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Forward light scattering to characterise structure of flocs composed of large particles

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Abstract

Forward light scattering has been a popular technique for measuring the fractal dimension of aggregated or flocculated particles. The method relies on the measurement of the slope of scattered intensity versus scattering vector (q) on a log–log plot. In the Rayleigh–Gans–Debye approximation, the negative of the slope has the value of the mass fractal dimension of the aggregates.

In this work, simulation results were used to test the idea that Fraunhofer diffraction can be used to describe scattering from fractal aggregates. Polystyrene latex of diameter 4.9 μm was aggregated in a forward light scattering instrument, and the fractal dimension was determined independently by the volume obscuration method. Comparison of the experimental data with simulations showed poor agreement. It is suggested that multiple scattering within the aggregate structure, ignored in the usual Fraunhofer formulation, is significant.

Keywords: Light scattering; Aggregation; Fractal; Flocculation

1. Introduction

The properties and behaviour of particle aggregates are of considerable interest to those concerned with solid–liquid separation operations, such as thickening and filtration. In these operations, flocculants are commonly added to increase the particle size (which increases the kinetics of the separation process) and to give the aggregated material sufficient strength to behave appropriately in the process. The agglomerate properties required (size, strength and structure) could change depending on the particular process which is being considered. It is believed that for processes, such as vacuum filtration a high strength, high porosity flocculated network is required to resist the applied hydrodynamic forces and maintain sufficient permeability to achieve the desired level of dewatering. Thickeners, on the other hand, subject the flocculated material to very different conditions and have a completely different mechanism for dewatering. It would be surprising indeed if exactly the same flocculated network properties were shown to be optimal in both cases.

The physical properties of flocculated particles and of the consolidated networks that they form are a function of the physical strength of the bonds between particles and the spatial arrangement of those particles. The spatial arrangement or structure of the flocs encompasses a large number of individual structural measures, such as the coordination number distribution, the number and size of loops in the structure and the fractal dimension.

This work concentrates on the structural measure known as mass fractal dimension, D_m, which describes the way that the mass of an aggregate or floc fills space. It describes the convolutedness or fluffiness of flocs, with smaller numbers (approaching a lower limit of 1) indicating very spread out, tenuous and stringy structures, and larger numbers (approaching an upper limit of 3) indicating structures that are usually mechanically stronger and quite dense. An ability to measure these properties and behaviours of flocculated material is critical to having proper control over solid liquid separation processes. Any technique that can measure relevant floc properties on-line would be a potentially very valuable tool in the improvement of process control.

The measurement of the fractal dimension of flocs can be achieved by a number of means [1], most of which are quite tedious laboratory procedures that will never be suitable for

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on-line applications. One of the methods that is commonly used is small angle light scattering. The idea behind this method is that the scattering pattern of light from particles depends on the details of the particle size distribution, optical property distribution (refractive index and absorption coefficient) and the particle structure. When used in commercial particle sizing instruments, the particles are assumed spherical, the optical properties are given by the user and assumed constant, and all of the variation in the observed scattering pattern is assumed to result from variations in particle size. These assumptions are quite good for most applications. However, one can make other assumptions about the nature of the particles that are scattering the light. For instance, the assumption that the scatterers are fractal aggregates is probably a better assumption for flocculated particles than assuming that they are spherical. This then gives us the possibility to determine structural information as well as size information from the scattering patterns. The main difficulty with making shape assumptions other than spherical is in modelling the scattering properly. Spherical particles have a well-known solution for light scattering that is valid for all particle sizes and optical properties, and can be calculated to arbitrary precision [2]. In assuming fractal aggregates, we have only one model to calculate scattering, known as the Rayleigh–Gans–Debye approximation [3]. This approximation is only accurate in the limit that the particles comprising the aggregate are smaller than the wavelength of the incident light and have a not-too-large refractive index. In practice, this means that the model is only really valid for particles somewhat smaller than a micron. This leaves out large classes of important materials, such as mineral tailings, which may have diameters of several microns and are usually of quite high refractive index. Individually, the scattering from such particles is well described by the Fraunhofer diffraction approximation. It is the aim of this work to discover whether this approximation is suitable for fractal aggregates of such particles.

2. Experimental

The aim of the experiment is to present large fractal aggregates of large particles to a scattering instrument, measure the resulting scattering pattern and to independently measure the structure of the aggregates. The observed scattering patterns can then be compared with the predictions of the Fraunhofer diffraction approximation. Polystyrene latex with sulfate surface groups was supplied by Interfacial Dynamics Corporation. The latex particles had a diameter of 4.9 μm and were white in colour. These particles have density close to that of water so there are no experimental difficulties associated with sedimentation, yet are large enough that their individual extinction coefficient is reasonably close to that of particles that are well described by the Fraunhofer diffraction approximation. What this means in this context is that the extinction coefficient is 2.25 μm (calculated from Mie theory), which is reasonably close to 2.0 (the expected value in the Fraunhofer limit). As the system aggregates, the extinction coefficient can only get closer to 2, leading to a maximum error of around 10% arising from uncertainty in the extinction coefficient of the aggregates.

Magnesium nitrate solution was prepared at 0.1 M using water from a millipore filtration system and then passed through a 0.22 μm filter to remove any particles associated with the salt.

Stock solution of flocculant (Floerger FO4800SH supplied by SNF Australia) was prepared with millipore water at 0.1 wt% and stored in a refrigerator at 4 °C. The flocculant was diluted from the stock to 10 ppm just before the experiments and the stock solution was discarded and freshly prepared after 4 days.

Prior to use the latex was shaken well to disperse sediment that collected at the bottom of the container and to ensure a uniform concentration for the experiment. Measurement of the shaken latex in a Malvern Mastersizer/S confirmed that the particles exist in a fully dispersed state, with a single sharp peak in the particle size distribution observed at 5 μm. The batch cell for the Malvern instrument was cleaned with millipore water and filled with the $MgNO_3$ solution to measure any background scattering. The magnetic stirrer supplied with the batch cell was operated at the slowest achievable speed (of the order of several hundred rpm) for the duration of the experiment. The exact stirring speed was not important to the experiment as no particular aggregate size or structure was required. Latex suspension as supplied was added to the cell in order to achieve an obscuration of around 50%. This is somewhat higher than the recommended range for analysing particle size, of 10–30%. The reason for this was that as the particles flocculate the obscuration will drop, and the aim here was to get aggregation states that can be considered fractal within the optimal range of 10–30%. If the obscuration was started at 30%, the upper end of the optimal obscuration range will be populated by small aggregates and individual particles that are not fractal in structure, and useful fractal aggregation information will be lost below the 10% obscuration level as the aggregation proceeds.

Aggregation was initiated by the addition of a small amount of diluted flocculant solution, achieving an overall flocculant concentration of 0.5 ppm in the cell.

3. Results and discussion

The fractal dimension of the aggregated latex was determined independently of the scattering pattern by the volume obscuration technique. The obscuration observed for a given sample, assuming that the particle concentration is low enough that the fraction of the total projected area obscured by other particles is small and that the particles are large enough that their extinction coefficient is constant with particle size, is given by:

$$\text{obscuration} \propto n_a A_a \quad (1)$$

where n_a is the number of aggregates and A_a is the projected area of an aggregate. If we have an aggregating fractal system, the radius of aggregates, R_a, is related to the number of particles in an aggregate N_a by

$$N_a \propto R_a^{D_m} \tag{2}$$

Since the total mass of the system is conserved, the total number of aggregates in the system is related to n_p, the total number of primary particles by

$$n_a = \frac{n_p}{N_a} \tag{3}$$

If the fractal dimension is higher than two and the aggregates are large enough, the projected area of an aggregate is related to N_a by

$$A_a \propto R_a^2 \tag{4}$$

Therefore, the total projected area seen by the instrument is

$$A_T = n_a A_a \propto \frac{n_p}{R_a^{D_m}} R_a^2, \text{ so that} \tag{5}$$

$$A_T \propto R^{2-D_m} \tag{6}$$

In other words, a plot of log of obscuration versus log of aggregate size should show a straight line with slope of $(2 - D_m)$. This plot is shown in Fig. 1, for the experiment with latex spheres. Obscuration is as reported by the instrument and size refers to the mass median size reported by the instrument, although the analysis is not sensitive, to which measure of size is chosen as long as the same measure is used for all points. The fractal dimension was evaluated to be 2.42 ± 0.06. In the case of large aggregates with fractal dimension less than 2, the projected area is constant and the plot would show constant obscuration as a function of aggregate size. A representative scattering pattern for the system is shown in Fig. 2. A clear power law dependence of the scattered intensity on the magnitude of the scattering vector, q, can be seen. The exponent of this power law is 2.42 ± 0.09 (hereafter referred to as the scattering exponent). In making this kind of analysis, there is a problem that arises in that the signal detected at the zero angle position inevitably includes some light scattered at very low angles. The effect of this would be to decrease the observed obscuration below the true value, and the effect would become larger as the particle size increases. This could lead to an underestimation of the fractal dimension by this method, although the effect has not been quantified in this analysis.

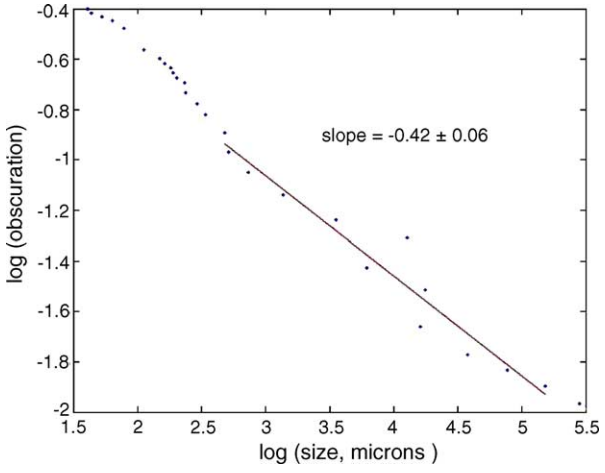

Fig. 1. Log–log plot of obscuration against particle mass median size showing the fractal dimension for the experimental system. The fractal dimension is $2 - (-0.42) = 2.42$.

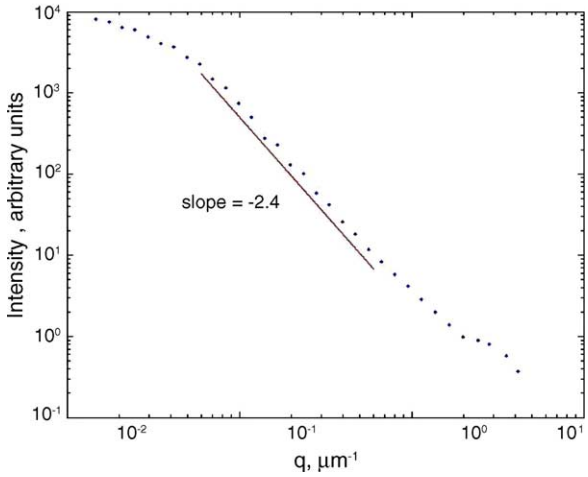

Fig. 2. Log–log plot of scattered intensity as a function of scattering vector magnitude. The scattering exponent is −2.4, which is the same as the value of the fractal dimension determined earlier.

Preliminary results were presented in an earlier work [4] that showed a relationship between the scattering exponent of simulated fractal aggregates and their fractal dimension. That work was extended here to cover a wider range of fractal dimension. Simulated fractal aggregates with 10,000 particles per aggregate were generated using a cluster–cluster algorithm similar to that developed by Thouy and Jullien [5]. Visualisations of some of the simulated aggregates can be seen in Fig. 3. To calculate the scattering patterns, images of the projection of each aggregate were obtained from a random orientation. Each image was represented by a pixel size of 10% of the primary particle diameter and the two-dimensional point-to-point correlation function was measured between pixels. The Fraunhofer scattering pattern was calculated from correlation function of the projection using the formulation of Cao and Watson [6].

A comparison between the simulated scattering exponent (the slope of the linear portion of a log–log plot of scattered intensity against q) with the true fractal dimension of the simulated aggregates is shown in Fig. 4. Clearly, the simulated results are not in agreement with the experimental data. According to the simulation results, a scattering exponent of 2.4 as was observed experimentally would be associated with a fractal dimension of around 2.05. Given that the simulated aggregate structures can be analysed for fractal dimension with a high degree of confidence, this implies that the calculation

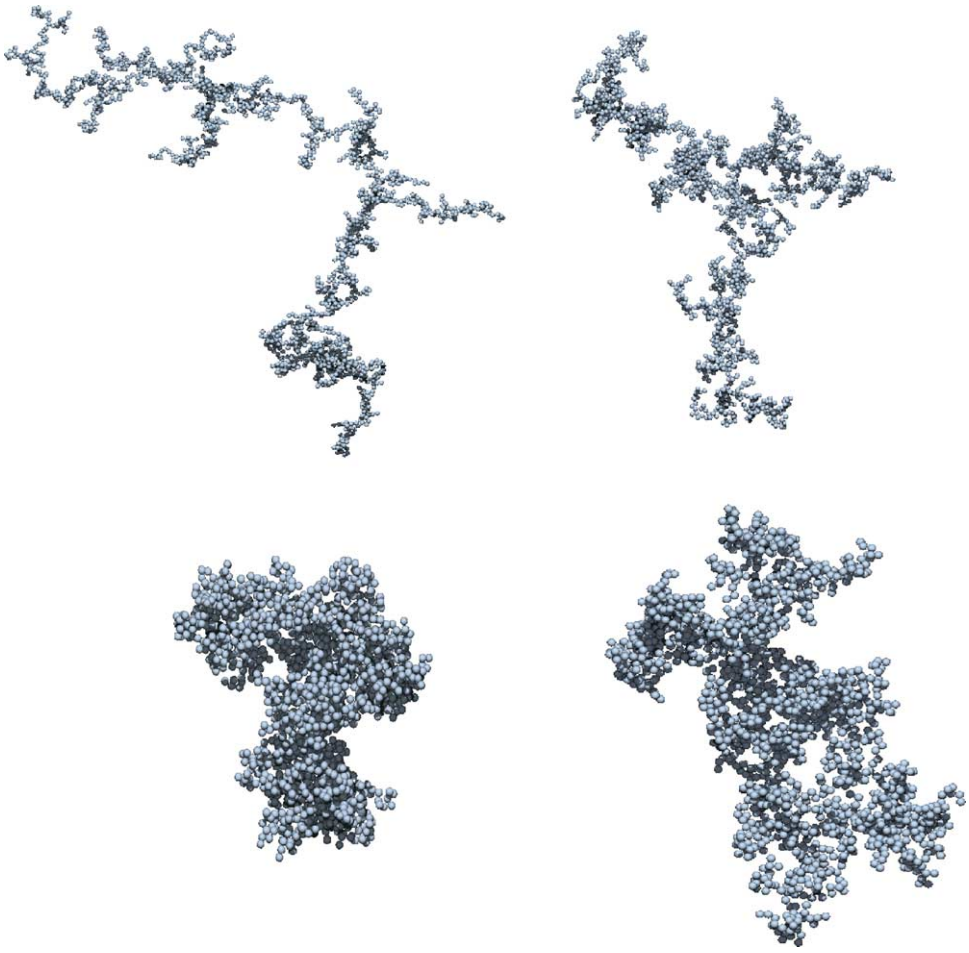

Fig. 3. Visualisations of simulated aggregates having different structures. Fractal dimensions are (clockwise from upper left) 1.544, 1.796, 2.071 and 2.390.

of the scattering pattern is not correct. This possibility was raised in the work of Stone et al. [4]. The work presented here seems to show that in fact the multiple scattering effects within an aggregate do make a significant contribution to the observed scattering pattern. Compressing an aggregate structure into a simple projected image ignores these important effects, and consequently, the predicted scattering patterns are incorrect. A more sophisticated approach to simulating scattering from these aggregates of large particles is required, such as the T-matrix approach [7] or a ray-tracing simulation.

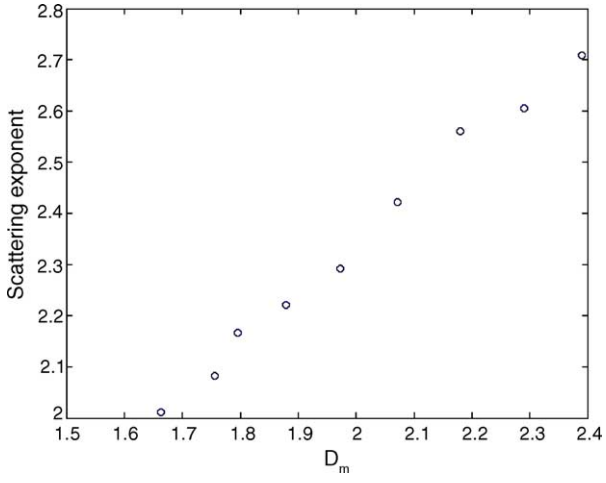

Fig. 4. A plot of simulated scattering exponent against fractal dimension for simulated aggregates with a range of different fractal dimensions.

Although the simulated results do not agree with the experimentally measured scattering, the fractal dimension as measured from the volume obscuration method appears to be consistent with the analysis of scattering using the Rayleigh–Gans–Debye formulation, which gives

$$I \propto q^{-D_m} \tag{7}$$

where q is the scattering vector, directly related to the sine of half the scattering angle. This is interesting because the RGD approximation has only been shown to be a reasonable approximation for fractal aggregates when the primary particles are very much smaller than a micron [8], although there is some evidence that as particle size and consequently aggregate internal multiple scattering increases, the q^{-D_m} dependence of scattering is maintained [9]. The limits to which this remains a reasonable approximation for the purposes of measuring the fractal dimension has not yet been established,

even though this is a matter of considerable practical interest. The results presented here suggest that the limit may apply at least as far as quite dense aggregates of 4.9 μm latex particles.

4. Conclusion

In order to establish whether small angle light scattering can be used to characterise the structure of aggregates of large particles, simulations were carried out to determine the scattering patterns shown by fractal aggregates using the Fraunhofer approximation. A relationship between this simulated scattering exponent and the fractal dimension was shown, broadly consistent with earlier work although the calculation approach was slightly different. Aggregates of 4.9 μm latex particles were made in the sample cell of a forward light scattering instrument. An independent measure of the fractal dimension was made, and was compared to the observed scattering exponent. The scattering exponent and the fractal dimension were shown to have the same value, at odds with the result of the simulation work. This suggests that the effects of multiple scattering within the aggregate structure, ignored in the traditional Fraunhofer scattering formulation for solid particles and apertures, are probably significant for aggregates examined here.

An alternative to the Fraunhofer approximation that can deal with multiple scattering is required to verify whether this apparent q^{-D_m} scattering is really reflective of aggregate structure for what are quite large primary particles. If it can be shown to be the case, this would be a highly significant result because it would mean that the structure of aggregates of quite large particles (compared to the wavelength of light) could be analysed by the same simple approach as aggregates of very small particles.

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