coherency, apparent particle size and strain with respect to ensemble population and diffraction angle. For the strain and size studies, they used the Williamson-Hall analysis, treating the Debye based diffraction spectra as experimental diffraction data from the ensemble. No comparison of the findings with an independent characterization technique was reported.

The two examples we cite above are typical of the current uses of the Debye scattering equation. The reasoning behind the choice of the Debye model in these studies is that the

resulting intensities are free of unwanted components of scattering contribution, such as background, statistical fluctuations due to photon counting and particle sampling. Hence, this model is appreciated as an ideal tool to isolate and investigate the effects of various parameters on the diffraction signature. However, the Debye equation destroys the link between sampling statistics and intensity statistics, as there is no concept of a particle and no allowance made for the uncertainty in the resulting intensities. Our results, presented in Chapters 3-5 show that, such uncertainties in intensities, even for ideal conditions and with perfectly controlled samples, are in fact quite large, especially when the ensemble size is small ($N_G \approx 10^3$ – 10^4) and individual particle size is above 10 nm (see Chapter 5 for details.). As a result, there is immense ambiguity resulting from the direct comparison of experimental diffraction profiles with the Debye equation without considering the uncertainties related to the measured intensities. The presence of these uncertainties may invalidate most of the findings reported in the past literature.

In this chapter, we will investigate the potential complications due to the incorrect use of the Debye equation in modeling the diffraction profile of ideal nanoparticle ensembles. Our discussion will start with revisiting the foundations of the Debye equation followed by a statistical analysis based on direct modeling and simulation.

6.2 Derivation of the Debye Equation

The derivation of the Debye equation has been summarized in numerous textbooks, some of which are classical references in the field of X-ray diffraction [60; 25]. However, in most of these references, the derivation has been given without emphasizing the assumptions used in the formulation. The lack of understanding of the basic assumptions in the derivation of the formula caused inappropriate uses of the equation by many groups. For this reason, we feel the need to follow the author's original derivation strictly and start with a quote of the author's original wording from his famous article [18] (English translation in [17]):

"In an amorphous body, all orientations of the atoms (molecules) are equally probable. If a part of this body, containing N atoms, is irradiated, the intensity to be observed at an arbitrary direction is secured by first finding the mean intensity scattered by one atom with

respect to all possible orientations, and subsequently multiplying by N ."

"... If now the atom assumes all possible orientations, any arrow rigidly connected with the atom will assume all directions in space with equal frequency."

As we see, we are to start with an amorphous structure, where atoms are distributed randomly within a given volume. Now, let the coordinates of those N atoms within the aggregate be known. If a plane monochromatic X-ray beam with a wavevector of $\vec{k}_i$ illuminates this aggregate, the intensity of the diffracted beam with wavevector $\vec{k}_d$ can be calculated by:

$$I(\vec{q}) = \sum_{m=1}^N \sum_{n=1}^N f_m f_n \exp(-2\pi i \vec{q} \cdot \vec{r}_{mn}) \quad (6.1)$$

where $\vec{q} = \vec{k}_d - \vec{k}_i$. As seen, this is the expression we derived in Chapter 2 for the intensity in the direction of $\vec{k}_d$ from a group of N atoms for a single, fixed orientation of the atomic aggregate. Now if we let this aggregate take any random orientation in space without changing the incoming and diffracted beam orientations and the relative positions of the atoms, the average intensity of diffracted beams can be computed by taking an orientation average of the intensity expression given above:

$$\langle I(\vec{q}) \rangle = \left\langle \sum_{m=1}^N \sum_{n=1}^N f_m f_n \exp(-2\pi i \vec{q} \cdot \vec{r}_{mn}) \right\rangle$$

This averaging operation can be conveniently performed if, without loss of generality, $\vec{q}$ is aligned parallel to the vertical axis of the coordinate system and that the angle between $\vec{q}$ and $\vec{r}_{mn}$ is chosen as the elevation angle ϕ , as shown in Figure 6.1. Expanding the dot product inside the exponential term, the orientation average can be converted to an area integral over the surface of a reference sphere:

$$\langle I(\vec{q}) \rangle = \frac{1}{4\pi |\vec{r}_{mn}|^2} \int_{\phi=0}^{\phi=\pi} \int_{\theta=0}^{\theta=2\pi} \sum_{m=1}^N \sum_{n=1}^N f_m f_n \exp(-2\pi i |\vec{q}| |\vec{r}_{mn}| \cos \phi) r_{mn}^2 \sin \phi d\theta d\phi \quad (6.2)$$

The above form of the expansion allows us to change the order of the double sum with the double integral. Once this is done, the new form can be interpreted as an averaging operation for the exponential term, involving the interatomic spacing vector $\vec{r}_{mn}$, over all orientations in 3D space, or equivalently over the surface of a sphere with radius $|\vec{r}_{mn}|$.

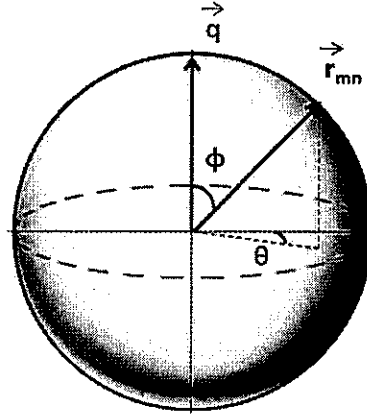


Figure 6.1: The schematic of the coordinate system used in deriving the Debye equation. $\vec{q}$ and $\vec{r}_{mn}$ stand for the momentum transfer vector and the interatomic spacing vector between atoms 'm' and 'n', respectively.

When it is performed for all $\vec{r}_{mn}$ vectors of all atomic pairs and the resulting terms are summed up, the average scattering intensity from the atomic aggregate in the direction of the momentum transfer vector $\vec{q}$ is obtained:

$$\langle I(\vec{q}) \rangle = I_D = \sum_{m=1}^N \sum_{n=1}^N f_m f_n \frac{\sin(2\pi|\vec{q}||\vec{r}_{mn}|)}{2\pi|\vec{q}||\vec{r}_{mn}|} \quad (6.3)$$

where I_D is the Debye-predicted intensity spectrum for the random aggregate including N atoms.

The double integral inside Eq. 6.2, which ultimately takes a sinc function form seen in the Debye equation, implies that all orientations in 3D space are sampled completely and uniformly by the orientation distribution of the $\vec{r}_{mn}$ vectors. For the whole aggregate, the sampling needs to be accomplished by all interatomic spacing vectors individually, as implied by the double sum. In practice, this type of a sampling can only be achieved by an infinite number of orientations for each $\vec{r}_{mn}$; which means that the statistical uncertainty due to particle sampling is completely eliminated in the derivation of the Debye equation. In reality, there is no feasible way to obtain a random powder ensemble including an infinite number of particles and measure its intensity signature; thus, the spectra represented by the Debye equation is not practically achievable. Hence, the Debye equation must be treated

purely as a model that yields the ultimate statistical limit for the diffracted intensities from a given atomic aggregate, rather than a realistic diffraction signature.

6.3 Challenges in Reaching the Debye Limit with a Numerical Model Based on a Discrete Rotation Algorithm

As an alternative discrete method, we can also formulate the total intensity diffracted from 'P' particles in the far field based on the kinematic sum:

$$I_{KS,tot}(\vec{q}) = \sum_{p=1}^P I_p(\vec{q}) = \sum_{p=1}^P \left[\sum_{m=1}^N \sum_{n=1}^N f_{p,m} f_{p,n} \exp[-2\pi i \vec{q} \cdot \vec{r}_{p,mn}] \right] \quad (6.4)$$

where $\vec{r}_{p,mn}$ refers to the interatomic distance between atom 'm' and atom 'n' in particle 'p' and $f_{p,m}$ is the atomic scattering factor. Now, assume that we assign each of these P particles an orientation vector, let these vectors take random orientations with respect to $\vec{k}_i$, compute each particle's contribution to the diffracted intensity and divide the total intensity by the number of particles P (This is the same procedure followed in previous chapters to generate an ideal powder ensemble.). Then by definition, the resulting intensity must be equal to the average intensity of a single particle over P different orientations. Since the average diffracted intensity from an aggregate of atoms over 'infinitely many orientations' is the Debye limit of this aggregate, we can write:

$$\lim_{P \rightarrow \infty} \frac{\sum_{p=1}^P I_p(\vec{q})}{P} = \langle I(\vec{q}) \rangle_{Debye} \quad (6.5)$$

But numerical algorithms can handle only a finite number of orientations or particles and therefore, there will always be a finite discrepancy between the Debye limit of the average diffracted intensity and the predictions of the discrete summation algorithms. Secondly, in Debye's original derivation, the double integrals generate all possible orientations for each $\vec{r}_{mn}$ separately and therefore, all interatomic spacing vectors are guaranteed to converge to their ultimate limit individually. This means that the diffracting 'unit' that is allowed to take all orientations randomly in space is a pair of atoms. In the summation based method (Eq. 6.4) the rotation operation is defined once for each particle and not for each interatomic

spacing vector inside the particle¹. The two methods, namely Eqs. 6.3 and 6.4, would, then, be equivalent only if the distribution of the atoms inside each particle is random, satisfying 'the amorphous body approximation', and the irradiated particle population is infinite, $P \rightarrow \infty$ so that averaging over particle orientation vectors guarantees convergence to individual ultimate limits for all $\vec{r}_{mn}$, as well.

The fact that crystalline particle aggregates do not satisfy the amorphous body assumption poses a great challenge. For these systems, '*any arrow rigidly connected with the atom will not assume all directions in space with equal frequency*', unlike Debye's original derivation. In crystalline particles, the positions of atoms are periodic, and therefore the interatomic spacing vectors take certain orientations with higher probability than others. Hence the statistical convergence rates of amorphous and crystalline particle aggregates must be different due to the initial bias in the orientation distributions of the interatomic spacing vectors within crystalline particles. Equivalently, for a fixed number (P) of particles in an ensemble, higher deviations from the Debye limit must be expected if the particles are crystalline than amorphous.

Furthermore, the Debye equation yields the diffracted intensities at each momentum transfer vector in the form of an average over the whole 3D space (a.k.a spherical average) and therefore, it does not impose an experimental geometry for collecting the diffraction spectra. This is a problem since there is no scanning mode available for 1 dimensional detectors that yields the intensities directly in such spherically averaged form, as most common scan types are linear scans, e.g. $\theta/2\theta$ scan. However, 2 dimensional flat detectors are able to overcome this challenge by collecting the diffracted intensities in the vicinity of the momentum transfer vector in 2 dimensions. By appropriate processing and reduction of these image data, one dimensional spectra can be obtained, which would, then, be comparable with the Debye-predicted spherically averaged diffraction intensities.

Finally, developing a metric for quantifying the deviation of the average diffraction spectra obtained by the discrete summation approach for a finite particle ensemble from

¹This is because in a random particle ensemble, what is randomly distributed is not necessarily the pool of all individual interatomic spacing vectors contained, but rather the orientation vectors attached to each particle.

its respective Debye-predicted spectra is not a trivial process. Ideally, the metric should be unbiased over the diffraction angles or the nominal value of the diffracted intensities and should allow for fair comparison between intensity data obtained from different particle ensembles irradiated at different conditions. Currently, there is some literature [6] reporting possible forms of such metrics, however there is no systematic study investigating the capabilities and shortcomings of these metrics.

In the following section, we will explain in detail how we generate the average diffraction spectra from crystalline and amorphous particle ensembles by the Debye equation and by the kinematic summation approach. The data generated by the discrete summation approach will, then, be processed and compared with the predictions of the Debye equation, and statistical convergence behavior of the discrete formulation will be investigated.

6.4 Modeling and Simulation Procedures for the Diffracted Intensities from Powder Ensembles

6.4.1 Creating the Particle Ensembles

Figure 6.2 illustrates individual amorphous and crystalline particles (a and c) along with the ensembles consisting of these particles (b and d). For both the amorphous and the crystalline cases, the powder ensembles were created from identical particles which differed only in their orientation with respect to $\vec{k}_i$. The shapes of the particles were chosen to be ideal spheres and any type of surface relaxation was disregarded. The crystalline particles were generated first by stacking unit cells inside a cube assuming gold FCC lattice structure with lattice parameter 4.08 Å and then by carving out spheres from these cubes; hence as the particle diameter decreased, the spherical shape looked more like a plus (+) sign. The amorphous gold particles, on the other hand, were generated by randomly distributing points inside the volume of a unit sphere and then stretching the diameter of this sphere by an appropriate amount such that the minimum inter-point distance was no less than 2.885 Å for all pairs of points. This distance was chosen since it is the shortest interatomic distance within the FCC lattice that is observed along [110] direction of the unit cell. Since FCC is the lattice type with the highest packing density, any two gold atoms in a crystalline

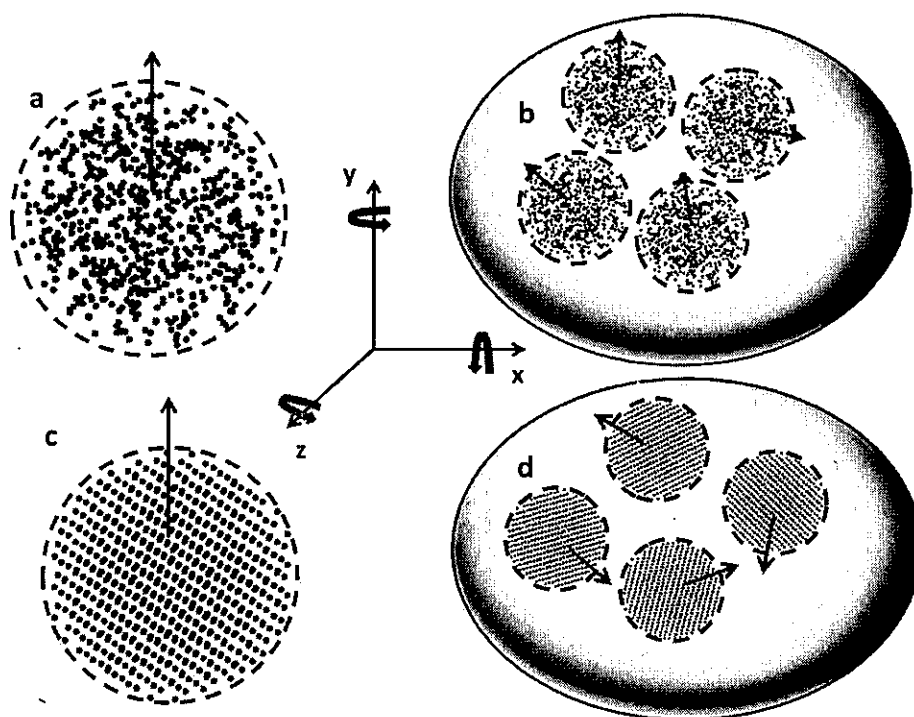


Figure 6.2: a) Isolated, spherical amorphous and c) crystalline nanoparticles. Each particle has an orientation vector that is initially parallel to the local y-axis of the particle and contains 736 atoms. b) Ideal powder ensembles containing four amorphous and d) four crystalline particles. The powder ensembles are generated by randomizing the orientation of a single nanoparticle by three rotation operations around the Euler axes of the particle. (see Appendix for details)

system cannot be closer to each other than this value [13].

The monodispersed ensembles for the crystalline and the amorphous particles were created in the same way: Initially the individual particles were assigned an orientation vector that was parallel to the y-axis ([010]) of their local coordinate system, as shown in Figure 6.2. Next, a randomization algorithm from literature [37] was adapted to our computation to form compound Eulerian rotation matrices that took care of x,y and z rotations of the orientation vector. Since the rotation operation did not impose any deformation on the particles, the relative orientation of all atoms inside the particle with respect to each

other was fixed; and the new coordinates of all atoms after the randomization could be obtained by applying the rotation matrix on the initial coordinates. There is one point to emphasize in this procedure: In Debye's original derivation, the $\vec{r}_{mn}$ vector was uniformly randomized by two angular rotations which were represented by two integrals over θ and ϕ angles. Implementing a similar procedure to randomize the orientation of a rigid body resulted in partial coverage of all possible orientations on the surface of the reference sphere [37]. Hence for our cases, the compound rotation matrices that were generated consisted of single rotation matrices around each of the three Euler axes of the particles.

6.4.2 Computation of the Diffraction Profiles

Once the atomic coordinates and the orientation distributions of the particles were generated based on the procedure described above, the average intensity spectra were computed by two methods, namely the Debye equation and Eq. 6.4. Throughout the analysis, only the coherent scattering intensity was considered and all incoherent and inelastic scattering components, absorption effects and unwanted background were neglected. Similarly, the positions of the atoms after the randomization operation were fixed, corresponding to a 0 Kelvin configuration of the particle systems and therefore, the Debye-Waller correction was neglected in the intensity computations.

Evaluation of the Debye Equation

As Eq.6.3 suggests, the computation of the Debye equation is trivial and requires only the magnitudes of the momentum transfer vectors $|\vec{q}|$ as input, in addition to the atomic coordinates. From the Ewald sphere construction introduced in Chapter 2, the magnitude of $\vec{q}$ can be related to half the scattering angle and the irradiation wavelength λ by $|\vec{q}| = \frac{2 \sin \theta}{\lambda}$. For our calculations, λ was chosen to be 1 Å and the scattering angles were equi-spaced in the interval $(0 < 2\theta \leq 53.13^\circ)$ (The reason why we chose this angular range will become clear in the next section.). For fair comparison of the average intensities, the diffraction spectra were computed at the same scattering angles (2θ) for both the Debye equation and the discrete summation method (Eqs. 6.3 and 6.4).

The evaluation of the Debye equation is computationally very expensive, albeit trivial,

even for monodispersed ensembles of monoatomic systems, since the number of terms to evaluate in the double sum scales quadratically with the number of atoms in a single particle. This issue has been discussed previously and there exist a number of articles suggesting possible ways to increase the computational efficiency for evaluation of the Debye equation. Some of these articles suggest a binning of the interatomic spacing vectors inside particles [24; 58] to speed up the calculations. This might be an acceptable solution if one does not need absolute accuracies in the calculated intensities from the Debye equation, since binning always introduces some systematic error into the intensities. Moreover, binning of the interatomic spacing vectors can be more demanding than expected when simulations are performed with particles consisting of polyatomic repeating units: in that case, those interatomic spacing vectors connecting like atoms and unlike atoms need to be differentiated since they need to be weighted by different scattering powers due to the differences in the atomic scattering factors ($f_1 f_2 \neq f_1^2$). Likewise for polydispersed ensembles, the Debye equation needs to be evaluated for a distribution of particle sizes, as discussed by Beyerlein *et al.* [6]. In our case, obtaining the Debye-predicted intensities accurately was crucial, therefore we did not resort to such approximations to ease the computations but instead we limited our analysis to monodispersed, spherical particle ensembles of gold crystallites with diameter below 10 nm².

Discrete Summation

Computation of the average diffracted intensities by the discrete summation method is relatively complicated in comparison with the Debye equation approach. For this case, the atomic coordinates from all particles were inserted into Eq. 6.4 and the respective diffracted intensities were computed from the ensembles at each $\vec{q}$ of interest. However, here we need to input not just the magnitudes but the individual components of the momentum transfer vectors into the equation, hence we used the geometry shown in Figure 6.3 to generate them. As seen, the incoming X-ray beam direction was set to +z direction in the laboratory coordinate system and each individual pixel on the 2D detector was associated

²The total number of different interatomic spacing vectors for 8.2 nm diameter crystalline gold nanoparticles was $\approx 1.4 \times 10^8$

with a diffracted wavevector $\vec{k}_d$, the coordinates of which were computed from the real space coordinates of the pixels on the flat detector. Assuming the distance between the diffracting crystallite and the center point of the detector (positioned at $[0, 0, L_{SD}]$) in the direction of $\vec{k}_i$ was L_{SD} and all pixels were periodically distributed identical squares of side length l_{pix} , the coordinates of the unit vector in the direction of $\vec{k}_d$ at a given pixel (t, j) became:

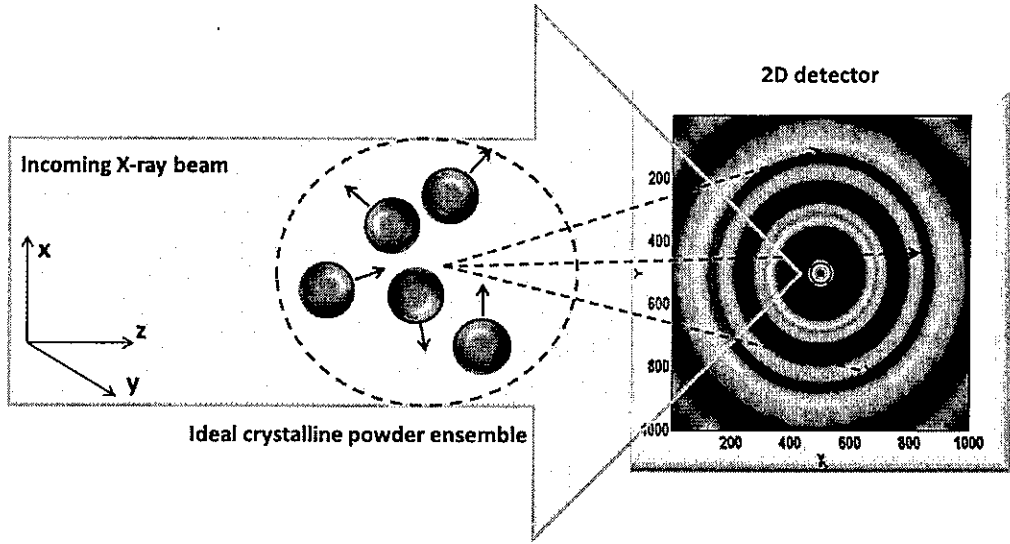


Figure 6.3: The schematic of the diffraction setup used in the simulations. Here, the incoming X-ray beam is directed towards the center of the 2D detector area, passes through the particles positioned at the origin and reaches to the detector. The detector center is positioned at $[0, 0, L_{SD}]$. The diffracted beams from all crystallites are collected by the 2D detector and as the number of irradiated crystallites increases, the Debye rings start to emerge. The 2D diffraction pattern shown on the detector area belongs to the simulated profile of an ideal powder ensemble of 10^4 spherical, gold particles, each with 2.86 nm diameter and irradiated by 1 Å X-ray beams. The coordinate axes designate the row and column numbers of the pixels.

$$\hat{k}_d^{t,j} = \frac{j l_{pix} \hat{x}}{\sqrt{L_{SD}^2 + (j l_{pix})^2 + (t l_{pix})^2}} + \frac{t l_{pix} \hat{y}}{\sqrt{L_{SD}^2 + (j l_{pix})^2 + (t l_{pix})^2}} + \frac{L_{SD} \hat{z}}{\sqrt{L_{SD}^2 + (j l_{pix})^2 + (t l_{pix})^2}} \quad (6.6a)$$

where j and t were the column and row numbers of the pixels respectively and, $\hat{x}$, $\hat{y}$ and $\hat{z}$ were the unit vectors in the direction of the coordinate axes as shown in Figure 6.3. From the definition of the momentum transfer vector, $\vec{q} = \vec{k}_d - \vec{k}_i$

$$\vec{q}^{t,j} = \frac{1}{\lambda} \hat{k}_d^{t,j} - \frac{1}{\lambda} \hat{z} \quad (6.6b)$$

Evaluating Eqs. 6.6 at each pixel position, the coordinates of all momentum transfer vectors were obtained for the whole area of the flat detector. As the equations imply, this procedure results in projecting a spherical surface patch onto a flat detector area. Therefore, the detector can be thought as a curved detector free of distortions in the diffracted intensities, which would, if the curvature was not properly treated, result from the extended paths taken by the diffracted X-rays captured by the pixels that are far from the center.

Once the coordinates of the atoms and the momentum transfer vectors were generated, the intensities from individual particles were calculated and added incoherently for the summation based method (Eq. 6.4), since each particle's orientation was independent from the remaining particles in the ensemble. This methodology, as well as the Debye equation, excluded the potential complications resulting from packing of the particles within the ensemble. Although Figure 6.2 depicts all particles together and inside a spherical volume that we call 'an ensemble', no coherency from packing of the particles is intended; the particles were illuminated one at a time for the simulations.

Following the calculation of the intensities, the 2D powder patterns were reduced to 1D spectra in order to compare the predictions of the Debye equation with the summation based method. This was achieved by azimuthally integrating the 2D patterns [27]. As illustrated in Figure 6.4, by azimuthal integration or caking, the diffracted intensities recorded by the detector pixels that were a constant radial distance away from the detector center were grouped together and summed up. Then this total diffracted intensity was normalized by the number of contributing pixels and was assigned to the corresponding radial distance. So in essence, a radial averaging of the diffracted intensities was accomplished for each diffraction angle. For the 2D powder diffraction geometry shown in Figure 6.3, the radial distance from the detector center was converted to the scattering angle 2θ by:

$$\tan 2\theta = \frac{r}{L_{SD}} \quad (6.7)$$

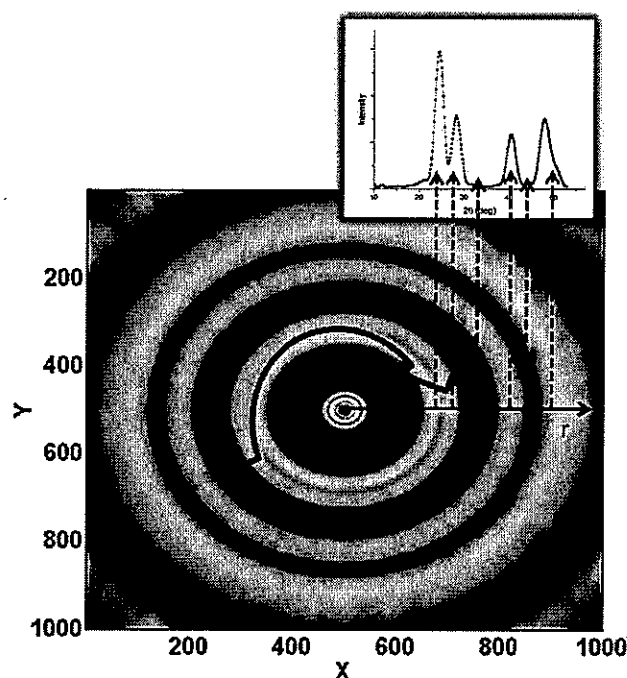


Figure 6.4: Azimuthal integration or caking process to reduce the 2D diffraction patterns to 1D spectra. The 2D data are presented in log scale whereas the reduced diffraction spectrum on top is plotted in linear scale. The intensity maximum at the center of the 2D pattern is usually filtered out by a beam stop and excluded from the measurements to protect the detector from radiation damage resulting from high intensity diffracted X-rays. Correspondingly, the reduced spectrum does not show the small angle range of the diffracted data.

where r and 2θ denoted the radial distance and the angle between the incoming and the diffracted beams, respectively.

6.5 Reaching the Debye Limit for Amorphous and Crystalline Particle Ensembles

In this part, the diffraction spectra computed by the Debye equation and by discrete summation approach (Eq.6.4) are compared. As the first case, we investigated the convergence

rates to the Debye limit for two powder ensembles consisting of 1000 particles where each particle had 736 atoms. In one ensemble, the atoms inside the particle volume were distributed randomly, and in the second one they were stacked within FCC unit cells, generating an amorphous and a crystalline particle ensemble, respectively. For the discrete summation, we collected the diffraction data on a 2D detector with dimensions of 0.4 m by 0.4 m, where 130321 pixels (361 pixels on each side) were distributed uniformly over the whole area.

Figure 6.5 presents the average intensities computed by the reduced 2D data from the discrete summation method and the Debye equation for amorphous (a) and crystalline (b) particle ensembles, as well as the percent absolute difference (c), $100 \times \frac{|I_D - I_{KS}|}{I_D}$, between the two spectra for both ensembles. First of all, the average diffraction spectra shown in Figure 6.5 are quite different for the two ensembles. For the amorphous powder, there are no intensity peaks except for the zeroth order peak ($2\theta \cong 0^\circ$) whereas for the crystalline powder, we observe broad, overlapping but distinguishable peaks. This is due to the fact that the random orientation of the atoms in the amorphous powder does not allow for constructive interference, unlike the crystalline powder. In the latter, the periodic stacking of the atoms enhances the coherent scattering intensity of the diffracted X-ray beams. As a result, the average intensities from the crystalline particles are orders of magnitude greater than those from the amorphous particles at the same scattering angles. Nonetheless, complete destructive interference is not observed even for the crystalline particle ensemble due to the small particle size and the presence of only a few coherently scattering atomic layers in the individual particles (There are only 7 atomic layers inside a 2.86 nm diameter spherical particle.).

The difference analysis shown in part (c) of Figure 6.5 suggests that the deviation from the Debye limit is highest in the small angle range, $2\theta \leq 20^\circ$, and stays below $\approx 10\%$ of the Debye predicted intensities beyond scattering angles of $2\theta = 20^\circ$ for both ensembles. However, there is almost an order of magnitude greater deviation from the Debye limit at the wide angle range ($2\theta > 20^\circ$), when the powder ensemble consists of crystalline particles than amorphous particles, even though both ensembles contain the same number of particles and all particles have the same number of atoms. For these two ensembles, the

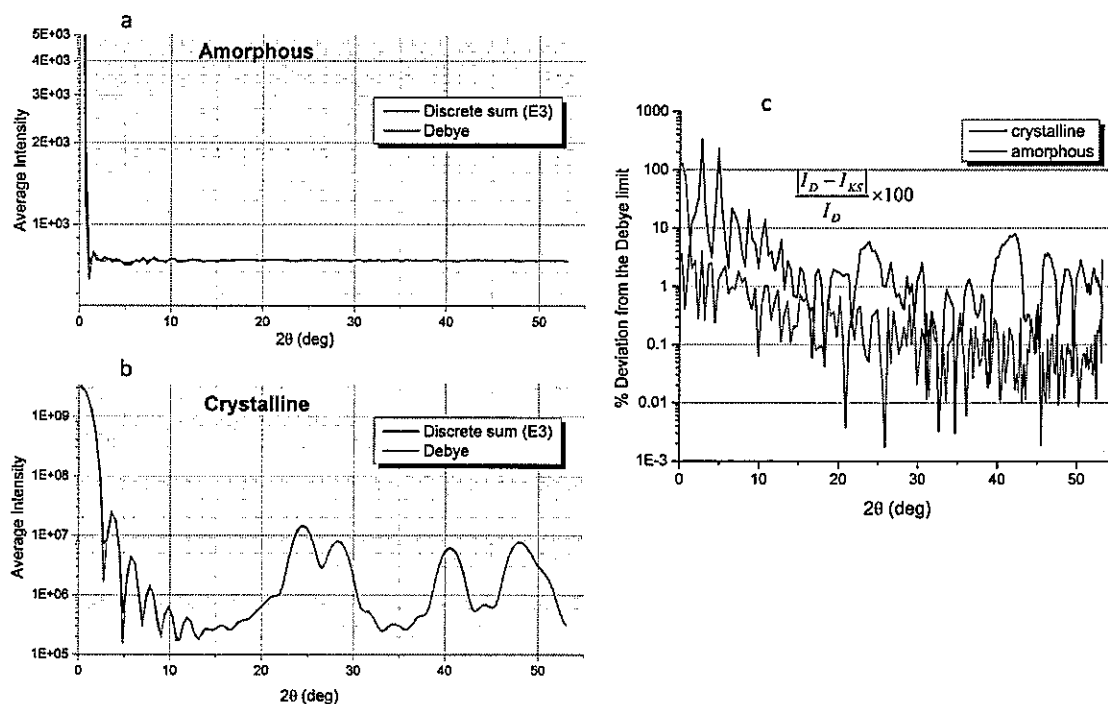


Figure 6.5: a) Average diffraction spectra computed by the Debye equation and by the discrete summation method for an amorphous gold powder sample. b) Same spectra computed for a crystalline gold particle ensemble. c) Absolute value of the percent difference, $100 \times \frac{|I_D - I_{KS}|}{I_D}$, between the intensity profiles calculated by the Debye equation and by Eq. 6.4. The profiles belong to powder ensembles of 1000 particles where each particle has 736 atoms that are distributed randomly (for the amorphous particle ensemble) or periodically (for the crystalline particle ensemble). The particle diameters are 2.86 nm and 24.58 nm for the crystalline and the amorphous particles, respectively. ($\lambda = 1 \text{ \AA}$)

only difference is the orientation distribution of the interatomic spacing vectors within each particle due to the different configurations of the atoms inside. Hence, this analysis confirms that not only does finite orientation sampling in particle ensembles with finite populations cause deviation from the Debye-predicted intensities, but also this deviation is greater in the crystalline particle ensembles due to the periodicity of the atoms within each particle.

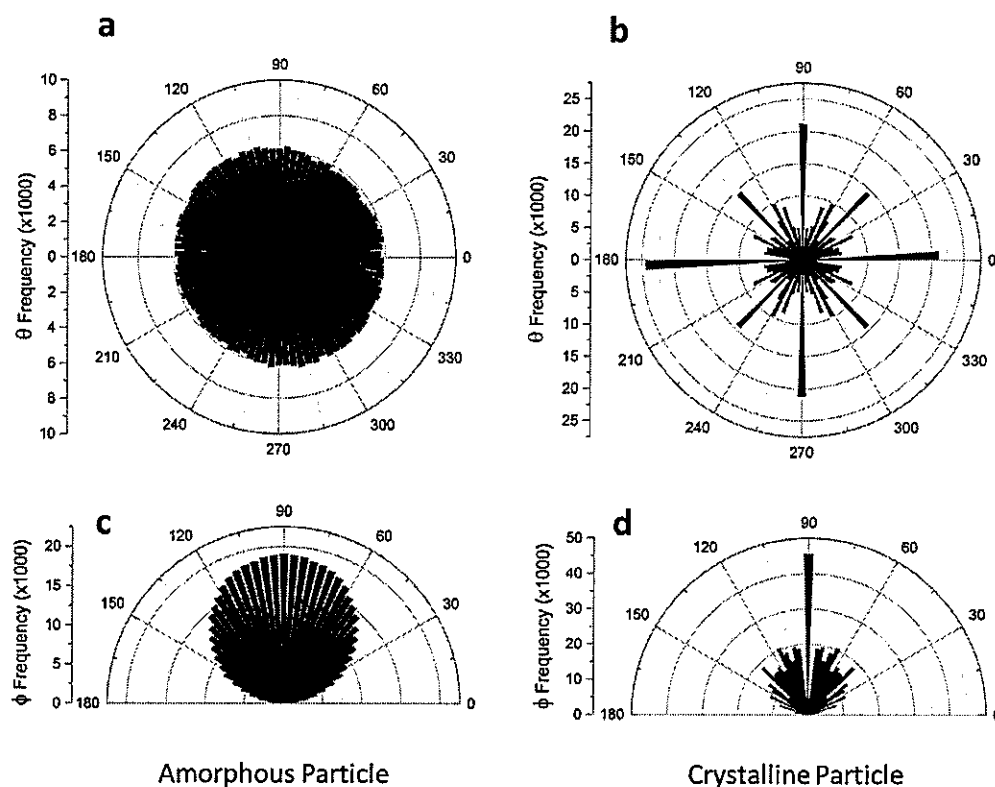


Figure 6.6: The orientation histograms (θ and ϕ angles) of all different interatomic spacing vectors within a single, spherical, amorphous (a, c) and crystalline (b, d) particle including 736 atoms. The angles θ and ϕ refer to the same angles shown in Figure 6.1.

To investigate how the atomic configuration within a particle modifies the convergence rate of the average diffraction spectrum to the Debye limit, we extracted the orientation angles of the interatomic spacing vectors within a single crystalline and an amorphous particle. Figure 6.6 illustrates the orientation histograms of all interatomic spacing vectors inside these particles including 736 atoms. The data presented in the sub-figures were generated by converting the Cartesian coordinates of $\frac{736 \times 735}{2} = 270480$ different $\vec{r}_{mn}$ vectors to spherical coordinates. As seen, the periodic stacking of the atoms in the crystalline particle imposes certain orientations of the $\vec{r}_{mn}$ vector to be better represented than others, introducing bias into the initial orientation distribution of the $\vec{r}_{mn}$ vector pool. This condition

is not compliant with the assumption used in the derivation of the Debye equation; since the likelihood of the $\vec{r}_{mn}$ vector to take any random orientation in space is non-uniform, unlike the (assumed) amorphous body. In the amorphous particle case, on the other hand, all orientation angles θ and ϕ are represented uniformly. For this system, similar amount of convergence to the Debye limit is achieved with ensembles including far fewer number of particles than crystalline particle ensembles.

These results emphasize that ordering of the atoms or the degree of crystallinity within the constituent particles in a powder ensemble must be properly treated when comparing the convergence rates of the average diffracted intensities to the Debye limit with respect to the ensemble size for different powder ensembles. Since an ideal crystalline and an ideal amorphous particle represent the two extremities of configuration of atoms inside a particle, the results presented here set the upper and lower limits of the deviation from the Debye equation due to finite particle sampling for any powder ensemble including 1000 particles, each containing 736 atoms and irradiated by X-rays of 1 Å wavelength.

6.5.1 Particle Size Dependency of the Deviation from the Debye Limit for Crystalline Particle Ensembles

In the last section, we discussed the effect of particle crystallinity in reaching the Debye limit for the average diffracted intensities computed by the discrete summation method. Here, we investigate whether adding more atoms to the constituent crystalline particles, thereby increasing the number of interatomic spacing vectors, modifies the orientation distribution of $\vec{r}_{mn}$ and improves the convergence of the average diffracted intensities to the Debye limit. To examine this problem, we computed the powder diffraction patterns on a 2D detector from monodispersed, spherical, nanocrystalline particle ensembles that differed only in particle diameter. The side length of the detector was set to 0.4 m and it was placed 0.15 m away from the irradiated particles. The reduced diffraction spectra had 181 datapoints and the scans covered an angular range up to $2\theta_{max} = 53.13^\circ$. Three ensemble sizes ($10^3, 10^4, 10^5$) were tested with 5 particle diameters, 2.86, 4.08, 4.90, 6.12, 8.16 nm. Due to extremely long computation times on desktop systems, the data presented here were collected at the High Performance Computing Center at Brookhaven National Laboratory with a remote access

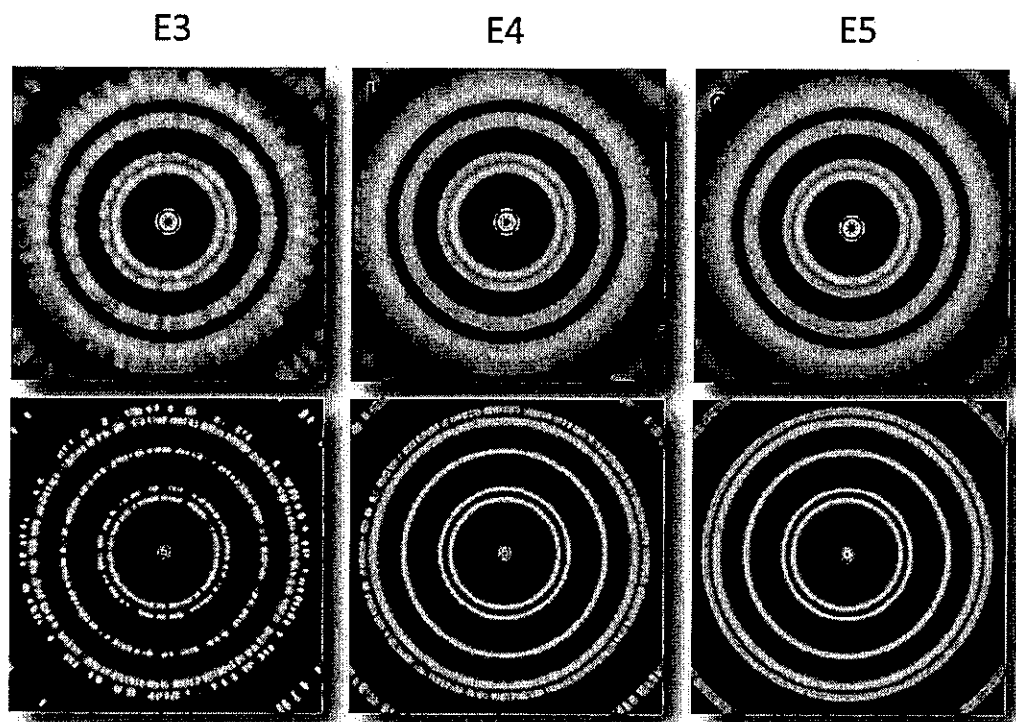


Figure 6.7: 2D Powder diffraction patterns computed by the discrete summation method assuming the irradiated ensembles contain a-d) 10^3 , b-e) 10^4 , c-f) 10^5 spherical, gold crystallites with 2.86 nm (a,b,c) and 8.16 nm (d,e,f) diameter. The irradiation wavelength is 1 Å. All patterns are normalized by the number of particles in the ensembles to emphasize the concentration of diffracted energy on the Debye rings and all data are presented in logarithmic scale (base 10). The central spots show the zeroth order intensity peak. (min: blue, max: red)

account. (The original codes were modified to enable parallel computing on the clusters with the help of BNL staff, Dave Stampf and Nicholas D'imperio.)

The 2D diffraction patterns computed as explained are shown in Figure 6.7 for the crystalline particle ensembles with the minimum (2.86 nm) and the maximum (8.16 nm) diameters for three ensemble populations, namely 10^3 , 10^4 and 10^5 particles. As seen, increasing the ensemble population causes the spottiness in the patterns to disappear for

both particle sizes. However, the decrease in spottiness is not uniform over the 2D pattern: it takes more particles for the outer Debye rings to smoothen completely, as these have the largest radii and the thickest width among other Debye rings, due to increasing Scherrer broadening with increasing diffraction angle. Thus, the diffracted spots are distributed over a larger area for higher angle Debye rings. Comparing the spottiness of the patterns for the two particle sizes at fixed ensemble populations, we observe that the patterns corresponding to the smaller particle are smoother than those of the larger particles. This is consistent with the smaller probability of diffraction for larger particles, since the particle acceptance angle decreases with increasing size as predicted by the Scherrer equation.

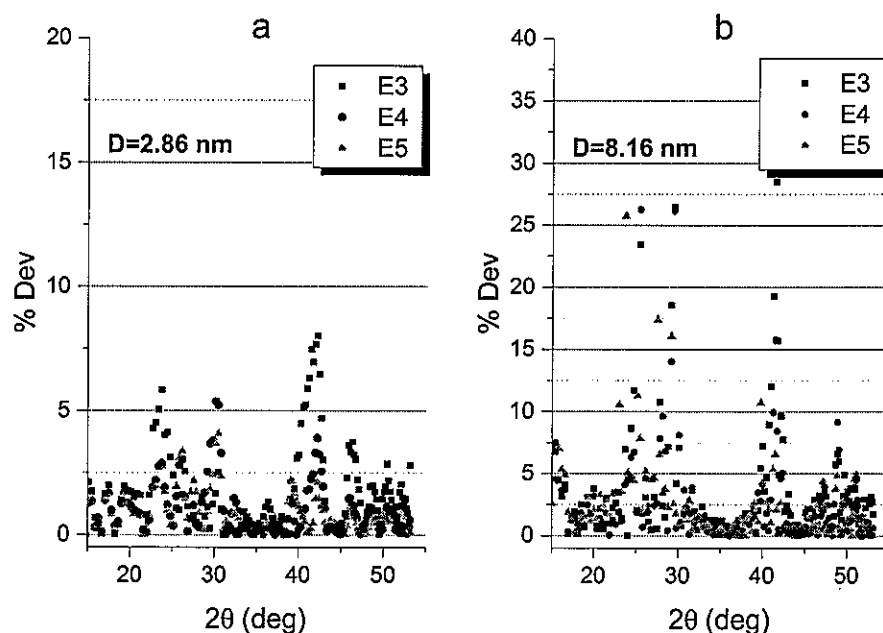


Figure 6.8: Percent deviation from the Debye limit for a) 2.86 nm and b) 8.16 nm diameter particle ensembles. Each color represents the data corresponding to a separate ensemble population. Note that the limits of the vertical axes are different.

Once all the 2D patterns were azimuthally integrated to 1D spectra and all Debye predicted intensities were calculated, the percent deviation from the Debye limit were computed for all particle sizes and ensemble populations. The results from this computation for the

powder ensembles with the limiting particle sizes are presented in Figure 6.8 over the whole angular range considered.

According to Figure 6.8, the deviation from the Debye limit is greater for the average intensities from the powder ensemble consisting of 8.16 nm gold crystallites than 2.86 nm crystallites for all scattering angles considered, $15^\circ \leq 2\theta \leq 55^\circ$. For both particle sizes, increasing the ensemble population from 10^3 particles to 10^5 results in better convergence to the Debye limit. Looking at the change in the percent deviations with respect to the angular range, we observe that the positions of the greatest deviations coincide with the positions of the Bragg peaks: For these ensembles the Bragg angles $2\theta_B$ computed from the Bragg equation are 24.5° , 28.4° , 40.6° , 48° , 50.2° for the 111, 200, 220, 311 and 222 reflections, respectively. The first two and the last two reflections in the 2.86 nm diameter case are not as well resolved as the 8.16 nm diameter case, due to larger Scherrer broadening; therefore the spikes in the percent deviation plot are not as clear for the powder ensembles with the smaller particles. The overlapping Bragg peaks also preclude any implication of better convergence to the Debye limit for the high multiplicity reflections. However, the larger amount of spottiness observed in the respective 2D profiles seems to be counterbalanced by the azimuthal integration operation, since we do not observe increasing percent deviation from the Debye limit with increasing diffraction angle, either.

In order to see how the particle size affects the required ensemble population for the average diffraction spectra to approach the Debye limit within a particular limit, the following parameter was defined and evaluated for all ensembles and particle sizes:

$$\epsilon = \sum_{i=1}^{i=E} \left| \frac{I_D(2\theta_i) - I_{KS}(2\theta_i)}{I_D(2\theta_i)} \right| \quad (6.8)$$

In this expression, I_D is the spectrum computed by the Debye equation as before, I_{KS} is the spectrum computed by Eq.6.4 and E is the number of data points in the diffraction spectra. For this computation, we excluded the small angel range from the diffraction profiles and included 157 data points (out of 181) that covered the angular interval of $10^\circ < 2\theta < 53.13^\circ$. As seen from its form, ϵ is inherently correlated with the number of data points considered in the diffraction spectra. Therefore this form of a parameter would introduce bias into comparative studies with multiple diffraction spectra when each spectra included a different

number of data points. To avoid this, all simulations in our case were performed assuming the same flat detector. The results of this difference analysis are plotted in Figure 6.9:

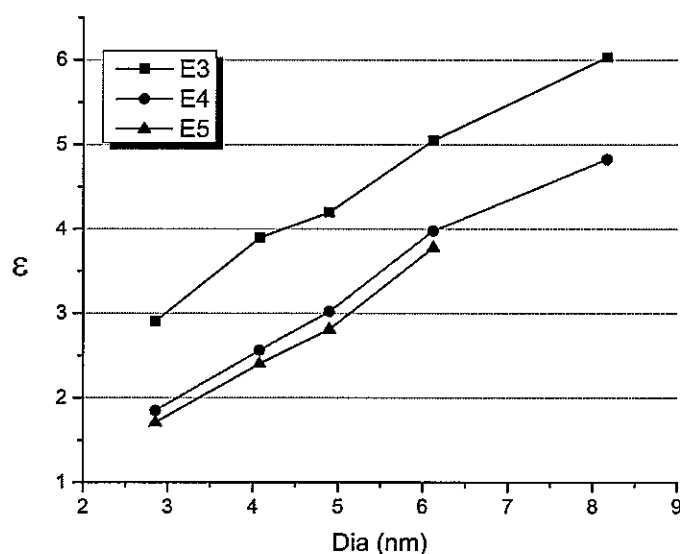


Figure 6.9: The difference parameter ϵ quantifying the deviation of the reduced diffraction spectra from the corresponding Debye limit with respect to the particle diameter for the angular interval $10^\circ \leq 2\theta \leq 53.13^\circ$ and for three ensemble sizes. All ensembles consist of monodispersed, spherical, crystalline gold particles and the irradiation wavelength is 1 Å.

As seen from Figure 6.9, the deviation from the Debye limit decreases as the ensemble population increases, for all particle sizes. This is expected and was justified also by the Lorentz based statistical analysis discussed in the previous chapters. Similarly, as the particle diameter increases, the deviation from the Debye limit increases as well at a given ensemble population. This means that expanding the interatomic spacing vector pool by adding more atoms to a crystalline particle without interrupting the crystallinity does not necessarily improve the randomness of the initial $\vec{r}_{mn}$ distribution. Although new orientations are included in the $\vec{r}_{mn}$ histograms by adding more atoms, the overall directionality in the orientation distribution of the $\vec{r}_{mn}$ pool increases, leading to further deviation from the amorphous body assumed in the Debye derivation. Consequently, more particles will be needed in the powder ensemble for a fixed convergence to the Debye limit, as the particle

size increases.

6.6 Summary and Conclusions

In this chapter, the Debye scattering equation has been rederived and rigorously tested against the average diffraction spectra calculated by the discrete summation method, where the diffracted intensities from each particle within an ideal powder ensemble are incoherently added up. The results of the systematic comparison between the analytical and discrete formulations show that the convergence of the average diffracted intensities from an ideal powder ensemble to the Debye limit depends not only on the ensemble population but also the particle crystallinity and size. For amorphous particle ensembles, convergence to the Debye predicted intensities is established with smaller ensemble populations, whereas for crystalline particle ensembles, the atomic ordering within each particle introduces bias into the intensity averaging operation, requiring far larger ensemble populations for identical convergence to the Debye limit. This bias stems from the directionality of the distributions of the interatomic spacing vectors for crystalline particles, which is incompatible with the assumption of an amorphous body in the original derivation of the Debye equation.

Although increasing the ensemble population causes the average diffracted intensities to agree better with the Debye-predicted spectra, our calculations show that adding more atoms to a crystalline particle without interrupting the atomic stacking and with keeping the ensemble size fixed, does not improve this agreement. For crystalline particle ensembles, we observe increasing deviation from the Debye limit with increasing particle diameter, which is consistent with our uncertainty analysis that was presented in Chapters 2,3 and 4. However, one must be careful when comparing the findings from our former uncertainty analysis with the Debye based intensity analysis, as there are critical differences between the two: Firstly, in the former analysis, the intensity spectra were generated directly from the pole and particle distributions; therefore, the intensity data could be easily traced back to the pole and particle populations. Since the Debye equation is a function of a pool of interatomic spacing vectors and lacks the concept of a particle, it is not trivial to relate any type of sampling statistics, pole or particle, quantitatively to the deviation from the Debye limit.

Additionally, when working directly with diffracted intensities from nanocrystalline particle ensembles, one cannot avoid the problem of overlapping peaks. Especially for very small crystallites, this effect exacerbates the problem of isolating individual reflections and linking their sampling statistics to the convergence to the Debye limit. This issue of overlapping peaks was suppressed in our previous analyses, as each intensity profile was generated from a single Patterson function. However, the Debye equation generates such features automatically in the analytical diffraction spectra. Finally, for realistic flat detectors, the intensity data suffer from curvature related distortions at the pixels that are far from the center of the detector. Hence, additional corrections must be applied on the 2D patterns before reducing them to 1D spectra.

Based on these results, we conclude that the findings reported in most of the previous literature that rely on the Debye equation as the representative intensity spectra from nanocrystalline particle ensembles are ambiguous. The statistical convergence to the Debye limit is very sensitive to the crystal structure of the irradiated particles and the uncertainties in the experimentally obtained diffracted intensities due to particle sampling are large enough for misinterpretation and incorrect characterization of the nanoparticle ensembles.

Chapter 7

Conclusions

Summary of the Presented Work

In this thesis, we presented a detailed theoretical investigation of the statistical aspect of idealized X-ray diffraction experiments performed with monodispersed powders of crystalline particles in the nanometer size regime. To accomplish that, we separated the sampling space from the intensity space and investigated them independently, which enabled us to trace an incoming X-ray beam from the irradiated particle up to a diffracted spot on a detector. In this regard, this is the first published work that examines how the diffracted intensity profiles are generated from a collection of randomly oriented particles interacting with X-rays, and which statistical models are applicable to analyze the convergence behaviors of the sampling and intensity space parameters.

From a broader perspective, the novel investigation of the diffraction process and the accompanying statistical analyses presented in this thesis lead to the following conclusions:

- In powder diffraction experiments, in which the sample consists of nanocrystalline particles, the integrated intensities are not directly proportional to the population of particles diffracting at the specified reflections. Even if the sample is an ideal and monodispersed powder, the irradiation wavelength and the crystal geometry promote the activation of poles belonging to certain reflections more favorably than others. As a result, the relative integrated intensities at various reflections from an untextured

nanocrystalline powder will be different than those from an untextured bulk powder, under identical experimental conditions.

- For a fixed particle size and wavelength, the activated pole populations and the integrated intensities at different reflections are directly proportional to the irradiated particle population and the multiplicity of the reflections. Such a proportionality is not present for the case of diffracting particle populations in the nanometer size regime.
- If the irradiated powder ensemble consists of crystalline particles having characteristic rocking curves which are non-uniform over the extent of the intensity peak (such as Patterson or Gaussian functions), the uncertainties in the integrated intensities will always be greater than the uncertainties in the population of diffracting particles contributing to that reflection. However, this dependency of the rocking curves on the diffraction angles can be suppressed if the particle size is large enough so that the total (relevant) extent (4β) of the intensity profile is recorded by a single pixel. This means that the classical statistical analysis proposed by Alexander, Klug and Kummer in 1948 is applicable only to the special case of diffraction experiments where the irradiated ensembles consist of 'bulk particles' ($4\beta_{hkl} < \Delta d$, where Δd is the acceptance angle of the detector pixel) and the one-grain one pole assumption holds.
- The uncertainties in the intensity space and sampling space estimated in this thesis are computed under the assumptions of ideal experimental setups, perfectly random and monodispersed powder samples and diffracted intensities that are purely in the kinematic regime with no contribution from incoherent and inelastic scattering modes. As a result, the numerical estimates for the uncertainties in integrated intensities and diffracting particle populations reported throughout this thesis establish the limits of ultimate accuracy one can achieve. In other words, it is not possible to collect diffraction data from nanocrystalline powders in a diffraction experiment with better precision than the limits reported here.
- Finally, the venerable Debye scattering equation that has been (and is currently be-

ing) used by numerous research groups to model the analytical diffraction spectra from nanoparticle ensembles, generates ideal diffraction signature with no uncertainty and therefore, does not accommodate for the statistical nature of the powder diffraction experiments. Hence, in most cases, the statistical uncertainties in the experimentally obtained intensity profiles from even the fully controlled, ideal and monodispersed particle ensembles may prevent these data from perfectly matching with the predictions of the Debye model. The convergence rates of the true diffraction spectra from nanoparticle ensembles to their Debye predicted profiles depend on the crystallinity of the particles, as well as the particle size and ensemble population. However, estimating the population of particles to be irradiated, in order to attain a particular uncertainty in the diffracted intensities is extremely difficult by analytical means, since the concept of particle is non-existent in the formulation of the Debye equation.

Extension of the Present Analysis to Realistic Applications

In order to focus our attention on the interaction between the powder sample and the incoming X-ray beam, we eliminated a great deal of complicating factors that are part of all realistic experimental setups. These factors can be divided into three groups, related to 1) **the experimental parameters**, such as the irradiation wavelength and the capabilities of the measurement equipment, 2) **the sample properties**, such as the presence of texture in the distribution of the particles, imperfections within the material and contributions from incoherent modes of interaction of the powder sample with the incoming X-ray beam and 3) **the treatment of the diffraction theory**. The outcome of introducing each of these factors into our analysis would be a substantial increase in the uncertainty budget on both the intensity space and the sampling space.

Experimental Parameters

First of all, our analysis is based on irradiation by X-ray beams that are purely planar, monochromatic and collimated. These types of beams are, in reality, impossible to achieve and there is always a finite amount of deviation from these ideal conditions. For example,

in real powder diffraction experiments, the sample is contained within a closed volume and all particles making up the powder are irradiated simultaneously. In such cases, the **finite divergence angle** of the incoming X-ray beam causes each particle within the powder sample to receive the incoming X-ray beam with a wavevector that is oriented slightly differently [42], depending on the position of the particle and the particular experimental geometry. This divergence, by contributing to the particle acceptance angle, would both increase the population of diffracting particles, and enhance the diffracted signal.

A similar effect is expected when the less than ideal efficiencies of the monochromators in the current synchrotron facilities are taken into consideration for the statistical formulations presented. In this case, a **range of wavelengths** needs to be included in the incoming X-ray beam, which results in a larger portion of the particles in the powder to participate in diffraction. However, unlike the previous case, here the enhancement in the selected particle populations would be due to the increased particle selection by the individual X-ray beams having slightly different wavelengths. Hence, the diffracted signals from these sub-population of particles selected by a different wavelength would not be coherent with each other and would contribute to the unwanted background intensity.

The downside of both the beam divergence and the polychromatic irradiation is the broken one-to-one correspondence that was established between the populations of diffracting particles, activated poles and the resulting intensities in the presented analysis. As a result, the formulations proposed to estimate the lower limits of the uncertainties for these quantities cannot be applied directly without proper adjustments.

There are also some instrumental factors that may enhance the uncertainties in the intensity space without affecting the selection process in the sampling space. As an example, the detectors that are used to measure the diffracted intensities, inherently introduce additional uncertainties in the data. **Photon counting uncertainty** in certain types of CCD detectors, in which reliable means of quantification is unavailable [64], is one such factor that may invalidate the accuracy and applicability of the statistical analyses presented in this work. When diffracted intensities are collected with such detectors, the contribution to the total uncertainty from particle sampling cannot be isolated and therefore, cannot be related to sampling statistics. The contribution of background scattering, losses and

inefficiencies in the photon detection and counting mechanism of the detectors are further examples where the diffracted intensities suffer from increased uncertainty.

In addition, the finite pixels sizes of the detectors in real experimental setups introduce more challenges into the interpretation of the integrated intensities and increase their uncertainty budget. In our analysis, we assumed that the angular positions of the activated poles and diffracted spots were known exactly with no uncertainty, which means that the pixel size on our hypothetical detector was practically zero. When the finite size of the detector pixel is incorporated into the current analysis, the positions of the diffracted spots include a finite uncertainty, which translates to orders of magnitude variation in their respective intensity contributions, especially when the spot position is very close to the exact Bragg angle. In such cases, the contribution of the uncertainty in the integrated intensities due to the pixel positions must be quantified and subtracted, before relating the statistics of particle sampling and diffracted intensities.

Sample Properties

In order to simplify our analysis, we assumed that the irradiated sample was a monodispersed, ideal nanocrystalline powder. Therefore, the orientation distribution of the particles making up the sample was assumed to be uniform and the probability of selecting any one particle was constant, satisfying the requirements of the Binomial selection process. In reality, obtaining such fully controlled, experimental samples is extremely challenging, especially when the particle size is on the order of a few nanometers. It has been reported in literature [9; 12] that the smaller sizes of nanoparticles result in higher chemical activity especially in their surface layers, due to the presence of dangling bonds. As a result, controlling the **shapes**, **sizes** and especially **monodispersity** of powder ensembles consisting of such particles can be hard to achieve. When the monodispersity in the particle ensemble is compromised, however, the selection probability for diffraction cannot be assumed to be constant: there would be an inherent bias, inversely proportional to the particle size due to the large acceptance angles of smaller particles, favoring their selection by the X-ray beam. However, the smaller selection probability of relatively larger particles in a polydispersed ensemble can easily be surpassed by their intensity contribution, since the intensities are

quadratically dependent on the particle size. For such powder samples, our uncertainty analysis fails largely and a more case-specific formulation is required.

Another property of nanocrystalline powder samples that may require further modifications on the statistical analysis presented here is the presence of **texture** in the sample. As detailed previously, our formulation treated each particle separately, so no accommodation was made for preferred orientations or packing of the particles. If the sample under consideration is textured, then the uniform particle and pole selection probabilities are no longer valid and there may also be enhancements in the diffracted intensities due to inter-particle coherency. Such situations would result in both the integrated intensities and activated pole populations being no longer proportional to the multiplicities of the reflections, unlike untextured ideal powders irradiated by purely monochromatic, planar X-ray beams.

Treatment of the Diffraction Theory

The formulations presented throughout this thesis were based on the assumption that the scattering phenomenon was strictly in the kinematic regime. This is a reasonable approximation for the case of nanocrystalline particle ensembles. However, when applying the current formulations to the analyses of nanoparticle ensembles, which are polydispersed in size and have wide particle size distributions, proper corrections might be required to account for the possibility of dynamic interaction of the larger particles with the X-ray beam. Similar logic follows when accounting for the incoherent and inelastic components of the interaction modes between the scattering materials and X-rays. As an example, absorption of the incoming X-ray beam, as it scatters from relatively larger particles, may lead to unexpectedly intense incoherent scattering, especially when the X-ray beam energy is close to the characteristic absorption edge of the material. If the ensemble polydispersity extends to atomic species and particle shapes, the individual crystallographic structures and acceptance angles of the particular species would further complicate the counting algorithm, and when coupled with divergent beams, would eventually invalidate our analysis. In the end, these complexities cause the direct link established between the diffracted intensities and the activated poles to be broken.

The small particle sizes of nanocrystalline particles, which have been mostly to our

advantage in simplifying our formulations, also introduce some challenges in the analytical formulations of the rocking curve functions. As mentioned in Chapter 2, the Patterson functions, that were used throughout our analysis, approximate the intensity profile of an isolated particle well in the immediate vicinity of the Bragg angle. This is because these functions are constructed from a single Fourier component related to the closest lattice point in reciprocal space. For nanocrystalline particles, the individual peaks in the intensity spectra are not always well resolved and peak overlapping is commonly observed; hence, multiple Fourier components are required to reconstruct the expected profiles for such peaks. Therefore, in the angular range where strong overlapping is expected, both the particle sampling and the intensity statistics may fail, as the direct link between individual intensity profiles and their corresponding pole and grain populations is interrupted.

Future Directions and Applicability of the Presented Analysis

Even though there are strong challenges against the direct application of the statistical analysis we proposed here, the effects of these challenges can be suppressed for certain types of diffraction experiments. One such example is coherent diffraction experiments with femtosecond X-ray free electron lasers (XFEL), that are newly being developed [22]. These experiments are intended to investigate the structure of samples that are difficult to crystallize and sensitive to radiation damage by enhancing their diffraction signature through intense, coherent X-ray beams with extremely short durations ($\approx 10^{-15}$ sec). Biological samples, protein structures and functional nanocrystalline particles are a few examples that are the focus of these experiments. The purpose here is to shorten the interaction time of X-rays with the irradiated material and obtain the diffraction pattern before the material gets destroyed.

To achieve this, the samples, which are usually in colloid form, are injected into the incoming X-ray beam path continuously, and the diffraction patterns corresponding to each batch are recorded in a serial way. Hence, it is required that the particle injection and the laser pulse be synchronized in such a way that the irradiated material is cleared away from the X-ray path after the interaction. Provided that each sample batch consists of

identical amounts of material, this procedure yields a finite number of 2D snapshots of the 3D reciprocal space, which are projections of the space along various planes.

Currently, the analysis of the diffraction data collected from XFEL experiments is performed in 3 steps [22]: 1) All diffraction patterns are classified according to particle orientations and sizes, and then an average pattern is obtained for each class, in which the statistical variation is minimized, 2) 3D diffraction data are generated by sorting and serially assembling these average patterns, 3) The sizes and shapes of the irradiated particle ensembles are reconstructed by refining the analytically obtained intensity distributions against the experimental data, until sufficient convergence is established [48]. For the reconstruction step, the expected intensity for an individual particle with a particular size and shape is calculated based on the Patterson functions and averaged over all possible orientations of the particle. Next, these analytical profiles are modified by incorporating the effect of size and shape polydispersity in the irradiated ensemble. These final intensity profiles are refined against the experimental data until sufficient convergence is obtained, and the structural parameters that enable convergence are declared as the 'structural solution'. This methodology is based on the direct correspondence of the diffracting particle populations and the resulting intensities, which we showed in this thesis to be invalid for particle sizes in the nanometer range. Hence, the structural solutions obtained from the refinements include a substantial amount of uncertainty.

As an example, see Figure 7.1 where the simulated 2D diffraction patterns from a single, gold nanoparticle of 2.86 nm diameter are shown. These profiles were obtained assuming an X-ray wavelength of 1 Å, and each pattern corresponds to a different orientation of the particle. Consistent with our previous discussions, the profiles are extremely different from each other, as the number of Laue spots that we can observe vary from 0 to 6, even though the number of irradiated particles equals one for all cases. This shows that by disregarding the consequences of the characteristically large acceptance angles of nanocrystallites and the statistical variations in the diffracted intensities due to particle sampling, the structural solution one can obtain from averaging over these 4 patterns would clearly overestimate the population of diffracting particles.

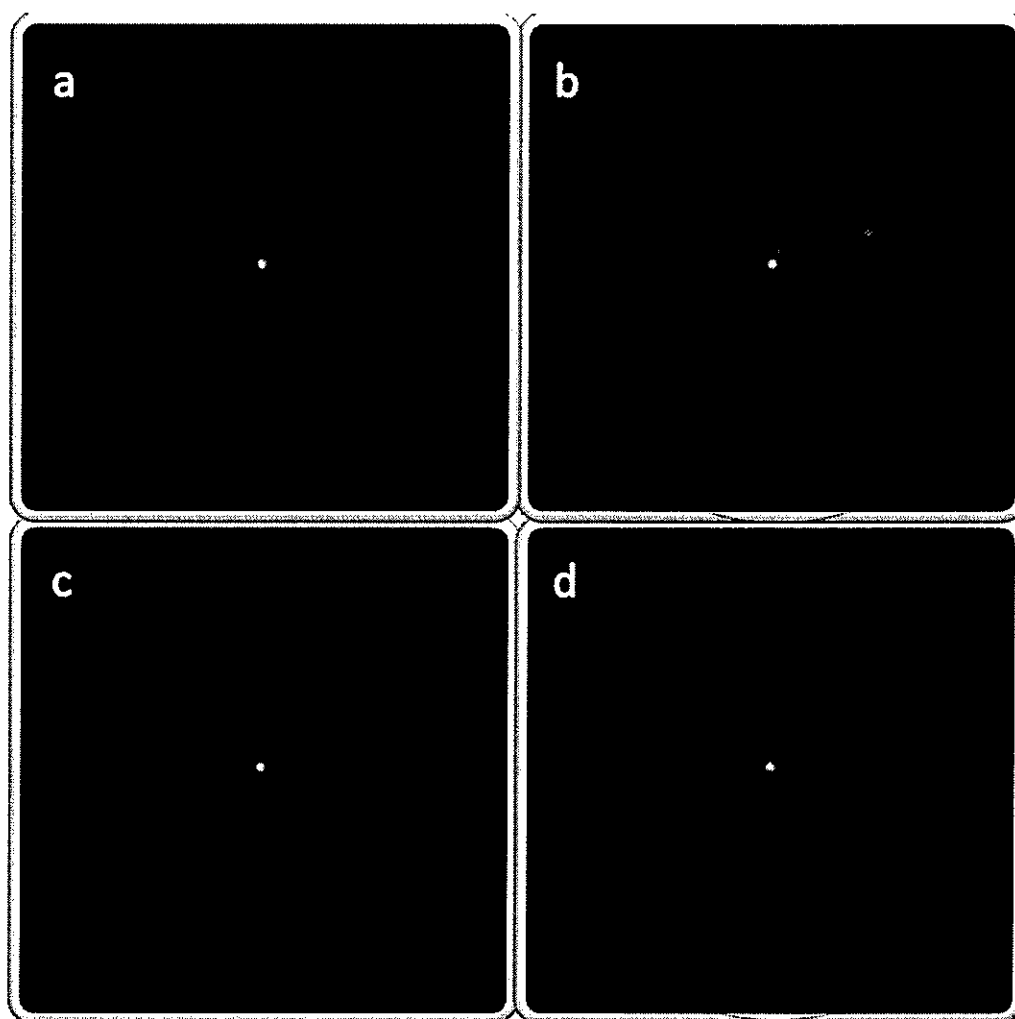


Figure 7.1: Simulated 2D diffraction profiles from a single, spherical gold crystallite with diameter 2.86 nm and irradiated by 1 Å wavelength X-rays in transmission geometry. Each pattern was obtained with an independent orientation of the particle. The central points enclosed by blue circles refer to the direct beam path and the remaining bright spots are the Laue spots belonging to the activated poles of the particle. The number of Laue spots that are diffracted from a single spherical particle is a) 0, b) 6, c) 1, d) 3. The red circles depict the expected positions of the Debye rings (Only those rings with observable Laue spots are shown).

Epilogue

Powder diffraction is a well-established characterization technique that proved its success over the last century [31]. This success is the collective outcome of invaluable contributions from numerous researchers. The current commercially available diffraction equipment is capable of almost semi-autonomous operation, automatically collecting and analyzing powder diffraction data and performing fairly complicated structural refinements with minimal operator intervention. However, the scientific and industrial advances which resulted in very successful structural characterization of bulk powder data also transformed the application of powder diffraction into a black-box standard practice. Unfortunately this transformation was accompanied by the loss of theoretical rigor by the practitioners. Few analysts know, or care, about the soundness of the error values attached to their refined parameters by the autonomous machines.

The theoretical developments presented in this thesis are intended to shed light on only a tiny part of powder diffraction: the statistical uncertainties associated with diffraction data due to particle sampling statistics. In going through the existing theory, however, we discovered many hidden-and unsuspected-complexities. We hope that our work will encourage further research into the proper application of uncertainty analysis to nanoparticle powder diffraction data, with simulations from rigorous physics based modeling and carefully performed test-case experiments.

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Appendix A

The Randomization Algorithm for Three Dimensional Rigid Bodies

The rotation matrices for the individual axes are as follows:

$$R_x(\eta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \eta & \sin \eta \\ 0 & -\sin \eta & \cos \eta \end{pmatrix}, \quad R_y(\theta) = \begin{pmatrix} \cos \theta & 0 & \sin \theta \\ 0 & 1 & 0 \\ -\sin \theta & 0 & \cos \theta \end{pmatrix}, \quad R_z(\phi) = \begin{pmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The compound rotation matrix then becomes

$$R_{x,y,z}(\eta, \theta, \phi) = R_x R_y R_z$$

$$\begin{aligned} \eta &= 2\pi \text{Rand}() - \pi \\ \theta &= \arccos(1 - 2\text{Rand}()) - \frac{\pi}{2} \\ \phi &= 2\pi \text{Rand}() - \pi \end{aligned} \tag{A.1}$$

where *Rand* signifies a random number within the interval (0, 1). For the purposes of this work, the random number generator algorithm embedded in Matlab was used.