A review of Debye Function Analysis

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The employment of the Debye function to model line profiles in the powder diffraction pattern from small crystallites is briefly reviewed. It is also demonstrated that for the case of very small spherical particles, it is necessary to average patterns from multiple constructions of the particle to have complete agreement with reciprocal space models. In doing so it is demonstrated that the technique of Debye function analysis is best suited for systems with only a few possible atomic arrangements.

Key words: nanocrystalline materials; line profile analysis; Debye function

I. INTRODUCTION

The Debye scattering function was derived in 1915 by Peter Debye in a paper showing that diffraction phenomena does not rely on a crystalline state, but also exists for molecules. Assuming an atomic arrangement is present in all orientations relative to the incident beam, the observable intensity is given by

$$I_P(s) = \frac{A(\theta)P(\theta)}{R^2} \sum_m \sum_n f_m(s) f_n^*(s) \frac{\sin(2\pi s d_{mn})}{2\pi s d_{mn}}. \tag{1}$$

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Here s is the magnitude of the scattering vector, defined as $s = 2\sin(\theta)/\lambda$, θ being the half scattering angle and λ the wavelength of incident radiation. Also, $A(\theta)$ is the absorption factor, $P(\theta)$ is the polarization factor, R is the goniometer radius, and $f_n(s)$ is the atomic scattering factor of the n-th atom. The interference of waves scattered by each atom is then expressed by the double summation, where d_{mn} is the distance between atoms m and n. The early work of Debye is the basis for understanding scattering from amorphous materials, including liquids and polymers, through the development of pair distribution function (PDF) analysis (Zernike and Prins, 1927). Nearly a century later, interest in nanotechnology, and an abundance of computing power, is leading scientists to revisit the Debye function. This has spawned another analysis method for powder diffraction data, sometimes referred to as Debye function analysis (DFA). In this approach, powder diffraction patterns are generated directly from atomistic descriptions of crystalline materials via the Debye function, and refined against measured data, to obtain detailed microstructural information.

As with any powder diffraction theory, the Debye function is found from taking the orientational average of the intensity from an atomic arrangement in a fixed orientation. However, It differs from other theories by taking this average before simplifying the expression for the intensity. While the Debye function is completely general with regard to the arrangement of atoms to which it can be applied, one downfall is that it requires a lot of computations as the particle size increases. The double sum in Eq. 1 implies that calculating the intensity via the Debye function scales as $O(N^2)$. Since the number of atoms scales with the volume, in terms of the particle radius, R, this calculation scales as $O(R^6)$!

With this incredible calculation burden, it is understandable why the Debye function was primarily used to calculate the intensity observed from small molecules until the advent of computers. Nonetheless, as early as 1941, Germer and White applied it to the study of nanocrystalline Cu films, and showed the transition of the peak shapes in a diffraction pattern from a few atoms to an appreciable crystallite size. Soon after, Berry (1952) used it to demonstrate that the powder pattern was sensitive to different particle shapes. However, it was not until the 1980s and 1990s that the Debye function began to take shape as a quantitative method of analyzing the powder intensity from small crystallites. This began with the works of Torchet on small molecular clusters (Fargas *et al.*, 1982; Torchet *et al.*, 1984) and Hall on multiply-twinned, icosahedral and decahedral nanoparticles (Hall et al., 1991). This application became even more robust as mixtures of size distributions were considered, as in the study of Gnutzmann and Vogel (1990). Advances in DFA of late have been extending the method to more material systems, like semiconductors, and modeling defects like faults and dislocations (Buljan *et al.*, 2009; Niederdraenk *et al.*, 2007; Oddershede *et al.*, 2008).

Parallel to the increasing robustness of the method, developments have been made to decrease its calculation time. The operation which takes the most time in the Debye function is calculating the sine function. Hall and Monet (1991) demonstrated that the fast Fourier transform (FFT) can be used to minimize this burden. Furthermore, the number of distances necessary to consider was shown by Cervellino *et al.* (2006) to be reduced dramatically utilizing a Gaussian binning strategy. Finally, the Debye function is ideal for parallelization, and lately the inexpensive computing power of GPUs has been shown to be extremely effective in its calculation (Gelisio *et al*., 2010).

The methods just mentioned to improve the calculation speed of the Debye function speed can be used on any arrangement of atoms. In the case of perfect crystals, the symmetry of the lattice can be used to find the multiplicities of interatomic distances without their explicit calculation. One of the first examples of this was shown for the case of a BCC lattice by Morozumi and Ritter (1953). Since then, Minami and Ino (1979) described how considering the symmetry of the lattice and the particle shape function, one can determine the appropriate multiplicities in fewer calculations. This approach extends the size limitations of the Debye function, and allows for the simulation of patterns from crystallites which are microns in size. The tradeoff is, of course, its generality -- as the method relies on the existence of a perfect crystal. Nonetheless, work on how to include defects and realistic strain fields is beginning (Thomas, 2011).

II. AVERAGE PATTERNS FROM DIFFERENT SHAPE FUNCTION OFFSETS

With the renewed interest in the Debye function, it is important to keep in perspective more traditional line profile analysis theories. The traditional description of the crystallite size and shape effect is based on intersecting a perfect atomic lattice with a volume defining a crystallite, the shape function (Patterson, 1939). This same reasoning can be used to generate particles for the Debye function calculation. At first glance this process is straightforward; one begins with an infinite lattice and uses the shape function to determine which atoms are included in the particle[1]. However, in doing so an immediate problem is faced: when the lattice is displaced with respect to the particle shape function, a different set of atoms describing the particle can be carved out. The resulting particles can have different total numbers of atoms, as well as, expose different surface structures and terminations. Two examples of such particles are shown in Figure 1. Furthermore, the powder patterns from these two particles are not exactly the same, as also depicted in Figure 1. So, the question becomes, “Which description is correct?”

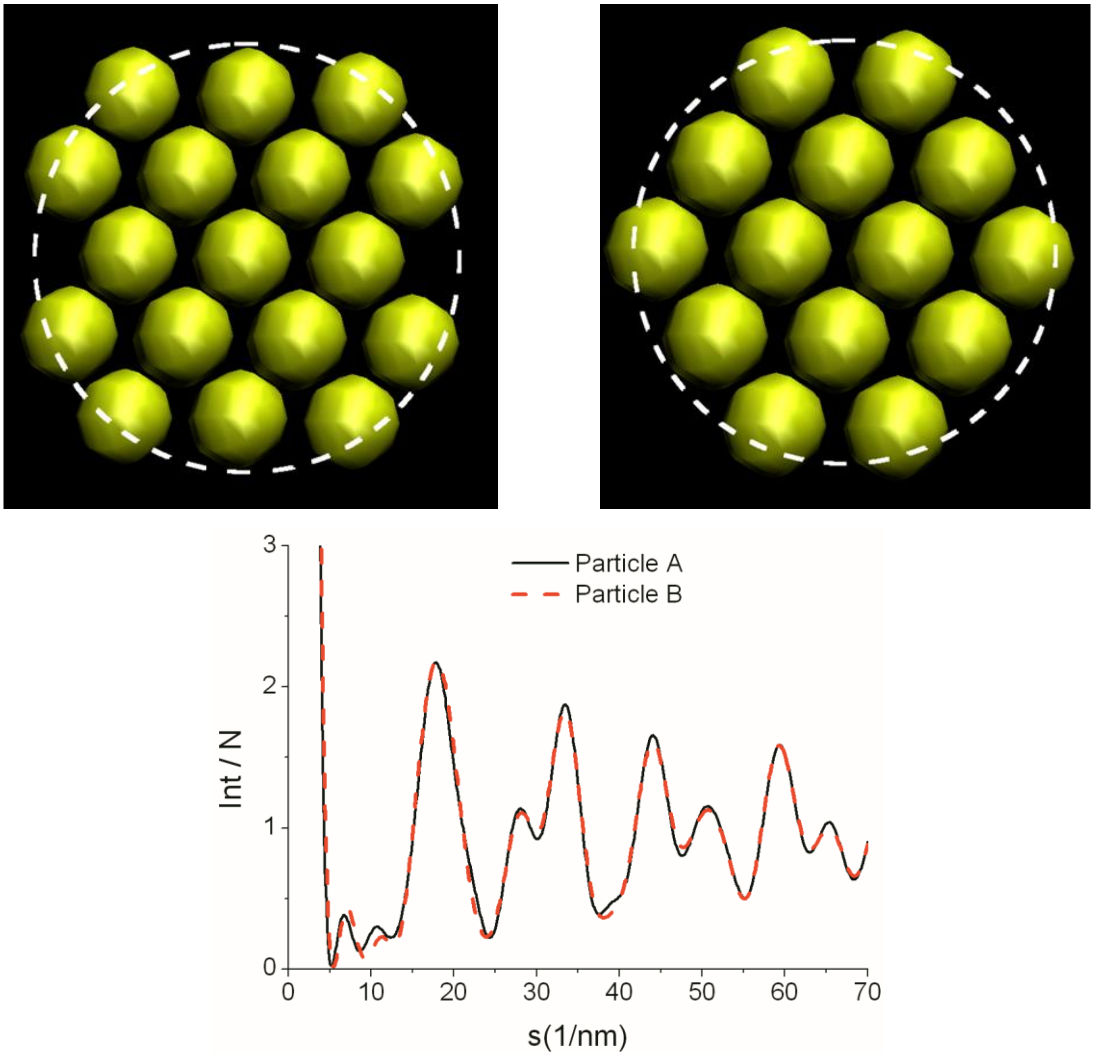

Figure 1. Cross sections of FCC spherical particles constructed assuming (a) no displacement of the shape function with respect to the lattice, and (b) a displacement of the shape function by t = [0.5a, 0.5a, 0.5a] are shown. (c) The corresponding Debye function calculated powder patterns are shown over the range of reciprocal space observable with Cu Kα_1 radiation.

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[1] In the case of molecular crystals, it is often times desirable to avoid including partial molecules at the crystal surface. Furthermore, finding crystal definitions which result in a realistic surface structure is another important part of constructing particles. However, this topic is beyond the aim of the present discussion, as it depends on the specific chemical properties of the molecules, as well as, the surrounding environment of the particles.

This question is neatly handled in the reciprocal space methods of line profile analysis through the random-shift assumption (Ino and Minami, 1979). Expressing the intensity as a product of the structure factor and shape function intrinsically assumes an average over all displacements of the lattice relative to the shape function. So, in order for the Debye intensity to be consistent with the reciprocal space description, the intensity from all possible constructions of the same shape should be averaged.

Due to the periodic nature of a lattice, the range of unique translational offsets of the shape function relative to the lattice is reduced to the confines of the unit cell. Then the average pattern from all possible translations can be expressed as the integral over the volume of the unit cell $\overline{I_P} = \frac{1}{V_{uc}} \int I_P\,(\mathbf{t})\,d\mathbf{t}$, where V_{uc} is the volume of a unit cell, $\mathbf{t}$ is a vector representing the shape function offset, and $I_P(\mathbf{t})$ is then the pattern from the particle described by the given offset.
Evaluating this average over the unit cell volume with Debye calculated intensities is burdensome as the particle size becomes large. Furthermore, the average in this form can be redundant as many translations can yield the same constructed particle. Therefore, a different Monte-Carlo sampling average might be more appropriate, with the average intensity becoming

$$\overline{I_P} = \frac{1}{N} \sum_{i=1}^{N} I_P(\mathbf{t}_i), \tag{2}$$

where the different translations, $\mathbf{t}_i$, are randomly sampled within the range of the unit cell. The question then becomes, “How many particle descriptions must be considered in the sample for the average Debye pattern to converge to the reciprocal space intensity?”

It can be reasoned that the number of particle patterns which must be averaged is intimately related to the similarity between the particle shape and the atomic lattice. For example, it has been proposed that for the case of cubic particles made up of an FCC lattice, a representative atomic construction exists, which results in the same pattern as the average pattern (Beyerlein *et al.*, 2011). On the contrary something like a sphere does not have cubic symmetry, so different shape function offsets are necessary to average to obtain a representative pattern.

To illustrate this point, the patterns of different spheres were calculated and averaged to study the convergence of the average pattern. Each sphere was constructed having an FCC lattice and the same shape function definition, but with a random offset bounded by the unit cell. Patterns were simulated over the small-angle and wide-angle range observable for Cu Kα radiation. The average pattern of from different numbers of constructions was compared to that given from the analytical solution to the peak shape (Scardi *et al.*, 2011), and the trend of the error function χ^2 is depicted in Figure 2a.

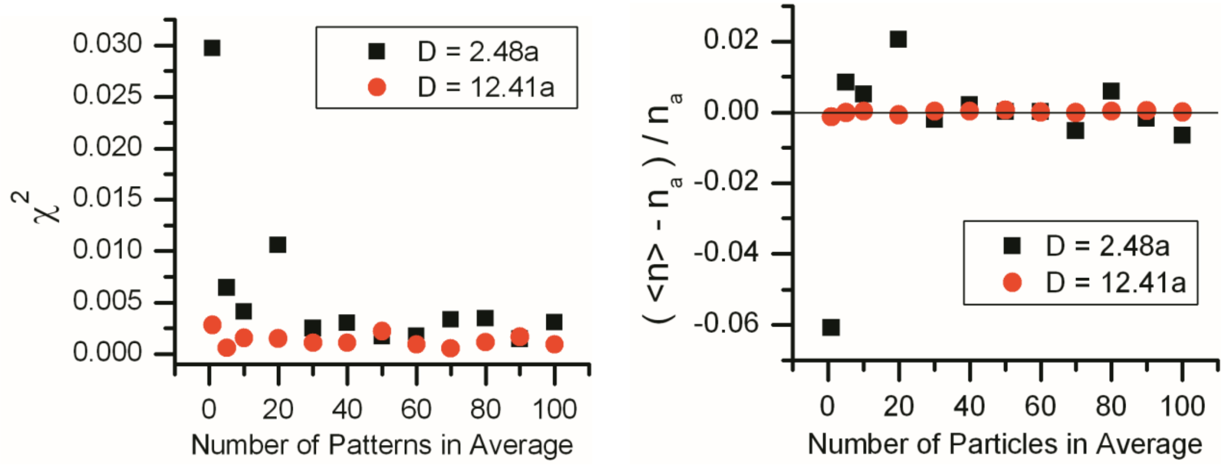

Figure 2. (a) The average Debye pattern from particles constructed by different shape function offsets is compared to the analytical pattern for a sphere and reported through the measure of the χ^2 error function, as the number of particles considered in the average increases. (b) The deviation of the average number of atoms in the particles, <*n*>, from the expected average number of atoms, $n_a = \rho V$ is also shown, considering the same sets of constructed particles.

The trend for spheres having a diameter of 2.48a, where *a* is the unit cell constant, shows that around 50 constructions were necessary before the average pattern converged. Also shown in Figure 2a are comparisons made considering larger spheres of diameter 12.41a. For this case of the larger spheres, the difference between patterns is nearly undistinguishable, and a single pattern is sufficient to describe the sphere.

Thus, it is found that as the size increases the deviation of a single pattern from the analytical reciprocal space pattern is diminished. Furthermore, the minimum number of particle patterns necessary to arrive to a representative pattern also depends on the particle size, increasing for smaller particles. Both findings can be reasoned to result from the increasing surface area to volume ratio with decreasing crystallite size. Two particles constructed from different translations of the shape function only differ in their atomic structure near the particle surface. So, the observed differences in the diffraction pattern must come from these surface atoms.

Then, as the particle becomes smaller, the fraction of atoms on the surface becomes larger, so a larger difference in the scattered intensity is seen. Therefore, to reach the same level of accuracy in the simulated patterns requires more averaging for smaller crystals than for larger crystals.

Plotted in Figure 2b are the trends of how the average number of atoms in the sum of constructed particles deviates from the expected value of $n_a = \rho V$, where ρ is the atomic density and V is the crystallite volume. It should be seen as no coincidence that the convergence of the average number of atoms in the constructed particle coincides with the convergence of the average pattern. This is because it is similarly sensitive to the different atomic constructions and extra surface atoms. Thus, the average number of atoms is a fast diagnostic to know how many particles should be averaged together to obtain a truly representative pattern.

III. CONCLUSION

With the averaging which is necessary to arrive to a true representative pattern, it is clear that the strength of the Debye function is that it describes the powder pattern from a specific particle construction. It is not limited to perfect crystals, nor reliant on lattice symmetries, but consequently does not scale well when many arrangements are necessary to consider. This complements the reciprocal space methods of powder pattern analysis, which are based on describing the intensity from the ensemble, and is one of the fundamental differences which can help scientists decide between these two analysis strategies. Admittedly when using the Debye function in practice one rarely considers the average of different particle descriptions, because the slight differences from each description might not be resolvable by the measurement, especially for small crystallites. However, with source brightness continually increasing, and the increasing study of subtle features in the diffraction pattern, it is important to consider the accuracy in assuming a single particle description when using the Debye function.

In any case, working with the Debye function inspires insight into the powder diffraction pattern. Since the works of Torchet and Hall, the method has been intimately linked to atomistic computer simulations. Today, scientists are routinely simulating complex systems of dense polycrystalline materials, to study their elastic and deformation properties. A notable work by Derlet *et al.* (2005) has shown how the Debye function can be reformulated to simulate the diffraction pattern from these simulations, providing a direct link between atomistic simulations and in situ diffraction measurements. Another notable application harkens back to the molecular origins of the Debye function, as it is being used to describe the wide-angle pattern from proteins in solution. In this approach, a collection of possible protein configurations are used to investigate the powder pattern via numerical approximations to the Debye function (Bardhan *et al.,* 2009). Then unique features in the pattern are identified and used to explain the measured pattern, to the level of attempting to extract some quantitative measure of each configuration in solution. This broad scope of future applications shows that the Debye function is a powerful tool that will surely continue to inspire and enlighten powder diffractionists.

Bardhan, J., Park, S. and Makowski, L. (**2009**). "SoftWAXS: a computational tool for modeling wide-angle X-ray solution scattering from biomolecules," J. Appl. Crystallogr. **42**, 932–943.

Berry, C. R. (**1952**). "Electron diffraction from Small Crystals," Phys. Rev. **88**, 596–599.

Beyerlein, K. R., Snyder, R. L. and Scardi, P. (**2011**). "Powder diffraction line profiles from size and shape of nanocrystallites," J. Appl. Crystallogr. **44**, 945–953.

Buljan, M., Desnica, U. V., Radic, N., Drazic, G. Matej, Z., Vales, V. and Holy, V. (**2009**). "Crystal structure of defect-containing semiconductor nanocrystals – an X-ray diffraction study," J. Appl. Crystallogr. **42**, 660–672.

Cervellino, A., Giannini, C. and Guagliardi, A. (**2006**). "On the efficient evaluation of Fourier patterns for nanoparticles and clusters," J. Comput. Chem. **27**, 995–1008.

Debye, P. (**1915**). "Zerstreuung von Röntgenstrahlen," Ann. Phys. (Berlin, Ger.) **351**, 809–823.

Derlet, P. M., Van Petegem, S. and Van Swygenhoven, H. (**2005**). "Calculation of x-ray spectra for nanocrystalline materials," Phys. Rev. B: Condens. Matter Mater. Phys. **71**, 024114.

Fargas, J., de Feraudy, M. F., Raolt, B. and Torchet, G. (**1983**). "Noncrystalline structure of argon clusters. I. Polyicosahedral structure of Ar clusters, 20<N<50," J. Chem. Phys. **78**, 5067–5080.

Gelisio, L., Azanza Ricardo, C. L., Leoni, M. and Scardi, P. (**2010**). "Real-space calculation of powder diffraction patterns on graphics processing units," J. Appl. Crystallogr., **43**, 647–653.

Germer, L. H. and White, A. H. (**1941**). "Electron diffraction studies of thin films. II. Anomalous powder patterns produced by small crystals," Phys. Rev. **60**, 447–454.

Gnutzman, V. and Vogel, W. (**1990**). "Structural Sensitivity of the standard Pt/SiO2 Catalyst EuroPt-1 to H2 and O2 Exposure by in situ X-ray diffraction," J. Phys. Chem. **94**, 4991–4997.

Hall, B. D., Flueli, M., Monot, R. and Borel, J. P. (**1991**). "Multiply twinned structures in unsupported ultrafine silver particles observed by electron diffraction," Phys. Rev. B: Condens. Matter Mater. Phys. **43**, 3906–3917.

Hall, B. D. and Monet, R. (**1991**). "Calculating the Debye–Scherrer diffraction pattern for large lusters," Comput. Phys, **5**, 414–417.

Ino, T. and Minami, N. (**1979**). "X-ray diffraction by small crystals," Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **35**, 163–170.

Minami, N. and Ino, T. (**1979**). "Diffraction profiles from small crystallites," Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **35**, 171–176.

Morozumi, C. and Ritter, H. L. (**1953**). "Calculated powder patterns from very small crystals: body-centered cubic cubes," Acta Crystallogr. **6**, 588–590.

Niederdraenk, F., Seufert, K., Luczak, P., Kulkarni, S. K., Chory, C., Neder, R. B. and Kumpf, C. (**2007**). "Structure of small II-VI semiconductor nanoparticles: A new approach based on powder diffraction," Phys. Status Solidi C **4**, 3234–3243.

Oddershede, J., Christiansen, T. L. and Stahl, K. (**2008**). "Modelling the X-ray powder diffraction of nitrogen expanded austenite using the Debye formula," J. Appl. Crystaollogr. **41**, 537–543.

Patterson, A. L. (**1939**). "Diffraction of X-rays by Small Crystalline Particles," Phys. Rev. **56**, 972–977.

Scardi, P., Leoni, M. and Beyerlein, K. R. (**2011**). "On the modeling of the powder pattern from a nanocrystalline material," Z. Kristallogr. **226**, 924–933.

Thomas, N. W. (**2011**). "A Fourier transform method for powder diffraction based on the Debye scattering equation," Acta Crystallogr., Sect. A: Found. Crystallogr. **67**, 491–506.

Torchet, G., Bouchier, H., Fargas, J., de Feraudy, M., and Raoult, B. (**1984**). "Size effects in the structure and dynamics of CO2 clusters," J. Chem. Phys. **81**, 2137–2143.

Zernike, F. and Prins, J. A. (**1927**). "Die beugung von Rontgenstrahlen in flussigkeiten als effekt der molekuhlanordnung," Z. Phys. **41**, 184–194.