Diffraction line broadening from nanocrystals under large hydrostatic pressures

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Atomistic copper nanocrystals were investigated via Molecular Dynamics (MD) under hydrostatic pressure to probe the relationship between applied load and structure deformation. The corresponding X-ray powder diffraction patterns were generated from the atomic coordinates. The analysis followed both the traditional Williamson-Hall approach based on pseudo-Voigt fitting and an alternative, more accurate method able to derive the integral breadths without applying a fitting. The Williamson-Hall results show discrepancies not fully associated with an issue of fitting.

Key words: Nanomaterials, High Pressure, Line Profile Analysis

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I. Introduction

Powder diffraction is a valuable tool for the non-destructive structural and microstructural characterization of nanoparticles. For example, recent works on measuring the compressibility of metal nanoparticles have shown anomalous softening (Zhang, *et al.*, 2007), stiffening (Gu, *et al.*, 2008) and behavior consistent with the bulk (Chen, *et al.*, 2001).

In this work we have undertaken a wide range of modeling covering a span of up to 1,000,000 atm (≈100 GPa), and set to evaluate the utility and accuracy of a traditional characterization by Line Profile Analysis (LPA). The most easily accessible and simple information on line profiles is the integral breadth Alalyzed by the so-called Williamson-Hall (WH) method (Williamson and Hall, 1953; Scardi, *et al.*, 2004), which is commonly used also in theoretical and simulation studies (Brandstetter, *et al.*, 2008; Derlet, *et al.*, 2005). While we know that the basic approximations of the WH method are not strictly valid, the issue of how these approximations hold up to an in situ study of high-pressure nanoparticles is still to be understood. In order to gain this insight, a series of simulations on ideally non-defected nanoparticles of copper with hydrostatic load in the vein of (Grünwald and Dellago, 2006) have been performed and analyzed. By using both the simulated powder pattern along with the knowledge of atomic arrangement, we can better understand the sensitivity of diffraction techniques to these structural changes and assess limits and applicability of LPA and of the WH method in particular.

II. Modeling

The series of simulations performed in this study were done using the LAMMPS molecular dynamics suite (Plimpton, 1995). A selection of copper nanoparticles of 5, 10, 15 and 20 nm in diameter was studied as an isothermal-isobaric (NPT) ensemble in the presence of a fluid atmosphere under periodic boundary conditions. As shown by Grünwald and Dellago (2006), a gas pressure bath can effectively simulate a hydrostatic load. Differently from Grünwald and Dellago we employed pair interactions (gas-metal as well as gas-gas atom pairs) to be closer to a real experimental environment.

A cross-sectional slice of the 20 nm system at 100 atm is shown in Figure 1: the picture is a 20 Å

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thick slice in the X-Y plane centered at Z=0. The starting box size was a cube of 50.61 nm on a side.

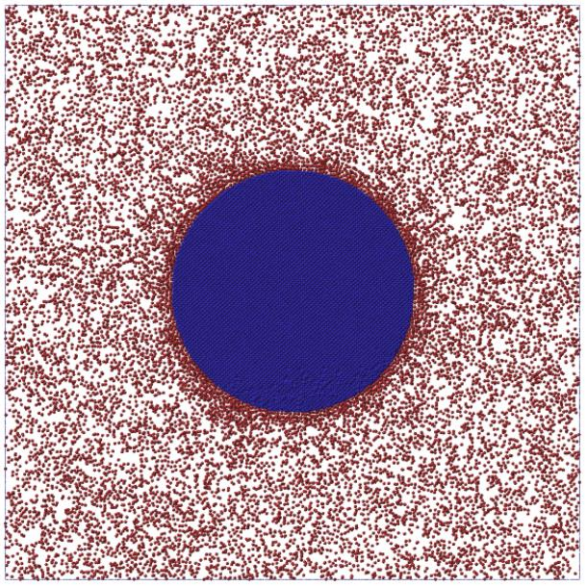


Figure 1: A 20 Å slice of the simulation system at 100 atm of pressure along the X-Y plane. Copper atoms are the central darker region(blue) and the Ar Lennard-Jones fluid atoms are the surrounding lighter (red).

The copper-copper interactions were modeled using an embedded atom method potential (Foiles *et al.*, 1986), with the fluid-fluid and fluid-metal interactions modeled by a Lennard-Jones potential (Lv, *et al.*, 2011) using values derived for Argon or Helium atmosphere. Even if, at room temperature, Argon goes through the liquid-solid phase transition at ~2 GPa (~20 GPa for Helium), using a method similar to that of Guo *et. al.* (2012) it was verified that the pressure on the nanoparticle surface is still hydrostatic. The reliability of the simulations has been assessed by changing the gas species (Argon or Helium) and the orientation of the copper nanoparticle. The Nosé-Hoover barostat and thermostat were applied to maintain the pressure and temperature of each simulation at the desired values, and the system was allowed to evolve and equilibrate over a time of 0.5 ns achieving an apparently stable configuration. The nanocrystals were allowed to freely move and rotate as governed by the pressure fluctuations; however, this behavior was removed following the work of Gullett *et al.* (2008). Coordination analysis of the atomic positions (Ackland, *et. al.*, 2006) showed that the nanoparticles retained an *fcc* structure at all pressures.

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III. Analysis

A. Debye patterns

Using the atomic position data for the last 100 ps of simulation, an average position set was generated in order to remove the dynamical component of the atomic displacements (Stukowski, *et al.*, 2009; Leonardi, *et al.,* 2011; Hosnaoui *et. al*. 2002). From these average positions X-ray powder diffraction patterns were generated using the Debye (1915) scattering function. These patterns represent an ideal powder diffraction experiment, noiseless and without thermal broadening thanks to the averaging performed. The series of patterns for the 15 nm diameter spheres is shown in Figure 2. The peak shift is due to the compression of the unit cell, whereas the variation in the peak broadening is a clear indicator of a severe microstructural modification. Figure 3 shows a detail of the peak broadening evolution for a selection of peaks: for an easier comparison peaks were shifted to remove the effect of cell parameter variation.

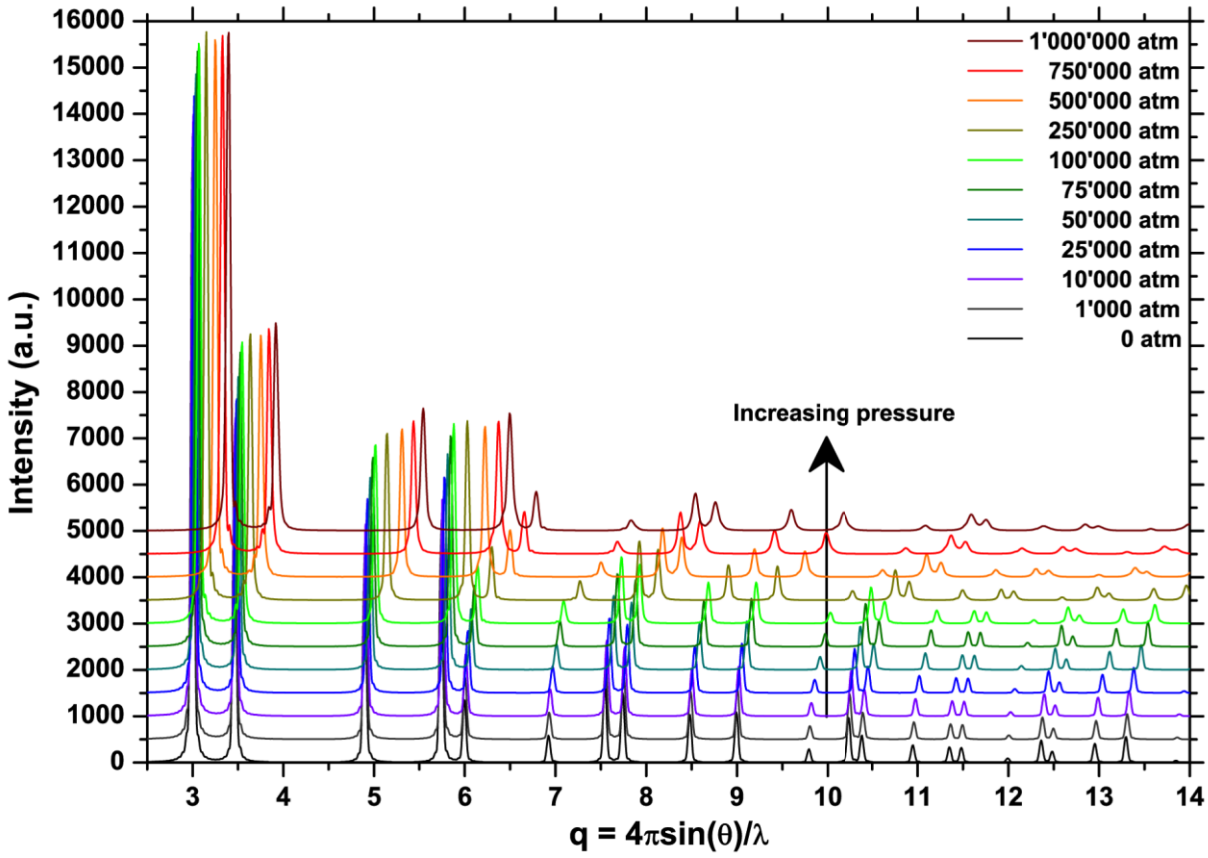


Figure 2: Debye function generated powder patterns of copper spheres 15 nm in diameter in Helium atmosphere. Different pressures shown with vertical offset, in ascending order: 0; 1000; 10,000; 25,000; 75,000; 100,000; 250,000; 500,000 and 1,000,000 atm.

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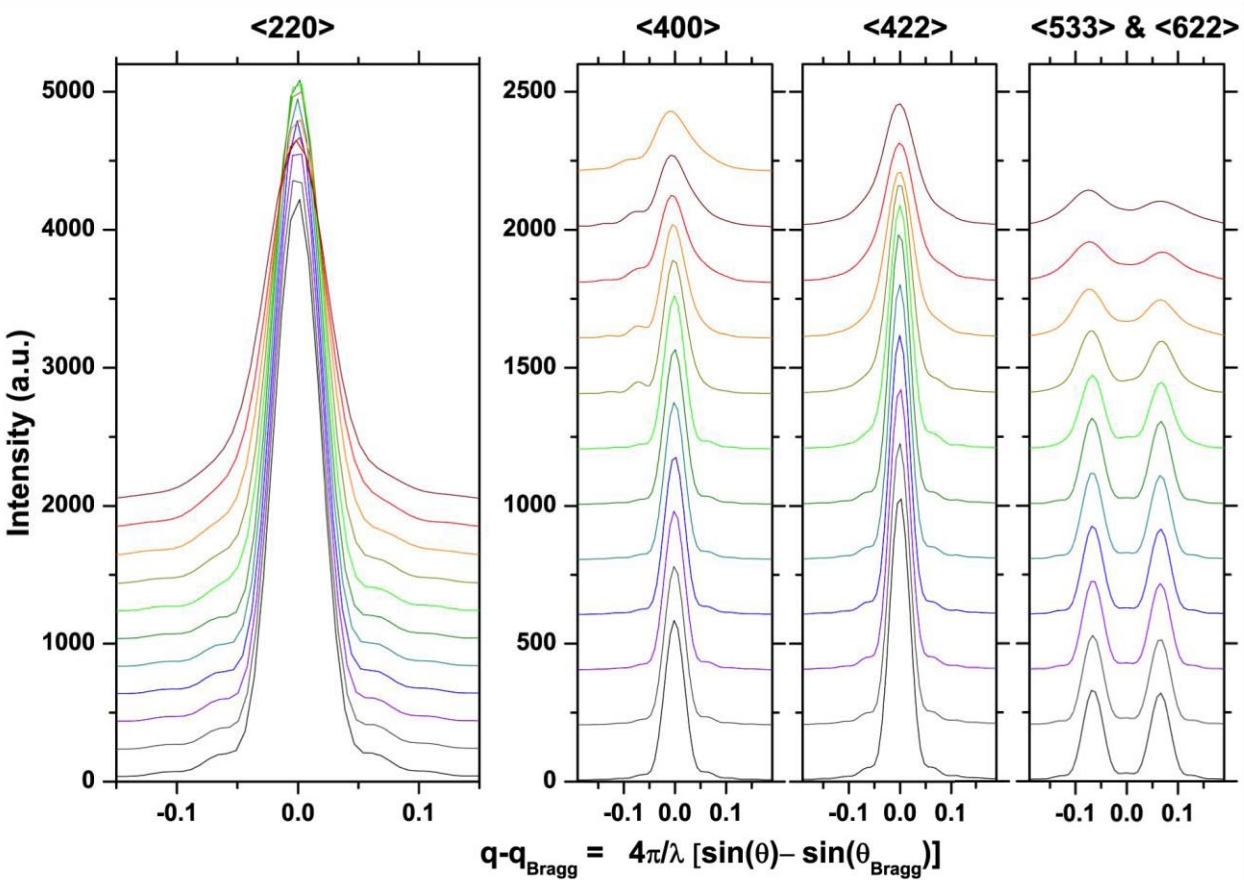


Figure 3: A detail of Figure 2, showing individual peaks across the reciprocal space range. Peaks are translated to offset shifting by a factor of the peak position at 0 pressure multiplied by the ratio of lattice parameters.

The isotropic component of the broadening is mostly related to a change in the particle size with the pressure (maximum *ca.* 10%). However, peak broadening increases with the depth into reciprocal space, with a pronounced peak-shape change most evident at around 250,000 atm; the high order peaks become exceedingly diffuse. Those phenomena are strong indicators of a non-uniform strain behavior with increasing pressure.

B. Williamson-Hall Analysis

Taking the Debye patterns as "experimental data" we applied a simple first-order analysis of the broadening using the software MarqX (Dong and Scardi, 2000) to perform a pseudo-Voigt fitting, and a calculation of the integral breadths for Williamson-Hall analysis. Representative cases are shown in Figure 4.

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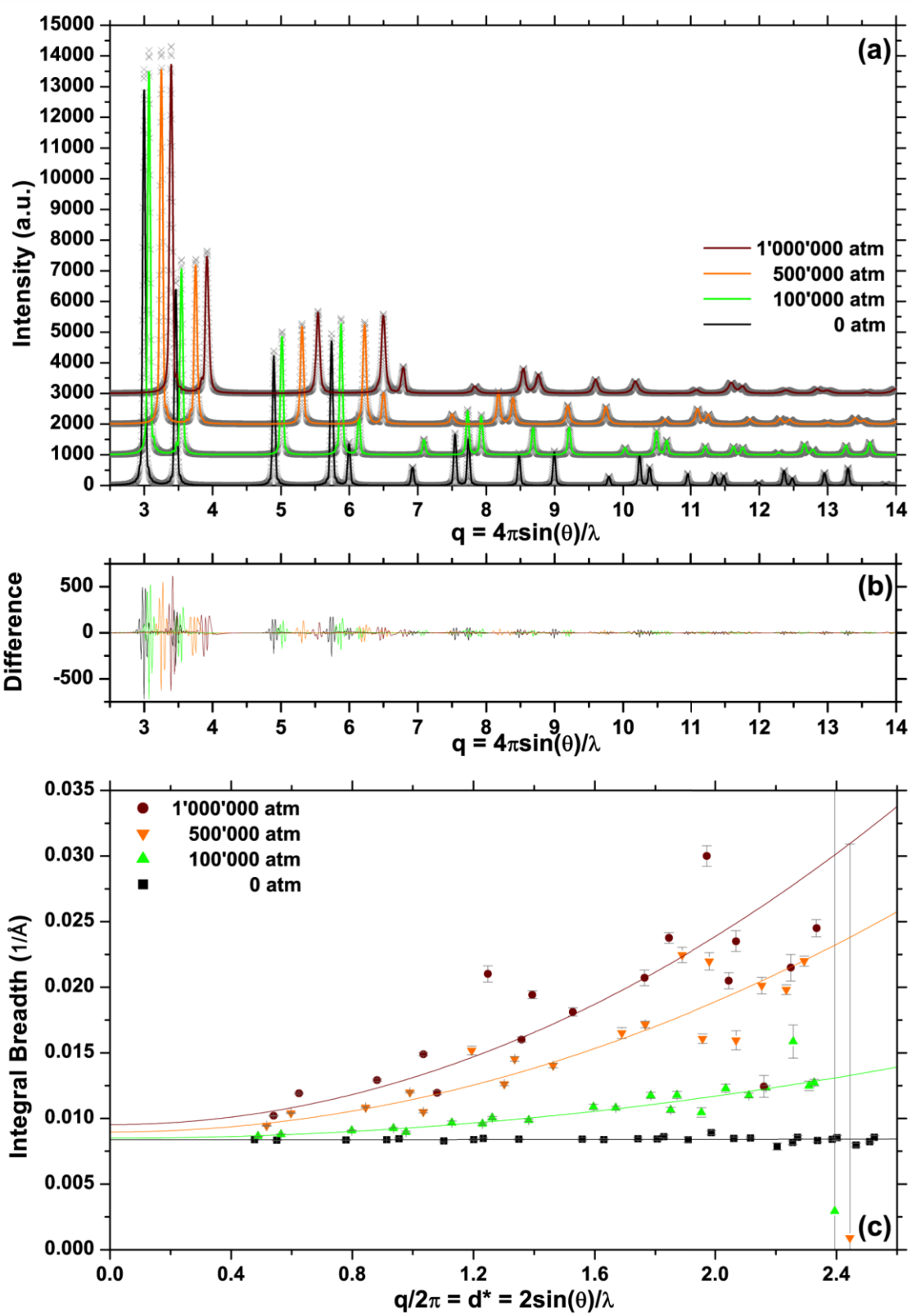


Figure 4: a: Representative pseudo-Voigt patterns and Williamson Hall fits for 15 nm spheres in Helium across the pressure range. b: Differences from the fitting. c: WH depressed quadratic fits.

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A fictitious “sample displacement” and a (second order) polynomial background were also independently refined for each pattern. Both to replicate a likely experimental procedure – ensuring that the fitting is not biased by information that would be hidden by an actual experimental procedure – and increase the quality of fit due to the “apparent lattice parameter” phenomenon seen in nanoparticles when simple profile functions are used to model the observed line profiles (Palosz *et al*., 2004).

The integral breadth data were fitted using both a linear, a depressed quadratic, an even power 4th order fit, and the modified Williamson-Hall (Scardi *et al.,* 2004) models. The latter, more than for dislocations (which do not exist in the present simulations), is intended in the sense of Stokes and Wilson (1944), as an expression of the anisotropy of the elastic medium. While there was considerable improvement in both goodness-of-fit and correspondence to the real size values moving from linear to depressed quadratic, the quality of the fit was not sufficiently improved using the higher order functions to justify their use. For the final modeling (cf. Figures 5 and 6), we have thus used the depressed quadratic model:

$$\beta\left(d^{*}\right)=\frac{1}{<L>_{V}}+\kappa\, d^{*2} \qquad (1)$$

where $<L>_V$ is the volume-weighted mean column length (equal to 3/4 of the diameter in the spherical case, as in Scardi and Leoni (2001)), and κ is a coefficient entailing several constants and quantities, but generally proportional to the r.m.s. strain (aka microstrain).

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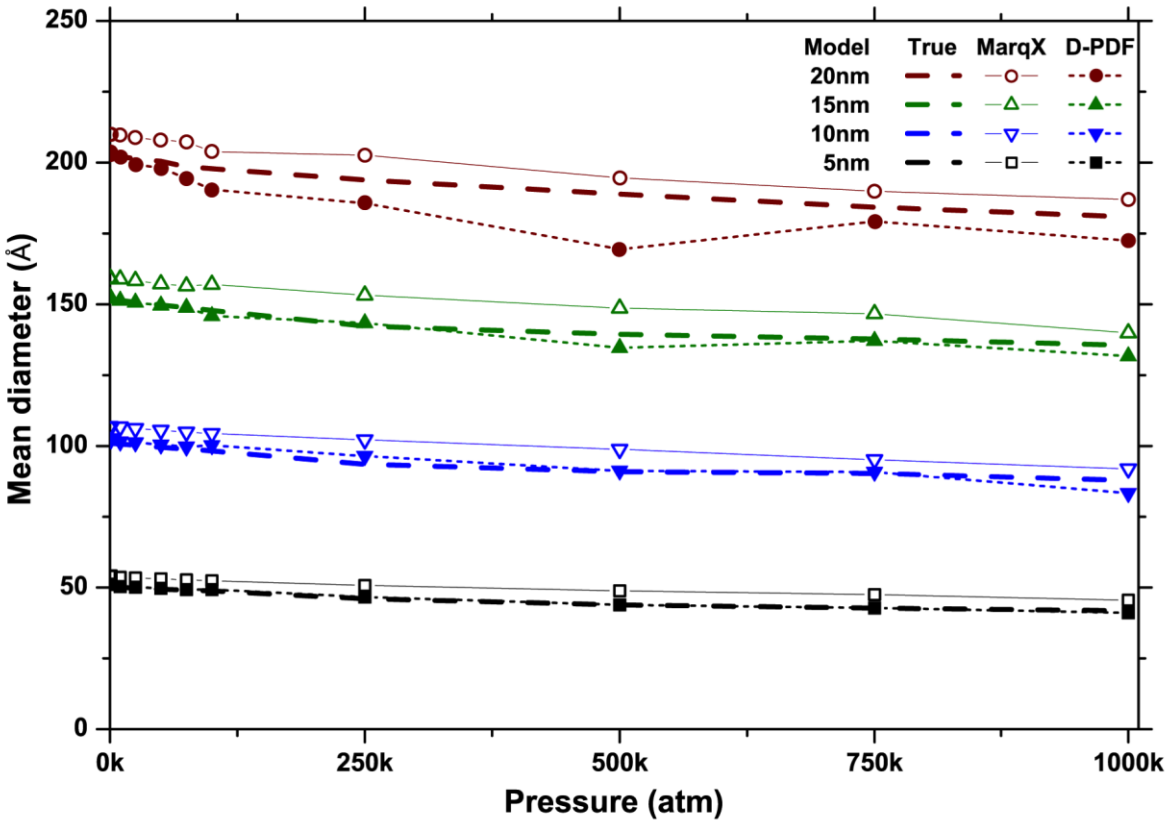


Figure 5: Size from WH intercept plotted against pressure. Sizes shown from both a pseudo-Voigt fitting (empty symbols) and D-PDF calculated integral breadths (filled symbols).

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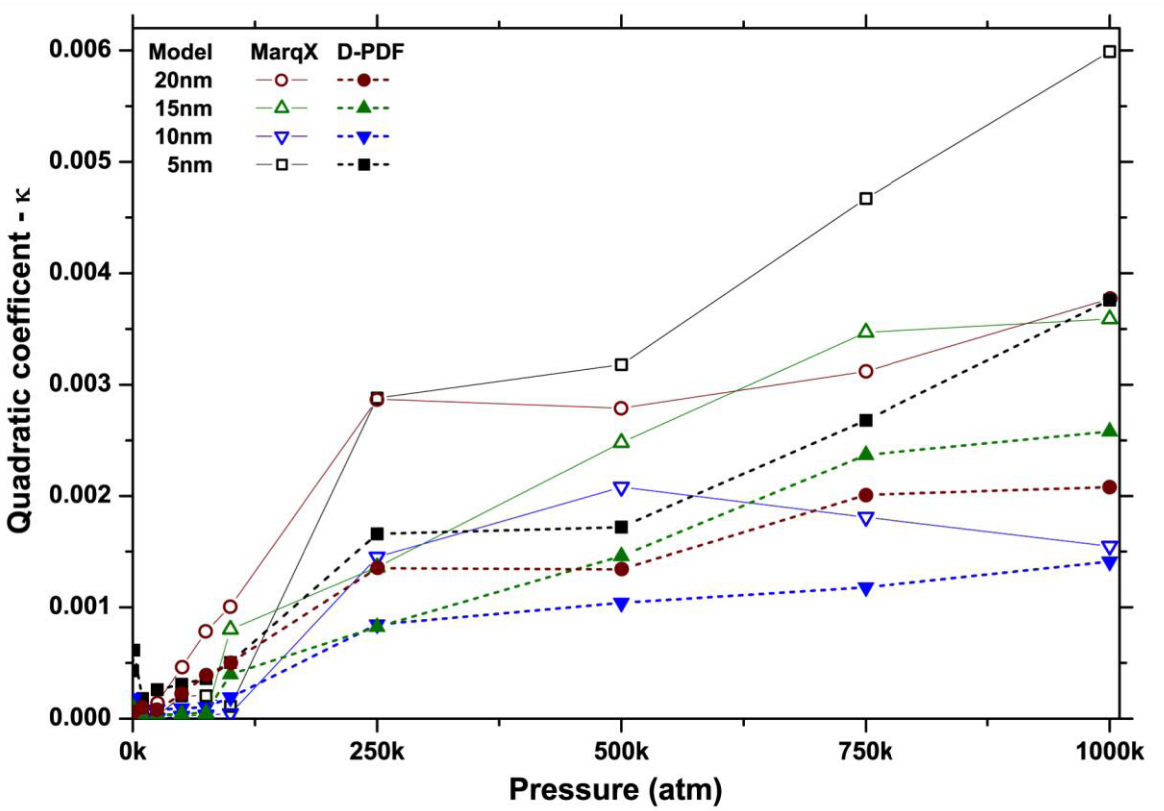


Figure 6: The quadratic coefficient from the WH fits plotted against pressure, for both the pseudo-Voigt fitted patterns using the software MarqX (empty symbols), and the direct D-PDF calculation of integral breadth (filled symbols).

The results shown so far were obtained under the assumptions and constraints of the MarqX profile fitting and of the Williamson-Hall method. To relieve at least partly the constraint and possible systematic errors caused by the arbitrary choice of the pseudo-Voigt fitting function, we calculated the integral breadth directly from the known atomic coordinates of the simulated nanocrystals using the procedure described in two recent papers (Leonardi *et al*. 2012, 2013). In brief, the atomic coordinates of a crystalline domain can be used to obtain the so-called Directional Pair Distribution Function (D-PDF), i.e.the atomic pair distribution calculated for a given [*hkl*] direction. The D-PDF can then be used to calculate the Fourier Transform of any required (*hkl*) peak profile, $A_{\mathrm{hkl}}(L)$, including both the size and any relevant lattice distortion effect. It is then straightforward to obtain the corresponding integral breadth of the (*hkl*) peak profile as:

$$\beta_{hkl}\left(d^{*}\right)=\left[2\int_{0}^{\infty}A_{hkl}\left(L\right)dL\right]^{-1} \qquad (2)$$

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where the actual integration limit is the maximum atomic pair distance, which in the present case is the diameter of the spherical domain. This gives us a "true" Williamson-Hall plot without any artifacts related to the use of an arbitrary fitting function such as the pseudo-Voigt (Scardi *et al.,* 2004). The results of the two fitting procedures, shown in Figure 7, agree quite well. The scattering in the high-angle results of the MarqX analysis is due to the intrinsic difficulty of properly isolate the contribution of the corresponding very broad and overlapping peaks.

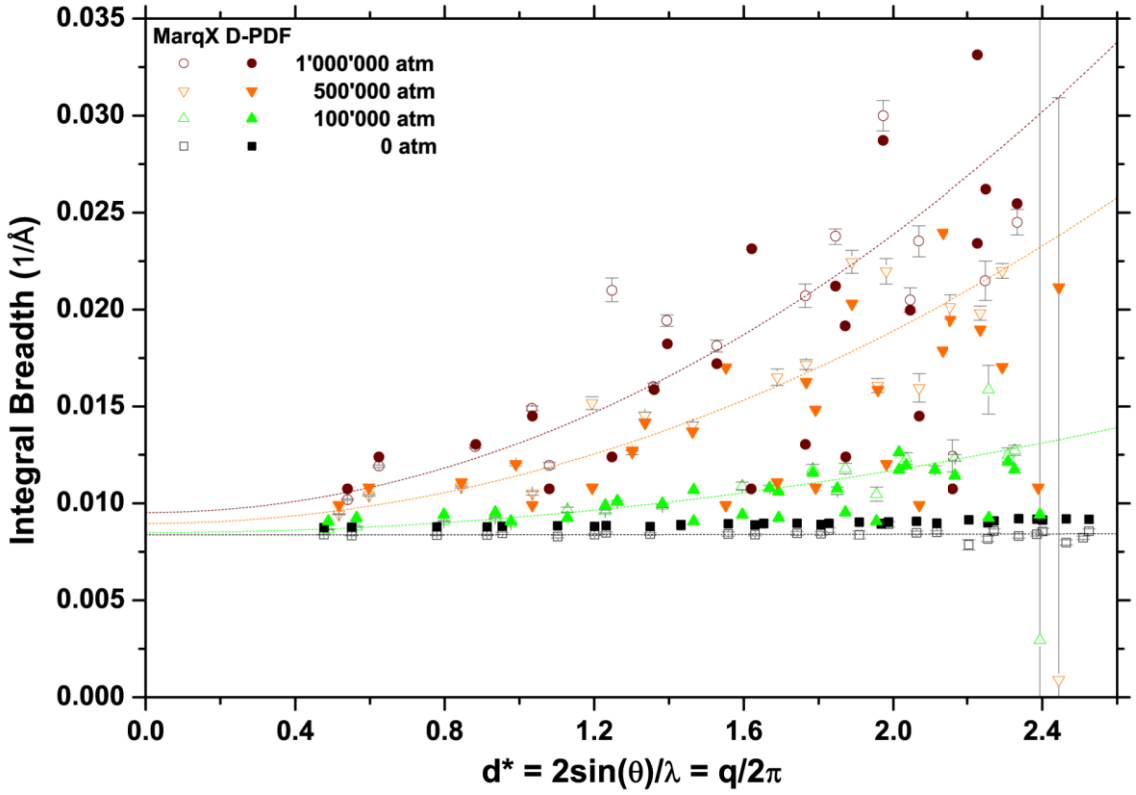


Figure 7: A comparison of Debye modeled and pseudo-Voigt fit integral breadths (empty symbols) with the D-PDF analysis method (filled symbols).

Using the depressed quadratic to model the WH plots, we observe an increasing strain with increasing load, reaching a saturation at ca. 250,000 atm. Beyond that limit, the strain does not increase at pace for the 10, 15 and 20 nm spheres despite a 4-fold increase in the applied load. The 5 nm spheres display a further significant increase at one million atmospheres; however, it still seems to reflect this saturation at intermediate pressures.

The microstrain term from the WH fit is the signature of a non-uniform atomic displacement due to the hydrostatic compression. This value is a non-trivial averaging of effects over all Fourier lengths (Stokes and Wilson, 1944). It seems likely that an increased decoupling of effects occurs

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with higher pressures causing the system to undergo higher strains at the long Fourier lengths, which are weighted more heavily to the surface region. The lack of saturation behavior in the smallest particles would then correspond with the fact that no strong surface-core dichotomy exists at that limit.

Further, in the case of the intercept, a considerable amount of uncertainty can be introduced simply by changing how far into reciprocal space the fit extends. While this is less of an issue for an X-ray measurement in which the far reaches of reciprocal space are difficult to access due to the need for higher energies and the presence of noise, extending the WH plot obtained with the D-PDF breadths from 2 to 4 nm^{-1} in q-space results in a heavy skewing to unrealistically smaller sizes at high pressure. This issue is thus one of weighting, by which is meant, not simply the statistical reliability of the data, which decreases with increasing q, but the degree of meaning of each peak to the WH model function.

The D-PDF derived patterns show a good degree of agreement with the MarqX data. With regards to strain it recreates the behavior seen in the MarqX results, although significantly rescaled to lower values (Figure 6). In the size the D-PDF follows the true diameters more accurately. However, even using the true integral breadths, the larger the dimension of the sphere the larger the discrepancy between true and estimated dimensions. This disparity is likely due to complexity of the strain field, which is inconsistent with the simplifications of the chosen WH model. Ultimately, these size discrepancies, though relatively small, are significant because we have effectively perfect noiseless XRD patterns with a monodisperse non-defected system; under these conditions – although at 0 atm – Beyerlein et al. (2011) showed an essentially perfect size correspondence can be found from fitting such data.

IV. Conclusion

Powder diffraction shows clear sensitivity to the subtle strain effects in nanocrystals at high hydrostatic pressures. A naive attempt to analyze line broadening effects using traditional Line Profile Analysis tools based on integral breadth runs into problems. The size values obtained by a Williamson-Hall analysis are systemically overestimated at low pressures by ca. 5%, and in some cases underestimated equally extreme at high pressures. However, the overall decrease of

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size with increasing pressure, expected from basic thermodynamics, is preserved. Second, while the analysis does generally reflect an increasing strain state against applied pressure, the correlation between the two is not particularly strong, under high loads. The Williamson-Hall method itself performs reasonably well at low pressures. However, a pseudo-Voigt peak function seems to introduce more error than under high loads, and overall we are left with little insight into the nature of the strain in the system. Further analysis of these effects however will necessitate a Fourier approach looking over different coherence lengths. When compared to the D-PDF, directly derived from the known atomic coordinates, the Williamson Hall method is a reasonable first-order analysis tool, and shows itself robust to the semi-arbitrary use of pseudo-Voigts as a fitting function.

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