

Scattering properties of dense clusters of nanoparticles

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ABSTRACT

In this work, we present a strategy aimed at improving the utilization of Small Angle Light Scattering (SALS) for the characterization of dense clusters of spherical particles. By making use of a tunable fractal dimension Monte-Carlo algorithm, we generate dense clusters with a desired fractal dimension (d_f). In order to analyze clusters with a d_f larger than 2.5, we introduce a new algorithm which is capable of making clusters progressively denser and reach d_f equal to 3. The cluster structure is then characterized by means of its pair-correlation function, which is used to compute their scattering properties through a mean-field version of the T-Matrix theory. The scattering profiles from mean-field T-matrix theory compensate for the limitations of the more commonly used RDG theory and are effectively used in the analysis of SALS data from coagulation experiments of polymer colloids.

Keywords: small angle light scattering, clusters, Monte-Carlo simulations, pair correlation function, T-Matrix theory

1 INTRODUCTION

In sheared induced coagulation processes of colloidal nanoparticles, which are customarily used in most industrial processes, dense clusters of particles are usually formed. The characterization of their size, structure and distribution is a key factor for the quality control of the final product. However, the challenges encountered in the characterization of suspensions of dense clusters are numerous. While several microscopy-based techniques have been proposed that can access information such as size, shape, and structure of clusters, their long analysis times and difficult preparation do not make them the ideal techniques for routine analysis. On the other hand, small angle light scattering (or laser diffraction) techniques are more commonly used to perform this characterization, because of their speed, excellent statistics and great simplicity. Nevertheless, a major obstacle in the effective utilization of this technique is the lack of realistic structural models for shapes other than spheres or cylinders. In the case of dense clusters of spheres, the commonly used Rayleigh-Debye-Gans (RDG) theory fails because of the intracluster multiple light scattering effects, which are particularly important for particles with a size comparable

to that of the wavelength of the incident radiation. These conditions are unfortunately more the rule rather than the exception in industrially relevant coagulation processes. In addition, there is also a lack of structural information on the morphology of dense clusters, which makes the determination of scattering profile even more difficult.

In this work, a methodology is presented that aims at overcoming these limitations. First of all, a tunable fractal dimension Monte-Carlo algorithm, initially proposed by Thouy and Jullien [1], is used to generate dense clusters with a desired fractal dimension. Since it is well known that the tunable fractal dimension algorithm cannot generate clusters with fractal dimension larger than 2.5, a new procedure has been developed to create cluster with fractal dimension up to 3. This procedure starts from clusters with a fractal dimension equal to 2.5 and creates a Voronoi tessellation of the space occupied by the cluster, which is made progressively denser by moving particles initially located on its surface to its interior. In this manner, the entire range of cluster fractal dimension encountered in typical aggregation processes, ranging from 1.8 to 3, is covered. The cluster structure is then characterized by means of its pair correlation function. The pair correlation function is finally used to compute scattering properties of cluster used a mean-field version of the T-Matrix theory, proposed by Botet et al.[2], which can provide reliable scattering behavior of dense clusters with arbitrary primary particle size. The predictions of the mean field T-matrix theory are compared to RDG theory predictions, to show the difference between these two approaches. In addition, the application of these results to the analysis of coagulation experiments of polymer colloids is discussed.

2 MONTE-CARLO GENERATION OF CLUSTERS

The Monte-Carlo tunable fractal dimension algorithm used in the first part of this work is virtually identical to that proposed by Thouy and Jullien [1]. According to the original idea, a given number of particles are sequentially connected to form progressively bigger clusters, making sure that at each step the clusters formed fulfill certain criteria, *i.e.* their fractal dimension and prefactor are assigned, so that the relationship between mass i and size:

$$R_g = R_p \cdot \left(\frac{i}{k}\right)^{\frac{1}{d_f}} \quad (1)$$

where R_g is the cluster radius of gyration, R_p is the primary particle size and k is the prefactor, gives directly the target radius of gyration for a given mass. During the formation of a cluster, several possible combinations are considered, until equation (1) is fulfilled within a given precision. The process is repeated by randomly selecting at each step one pair of clusters.

However, it is well documented that this strategy is very effective in generating clusters with a fractal dimension up to 2.5 [1]. Above this value, it is highly unlikely to find a random combination of clusters that can form an extremely dense cluster. However, since in the case of clusters formed during shear aggregation processes it is not unusual to form cluster with a fractal dimension of 2.6 or higher, an alternative algorithm is introduced in order to form highly dense clusters. In real shear aggregation processes, the high fractal dimension values are obtained as a result of a combination of aggregation, breakage and restructuring of each cluster due to the action of the fluid. Since a realistic simulation of the real phenomenon is physically very challenging, once again a totally empirical approach is followed. The densification process starts from a cluster with a $d_f=2.5$, and first creates a Voronoi tessellation of the space occupied by the cluster. The Voronoi tessellation is then used to find the amount and position of empty spaces inside the cluster. Then, particles located on the outer surface of the cluster are progressively moved to its interior, until all empty spaces are occupied. The procedure is extremely effective, and leads to the generation of clusters up to $d_f=3$. As an example, Figure 1 shows a typical cluster made of 1000 particle with a $d_f=2.5$.

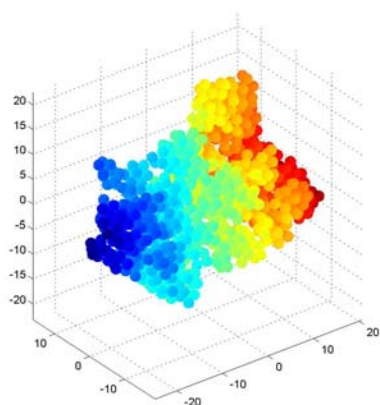


Figure 1. MC cluster with 1000 particles and $d_f=2.5$.

The structural characterization of the clusters is carried out by determining the average particle-particle correlation function $g(r)$, which gives the probability of finding a particle at a distance r from the average particle. The $g(r)$ function contains all most important structural properties of clusters, such as number of nearest neighbors, fractal

regime and upper size [3]. An example of particle-particle correlation function is given in Figure 2 for a cluster made of 10000 particles and with $d_f=2.2$.

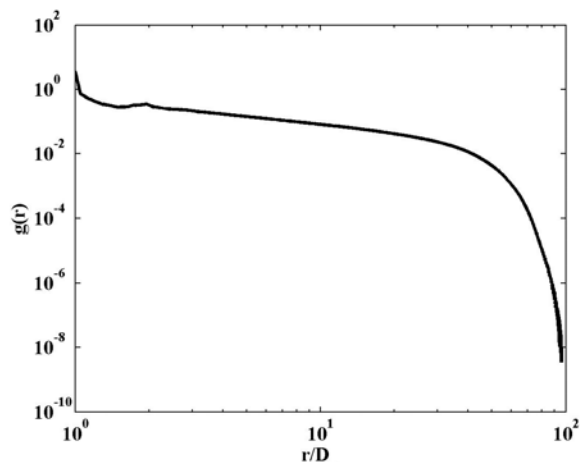


Figure 2. Particle-particle correlation function $g(r)$ of a cluster with 10000 particles and $d_f=2.2$.

3 LIGHT SCATTERING THEORY

According to the simplified RDG theory [4], which neglects any multiple scattering effects, the intensity of the radiation scattered by one cluster made of identical subunits is proportional to the square of the cluster mass. The angular dependence of the scattered radiation $I(q)$ (where q is the scattering wave vector), contains two contributions: the form factor of one single subunit $P(R_p, q)$, depending upon the subunit size and shape, and the structure factor $S(q)$, which depends upon the relative positions of the subunits. Quantitatively, this reads:

$$I(q) \sim i^2 P(R_p, q) S(q) \quad (2)$$

where i is the number of particles in the cluster. The consequence of equation (2) is that in a suspension containing a large number of clusters with different masses, the bigger cluster will contribute much more to the total intensity of the scattered radiation compared to the small clusters. The above mentioned description, however, fails to provide the correct description in the case when multiple light scattering is playing a role, as it happens in the case of dense clusters, or in the case of clusters made of large particles. In this case, it is not possible anymore to factorize the form factor from the structure factor, since the intensity of light scattered by any particle depends specifically on its location inside a cluster. The rigorous T-matrix theory [4] accounts for this effect, and uses an extension of Mie theory accounting for the contribution from all the neighbor particles to scattering of any specific particle.

However, in the case of fractal clusters, where there can be several realizations of clusters with the same mass and structural properties, Botet et al [2]. proposed a mean-field version of T-Matrix theory, which used a similar formulation as the RDG one, except that the form factor is corrected to account for the multiple light scattering contribution that the average particles experiences in the cluster. In other words, the form factor is not anymore just a function of size and optical properties of the particle, but is also a function of the cluster structure. The correction factor can be determined if the particle-particle correlation function is known. It is worth noting that the structure factor is not changed from RDG to mean-field T-matrix theory.

4 RESULTS AND DISCUSSION

One of the consequences of the mean-field T-matrix theory is that the intensity of the scattered radiation is not anymore proportional to the square of the mass of the cluster, but to a power of the mass which depends on its fractal dimension and on its primary particle size. This implies that:

$$I(q) \sim i^\alpha P(R_p, q) S(q) \quad (3)$$

where α is a number that can be as low as $2/3$ in the case of very large spheres. For clusters with d_f up to 2.5 and particle size of 700nm, the zero angle scattered intensity is plotted in Figure 3. It can be clearly seen that the exponent is decreasing as the fractal dimension increases, going to 1.5 for $d_f=2.5$. This means that large clusters will contribute much less to the overall scattering in a solution compared to what RDG theory predicts.

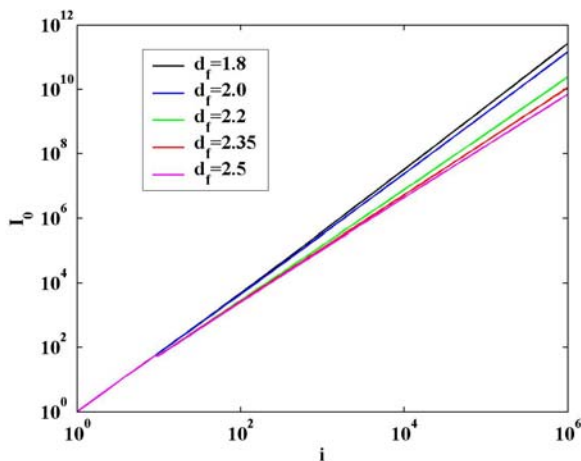


Figure 3. Zero angle scattered as a function of the cluster mass for cluster with different d_f values, made of 700nm polystyrene particles (incident light having a wavelength of 633nm)

In order to give a flavor of what can be done with the broad collection of structural and scattering properties we have available, we have chosen to treat a couple of sets of experimental SALS data of coagulating polymeric colloidal particles. The first case is that of a dispersion of particles undergoing DLCA aggregation. We have used our library of structural properties to invert SALS data collected from a sample of 70nm polystyrene particles in DLCA conditions (fractal dimension 1.8). The inversion of the data, in order to recover the cluster mass distribution, has been achieved using CONTIN algorithm. CONTIN [5] is a well known powerful algorithm for the solution of ill posed integral equations, such as the one arising from the inversion of scattering data. In order to provide a clear idea of the substantial advantage of our approach over conventional structural models, we have treated the same data using both the fractal model we have developed and the conventional one which assumes that the dispersion is made of a population of spheres, instead of a population of clusters. The results are shown in Figure 4. Figure 4a shows the experimental data and all the fittings, while Figure 4b shows the distributions. Clearly, using the scattering profiles of spheres leads to a totally meaningless distribution, whereas the use of fractal scattering profiles give a distribution quite close to the one predicted by Population Balance Equations [3]. Interestingly, all of the fittings of the experimental data are almost equivalent. This results show the importance of using the correct structural model to invert SALS data.

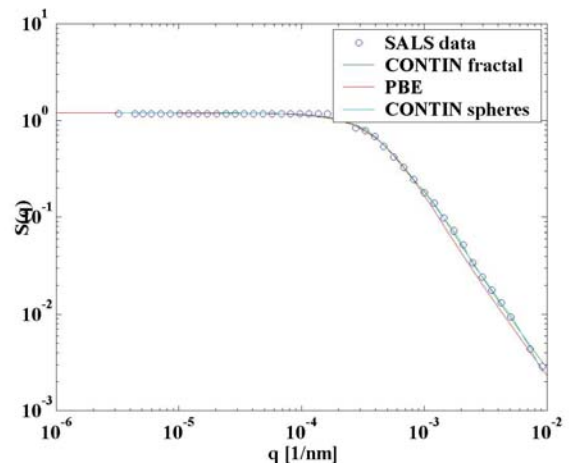


Figure 4a. SALS experimental data from DLCA cluster of 70nm particles ($d_f = 1.8$). Fitting using distributions calculated from PBE, extracted using CONTIN and both fractal model and sphere model are shown.

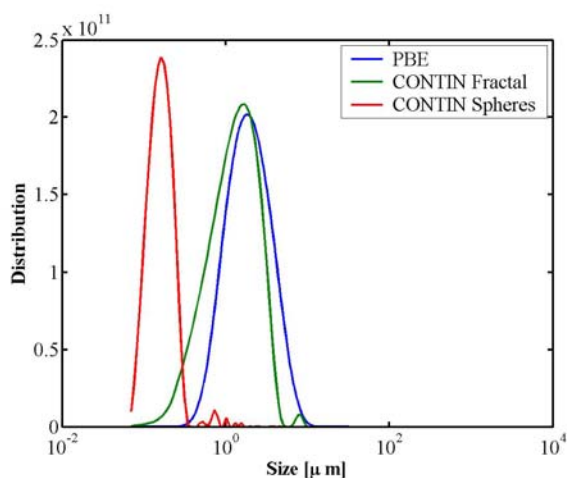


Figure 4b. Comparison of cluster mass distributions calculated and extracted from data shown in Figure 4a. PBE calculations results, and CONTIN results with both fractal model and sphere model.

5 CONCLUSIONS

We have shown in this work a methodology to better treat SALS data from cluster of particles. First of all, a library of cluster structures has been generated using a tunable cluster-cluster aggregation Monte-Carlo algorithm, which generates clusters with a fractal dimension up to $d_f = 2.5$. In order to go beyond that limit, a densification algorithm has been proposed, which using a Voronoi tessellation of space to find the empty space inside the cluster and fill it. The structure of the fractal clusters is then characterized in terms of particle-particles correlation function. The correlation function is also the required information for computing scattering properties of clusters within the framework of mean-field T-matrix algorithm, which provides realistically into account the intra-cluster multiple scattering. These properties have been shown to be effectively used in combination with CONTIN algorithm to invert experimental SALS data of colloidal clusters in order to extract the cluster mass distribution.

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