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# Structure of nanoparticles from powder diffraction data using the pair distribution function

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## Abstract

The local structure of nanoparticles can be determined by a direct interpretation of the first peaks observed in the radial distribution function obtained from powder diffraction data measured to high  $Q$  values. Single peak fits to these maxima yield the mean distances and width of the distribution in the first few neighbouring shells. An algorithm is presented to calculate the radial distribution function based on the simulation of a single nanoparticle. This algorithm allows a flexible description of nanoparticle size and shape. Based on this algorithm the structure of CdS:glutathione nanoparticles of less than 2 nm diameter is presented. This structure consists of a CdS core with tetrahedrally coordinated first neighbours and a shell of glutathione molecules. Within the core several stacking faults lie in different orientations with a stacking fault probability of 40%.

## 1. Introduction

Nanoparticles are defined as solid aggregates of matter intermediate in size between molecules and clusters on the one hand and extended crystals or glass on the other hand. Thus they fall into a size ranging from a few nanometres to several hundred nanometres. The main definition besides size, however, is that these particles exhibit size dependent properties [1]. Besides these fundamental properties interest in nanoparticles stems from the many applications that have been developed [2, 3] and the recognition of their importance in natural environments [4].

The limited size of nanoparticles of much less than one cubic micron presently does not allow the application of single crystal techniques to study the structure of nanoparticles. Therefore, the investigations are currently limited to powders, both for diffraction experiments as well as spectroscopic investigations.

If the nanoparticles are available in sufficient quantity as dry powders, such a powder diffraction experiment on these particles does not require any special methods that would

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distinguish it from a powder diffraction experiment on crystalline material or a glass or liquid sample. It may be carried out as an x-ray as well as a neutron diffraction experiment.

The finite size of the particles, however, is responsible for specific features within the diffraction experiment that distinguish this diffraction pattern from other classes of materials. The finite size of the particles causes a line broadening of the diffraction peaks. The Scherrer equation [5] is often used to determine particle sizes from the peak width. Difficulties in applying this formula to nanoparticles have been noted by several authors [6–8]. The Scherrer equation is based on the assumption of a perfect lattice limited in size. Besides the finite size, nanoparticles are often terminated by a variety of different *hkl*-planes, have a very large fraction of their atoms on the surface of the particle and will often contain a high degree of disorder. All these features contradict the basic assumptions of the Scherrer equation. Hall [9] presented a method to nevertheless determine the nanoparticle size from powder diffraction data. The Fourier transform of the powder diffraction data will yield maxima that correspond to the interatomic distances. By analysing the longest interatomic distances that correspond to significant maxima, Hall was able to determine the nanoparticle size.

By reducing the size of an otherwise perfect crystal, the finite size broadening will widen the reflections to cover several degrees of  $2\Theta$ . A diffraction pattern of a nanoparticle of less than some 5 nm shows just a few broad maxima and resembles the diffraction pattern of an amorphous substance. The presence of defects, like stacking faults, leads to an additional line broadening, superimposed on the pure size effect. The number of ‘reflections’ in such a powder diffraction pattern is too small to apply structure determination and refinement methods that may be used on powders of crystalline materials, like the Rietveld method. In addition to the small number of peaks, one has to keep in mind that each peak consists of overlapping ‘Bragg’ reflections, thus obscuring the intensity of the individual reflections. Even in the absence of any defects, a nanoparticle of 30–50 nm diameter will consist of merely 50–100 lattice planes. This small number is too small to warrant the description of the particle as a ‘periodic’ arrangement of lattice planes. Accordingly the diffraction should rather be described as the interference of the diffraction by individual atoms, as described by the Debye equation.

## 2. Pair distribution function of nanoparticles

The structural features of nanoparticles may be determined by analysing the Fourier transformation of the diffraction pattern, which yields the radial distribution function (RDF) [5, 10, 11], also called the pair distribution function (PDF) [12, 13]. See Keen [14] for a review of commonly used definitions for the correlation functions. For the calculations in this presentation the definition according to [13] was used:

$$G(r) = 4\pi r [\rho(r) - \rho_0] = \frac{1}{2\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dr \quad (1)$$

where  $\rho(r)$  is the density at distance  $r$  and  $\rho_0$  the average number density. By subtracting the average number density, the pair distribution function oscillates around zero. With increasing distance  $r$  the oscillations become smaller. The pair distribution function can be calculated [15] from a structural model via

$$G_{\text{calc}}(r) = \frac{1}{r} \sum_{i,j} i \left[ \frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \right] - 4\pi r \rho_0 \quad (2)$$

where  $b_i$  is the scattering power of atom  $i$  and  $\langle b \rangle^2$  is the average scattering length of all atoms.

Alternatively, a slightly modified pair distribution function has been used [16]:

$$G'_{\text{calc}}(r) = \sum_{i,j} i \left[ \frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \right] - 4\pi r^2 \rho_0. \quad (3)$$

The pair distribution function is a diagram of the weighted interatomic distances within the sample. The location of the maxima reflects the interatomic distance  $r$ , while the intensity is proportional to the number of atom pairs at the given distance and their corresponding scattering power. The interpretation of the pair distribution function yields information on the local structure, i.e. the mutual arrangement of the atoms at short distances. The original applications concerned the study of amorphous bulk materials like glasses and liquids. More recently the analysis of the pair distribution function to disordered crystalline materials was introduced [13].

Only a few studies on the pair distribution function of nanoparticles have been performed so far. Hall *et al* [9] studied the pair distribution function solely in order to determine the particle size. Since the study was applied to nanoparticles of metals, whose internal local structure is close to that of the bulk material, no additional structural features were derived.

Petkov [17] analysed the local structure of nanocrystalline  $\text{LiMoS}_2$ . They observed that the Bragg reflections were significantly broadened compared to those of  $\text{MoS}_2$  and merged into a slowly oscillating diffuse component at approximately  $8 \text{ \AA}^{-1}$ . The structural coherence of the  $\text{LiMoS}_2$  compound was listed as approximately  $50 \text{ \AA}$ , yet no information was given on the particle size. The local structure, however, was well defined with Mo atoms residing in distorted octahedra of sulfur. The local structure was determined up to  $17 \text{ \AA}$ , a much smaller distance than the structural coherence length. For this reason Petkov *et al* were able to fit the local  $\text{LiMoS}_2$  structure based on a periodic model. The finite size of the structural coherence did not influence the analysis.

Korsounski *et al* [18] determined the local structure of very small CdS nanoparticles capped by glutathione. These particles measured less than  $2 \text{ nm}$  in diameter. The pair distribution function was determined up to  $25 \text{ \AA}$ , well beyond the particle diameter. Significant maxima were observed to distances up to  $17 \text{ \AA}$ . The analysis of such a small finite particle required a different approach compared to [17]. The nanoparticles consist of a core of CdS stabilized by an outer shell of glutathione molecules. These molecules were bound to the inorganic core through the sulfur atom. The core can best be described as a disordered tetrahedral network of CdS.

To analyse the structure of amorphous bulk materials like glasses and liquids, the reverse Monte Carlo (RMC) simulation [19] is commonly applied to the pair distribution function as well as directly to the powder diffraction data. The current implementations of this algorithm require periodic boundary conditions and, even more restricting, a homogeneous material. Thus they cannot yet be applied to the study of very small nanoparticles. Despite these drawbacks the local structure of nanoparticles may be derived from a careful study of the pair distribution function.

A prerequisite of the current analysis of small nanoparticles is the availability of a high quality pair distribution function. To obtain such a pair distribution function, diffraction data with excellent counting statistics up to high  $Q$ -values are required. From such data a pair distribution function can be calculated that yields reliable pair distribution function peak positions as well as peak intensities.

The nanoparticle studies so far were of comparatively simple chemical nature to allow a direct interpretation of the pair distribution function maxima at short interatomic vectors, and the main steps in such an analysis are reviewed in the remainder of this section. Figure 1 shows the pair distribution function of CdS:glutathione, obtained from high energy x-ray diffraction

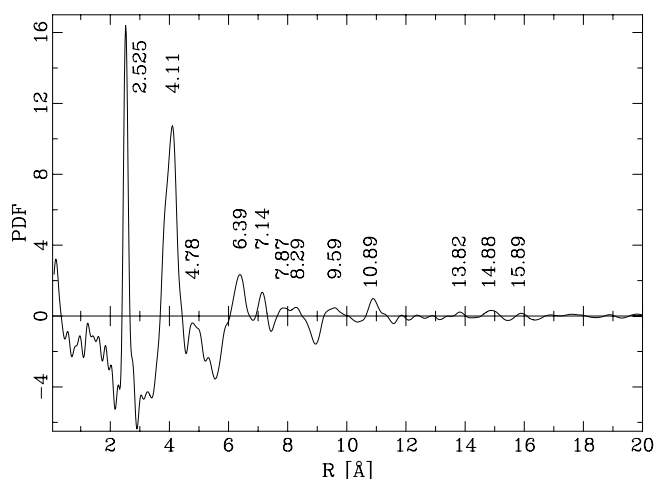


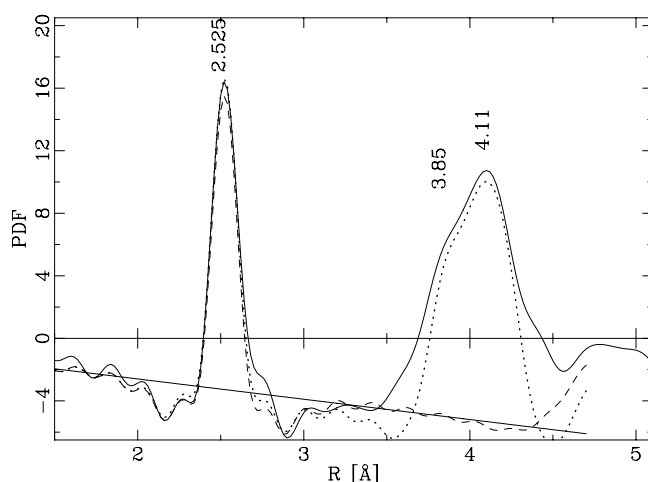
Figure 1. Experimental pair distribution function of CdS:glutathione.

data [18]. The x-ray derived pair distribution function of such a compound is dominated by the interatomic vectors between the heavy atoms. The Cd–Cd partial pair distribution function and the Cd–S partial pair distribution function produce the most intense maxima, while the S–S partial pair distribution function produces maxima of minor intensity. The interatomic vectors within and between the glutathione molecules are so weak that they may, in a first approximation, be neglected.

The first maximum at 2.53 Å corresponds to the Cd–S bond length observed in crystalline CdS. Thus this first maximum can be interpreted to correspond to the Cd–S bond distance in the nanoparticle. Due to the domination of the Cd–Cd partial pair distribution function, the next nearest neighbour peak at 4.11 Å can be assigned to the Cd–Cd distances between the Cd atoms around a central S atom. Given the Cd–S bond length and the Cd–Cd distance, it follows that the bond angle Cd–S–Cd is approximately 109°. This bond angle requires a tetrahedral coordination of sulfur by cadmium. By comparing this partial structural model with known Cd–S compounds it is reasonable to assume that Cd is likewise tetrahedrally coordinated by sulfur. This would produce a S–S peak at 4.11 Å as well. Since the S–S partial pair distribution function is too weak to produce a significant maximum, this model is based on chemical intuition. For structures with atoms of similar scattering power, the mutual coordinations could be assigned more unambiguously on the presence or absence of next neighbour peaks.

In combination with further information, the structural model can be developed further and be put onto a more quantitative basis. A quantitative chemical analysis yielded a chemical formula of CdS<sub>0.5</sub>glutathione<sub>0.5</sub>, where the Cd:S ratio is 1:1 and half the sulfur atoms are part of the glutathione molecule. IR spectra did not show any S–H modes. A structural model of a CdS core with glutathione molecules attached to its surface is in agreement with the pair distribution function and the chemical and spectroscopic data. In order to fulfil the Cd:glutathione ratio, at least half of the sulfur atoms must be on the surface of the core and be part of the glutathione molecule.

A quantitative assessment of the local structure is achieved by fitting a calculated pair distribution function to the experimental data. The first neighbour maximum in figure 2 is very narrow and of symmetrical shape. It can be described by a pair distribution function calculated from a Cd–S distribution centred at 2.525 Å and a  $\sigma$  of 0.063 Å. The number of nearest



**Figure 2.** Experimental (solid curve) and calculated pair distribution function for CdS:glutathione from [18]. The dotted curve represents the calculated total pair distribution function, the broken curve the Cd–S partial pair distribution function, and the straight line  $-4\pi r\rho_0$ .

neighbours was fitted to 3.25. This value is smaller than the bulk value of four tetrahedrally coordinated neighbours both in the zincblende and the wurtzite structure. This lower number is to be expected for a nanoparticle of finite size, since a large part of the atoms is located on the surface and thus has a lower number of neighbours.

The second neighbour maximum in figure 2 is much wider and asymmetric, with a shoulder on the low- $R$  side. Since the pair distribution function is dominated by the Cd–Cd distances these two components in the peak at 4 Å correspond to two different Cd–Cd distances and respectively to two different Cd–S–Cd bond angles of  $100^\circ$  and  $109^\circ$ . A fit yields distances of 4.13 and 3.85 Å with widths of 0.15 and 0.12 Å and 4.3 neighbours. The longer distances correspond to an ideal tetrahedral coordination with  $109^\circ$  Cd–S–Cd bond angles. This environment describes the inorganic core of the nanoparticle. The shorter distances of 3.85 Å, i.e.  $100^\circ$  Cd–S–Cd angles, correspond to the cadmium neighbours around those sulfur atoms that are part of the glutathione molecule. Similar distance and angle schemes are observed in metal organic compounds that contain small CdS clusters.

### 3. Structure of the whole particle

Such a fit, based on well resolved PDF maxima, can accurately describe the local structure of the nanoparticle. The pair distribution function peaks at longer distances overlap too much to allow such a direct interpretation. The overall structure of the particles must be derived from a comparison between the experimental pair distribution function and a pair distribution function calculated from structural models of the whole nanoparticle. The calculation of the pair distribution function of a finite nanoparticle requires an important modification of the usual algorithm used to calculate the pair distribution function. For an infinite object of homogeneous density the average number of interatomic vectors increases with  $r^2$ . By subtracting the average number density in equations (2) and (3) the pair distribution function is equal to zero at large distances.

For a single finite nanoparticle, however, a longest interatomic vector  $R_D$  exists. Accordingly the actual density  $\rho(r)$  is zero for distances longer than the longest diameter

of the particle. For distances shorter than the shortest interatomic vector,  $\rho(r)$  is zero. For intermediate vectors the density reaches a maximum. The exact shape of the distribution depends on the atomic structure as well the shape of the nanoparticle. If one assumes a homogeneously filled particle, the shape of the distribution may be calculated analytically or numerically for a given shape like a sphere, cube, etc. Since real nanoparticles will be of a more complicated shape and this shape will underlie a size and form distribution, one can in general not define this average distribution very well.

The pair distribution function  $G(r)$  in equation (2) calculated for a single nanoparticle will accordingly fall off with  $-4\pi r\rho_0$  for distances longer than the longest diameter of the particle.

In the experiment a different situation is encountered. The nanocrystalline particles form a powder sample, in which the particles will be in contact, yet without any interparticle orientation correlation. Thus for distances longer than the nanoparticle diameter, the sample is essentially a homogeneously filled object. Interatomic vectors within each particle are well defined, while interatomic vectors from one particle to the next are randomly distributed at a probability given by the average number of interatomic vectors for the given distance. The pair distribution function therefore has negligible oscillations and is equal to zero for all distances larger than the particle diameter. The pair distribution function calculated from a powder diffraction pattern of such a sample will therefore also have to be equal to zero for distances longer than the particle diameter.

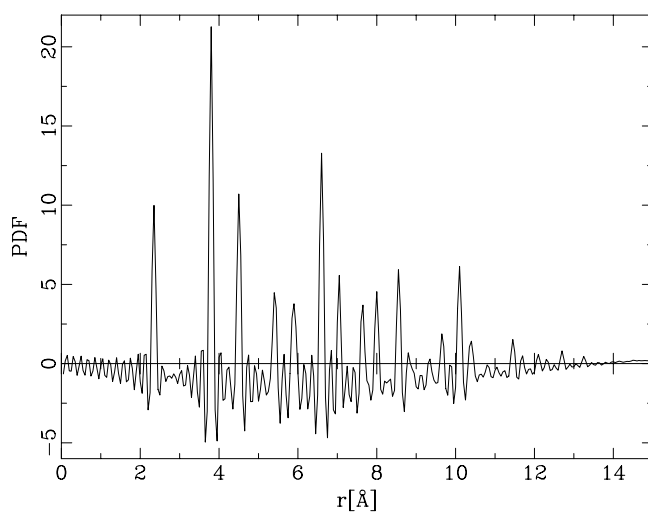
The calculated pair distribution function of finite nanoparticles can be calculated following two different strategies. The simulated nanoparticles can be stacked in random orientation within a large supercell with periodic boundary conditions. Unless the shape of the particles is very regular, it is computationally expensive to achieve a tight packing. This holds even more, if the nanoparticles are to be modified by for example an RMC algorithm to optimize the fit to the experimental pair distribution function. Since no interparticle interaction has been observed in an experimental pair distribution function, disadvantages of such a model of stacked nanoparticles outweigh the advantage of having a realistic simulation of the nanoparticle powder sample.

Alternatively the pair distribution function can be calculated from a single nanoparticle. In order to achieve a fit to the experimental pair distribution function the average density of the interatomic neighbours must be modified. The interatomic vectors that arise from within the particle will produce the peaks of the pair distribution function. To simulate the non-correlated randomly oriented interatomic vectors between atoms in neighbouring nanoparticles, an additional smooth function added to  $G(r)$  is required. This function must be zero for small distances  $r$  and equal to  $4\pi r\rho_0$  for distances larger than the nanoparticle diameter. Additionally this function must be flexible enough to describe the effect of different nanoparticle shapes. This can be achieved by modifying equation (2) to

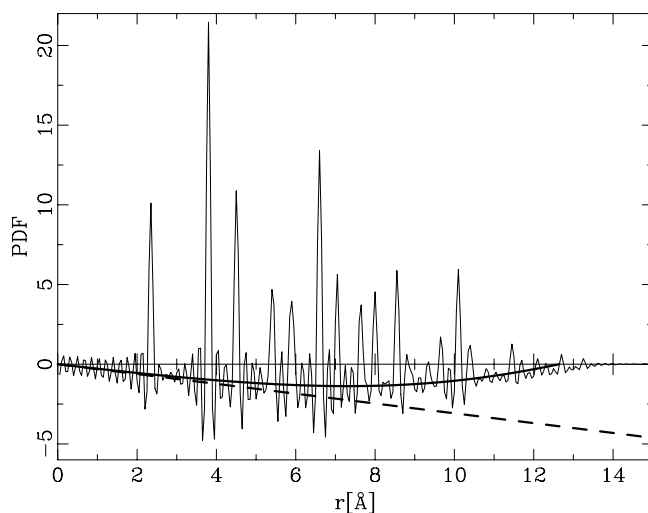
$$G_{\text{calc}}(r) = \begin{cases} \frac{1}{r} \sum_{i,j} i \left[ \frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \right] - 4\pi r\rho_0 \tanh(S(R - r)) & \text{for } r < R \\ \frac{1}{r} \sum_{i,j} i \left[ \frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \right] & \text{for } r \geq R \end{cases} \quad (4)$$

where  $R$  is the nanoparticle diameter, and  $S$  a parameter related to the nanoparticle shape.

Figure 3 shows the pair distribution function for a periodic stacking of randomly oriented zincblende nanoparticles, while figure 4 shows the pair distribution function of a single nanoparticle calculated according to equation (4). Since the two graphs match perfectly well, they have been printed separately. Inspection of figure 4 shows that the difference between  $-4\pi r\rho_0$  and  $-4\pi r\rho_0 \tanh(S(R - r))$  is negligible up to approximately half the nanoparticle



**Figure 3.** Calculated pair distribution function for a packing of spherical CdS nanoparticles with diameter of 13.25 Å. The particles are stacked with random rotation in an fcc lattice of 22.63 Å lattice constant. The internal particle structure is a perfect zinblende structure.

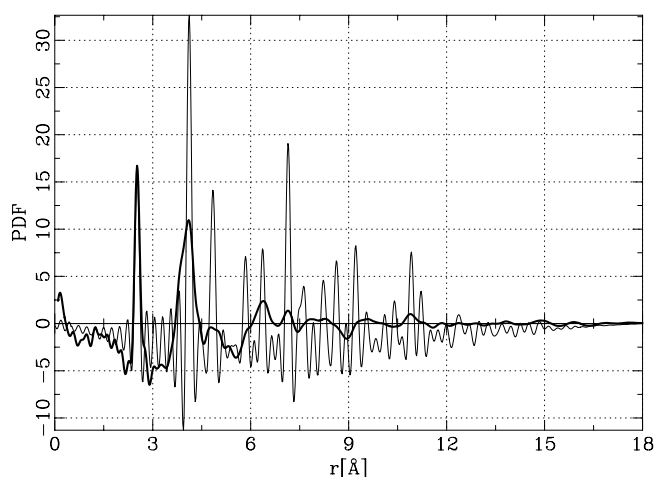


**Figure 4.** Calculated pair distribution function for a single CdS nanoparticles with diameter of 13.25 Å. The broken curve represents  $-4\pi r\rho_0$ , the continuous thick curve the modified function  $-4\pi r\rho_0 \tanh(S(R-r))$  with  $S = 0.133$ ,  $R = 12.64$  Å.

diameter, especially if experimental noise is taken into consideration. Thus the modified calculation according to equation (4) needs to be carried out for nanoparticles, whose pair distribution function has been determined for distances longer than half the particle diameter. Accordingly, the analysis of the  $\text{LiMoS}_2$  structure by [17] did not need to take this finite size effect into account.

The structure of a very small and highly distorted nanoparticle can qualitatively be derived by comparison between the calculated and experimental pair distribution functions. In order to achieve a quantitative determination, the structural parameters must be obtained from a fit to





**Figure 5.** Calculated pair distribution function for a single CdS 19 Å nanoparticles with perfect zincblende structure (thin curve) in comparison to the experimental pair distribution function (thick curve). Except for the first maximum, all calculated maxima are too narrow and too high.

the experimental pair distribution function. Two approaches are currently being investigated. In the first approach, many nanoparticles with a given initial configuration are stored in a large supercell. The unit cell lengths are chosen long enough to prevent any overlap between the individual nanoparticles. Since this introduces an artificially low average number density the subtraction of  $4\pi r \rho_0$  is adjusted accordingly. To take the finite size of the particles into consideration, equation (4) is used. An RMC algorithm is applied to modify the nanoparticles. The algorithm is modified to restrict the modification to those within an individual nanoparticle, like shifting of atoms, changing the particle size, etc.

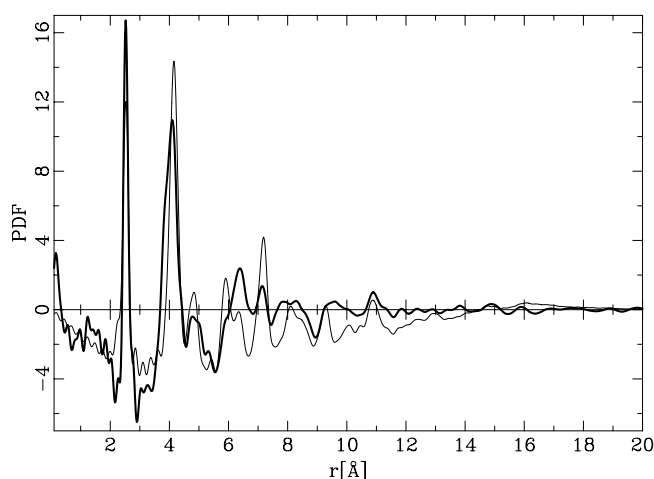
Since the particle size and the particle size distribution are to be determined as well as the atomic structure of the nanoparticles, this first approach requires extensive deviations from a standard RMC algorithm. If capped nanoparticles are studied, a change of the particle size requires the addition of atoms to the nanoparticle core and simultaneously a corresponding shift of the molecules in the shell to avoid physically impossible short distances. The second approach facilitates this requirement. Now parameters like size, composition, average short distance distributions, coordination spheres, defect types and densities are defined that are used to construct a nanoparticle and calculate the corresponding pair distribution function. A differential evolution algorithm is used to modify the parameter set to achieve an optimal fit to the experimental pair distribution function.

#### 4. Estimation of nanoparticle disorder

Figure 5 shows the pair distribution function of a nanoparticle with 16 Å diameter based on the perfect zincblende structure. It is obvious that the maxima at longer distances are too narrow compared to the experimental maxima. Thus a high degree of disorder must be present in the nanoparticles. Qualitative results are presented in this study.

Several models can be constructed to introduce disorder. The most simple model includes only the different Cd–S–Cd bond angles within the core and at the surface. Calculated pair distribution functions still show maxima that are too narrow.

A second model allows for the presence of one or several stacking faults mixing zincblende and wurtzite layers along the [111] direction. Along this [111] direction the ‘long range’ order



**Figure 6.** Calculated pair distribution function for an average of disordered particles (thin curve) compared to the experimental pair distribution function (thick curve).

is lost and this leads to a broadening of the pair distribution function maxima. Within the individual layers, however, the structure remains perfect and as a consequence the calculated pair distribution function maxima are still too narrow.

Similarly, a model consisting of a perfect tetrahedrally shaped zincblende core and wurtzite layers on the  $\langle 111 \rangle$  surfaces does not yield a pair distribution function with sufficiently wide maxima.

A model that allows for multiple stacking faults to occur along any of the  $\langle 111 \rangle$  directions is able to explain at least qualitatively the observed pair distribution function. This model was constructed by adding individual atoms to a pair of atoms, until a nanoparticle of approximately 80 cadmium atoms was obtained. The particle was relaxed to give 2.525 Å distances between nearest Cd–S neighbours, 109° Cd–S–Cd bond angles for fully tetrahedrally coordinated S atoms and 100° Cd–S–Cd bond angles for twofold and threefold coordinated sulfur atoms on the surface of the nanoparticle. The growth algorithm introduces several independently placed and oriented stacking faults within the nanoparticle. Averaging the pair distribution function of ten nanoparticles gave the pair distribution function shown in figure 6. This pair distribution function reproduces the main features of the experimental pair distribution function.

The structure of the CdS:glutathione nanoparticle can be described by a highly disordered ‘inorganic’ CdS core. The core consists of approximately 70 to 90 cadmium atoms. Cadmium and sulfur are tetrahedrally coordinated by the opposite species. The Cd–S bond length distribution is a narrow distribution with a single mode at 2.525 Å and a width of 0.063 Å. The stacking fault probability is approximately 40%. This high stacking fault probability destroys the long range order and thus widens the pair distribution function maxima at longer distances. On the surface of the particle glutathione molecules are located. Their sulfur atom forms a bond to the cadmium atoms. The smaller Cd–S<sub>glutathione</sub>–S bond angle of 100° causes a distortion of the local Cd environment.

## 5. Conclusion

It has been shown that the first neighbour peaks in a pair distribution function of very small nanoparticles with diameters of less than 2 nm can be interpreted based on single peak fitting

procedures. Such a fit yields the average distance and distance distribution of the interatomic vectors in the first few neighbour shells. By comparing the observed distances with known periodic structures of similar composition, a reliable short range order model can be derived. For longer distances beyond the third neighbour shell single peak fits are no longer reliable due to the high overlap between adjacent peaks. Unless very high quality partial pair distribution functions are available, these peaks cannot unambiguously be assigned to individual pairs. To model the pair distribution function of small nanoparticles, the finite size must be taken into consideration. If the pair distribution function has been determined to distances longer than about half the particle diameter, the deviation of the average neighbour density from the straight line  $4\pi r\rho_0$  must be taken into account. The empirical function presented in equation (4) allows a flexible adjustment of the particle size and shape.

### Acknowledgment

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