A novel real space scattering theory: efficient characterization of colloidal crystals

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Abstract. Recent advances in self-organized 3D ordered structures of submicron particles as colloidal crystals demand a precise quantitative characterization of the produced nanostructures. Small angle scattering is the technique of choice for such a task but a comprehensive quantitative modeling of the measurements is far from being straightforward. We have developed a theory based in the pair distances distribution which take into the account orientational, positional and staking disorder as well as finite size effects. We show also how the radial scattering length density of the constituent particles, essential for a comprehensive modeling of the experimental data, can be estimated from the position of the form factor local minima. The results reduce to sums of analytical functions over the distribution of pair distances and as such, are suitable for easy (automatic) parallelization.
1. Introduction

Monodisperse latex particles, i.e., microspheres of controlled size and variable composition, can be induced to self-organize into 3D ordered structures (colloidal crystals). This remarkable behaviour is not only outstanding from the fundamental point of view [1, 2, 3, 4] but it is also of a great applicability. The ordered 3D arrays can be used as templates for nano-structured porous materials made of a variety of compounds (inorganic oxides, carbon, metals or polymers [5]) with a broad range of applications: optical switches [6], chemical sensors [7] or photonic band gap materials [8]. For these applications the main effort is addressed to obtain large single crystal possessing long-range order, with a low density of defects and small fluctuations of the particle positions. Many properties of colloidal crystals are correlated with the crystal structure, and according to this, it is important to elucidate the mechanism of crystal formation and to develop methodological tools for structural analysis of these systems (see, for instance, [9] for the use of subcritical adsorption isotherms for identifying structural information of colloidal crystals).

Small angle scattering is probably one of the most used techniques for structural characterization of colloidal crystals [10, 11, 12, 13, 14] due to its microscopic sensibility to the structural details. Given its high informative content and the complexity of the structures studied it is not an easy task a quantitative description of the measurements. The traditional approach to the theoretical developments is to work in the the reciprocal space making recourse of the powerful analytical properties of the imaginary exponentials [15]. Orientational average is left to the latest stage of the calculation in order to preserve analytical advantages of the exponentials. Following this line, elaborated calculations have produced significative advances in the quantitative description of the diffraction patterns [16, 17]. However, the production of higher quality crystals is still hampered by the lack of numerically efficient quantitative assessments of the measurements. Here, we propose an alternative theoretical route, akin to the Debye approach (see pag. 49 in [15]), that begins with the orientational average so that the theoretical development is based on the pair distances distribution. Since the final expressions are expressed as sums of analytical terms they profit of the automatic parallelization capabilities of modern multicore processors. These formulae are complemented with a method to extract from the diffractogram an effective radial scattering length density of the constituent particles, essential for a comprehensive modeling of the experimental data.

2. Theory

Let us start by assuming an arrangement of scattering entities of finite size, each characterized by a scattering length \( b_i(Q) \) being \( Q \) the scattering vector for the given radiation. The sample is such that all the orientations are well represented or else they are efficiently explored during the measurement (for instance, by an adequate rotation of the sample). Under such circumstances the singly scattered radiation by such an object is given by,

\[
I(Q) = N \langle |b(Q)|^2 \rangle + \langle \sum_{i \neq j} b_i(Q) b_j^* (Q) e^{-iQ \cdot (r_i - r_j)} \rangle ,
\]

where the \( r_i \) vectors point to the positions of the “centers” (the centers of mass, for instance) of the \( N \) entities illuminated by the radiation, the bar denotes orientational average and the angular brackets denote ensemble average over the rest of needed statistical distributions, typically center positions and size. As a first approximation we will assume that the various distributions are uncorrelated, a reasonable assumption for colloidal crystal of quasi-spherical particles. Then,

\[
I(Q) = N \left( \langle |b(Q)|^2 \rangle - |\langle b(Q) \rangle|^2 \right) + N |\langle b(Q) \rangle|^2 S(Q) ,
\]
where \( S(Q) \) is the orientationally averaged structure factor given by

\[
S(Q) = 1 + \frac{1}{N} \sum_{i \neq j}^{N} \langle \text{sinc}(Q d_{ij}) \rangle, \tag{3}
\]

being \( d_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \). Disordered systems with large size dispersion are not accurately reproduced by Eq. (2) since correlations between size and pair distances develop. Dilution of the system leads to \( S(Q) \to 1 \) so that the \( I(Q) = N \langle |\mathbf{b}(Q)|^2 \rangle = NP(Q) \) being \( P(Q) \) the average form factor of the constituent entities. For small enough scattering length variance, \( P(Q) \simeq \langle |\mathbf{b}(Q)|^2 \rangle \), the first term in Eq. (2) vanishes, and \( I(Q) \) can be approximated by \( NP(Q)S(Q) \). In such a case, measuring the scattering of a dilute version of the system allows for the estimation of the structure factor by simple division.

We will now address the various effects shaping the structure factor, i.e., affecting the pair distances distribution, leaving for the next section those related with the scattering length.

### 2.1. Structure factor

Characteristic of an ideal crystal is a definite deterministic set of pair distances \( \{d_{ij}\} \). In a real crystal, on the contrary, the \( d_{ij} \) are statistically distributed. Let as assume that the corresponding probability distributions, \( g_{ij} \), are of the Schulz (or Gamma) kind, that is,

\[
\gamma(x; \alpha, \bar{x}) = \frac{1}{\Gamma(\alpha)} \left( \frac{\alpha}{\bar{x}} \right)^\alpha x^{\alpha - 1} \exp \left( -\frac{\alpha x}{\bar{x}} \right), \tag{4}
\]

where \( \bar{x} \) is the mean value of the random variable \( x \) and \( \alpha \) is a shape factor such as the variance is given by \( \sigma^2 = \bar{x}^2 / \alpha \). The inverse of the squared root of shape factor, \( \sigma_p = 1/\sqrt{\alpha} \), is in fact the dispersion normalized to the mean. The subindex \( p \) refers to polydispersity since, following Pusey [18], we will use it as an index of polydispersity within the context of colloidal particles. It should not be confused with the polydispersity index coefficient (PDI) a more common characterization of polydispersity (see section 3). The advantage of the Schulz distribution is that allows for analytical integration of products of trigonometric functions with powers of the random variable. In particular,

\[
\langle \text{sinc}(Q d_{ij}) \rangle = \int \gamma(d_{ij}; \alpha_{ij}, \bar{d}_{ij}) \text{sinc}(Q d_{ij}) \, d d_{ij} = \alpha_{ij} \left( 1 + \frac{Q \bar{d}_{ij}^2}{\alpha_{ij}} \right)^{-\frac{\alpha_{ij} - 1}{2}} \sin \left[ (\alpha_{ij} - 1) \arctan \left( \frac{Q \bar{d}_{ij}}{\alpha_{ij}} \right) \right]. \tag{5}
\]

Choosing different relations between the \( \alpha_{ij} \)'s and the \( \bar{d}_{ij} \)'s we can choose the type of disorder. Thus, disorder of the first type, such us thermal spreading, lead to the same dispersion for all the \( \bar{d}_{ij} \) since on average a lattice with long range order is preserved and the positions just spread with a given \( \sigma \) around the sites of the lattice. Therefore \( \alpha_{ij} = \bar{d}_{ij}^2/(4\sigma^2) \), that is, \( \alpha_{ij} \) is quadratic on the distance. In disorder of the second type, typical of colloidal crystals, no average lattice with long range order is defined but only the mean and dispersion of the first neighbors distances. For a \( d_{ij} \) corresponding to positions of a linear chain in the crystal of first neighbors \( n \) sites apart, the distribution is that of a random variable sum of \( n \) variables following the distribution of the close neighbor distance, \( d \). Being such a distribution a Schulz one with scale parameter \( \alpha \), \( d_{ij} \) follows simply \( \gamma(d_{ij}; n \alpha, \bar{d}_{ij}) \). Since \( \bar{d}_{ij} = nd \), we have \( \alpha_{ij} = (\alpha/d)\bar{d}_{ij} \), i.e., \( \alpha_{ij} \) is linear with the distance. As a first approximation we will assume the same proportionality for every direction in the crystal (or more correctly paracrystal). This will suffice to grasp the structure factor lineshapes characteristic of this type of disorder.
Typically for colloidal crystals the structure will be of the closed packaged kind such as the fcc lattice. Let us suppose that the colloidal particles are quasi-spherical with a mean diameter $d$ and a polydispersity $\sigma_p$. As far as the lattice is concerned, we will assume that the lattice parameters are those corresponding to a diameter $d_l$, not necessarily equal to $d$. This extra degree of freedom allows up to a certain extend to deal with deformed particles by action of stress forces during self-assembly of the particles. To calculate the $S(Q)$ of a fcc paracrystal we first generate the discrete pair correlation function for the fcc structure, i.e., a lookup table with entries of the form $g_n = \{d_{ij}, m_{ij}\}$ where $m_{ij}$ is the multiplicity of $d_{ij}$ per particle. $S(Q)$ is then calculated as,

$$S(Q) = 1 + \sum_{n}^{M} g_n(2) \langle \text{sinc} \ [Q g_n(1)] \rangle,$$

where $g_n(1)$ and $g_n(2)$ denote the first and second elements of the $g_n$ entry, $M$ is the size of the table and the average is calculated using Eq. (5) with $\alpha_{ij} = d_{ij}/(d\sigma_p)$. However, generating the lookup table for not very small structures is rather time consuming since its size goes as the square of the number of sites and we need to explore a rather dense set of crystal sizes to match the effective grain size of our polycrystalline sample. The table for the infinite fcc structure is far less expensive to calculate since only the distances to one of the points of the Bravais lattice have to be calculated. The table will be of a finite size and therefore suitable only above a minimum $Q_{\text{cut}}$ but very large tables can be generated rather quickly. The $m_{ij}$’s of a finite crystal decay to zero as the $d_{ij}$’s approach the size of the crystal. They are also below those of the infinite crystal so that the ratio between both multiplicities also decay to zero. Such a decay depends on the crystallite shape but once normalized to the maximum pair distance it follows a universal curve independent of the size. We have explored master curves for many different crystallite shapes and found that all of them fit well with the mono-parametric family (see fig. 1),

$$f_{a}(x) = \exp \left( -\frac{ax}{1-x} \right),$$

where $a$ is the slope at the origin. Therefore, from the lookup table corresponding to the infinite crystal, we can approximate the structure factor of a crystal of size $s$ by,

$$S(Q) = 1 + \sum_{n}^{M} f_{a} \left( \frac{g_n(1)}{s} \right) g_n(2) \langle \text{sinc} \ [Q g_n(1)] \rangle.$$
yield the same hcp crystal. Any alternate series will represent a closed packed structure. The 2D lattice is generated by the lattice vectors $\mathbf{a} = \hat{x}$ and $\mathbf{b} = (1/2)\hat{x}+ (\sqrt{3}/2)\hat{y}$. The third component necessary to span the 3D structure is given by $\mathbf{c} = \sqrt{2/3}\hat{z}$, again in terms of the diameter being $\hat{z}$ perpendicular to the layers. Now, any given structure is determined giving the set of probabilities $P_k$ that two layers separated by a distance $k\sqrt{2/3}$ being identical. For the closed packed structures $P_k$ can be calculated as a function of $k$ parametrized by the probability $\beta$ that layers $n$ and $n+2$ have the same lateral position. More explicitly, $P_k(\beta) = 1/3 + q_1|\rho_1|^k + q_2|\rho_2|^k$ being $\rho_{1,2}$ the roots of the equation $\rho^2 + (1-\beta)\rho + 1-2\beta = 0$ and $q_1$ and $q_2$ determined by the the conditions $P_0(\beta) = 1$ and $P_1(\beta) = 0$ (see page 49 in[15]. See also [20, 21]) Each closed packed structure is, then, determined by a unique parameter, $\beta$, with $\beta = 0$ for the fcc lattice, $\beta = 1$ for the hcp and $\beta = 0.5$ for a random stacking sequence. We need, now, to construct the $S(Q)$ from the pair distances of the infinite crystal. From any sphere in the reference layer, $k = 0$, any distance to any other sphere in a no displaced layer adopt the form $\sqrt{(i+j/2)^2+(3/4)^2+(2/3)k^2}$ where $i, j, k$ are the indexes of the lattice vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$. To a displaced layer we have, irrespectively of being a $t_+$ or a $t_-$ displacement, $\sqrt{(i+j/2+1/2)^2+(3/4)(j+1/3)^2+(2/3)k^2}$. If we generate a lookup table, $G_{n_0}^0$, for the “squared” 2D distances $(i+j/2)^2+(3/4)j^2$ and $G_{n_0}^1$ for the displaced

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**Figure 1.** (color online) Ratio between the multiplicities of finite size crystals, $g_{n}(2)$, and those of the corresponding infinite crystal, $g_{n}(2)$, as function of the pair distance normalized to the longest for three different crystallites. The corresponding fits with $f_a$ are also shown. The data set in black corresponds to a crystallite with the symmetry of a symmetric primitive cell (upper right corner). For this crystallite the scaling with the crystallite size is shown for three different sizes in the inset. The lower left crystallite is of the same type but with and elongated aspect ratio.
version \((i + j/2 + 1/2)^2 + (3/4)(j + 1/3)^2\), we finally have,

\[
S(Q) = \sum_k \left\{ P_k(\beta) \sum_n f_n \left( \sqrt{G_n^0(1) + (2/3)k^2} \right) \right. \\
\left. + \frac{G_n^0(2)}{s} \left( \sin \left[ Q\sqrt{G_n^0(1) + (2/3)k^2} \right] \right) \right\}.
\]

The average over the statistical distribution of stacking faults given by the \(P_k(\beta)\)'s do not allow
making recourse of a complete 3D pair distances table. At any rate, Eq. (9) is amenable to
automatic parallelization allowing a fast calculation for rather large lookup tables.

2.2. Scattering length terms

In order to compute Eq. (2), we now need to calculate \(\langle |b(Q)|^2 \rangle\) and \(\langle b(Q) \rangle\). Assuming isotropic
particles the orientational average is automatic. For spheres of constant scattering length density \(\rho\) and radius \(R\), the corresponding scattering length is \(\rho b^{ph}(Q, R) = \rho(4\pi R^3/3) 3 \sin(QR) / (QR)^3\). Again, using a gamma distribution for the radii both \(\langle b(Q) \rangle\) and \(\langle |b(Q)|^2 \rangle\), although cumbersome, admit analytic expressions [22, 23]. If the particles are isotropic but with
a varying scattering length profile, they can be approximated by a finite number, \(M\), of shells
of constant \(\rho\) so that the scattering length reads, \(b(Q) = \sum_{m=1}^{M} c_m b^{ph}(Q, mR/M)\), where the
coefficients fulfill \(c_m = \rho_m - \rho_{m+1}\), being \(\rho_m\) the length density of the \(m\) shell (\(\rho_{M+1} = 0\)).
This decomposition allow us to calculate averages over radii distributions. The problem now is
how to determine the number of shells, \(R\) and the \(c_m\)'s coefficients. In principle we could
think of some fitting procedure provided we have measurements of the average form factor from
small angle scattering of the particles in dilution. However, the radial profile and radius of the
particles in dilution can be substantially different from those of the dried counterparts present
in the crystal. Nevertheless, in many cases we can estimate some of the minima of the average
form factor since they are particularly conspicuous features in the diffraction patterns. But the
minima of the form factor are dominated by the zeros of \(b(Q)\) event for rather large dispersion
in the radii. Let us suppose we know an estimation of the \(M\) first minima which in turn are
a good approximation to the first \(M\) zeros of \(b(Q)\). We can construct a radial profile with \(M\)
shells given rise to a \(b(Q)\) passing by the zeros in the following way. First, notice that the \(c_m\)'s
must fulfill the linear system:

\[
0 = c_1 b^{ph}(Q_1, R/M) + \ldots + c_m b^{ph}(Q_1, R) \\
\vdots \\
0 = c_1 b^{ph}(Q_M, R/M) + \ldots + c_m b^{ph}(Q_M, R),
\]

being \(Q_1, \ldots, Q_M\) the estimated zeros. Therefore, the matrix of coefficients, \(A_{ij} = b^{ph}(Q_i, jR/M)\), of the linear system must have null determinant. Finding the first zero of
\(\det(A)\) give us the minimum \(R\) to accomplish the task. Solving, then, Eq. (10) determine the
\(c_m\)'s up to a constant factor. In practice, since the zero of \(\det(A)\) is determined numerically,
it is better to solve the underdetermined system corresponding to only \(M - 1\) zeros. Having
estimated the zeros of \(b(Q)\) from experimental data does not make sense the very high numerical
precision necessary to \(\det(A) = 0\) in order to obtain a non null solution of Eq. (10).
3. Sample preparation

Spherical particles of Polystyrene-Methacrylic acid (PS-MAA) latexes were prepared from surfactant-free emulsion by a standard copolymerization process of styrene and methacrylic acid [9, 24]. Small changes of the original recipe, by increasing the hydrophilic monomer to 9.2 wt% of the total monomer, allowed a reduction of particle size to less than 200 nm which facilitated allocation of the corresponding diffraction patterns within the SAXS Q-range window. The synthesized PS-MAA particles were spheres with a smooth surface morphology. A disk centrifuge photosedimentometer (DCP) (Brookhaven BI-DCP) operating in the line start mode yielded a diameter of $d = 195 \pm 7$ nm. The particle size dispersion expressed by the polydispersity index coefficient (PDI), that is, the ratio $d_v/d_n$ where $d_v$ and $d_n$ are the volume and number average diameters, respectively amounts to PDI = 1.007. This value qualifies the sample as mono disperse (PDI < 1.05). On the other hand, the standard deviation normalized to the mean yielded $\sigma_p = 0.036$. When the suspension was dried the particles self-assemble in nice crystals, as it corresponds to monodisperse spheres (fig. 2).

4. Comparison with the experiments

The diffraction measurements were performed in the BW4 line of the HASYLAB at the DESY synchrotron in Hamburg, Germany. The wavelength used were 1.38 Å. The setup was the USAXS configuration corresponding to a distance from the sample to the detector of 8 m with a beam size of 400 µm. The detector was a marCCD165 camera with and active area of 165 mm of diameter. The pixel size was 79.1 µm what yields in this setup a $\Delta Q$ resolution of $4.5 \times 10^{-5}$ Å. With such a high resolution there is no need of including it in the calculations. The sample was introduced as a powder in a standard quartz sample holder for liquids. Fig. 3 shows the diffraction pattern obtained by angular average of the raw 2D digital patterns actually yielded by the machine. It is a particularly useful example since it allows for a comprehensive study of the structure from the first diffraction peak at low Q’s, to the complete damping of the structure factor at large Q’s. The modeling of the data has been done making recourse of the MINUIT [25] package in its FORTRAN version complemented with manual tweaking and partial fits with Mathematica when necessary.

Centering the modeling just to a few oscillations at large Q’s so that the effect of the $S(Q)$ can be neglected, a fit to the data yields a constant background (subtracted from now on in all the shown diffractograms) as well as preliminary values for the mean diameter, $d = 181.1$ nm and polydispersity, $\sigma_p = 0.019$. Adding a simple background representing the tail of the form factor
of a distribution of very large size aggregates, namely a pure Porod dependence ($\sim 1/Q^4$), we proceed with a first attempt of a complete fit assuming spherical particles with constant scattering length density, $\rho$. As shown in fig. 4, the model fails to fit the three main peaks, firstly because the background is too high at those Q’s and secondly because the minima of the form factor do not match those of the data.

Figure 4 also illustrate how the minima of the data are dominated by the minima of the form factor. A simple graphical estimation of the positions of the thirteen minima was done. The obtained values were then used as an input to Eq. 10 yielding an underdetermined system corresponding to the twelve first zeros of $b(Q)$. The obtained $b(Q)$ showed indeed, a zero at the position of the thirteen minimum. No background can be determined unambiguously from the data. In particular, a pure Porod contribution, although fitting the highs of most of the minima as stated above, fails at low Q’s. So the Porod profile, which can be understood as the diffuse scattering coming from large disordered aggregates, must be corrected with some other contributions reflecting the diffuse scattering coming from smaller aggregates and any other kind of disorder not included in the theory. To fix the matter in a simple manner we added to the Porod dependence, a broad distribution of finite diameter spherical particles. In fact, we used the broadest possible distribution of diameters giving a null probability of zero diameter, that is, one with $\alpha = 2$. The amplitudes of both contributions plus the mean diameter of the broad distribution were then chosen to fit of the highs of the experimental minima. A mean diameter of just 19 nm led to a reasonable background as shown in fig. 5.
\[ I(Q) \]

Figure 4. Comparison of the model with constant \( \rho \) (thickest red line) to the data (blue circles) for the values shown of the fitted parameters. Also shown are the form factor (thick red line), the background (thick black line) and the \( S(Q) \) (thin black line). \( d \) is the mean diameter of the particles, \( \sigma_p \) is the diameter dispersion normalized to the mean, \( d_l \) is the lattice constant of a triangular layer of the closed packaged structure, \( \beta \) is the probability of two alternate layers being in the same lateral position (\( \beta = 0 \) implies fcc, \( \beta = 1 \) implies hcp), \( a \) parametrizes the decay of pair distances multiplicities and \( s \) is an effective grain size.

As shown in fig. 5, except for the first peak, excellent fits can then be obtained. The high of the first peak, on the other hand, is anomalously low and incompatible with the height of any reasonable form factor. This points to some kind of shadowing of the signal at the lowest angles. Certainly, comparing the model and the signal leads to a multiplicative correction akin of some kind of shadow (see fig. 6). That the experimental setup produced such a shadow in some way we were not aware of seems improbable. Preliminary analysis seems to indicate it is due to specular reflection over crystalline planes. Indeed, below a small enough angle of incidence, the planes shown in fig. 2 will look like a uniform medium. Reflection on such a surface could well produce a similar effect to the mask pictured in the inset of fig. 6 as attested by the aspect of the reflectivity in the Fresnel approximation for this kind of systems [26]. At any rate, further study will be necessary to clarify the matter.

5. Discussion
Table 1 summarizes the final values of the fitted parameters. Some comments regarding their relevance and corresponding consequences seems in order.

Beginning from the size distribution the mean diameter obtained is below that given by DCP (195 nm). This is something to be expected since DCP is giving the hydrodynamic size in
Figure 5. Comparison of the model (thick red line) to the data (blue circles) for a radial distribution of $\rho$ as shown in the inset. Also shown are the background (up thick black line) and the $S(Q)$ (down thick black line). The values of the fitted parameters are the same than in the constant $\rho$ case except for the diameter now slightly reduced: $d = 180.8$ nm. The vertical lines mark the positions of the Bragg peaks of a pure ($\beta = 0$) fcc structure.

suspension known to be larger than the size of the dried particle [27]. The fitted $\sigma_p$ is also half of DCP value pointing to a segregation out of the crystal of particles with sizes far from the mean. On the other hand, not surprisingly [28, 29, 11], the SEM images show deformed particles towards dodecahedral cells within the crystalline parts (see inset in fig. 3). Estimation of the size of the particles from the SEM picture lead to a major diameter of $d_M = 176 \pm 5$ nm and a minor diameter $d_m = 154 \pm 5$ with a corresponding $\sigma_p$ of 0.03. Since the fitted diameter corresponds to that of a spherical particle representing an orientational average of the real particles the sensible comparison is with $d_M$ which certainly is compatible with the fitted diameter. The value of $\sigma_p$, however, depart substantially from the that of table 1 but still is lower than the one obtained by DCP.

A key point of the theory to successfully model the data is the allowance of a lattice parameters independent of $d$. Although the value $d_l$ is only smaller than $d$ by a 3 %, the fit is very sensible to it and certainly a $d_l = d$ is ruled out. It is rewarding that this simple isotropic modification with respect to the ideal case of spherical particles is enough to grasp the effect of the particle deformation. The polydispersity, on the other hand, do not need to be altered. The fitted value of $\beta$ indicates a clear preponderance of the fcc structure giving further support to the rational of Norris et al.[30] in favor of such a lattice for this kind of colloidal crystals.
Figure 6. As in the previous figure but with the model masked by the “shadowing” function shown in the inset.

With respect to the effective crystallite size the fit render a grain size of $s = 13.1$ ordered triangular layers before any dislocation breaks the coherence of the crystal. Although substantial, such a coherence length is not enough to separate the first two Bragg peaks (see fig. 5) which would be otherwise split in the infinite crystal. As a matter of fact, we have also checked that the experimental lineshapes cannot be reproduced with disorder of the first kind (too narrow lineshapes at high Q’s).

In regarding the shape of the grains, the modeling is fairly sensible to the type of crystallite but only up to a certain degree. From the $a$ value corresponding to the symmetric primitive cell shown in fig. 1, i.e., $a = 4.34$, to above, decently good fittings are obtained choosing the adequate value of $s$, although the best values are near $a = 4.34$ (the final quoted value of $a = 4.09$ yields only a marginally better fit than $a = 4.34$). As shown in the figure for the case $a = 5.79$, values of $a$ above 4.34 can be obtained from the symmetric primitive cell case simply changing the aspect ratio of the crystallite. The character of the boundary planes of the symmetric primitive cell case, which are all $\{111\}$, are still retained. However, the case $a = 2.93$, corresponding to the best approximation to a pure cubic crystallite, does not fit at all. We see, then, that there is more information in the lineshapes than the mere overall size of the grains given by the $s$ parameter. The densest planes (the $\{111\}$ planes are the densest of a fcc structure) are preferred for the grain boundaries. This makes sense given the feeble interactions among the colloidal particles. Indeed, the claveage planes pictured in the SEM images (fig. 2) in which only planes $\{111\}$ and $\{100\}$ (the next densest) are seen, show this preference.

In regarding the scattering length density, in view of the apparently slight deviation in the minima, it is rather surprising how large is the deviation with respect to the constant case. It makes a strong case towards the necessity of comprehensive modeling of the diffractograms.
Table 1. Final fitted values

| Size distribution parameters | Lattice parameters | Effective crystallite parameters |
|-----------------------------|--------------------|---------------------------------|
| $d = 180.4 \text{ nm}$ | $d_l = 0.97 \, d$ | $a = 4.09$ |
| $\sigma_p = 0.019$ | $\beta = 0.11$ | $s = 13.1 \text{ layers}$ |

Certainly, from the changing rate of polymerization as well as the increasing area during the particle formation we cannot expect a final constant density. At any rate, it should be taken into the account that $\rho$ corresponds to a representative spherical particle representing the average of the real entities and as such it is also affected by the deformation of the real particles.

A part from the deviation of the main peak possibly owing to specular reflection in the cleavage planes of the crystallites, the second main deviation is the shoulder appearing in the second peak not present at all in the data. We do not know the origin of such deviation. We have detected texture in the isolated 2D images actually yield by the diffractometer but it disappears when added up due to the wandering of the X-ray beam. Still, that does not guarantee a negligible influence of texture something that would require a three dimensional scanning of the sample orientation. Perhaps, the detailed structure of the specular refection due to the three dimensional variations of the scattering owing to the crystal structure can lead to extinction of the shoulder. A more accurate account of the particle deformation could contribute also, to correct the deviation.

Finally some words about the computational efficiency. To compute one instance of the $I(Q)$ shown in fig. 4 takes just 0.75" in a laptop with a dual core processor at 2.2 GHz. The code was written in FORTRAN compiled with automatic parallelization. Probably the mayor efficiency enhancement comes from the treatment of the grain size. Based on expression (7) it allows to rely in a table of distances to a given origin which grows as the number of particles and therefore as the cube of the size representing a huge improvement with respect to the pair distances table which grows as the size to the sixth.

6. Conclusion

In conclusion, we have developed a scattering theory capable of a comprehensive quantitative account of the small angle scattering diffractograms of colloidal crystals. We have shown how critically it depends not only in the structure of the crystal but in the internal structure of the scattering particles, at the same time giving a method to extract the radial distribution of scattering length from the diffraction pattern. The implementation proposed is numerically efficient smoothing the way to quantitative characterization and comparison of samples prepared under different conditions.

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