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Scattering of clusters of spherical particles—Modeling and inverse problem solution in the Rayleigh–Gans approximation

Guillermo E. Eliçabe*

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J.B. Justo 4302, 7600 Mar del Plata, Argentina

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ABSTRACT

In this work, an exact scattering model for a system of clusters of spherical particles, based on the Rayleigh–Gans approximation, has been parameterized in such a way that it can be solved in inverse form using Thikhonov Regularization to obtain the morphological parameters of the clusters. That is to say, the average number of particles per cluster, the size of the primary spherical units that form the cluster, and the Discrete Distance Distribution Function from which the *z*-average square radius of gyration of the system of clusters is obtained. The methodology is validated through a series of simulated and experimental examples of x-ray and light scattering that show that the proposed methodology works satisfactorily in unideal situations such as: presence of error in the measurements, presence of error in the model, and several types of unideallities present in the experimental cases.

1. Introduction

The characterization of clusters of small particles by scattering techniques is important in many scientific and technological applications that involve the morphological study of soot agglomerates and aggregated colloidal particles [1]. For instance, the characterization of aerosols of soot emitted from combustion devices has driven great attention because of its effects on public health and the environment [2,3]. Morphological studies of clusters of colloidal particles can be useful in the design of building blocks for new types of colloidal assemblies or of model particles to understand the fundamental physics of particulate systems [4]. Also the stability and controlled aggregation of colloidal systems for toner applications is another area in which cluster characterization plays an important role [5].

Scattering characterization techniques require the use of a model that represents the scattering event that happens between the incoming beam, i.e. light, x-rays or neutrons, and the system of clusters that is been analyzed. Exact models derived from Maxwell's equations give a precise description of diluted systems of clusters, but are computationally complex [6,7]. Concentrated systems can also be analyzed with these models, but the computational load is so heavy that realistic simulations are unrealizable. On the other hand, the Rayleigh Gans (RG) approximation has been developed for many years and applied with success to model scattering by systems of clusters [1,8,9]. Indeed, x-ray and neutron scattering can be analyzed using the RG approximation without resigning precision [10]. In the case of light, the optical contrast between particles and the suspending medium must be low and the phase shift parameter must be $\ll 1$, for the RG model to be valid [11].

A vast bibliography on the modeling of scattering by systems of clusters under the RG approximation has been developed in recent years [2,12–15].

In order to characterize the clusters, the model that describes the scattering process, together with the measured scattering spectra, must be used in order to infer the morphological parameters of the clusters. This procedure

* Tel.: +54 2234816600.
E-mail address: elicabe@fi.mdp.edu.ar

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is generally known as the solution of the inverse scattering problem. The solution of this problem is in many cases unstable and requires what is known as regularization.

In this work, an exact model under the RDG approximation is used to derive an inverse methodology that allows one to estimate, for a system of arbitrary clusters in diluted concentration, the parameters that characterize morphologically the clusters; i.e. the average number of particles per cluster, the size of the primary spherical units that form the cluster, and the Discrete Distance Distribution Function (DDDF) from which the z-average square radius of gyration of the system of clusters is obtained. The model, cast in appropriate form, is solved in an inverse fashion using Thikonov Regularization [16] to estimate the aforementioned parameters. The methodology is validated through a series of simulated and experimental examples of x-ray and light scattering.

2. Scattering model of a system of clusters of spherical particles in the RDG approximation

A group of N arbitrary non-overlapping particles located at positions given by $\mathbf{R}_j$ ($j=1,\ldots, N$), scatters light with amplitude electric field, E_S, given by [10]

$$E_S(\mathbf{R}) = -E_0 \frac{\exp(ikR)}{R} \sum_{j=1}^{N} b_j(\mathbf{q}) \exp(-i\mathbf{q}\cdot\mathbf{R}_j) \tag{1}$$

where vector $\mathbf{R}$ ($|\mathbf{R}| = R$) indicates the position of the detector, E_0 is the magnitude of the incident field (which in this case is assumed to be polarized perpendicularly to the scattering plane), $\mathbf{q}$ is the scattering vector, and b_j is the scattering length of particle j. Note that time dependence has been omitted. If the particles are spherical and all of the same radius

$$E_S(\mathbf{R}) = -E_0 \frac{\exp(ikR)}{R} b_r(\mathbf{q}) \sum_{j=1}^{N} \exp(-i\mathbf{q}\cdot\mathbf{R}_j), \tag{2}$$

where the scattering length is given by

$$b_r(\mathbf{q}) = \frac{k^2}{2\pi} \frac{(n_1 - n_0)}{n_0} V_r F(q,r) \quad \text{with}$$

$$F(q,r) = \left[\frac{3}{(qr)^3} (\sin\, qr - qr\cos\, qr) \right] \tag{3}$$

Here, n_0 and n_1 are respectively the refractive indices of medium and particles, r is the radius of the particles; q is the absolute value of the scattering vector ($q = |\mathbf{q}| = (4\pi n_0/\lambda_0)\sin(1/2)\theta$); $k = 2\pi n_0/\lambda_0$ is the magnitude of the propagation vector of the incident radiation; θ is the scattering angle; λ_0 is the wavelength of the incident radiation in vacuum; and $V_r = \frac{4}{3}\pi r^3$ is the volume of particles. Thus, the Differential Scattering Cross Section (DSCS) for this generic cluster of particles (i) is given by

$$\frac{d\sigma(q)^{(i)}}{d\Omega} = \frac{|E_S(\mathbf{R})|^2 R^2}{E_0^2} = \frac{k^4}{4\pi^2 n_0^2} (n_1 - n_0)^2 V_r^2 F(q,r)^2 \times \left[N + \sum_{j=1}^{N} \sum_{\substack{k=1 \\ k\neq j}}^{N} \cos(\mathbf{q}\cdot\Delta\mathbf{R}_{jk}) \right] \tag{4}$$

with $\Delta\mathbf{R}_{jk} = \mathbf{R}_j - \mathbf{R}_k$. This formula is valid for a cluster of particles in fixed positions, $\mathbf{R}_j$ ($j=1,\ldots, N$). If one wants to compute the DSCS of either a diluted system of N_c geometrically identical clusters whose orientations are randomly distributed in all possible directions, or a single cluster that is rapidly moving in all possible orientations, such as that the interesting quantity in these two cases is the average value of the DSCS, orientational average, denoted $\langle\,\rangle$, must be taken on the DSCS given before, as follows:

$$\left\langle \frac{d\sigma(q)^{(i)}}{d\Omega} \right\rangle = \frac{k^4}{4\pi^2 n_0^2} (n_1 - n_0)^2 V_r^2 F(q,r)^2 \times \left\langle N + \sum_{j=1}^{N} \sum_{\substack{k=1 \\ k\neq j}}^{N} \cos(\mathbf{q}\cdot\Delta\mathbf{R}_{jk}) \right\rangle \tag{5}$$

where the orientational average can be calculated analytically and is given by

$$\left\langle N + \sum_{j=1}^{N} \sum_{\substack{k=1 \\ k\neq j}}^{N} \cos(\mathbf{q}\cdot\Delta\mathbf{R}_{jk}) \right\rangle = \left(N + \sum_{j=1}^{N} \sum_{\substack{k=1 \\ k\neq j}}^{N} \frac{\sin(q\Delta R_{jk})}{q\Delta R_{jk}} \right) \tag{6}$$

with $\Delta R_{jk} = |\Delta\mathbf{R}_{jk}|$. Finally, the orientationally averaged DSCS of a cluster of spherical particles is given by

$$\left\langle \frac{d\sigma(q)^{(i)}}{d\Omega} \right\rangle = \frac{k^4}{4\pi^2 n_0^2} (n_1 - n_0)^2 V_r^2 F(q,r)^2 \times \left[N + \sum_{j=1}^{N} \sum_{\substack{k=1 \\ k\neq j}}^{N} \frac{\sin(q\Delta R_{jk})}{q\Delta R_{jk}} \right] \tag{7}$$

In any practical application the sample to be proved experimentally will consist of a system of clusters. Assume the standard situation in which the system is made of N_c clusters and the size of the spherical particles that make up the clusters is the same. In this situation, there are three possible cases with regards as to how the system is built: (i) all the clusters have the same number of particles and spatial configuration; (ii) the number of particles in each cluster is the same but the geometrical configuration differs from one cluster to the other; and (iii) the number of particles in each cluster is not the same and consequently the spatial configuration between clusters is different. One could also consider that each cluster in the sample moves so rapidly that during the measurement process it takes all possible positions. Under these assumptions, the DSCS of the system of clusters, i.e. the measured quantity, is given by

$$\left\langle \frac{d\sigma(q)}{d\Omega} \right\rangle = \sum_{i=1}^{N_c} \left\langle \frac{d\sigma(q)^{(i)}}{d\Omega} \right\rangle = \frac{k^4}{4\pi^2 n_0^2} (n_1 - n_0)^2 V_r^2 F(q,r)^2 \times \sum_{i=1}^{N_c} \left[N_i + \sum_{j=1}^{N_i} \sum_{\substack{k=1 \\ k\neq j}}^{N_i} \frac{\sin(q\Delta R_{jk}^{(i)})}{q\Delta R_{jk}^{(i)}} \right] \tag{8}$$

In Eq. (8), the N_i's ($i=1,\ldots, N_c$) are the numbers of primary particles in each cluster.

In order to reduce the number of parameters of the model, Discrete Distance Distribution Functions (DDDF's) $f_j^{(i)}(j=1,\ldots,M)$ are defined for each cluster ($i=1,\ldots,N_c$). Also a set of distances between particles in the clusters $\Delta r_j(j=1,\ldots,M)$is defined. The set of Δr_j's is selected to be the same for all clusters and to cover at least the range defined by the minimum and maximum $\Delta R_{jk}^{(i)}$. The Δr_j's are chosen as $\Delta r_j = \Delta r_{j-1} + \delta\Delta r \quad (j=1,\ldots,M)$, where $\delta\Delta r$ is the discretization step. The$f_j^{(i)}$'s ($j=1,\ldots, M$) represent the number of distances between particles in cluster i that are in the range of distances $\Delta r_j \pm \delta\Delta r$. M is selected to be less than the maximum theoretical number of different distances in a cluster that is equal to $N(N-1)/2$. With these definitions it is possible to write

$$\sum_{j=1}^{N_i}\sum_{\substack{k=1\\k\neq j}}^{N_i}\frac{\sin(q\Delta R_{jk}^{(i)})}{q\Delta R_{jk}^{(i)}} \approx \sum_{j=1}^{M} f_j^{(i)}\frac{2\sin(q\Delta r_j)}{q\Delta r_j} \tag{9}$$

Under these assumptions

$$\left\langle\frac{d\sigma(q)}{d\Omega}\right\rangle = \frac{N_c k^4}{4\pi^2 n_0^2}(n_1-n_0)^2 V_r^2 F(q,r)^2\left(\overline{N}+\sum_{j=1}^{M}\overline{f}_j\frac{2\sin(q\Delta r_j)}{q\Delta r_j}\right) \tag{10}$$

with $\overline{N}=(1/N_c)\sum_{i=1}^{N_c}N_i$ and $\overline{f}_j=(1/N_c)\sum_{i=1}^{N_c}f_j^{(i)}$. $\overline{N}$ is the average number of particles per cluster and the $\overline{f}_j$'s are the average number of distances per cluster that are in the range $\Delta r_j \pm \delta\Delta r$ for $j=1,\ldots,M$. It is clear from the previous discussion that

$$\sum_{j=1}^{M} f_j^{(i)} = \frac{N_i(N_i-1)}{2} \tag{11}$$

3. Inverse problem formulation

In what follows it will be addressed the problem of obtaining the relevant parameters of a system of clusters of spherical particles from measurements of the DSCS of the system. The scattering model of the system is the one developed in the previous section in Eqs. (10) and (11). Assume that relative measurements of the DSCS, $\langle d\sigma(q)/d\Omega\rangle^{(r)}$, which are the ones more commonly found, are considered. In that, case the model of Eq. (10) must include a constant K_1 that depends on the experimental set up, as follows:

$$\left\langle\frac{d\sigma(q)}{d\Omega}\right\rangle^{(r)} = K_1K_2a(q,r)\left(\overline{N}+\sum_{j=1}^{M}\overline{f}_j\frac{2\sin(q\Delta r_j)}{q\Delta r_j}\right) \tag{12}$$

with $K_2=(N_ck^4/4\pi^2n_0^2)(n_1-n_0)^2$ and $a(q,r)=V_r^2F(q,r)^2$.

Define now a vector of relative measurements of the DSCS taken at different moduli of the scattering vector, q_i ($i=1,\ldots, L$),

$$\mathbf{i}=\left[\left\langle\frac{d\sigma(q_1)}{d\Omega}\right\rangle^{(r)} \quad \left\langle\frac{d\sigma(q_2)}{d\Omega}\right\rangle^{(r)} \quad \ldots. \quad \left\langle\frac{d\sigma(q_L)}{d\Omega}\right\rangle^{(r)}\right]^T \tag{13}$$

With this definition, Eq. (12) can be written using matrix notation, as

$$\mathbf{i}=\mathbf{A}(r)\mathbf{S}\mathbf{f}' \tag{14}$$

where $\mathbf{f}'=\left[K\overline{N} \quad K\overline{f}_1 \quad K\overline{f}_2 \quad \cdots \quad K\overline{f}_M\right]^T=\left[K\overline{N} \quad \mathbf{f}^T\right]^T$ is a vector of unknowns, $K=K_1K_2$, and matrices $\mathbf{S}$ and $\mathbf{A}$ are given by

$$\mathbf{S}=\begin{bmatrix}1 & S_{11} & S_{12} & \ldots & S_{1M}\\ 1 & S_{21} & S_{22} & \ldots & S_{2M}\\ \ldots & \ldots & \ldots & \ldots & \ldots\\ 1 & S_{L1} & S_{L2} & \ldots & S_{LM}\end{bmatrix} \quad \text{with} \quad S_{ij}=\frac{2\sin(q_i\Delta r_j)}{q_i\Delta r_j} \tag{15}$$

$$\mathbf{A}(r)=\begin{bmatrix}a(q_1,r) & 0 & \ldots & 0\\ 0 & a(q_2,r) & \ldots & 0\\ \ldots & \ldots & \ldots & \ldots\\ 0 & 0 & \ldots & a(q_L,r)\end{bmatrix} \tag{16}$$

With these definitions, it can be noticed that except for r, all the unknowns of the model are in vector $\mathbf{f}'$. Assume for the time being that r is known. Under this assumption, the solution for $\mathbf{f}'$could be obtained in principle by linear least squares. However, the structure of matrix $\mathbf{S}$ guarantees that the problem has some degree of ill-conditioning that will require a regularization scheme. If the so called constrained Tikhonov regularization is adopted [16], the following minimization problem must be solved:

$$\min_{\mathbf{f}'} J(\mathbf{f}',r)=\{|\mathbf{A}(r)\mathbf{S}\mathbf{f}'-\mathbf{i}^{(m)}|^2+\gamma g(\mathbf{f})\}$$

Subjected to

$$\mathbf{f}'\geq 0 \tag{17}$$

where $\mathbf{i}^{(m)}$ is a vector with the measured values of the relative DSCS defined by the model of Eq. (12). The solution of this problem will give the estimated vector of unknowns $\hat{\mathbf{f}}'=\left[\widehat{K\overline{N}}\,\hat{\mathbf{f}}^T\right]^T$. In the functional of Eq. (17), g penalizes the spurious oscillations in the elements of $\mathbf{f}$, which are proportional to the average number of distances $\Delta r_j(j=1,\ldots,M)$ per cluster, $\overline{f}_j$. The function g is selected so that to constrain the second differences of $\mathbf{f}$, a rather natural requirement for distributions. Thus, the penalty function is given by

$$g(\mathbf{f})=\mathbf{f}'^T\begin{bmatrix}0 & \mathbf{0}_M^T\\ \mathbf{0}_M & \gamma\mathbf{H}\end{bmatrix}\mathbf{f}' \tag{18}$$

with matrix $\mathbf{H}$ ($M\times M$) given by

$$\mathbf{H}=\begin{bmatrix}1+\beta^2 & -2 & 1 & 0 & 0 & \ldots & 0\\ -2 & 5 & -4 & 1 & 0 & \ldots & 0\\ 1 & -4 & 6 & -4 & 1 & \ldots & 0\\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots\\ 0 & \ldots & 1 & -4 & 6 & -4 & 1\\ 0 & \ldots & 0 & 1 & -4 & 5 & -2\\ 0 & \ldots & 0 & 0 & 1 & -2 & 1+\beta^2\end{bmatrix} \tag{19}$$

where β, which is selected to be $\gg 1$, restricts the first and last values of $\mathbf{f}$ ($K\overline{f}_1$ and $K\overline{f}_M$) to be 0, in accordance with what it is expected of distributions. $\mathbf{0}_M$ is a vector of zeros of dimension M and γ is the regularization parameter that

equilibrates the amount of regularization with the amount of fitting. The regularization parameter may be selected using several methods as discussed in reference [17].

To also estimate r, the previous scheme is incorporated into the following algorithm which is similar to the one reported in reference [17]:

1) Select q_i, $i=1,\ldots, L$ and Δr_i, $i=1,\ldots, M$.
2) Calculate $\mathbf{S}$.
3) Give a range of possible values for the radius of the particles in the clusters (r_{min} to r_{max}), and from that range select a set of N_r values of r (r_i, $i=1, \ldots, N_r$).
4) Calculate $\mathbf{A}(r)$ for the N_r values of r.
5) Obtain N_r estimations of $\mathbf{f}'$ ($\hat{\mathbf{f}}'(r_i)$, $i=1, \ldots, N_r$) for each one of the selected values of r using constrained Tikhonov regularization as described before.
6) From the N_r generated pairs ($\hat{\mathbf{f}}'(r_i)$, r_i) select as a solution to the problem ($\hat{\mathbf{f}}'(\hat{r})$, $\hat{r}$) the one for which $J(\hat{\mathbf{f}}'(r_i),\ r_i)$ is minimum.

4. Estimated parameters

With the previous procedure, two estimated variables are obtained: the estimated radius of the primary particles in the clusters, $\hat{r}$, and the vector of estimates $\hat{\mathbf{f}}' = \left[\widehat{K\overline{N}}\ \widehat{K\overline{f}}_1\ \widehat{K\overline{f}}_2 \cdots \widehat{K\overline{f}}_M\right]^T$. It is clear that the elements of $\hat{\mathbf{f}}'$ are estimates which are just proportional to the sought parameters, i.e. $\overline{N}$, $\overline{f}_1$, $\overline{f}_2$, $\ldots\overline{f}_M$. For this reason Eq. (11) together with $\hat{\mathbf{f}}'$ must be used to extract useful information from this vector of estimates. It must be noticed, however, that if K were known the problem would not require the use of Eq. (11) and it could be directly solved. Nevertheless, the most common situation is the restrictive one in which K is unknown, and then this restriction will be assumed.

4.1. Number of particles per cluster

From the result of the estimation, now define $\mathbb{Q} = \widehat{K\overline{N}} / \sum_{j=1}^{M} K\overline{f}_j$. Using Eq. (11) and after a few manipulations, it can be shown that, if the estimation is exact

$$\mathbb{Q} = \frac{2\overline{N}}{1/N_c \sum_{i=1}^{N_c} N_i^2 - \overline{N}} \tag{20}$$

In Eq. (20), the N_is can be written as $N_i = \overline{N} + \Delta N_i$, where $\sum_{i=1}^{N_c} \Delta N_i = 0$. This representation for the N_i's is replaced in Eq. (20) and, after solving for $\overline{N}$, the following expression is obtained:

$$\overline{N} = \frac{\mathbb{Q}+2}{2\mathbb{Q}} + \sqrt{\left(\frac{\mathbb{Q}+2}{2\mathbb{Q}}\right)^2 - V_N} \tag{21}$$

where $V_N = (1/N_c)\sum_{i=1}^{N_c} \Delta N_i^2$ is the variance of the number of particles per cluster. Eq. (21) gives an estimate of $\overline{N}$, i.e. $\widehat{\overline{N}}$, which is a function of $\mathbb{Q}$ and the variance of the number of particles per cluster, V_N. In order to calculate $\overline{N}$, the value of V_N should be externally provided. If the value of V_N is not precisely known, something that is expected, but instead, a lower and an upper bound for V_N, say $V_N^{(l)}$ and $V_N^{(u)}$, are available, then the following lower and upper bounds for $\overline{N}$ can be obtained:

$$\frac{\mathbb{Q}+2}{2\mathbb{Q}} + \sqrt{\left(\frac{\mathbb{Q}+2}{2\mathbb{Q}}\right)^2 - V_N^{(u)}} = \widehat{\overline{N}}^{(l)} < \overline{N} < \widehat{\overline{N}}^{(u)} = \frac{\mathbb{Q}+2}{2\mathbb{Q}} + \sqrt{\left(\frac{\mathbb{Q}+2}{2\mathbb{Q}}\right)^2 - V_N^{(l)}} \tag{22}$$

In this case, the estimated average number of particles per cluster, $\widehat{\overline{N}}$, will be represented by the interval $[\widehat{\overline{N}}^{(l)}, \widehat{\overline{N}}^{(u)}]$, in which the real $\overline{N}$ lies. This interval is expected to be small in order to obtain a useful estimate of $\overline{N}$.

4.2. Radius of gyration of the clusters

From the estimated vector $\hat{\mathbf{f}}' = \left[\widehat{K\overline{N}}\ \widehat{K\overline{f}}_1\ \widehat{K\overline{f}}_2 \cdots \widehat{K\overline{f}}_M\right]^T$ another important parameter can be obtained. First define $\mathbb{C} = \sum_{k=1}^{M} \widehat{K\overline{f}}_k \Delta r_k^2 / (\widehat{K\overline{N}} + 2\sum_{j=1}^{M} \widehat{K\overline{f}}_j)$ which is calculated from the estimated vector and the $\Delta r_k's$. Then it can be demonstrated that, theoretically, $\mathbb{C} = R_{g_z}^2$, with

$$R_{g_z}^2 = \sum_{i=1}^{N_c} \left[\frac{N_i^2}{\sum_{k=1}^{N_c} N_k^2}\right] R_{g_i}^2 \tag{23}$$

which is the z-average square radius of gyration of the system of clusters. Thus, $\sqrt{\mathbb{C}}$ gives an estimate of R_{g_z}, i.e. $\widehat{R}_{g_z}$. In Eq. (23)

$$R_{g_i}^2 = \frac{\sum_{j=1}^{N_i} \sum_{\substack{k=1 \\ k\neq j}}^{N_i} [\Delta R_{jk}^{(i)}]^2}{2N_i^2} \approx \frac{\sum_{j=1}^{M} f_j^{(i)} \Delta r_j^2}{N_i^2} \tag{24}$$

is the squared radius of gyration of cluster i. If the clusters have different spatial configurations but the same number of particles per cluster, N, then $\mathbb{C} = (1/N_c)\sum_{i=1}^{N_c} R_{g_i}^2$, i.e. the number average squared radius of gyration of the different clusters. If all the clusters are identical, $N_i = N$ and $R_{g_i}^2 = R_g^2$ for $i=1,\ldots, N_c$, and in this case $\mathbb{C} = R_g^2$, where R_g^2 is the squared radius of gyration of the cluster.

5. x-Ray simulated example

In this section, the methodology developed before is applied for the estimation of the parameters of a system of clusters computed using the fractal law

$$N = k_f \left(\frac{R_g}{r}\right)^{D_f} \tag{25}$$

where k_f and D_f are the fractal parameters, prefactor and fractal dimension respectively. The system, which is evaluated using small angle x-ray scattering techniques, is composed of four fractions of the same number of identical clusters each one. All clusters in the system are made of spherical primary particles of radius $r=6$ nm. Each one of the four fractions, with 1/4 of the total clusters in the system, is described by the following parameters: (1) fractal parameters $k_f=2.3$ and $D_f=1.78$, $N=60$

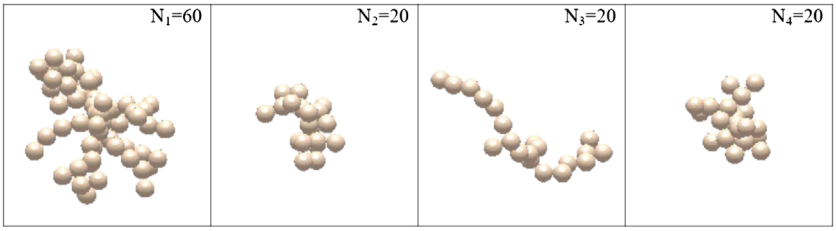

Fig. 1. The four types of clusters used in the simulations of the x-ray example. They correspond, from left to right, to the ones indicated in the text as (1), (2), (3) and (4).

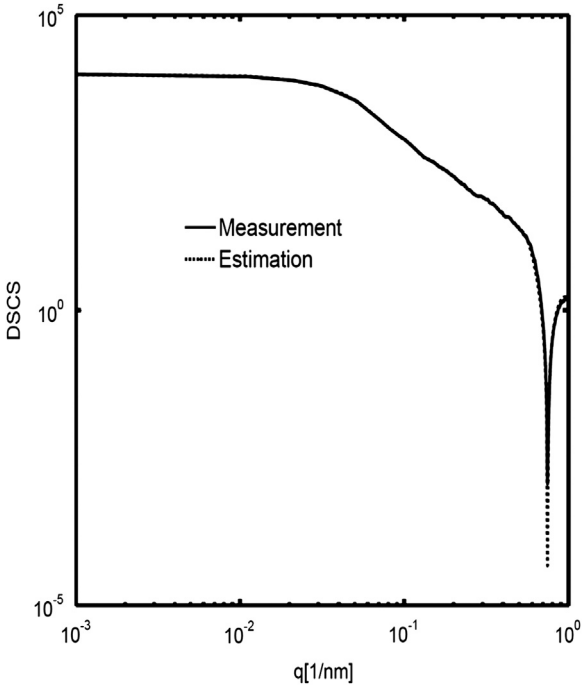

Fig. 2. "Measured" (—) and estimated (——) x-ray relative DSCS spectra as a function of q for the x-ray example for an error level of 5%.

and $R_g = 37.1$ nm; (2) $k_f = 2.3$ and $D_f = 1.78$, $N = 20$ and $R_g = 19.6$ nm; (3) $k_f = 1.5$ and $D_f = 1.3$, $N = 20$ and $R_g = 43.3$ nm; and (4) $k_f = 2.3$ and $D_f = 1.78$, $N = 20$ and $R_g = 19.6$ nm, but in a different spatial configuration than in (2). In Fig. 1, the four types of clusters that compose the system are illustrated. With these parameters for the individual clusters, the parameters to be estimated are $r = 6$ nm, $\overline{N} = 30$ and $R_{g_z} = 35.4$ nm.

In Fig. 2, the simulated measurement of the x-ray relative DSCS spectrum is shown in a full line as a function of q. To compute this "measurement", the theoretical values from Eq. (12) were corrupted with a random error from a zero mean uniform distribution. The error has a q dependent value in the range $\pm 0.05 \langle d\sigma(q)/d\Omega \rangle^{(r)}$; i.e. 5% noise relative to current measurement. The values of q range from 0.001 nm^{-1} to 1.0083 nm^{-1}, and $\lambda_0 = 0.2$ nm. The value of n_0 was taken to be equal to 1.

In order to apply the proposed methodology, the relative measurements of the DSCS of the system of clusters were discretized at $L = 101$ different values of q in the range mentioned before. On the other hand, the

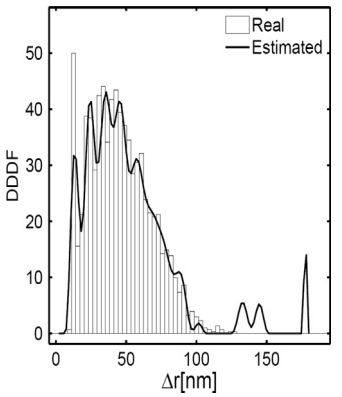

Fig. 3. Real and estimated average DDDF's of the system of clusters for the x-ray example for an error level of 5%.

average DDDF of the system is discretized at $M = 101$ different equidistant values of Δr in the range of distances from 2 nm to 180 nm. This range is usually obtained from previous knowledge of the system and its minimum value should not be larger than $2r$ and its maximum value depends on the type of clusters analized and should be larger than the maximum distance between the two most distant primary particles in all clusters in the system. Usually, the solution of the inverse problem is sensitive to this value.

In Fig. 3, the real and estimated average DDDF's of the system of clusters are shown. The real distribution was calculated from the coordinates of the particles that make up the clusters. Indeed, the real distribution is only available in a simulated set up. The estimated distribution is calculated in a range of distances that is larger than the range of distances of the real distribution, which in a real example is not known. The oscillations at the tail of the estimated distribution, where the real distribtuion is zero, are artifacts related to the ill-conditioning of the inverse problem.

The other estimated parameters are $\widehat{R}_{g_z} = 41.6$ nm and $\widehat{\overline{N}} = 34.3$ nm. In this example, we have assumed that the variance of the N_i, which in this case is 300 nm^2, is known. In Table 1, the estimated parameters are shown for the cases in which the measurement error is 0%, 1%, 5%, and 10%. Lower bounds and upper bounds, $\widehat{\overline{N}}^{(l)}$ and $\widehat{\overline{N}}^{(u)}$ respectively, are reported for $\widehat{\overline{N}}$, for three different levels of knowledge of the variance of the N_is, expressed by the range $[V_{N_i}^{(l)}, V_{N_i}^{(u)}]$: 300–300 nm^2, 250–350 nm^2, and

Table 1

Estimated parameters of the system of clusters for the x-ray example for different levels of measurement error. Lower bounds and upper bounds, $\hat{\overline{N}}^{(l)}$ and $\hat{\overline{N}}^{(u)}$ respectively, are reported for $\hat{\overline{N}}$, for three different levels of knowledge of the variance of the N_i's, expressed by the range $[V_N^{(l)}, V_N^{(u)}]$: 300–300 nm^2, 250–350 nm^2, and 200–400 nm^2.

% error	$[V_N^{(l)}, V_N^{(u)}]$ [nm^2]						$\hat{R}_{g_z}$ [nm] ($R_{g_z}=35.4$)	$\hat{r}$ [nm] ($r=6$)
	$\hat{\overline{N}}^{(l)}$ [part.] ($\overline{N}=30$)			$\hat{\overline{N}}^{(u)}$ [part.] ($\overline{N}=30$)				
	300–300	250–350	200–400	300–300	250–350	200–400		
0[a]	33.6 (12)	31.4 (5)	28.5 (−5)	33.6 (12)	35.5 (18)	37.2 (24)	35.4 (0)	5.98 (0)
1[b]	33.8 (13)	31.6 (5)	28.8 (−4)	33.8 (13)	35.7 (19)	37.4 (25)	36.7 (4)	5.95 (−1)
5[c]	34.3 (14)	32.2 (7)	29.5 (−2)	34.3 (14)	36.2 (21)	37.8 (26)	41.6 (18)	6.02 (0)
10[d]	42.9 (43)	41.5 (38)	39.9 (33)	42.9 (43)	44.3 (48)	45.5 (52)	46.5 (31)	5.95 (−1)

[a] $\gamma=0.001$.
[b] $\gamma=0.01$.
[c] $\gamma=0.1$.
[d] $\gamma=1$.

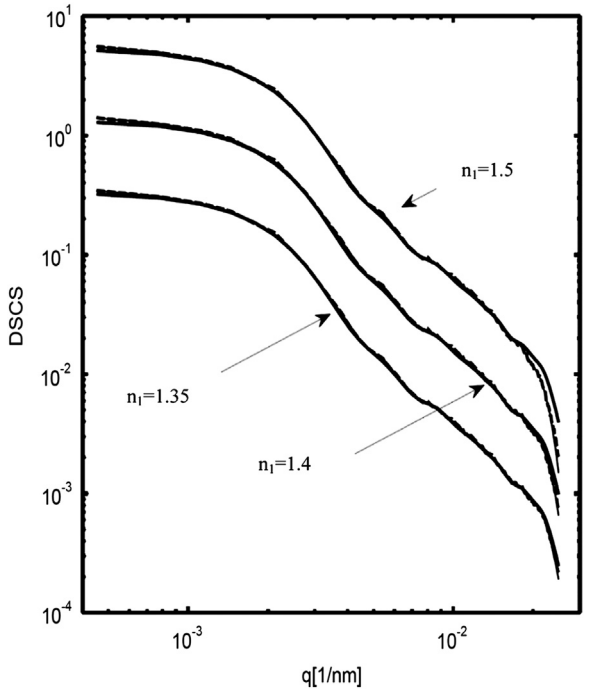

Fig. 4. "Measured" (T-matrix) (——), estimated (—) and calculated with RDG (—) light scattering relative DSCS spectra as a function of q for the light scattering example for a measurement error level of 5%, for $n_1=1.35$, 1.4, and 1.5.

200–400 nm^2. Also the values of $\hat{R}_{g_z}$ and $\hat{r}$ are listed in the table. The estimated parameters agree well with the real ones in the cases in which the uncertainty is low, i.e. low measurement error and narrow knowledge ranges for the variance of the N_i's. As it can be noticed, the estimated values of the $\hat{\overline{N}}$'s deteriorate as the uncertainty increases, resulting the estimations in all cases with a positive error. The same happens with the estimated $\hat{R}_{g_z}$'s but the percentage error is smaller as the measurement error increases. On the contrary, the estimation of the radii of the primary spherules remains hardly affected by the uncertainty increase. The percentage of error with respect to the real value is indicated between parentheses next to the reported estimation.

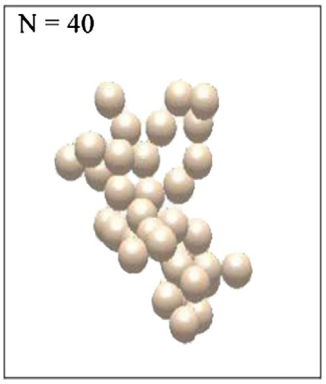

Fig. 5. Cluster of 40 primary spherules used in the simulations of the light scattering example.

6. Simulated light scattering example

Contrary to x-ray static scattering in which the conditions for the RG approximation to be valid are always fulfilled, in static light scattering these conditions generally imply in that a low optical contrast between the suspending medium and the clusters must be achieved, and that the phase shift parameter, $(4\pi r n_0/\lambda_0)((n_1/n_0)-1)$, must be $\ll 1$.

In Fig. 4, the simulated scattering spectra of a fractal cluster in random orientation calculated with the RG approximation and using the exact result provided by the T-matrix method are compared for a range of q values from 0.0005 nm^{-1} to 0.025 nm^{-1}. The value of λ_0 for this example was taken as 632 nm. The "measurements" were discretized at $L=101$ different values of q in the range mentioned before. The average DDDF of the system was discretized at $M=101$ different equidistant values of Δr in the range distances from 2 nm to 5000 nm.

The cluster is the one shown in Fig. 5. It consists of $N=40$ spherical primary particles of $r=150$ nm, and it was generated using a fractal law with $k_f=2.3$ and $D_f=1.78$. In this example, the refractive index of the medium was $n_0=1.3$ and the refractive indices of the particles that make up the cluster were taken as $n_1=1.35$, 1.4 and 1.5. The phase shift parameters are for each of these cases: 0.02, 0.05 and 0.09, respectively. If these values are $\ll 1$ or not, as required by the theory, will be confirmed in the analysis performed below. In Fig. 4 the curves in dotted lines represent the values calculated using the exact result provided by the T-matrix method to which a random error of magnitude 5% calculated in the same form as in the x-ray example was added. The thick solid curves represent the same scattering spectra but calculated using the RG approximation. As it may be noticed, the spectra calculated using the RG model agree well with the exact scattering spectra except for the very small and very large angles in which a small difference is noticed. This difference becomes more pronounced as the optical contrast of the particles with the medium increases, as expected. This result confirms, for this example, the validity of the conditions for RG scattering to be applicable and the weak effect of multiple scattering in this case.

Now, the methodology developed to estimate the clusters parameters is applied to the three cases considered for this cluster, i.e. $n_1=1.35$, 1.4 and 1.5. In Fig. 6 the DDDF's estimated for each case are shown for an error level of 5%. As in the x-ray example, oscillations at the tail of the distributions beyond the upper value of the range of the real distribution are present. As mentioned before, these oscillations are related to the ill-conditioned nature of the solved inverse problem. The parameters to be estimated are: $R_{g_z}=735$ nm, $N=40$ and $r=150$ nm. The results of the estimations are shown in Table 2. In this table the results corresponding to 0%, 1% and 10% measurement error are also illustrated. The spectra fitted to the measurements are shown in Fig. 4 in thin full line for the 5% error case. The estimated parameters agree well with the real ones in the cases in which the uncertainty is low, i.e. low measurement error and low contrast between medium and particles. When the uncertainty is not low, the estimated $\overline{N}$'s slightly deteriorate giving values that are consistently larger than the real ones but do not follow a particular pattern with respect to the uncertainty introduced by the measurement error and the refractive index

Table 2
Estimated parameters of the cluster for the light scattering example for different levels of measurement error for the three cases studied here: $n_1=1.35$, 1.4, and 1.5.

% error	n_1	$\hat{\overline{N}}$ [part.] ($\overline{N}=40$)	$\hat{R}_{g_z}$ [nm] ($R_{g_z}=735$)	$\hat{r}$ [nm] ($r=150$)
0[a]	1.35	43.4 (9)	735 (0)	149 (−1)
	1.4	41.4 (4)	736 (0)	152 (1)
	1.5	39.7 (−1)	740 (1)	157 (5)
1[b]	1.35	44.2 (11)	796 (8)	149 (−1)
	1.4	47.4 (19)	797 (8)	149 (−1)
	1.5	40.4 (1)	801 (9)	157 (5)
5[c]	1.35	47.9 (20)	990 (35)	149 (−1)
	1.4	43.0 (8)	994 (35)	154 (3)
	1.5	41.8 (5)	996 (36)	159 (6)
10[d]	1.35	43.9 (10)	1171 (59)	155 (3)
	1.4	45.1 (13)	1169 (59)	157 (5)
	1.5	42.8 (7)	1178 (60)	160 (7)

[a] $\gamma=0.1$, 1 and 1.
[b] $\gamma=1$, 10 and 10.
[c] $\gamma=10$, 10 and 100.
[d] $\gamma=10$, 100 and 100.

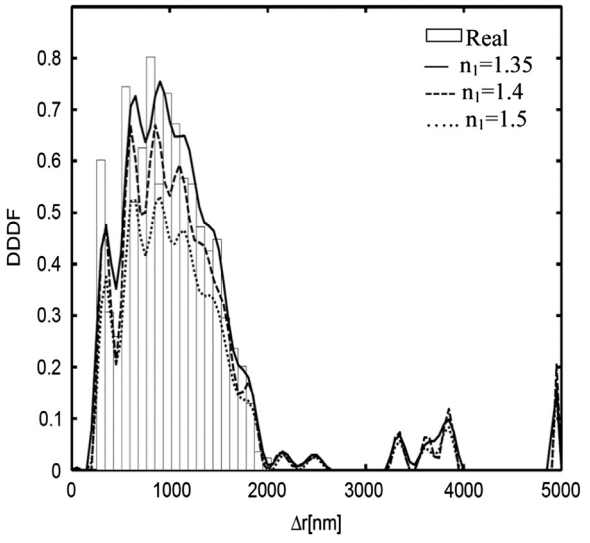

Fig. 6. Real and estimated DDDF's of the cluster for the light scattering example for an error level in the measurement of 5%. (—) $n_1=1.35$, (– –) $n_1=1.4$, and (●●●●) $n_1=1.5$.

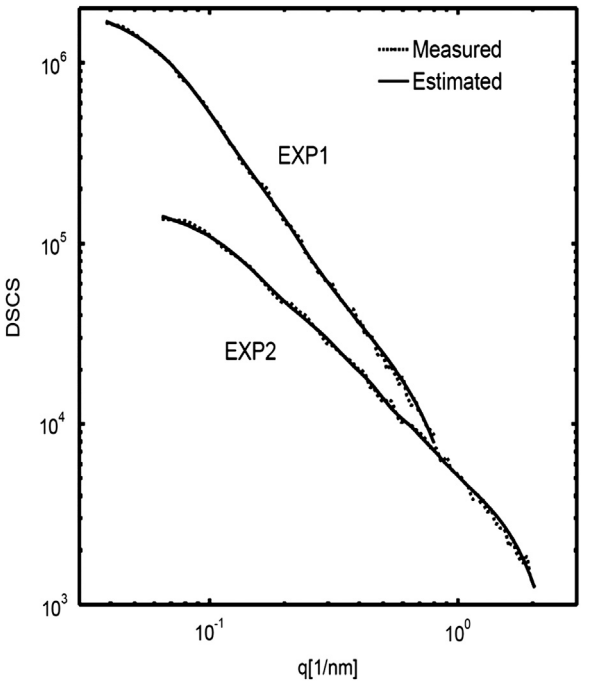

Fig. 7. Measured (●—) and estimated (—) x-ray relative DSCS spectrum as a function of q for the experimental x-ray examples, labeled EXP1 and EXP2.

contrast. As the measurement error increases, the estimations have in all cases a positive error. With respect to estimated R_{g_z}'s, they follow a clear deterioration pattern with uncertainty. Errors in this case are also always positive. Contrarily, the estimation of the radii of the primary spherules remains hardly affected by the uncertainty increase. In the table, also the percentage of error with respect to the real values is indicated between parentheses next to the reported estimations.

7. Experimental x-ray examples

A final application of the methodology developed here will be applied to a couple of experimental small angle x-ray scattering spectra of colloidal samples of aluminum hydroxide made by partial hydrolysis of aluminum chloride solution with sodium hydroxide. The spectra were taken from reference [18] and correspond to a sample characterized by a hydrolysis ratio, x, of 2.6 (EXP1) and to a sample with $x=2.5$ (EXP2). At these values of x the colloidal particles aggregate to form systems of clusters which exhibit fractal dimension $D_f=1.45$ for $x=2.5$ and $D_f=1.86$ when precipitation starts at $x=2.6$.

In Fig. 7 the experimental x-ray relative DSCS spectra of the two samples are shown in dotted line. The collected data cover the q-range 0.0383–0.800 nm^{-1} for EXP1 and 0.0643–2.033 nm^{-1} for EXP2 and the wavelength of the incident x-ray beam is $\lambda_0=0.16$ nm. These experimental values were discretized at $L=121$ different points in the range of q considered for each example. Also the average DDDF's were discretized at $M=101$ equidistant values of Δr over a range of 1–120 nm for EXP1 and over a range from 1 to 60 nm for EXP2. In Fig. 8 the estimated average DDDF's of the systems of clusters are shown for each example. The other estimated parameters were: $\widehat{\widetilde{N}}=62$, $\widehat{R}_{g_z}=23.5$ nm and $\widehat{r}=3.2$ nm for EXP1 and $\widehat{\widetilde{N}}=23$, $\widehat{R}_{g_z}=12$ nm and $\widehat{r}=1.36$ nm for EXP2. These estimations give, using the fractal law of Eq. (25), and for the fractal dimensions reported in [18] for the colloidal samples of aluminum hydroxide analyzed here, the following structure prefactors: $k_f=1.5$ for EXP1 with $D_f=1.86$ and $k_f=0.98$ for EXP2 with $D_f=1.45$. These values for the prefactor parameters are within the range of reasonable values for this quantity [19].

In each case the clusters were considered to have the same number of subunits, i.e. the variance of the number of particles per cluster, V_{N_i}, was set to zero in the estimation scheme. In Fig. 7, the estimated spectra are shown in solid line for both examples.

In these examples the regularization parameters are $\gamma=5.5\times10^9$ for EXP1 and $\gamma=8.6\times10^6$ for EXP2 which were calculated using the Generalized Cross Validation [20]. The authors of the article from which these experimental values were taken also calculated the size and number of the subunits forming the clusters. Their results differ quantitatively from the ones obtained here. These authors assumed that the subunits forming the clusters are of the same size for both experiments, and estimated their size as ~1 nm independently from the scattering data. With this value calculated the number of particles and obtained $\widehat{N}=512$ for EXP1 and $\widehat{N}=64$ for EXP2. The estimation method used in that article is based on an approximated model which may justify the observed differences with the results obtained here.

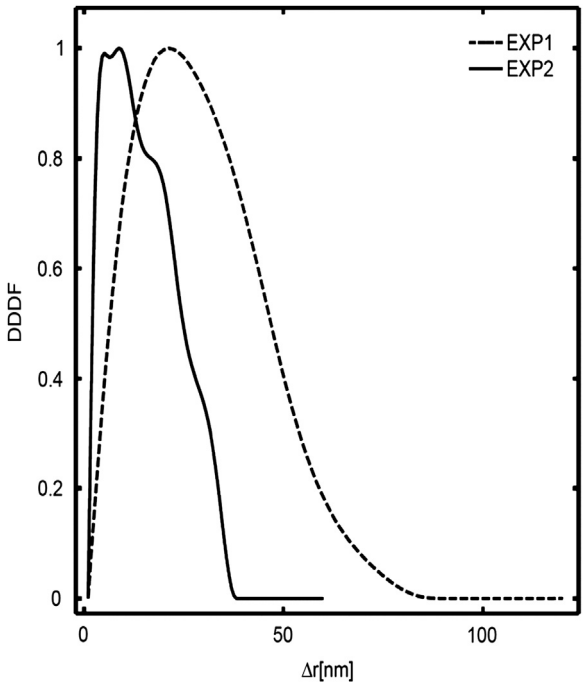

Fig. 8. Estimated normalized average DDDF's of the system of clusters for the experimental x-ray examples, EXP1 and EXP2.

8. Conclusions

In this work, an exact scattering model for a system of clusters, based on the RG approximation, has been parameterized in such a way that it can be solved in an inverse form using Thikhonov Regularization. With the methodology developed here, all the relevant parameters of the clusters can be estimated in a single step procedure without any assumption. Although natural clusters of particles are usually the result of a fractal aggregation process, no assumptions on the relationships between the parameters of the clusters have been made in this work. Thus, the results presented here also apply to non-fractal clusters. The simulated as well as the experimental examples presented in this work show that the proposed methodology performs satisfactorily in unideal situations such as: presence of error in the measurements, presence of error in the model, and several types of unideallities present in the experimental example.

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