Fractal Cluster Size Distribution Measurement Using Static Light Scattering

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For qRc < 1. In Eq. [1], I(q) is the scattered intensity at wave vector q. Equation [1] holds regardless of refractive index or morphology and hence is very useful for determining cluster or particle size through Rc. It has been used widely for spread applications (1-5).

We have used Eq [1] to determine Rc values for soot aerosols (4-6). We found it conceptually useful to plot the inverse, normalized scattered intensity, I(q)/I(q=0), versus q2 because such graphs should be linear with a slope of Rc2/3 and remain quite linear even when qRc > 1. This plot is similar to a Zemans plot (7, 8) except that the cluster concentration extrapolation is carried out since our soot clusters are near zero concentration. The linearity for qRc < 1 is puzzling, as Eq. [1] should only hold for qRc < 1 and plots of the complete structure factor begin to curve severely for qRc > 1. Further numerical analysis showed that inclusion of polydispersity lessened this variance and that the transition from the Guinier to the power law regime, i.e., as qRc passed through unity, was sensitive to a number of details regarding the morphology of the individual clusters and, most importantly for our purposes here, the cluster size distribution. A subsequent review of the literature showed that this knowledge was not new. Shull and Ross (9) used graphical methods different than those we will present here, to show for a system of spherical particles how the Guinier power law, which for spheres is a q6-8 Pored law, transition is sensitive to the size distribution of spherical particles. Schmidt and coworkers (10, 11) showed how Fourier inversion of small angle X-ray scattering data in this regime could yield the particle size distribution. However, we have shown that the shape of the particles, e.g., eccentricity, also affected scattering in this regime and hence could confound the size distribution determination. In this work we were for uniform density, spherical particles, i.e., no aggregates. Thus, the usefulness of this crossover regime for size distribution measurements for fractal aggregate clusters remains to be explored. That is the purpose of this paper. We will show that if the morphology of the aggregate is well known, an effective measurement of the size distribution width can be made. Uncertainty in the morphology, however, can seriously limit

1. INTRODUCTION

Optical particle sizing is a valuable technique for in situ, non-invasive diagnostics of particulate systems. The desired information is a complete description of the particle size distribution, but this can be very difficult to obtain. Practically, we are satisfied with accurate mean size information and some degree of knowledge regarding the nature of the distribution, usually in width. In this paper we describe a graphical method to obtain the size distribution width of fractal aggregates via light scattering measurements which we have found useful in our studies of soot aerosols.

The scattering of light, or any other wave, from particles or clusters can be divided into three regimes (1-3) based on the magnitude of qRc, where Rc is the particle or cluster radius of gyration and q = 4πka sin θ/2, where k is the wavelength of light and θ is the scattering angle, is the scattering wave vector. These regions are the Rayleigh regime where qRc < 1, in which the scattered intensity is constant, independent of the scattering angle, the Guinier regime where qRc < 1, in which a small angle dependence is seen due to the overall size of the particle, and, typically, a power law regime for qRc > 1, in which the intensity angular dependence contains information regarding the particle’s or cluster’s structure. The particle or cluster mean size can be obtained in the Guinier regime where

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the accuracy of this measurement. Our method will be a graphical analysis of the shape of curves plotted in accord with Eq. [1].

II. ANALYSIS

A. Scattering and the qRc< 1 Regime

We consider a noninteracting ensemble of clusters with monomers small enough to be Rayleigh scatterers. For such a system, intraclass multiple scattering is not a significant fraction of the scattering (12, 13). We assume the cluster number density is small enough so that there is no interclass multiple scattering. These conditions are commonly satisfied for most colloidal and aerosol systems. In general, the scattered light intensity from an ensemble of clusters with various numbers of monomers per cluster N and size distribution n(N) is

\[ I(q) = c \int n(N)N^2S(qRc)dN. \]  

In Eq. [2], c is a constant including functions of the refractive index, collection solid angle, detector efficiency, etc. \( S(qRc) \) is the static structure factor of the cluster. For fractal clusters, \( N \sim Rc^D \) where \( D \) is the fractal dimension. Since \( S(qRc) = 1 \) as \( qRc \to 0 \), one may eliminate \( c \) to obtain

\[ \frac{I(q)/I(0)}{1} \approx \frac{\int n(N)N^2S(qRc)dN}{\int n(N)N^2dN}. \]  

In the Guinier regime, \( qRc < 1 \), the structure factor is given by \( S(qRc) = 1 - q^2Rc^2/3 \), and this may be substituted into [3]. We define the moments of the size distribution by

\[ M_q = \int R^q n(N)dN. \]

Then Eq. [7] becomes

\[ \frac{I(q)/I(0)}{1} = 1 - \frac{(1/3)}{2}q^2 Rc^2 M_2/M_q. \]  

In Eq. [5] we have used \( N = k_R Rc/a_0 \) where \( a_0 \) is the monomer radius and \( k_R \) is a constant. Equation [5] shows that a measurement of \( Rc \) obtained by studying the q dependence of the light scattered in the Guinier regime yields an average radius of gyration related to the moments of the distribution by

\[ (Rc)^2 = \frac{q^2}{2} M_2/M_q. \]

The functional dependence of the Guinier formula may be used to find average \( Rc \) values. A convenient graphical method is to plot the inverse of the scattered intensity, \( 1/I(0)/I(q) \), versus \( q^2 \). Then the slope is 1/3 \( (Rc)^2 \). We used inverse \( I(q) \) because \( I(q) \) is not bounded whereas \( I(q) \) is, hence \( 1/I(q) \) versus \( q^2 \) tends to be more linear and easier to analyze. An example for a R66 aerosol is shown in Fig. 1, which has been used to yield accurate \( Rc \) values (4).

A close look at Fig. 1 shows that we have used data for which \( qRc > 1 \), beyond the Guinier regime, yet \( 1/I(q) \) versus \( q^2 \) is still surprisingly linear. Linearity is expected only for \( qRc < 1 \). This curious fact and our desire to understand the effect of \( n(N) \) on these plots led us to realize that the \( qRc > 1 \) region of these graphs is very sensitive to the functions that go into Eq. [1], the functions \( n(N) \) and \( S(qRc) \).

B. The qRc \( \gg 1 \) Regime

Two major parameters determine the form of \( S(qRc) \) for a cluster. They are the fractal dimension \( D \) and the cutoff function of the cluster density–density correlation function. The fractal dimension essentially determines the limiting slope as \( S(qRc) \sim (qRc)^{-D} \) for \( qRc \gg 1 \) regardless of the cutoff function. For diffusion limited cluster aggregates (DLCA) \( D = 1 \) to 1.8. The fractal dimension is readily measured if \( qRc > 1 \) data are available, and it is not measurable if not, provided one knows about the cutoff function and the size distribution (6, 14). The density correlation function \( g(r) \) may be written as

\[ g(r) = r^{-D} \cdot \delta (r/\xi), \]

where \( \delta \) is the spatial dimension. The cutoff function is \( h(r/\xi) \) where \( \xi \) is a characteristic cluster size related to \( Rc \). It describes the manner in which the density of the cluster terminates at the perimeter. It is important because \( S(qRc) \) is the Fourier transform of \( g(r) \). Regardless of \( h(r/\xi) \),

FIG. 1. Normalized inverse scattering intensity versus wave vector squared for light scattered from two aggregates in a pressurized CH3O/O2 flame. The parameter \( \theta \) is the height above the burner surface from which the data were obtained. Linearity is in accord with the Guinier approximation, Eq. [1], and the slopes are \( (Rc)^2/3 \).
S(\phi) will have the same Rayleigh and Gaussian (\phi_r < 1) and power law (\phi_r > 1) limits. It is the shape of the Gaussian to power law crossover regime \phi_g > 1 that is affected by S(h(\xi)).

The problem is, what is h(\xi) here? Most earlier workers used an exponential \( h(\xi) = \exp(-r \xi) \) for (15, 16). Mountain and Mullerholm (17) used simulated clusters and found h(\xi) = \exp(-c r \xi) with c = 2.5 \pm 0.3. A reasonable physical mechanism for the cutoff can be obtained by considering two overlapping spheres, which yields h(\xi) \approx (1 + r^2 \xi^2) \exp(-c r \xi), r = 2 \xi, otherwise zero (2, 18).

We have studied h(\xi) in two different ways. First, we computed measured structure factors from scans to various structure factors derivable from the different cutoffs (6). We found the most reasonable fits were obtained for a structure factor derivable from a Gaussian cutoff, h(\xi) = \exp(-c r \xi). Second, we captured slow particles on electron microscope grids, photographed them with the electron microscope, computer digitized their images, and then calculated g(\mathbf{r}) from which h(\xi) was determined directly (14). We found both the Gaussian cutoff and the overlapping spheres cutoff described the data accurately. These two cutoffs are nearly identical in the range h(\xi) \approx 0.01. Given our numerical evidence for a Gaussian cutoff and the physical reasoning that leads to the overlapping sphere cutoff and their essential equivalence, we shall use a structure factor derivable from the Gaussian cutoff (the overlapping sphere cutoff does not allow for an analytic expression for S(\phi)) which is

\[ S(\phi) = e^{-\kappa_0 \phi} \left( \frac{3 - D_s}{2 \phi} \right)^{\frac{3}{2}} \left( \frac{\phi_0}{D_s} \right)^{\frac{3}{2}}. \]  

where \( F_s \) is the convex hypogeometric series.

The other functionality is Eq. [3] for the size distribution n(N). Since our method will not yield n(N) directly, the test to which we can apply is to measure an effective width. Thus a functional form for n(N) must be assumed which will have a width parameter. In this work we have used two different size distribution functional forms: the Serfling-Binder Log Normal (ZOLD) (1, 19) and the scaling distribution (20).

The functional form for the normalized ZOLD is

\[ n(N) = \frac{2}{\sqrt{2\pi} N_0} \ln \sigma \exp\left(\frac{1}{2 N_0^2} \sigma^2 \right) \exp\left(\frac{-\ln(N/N_0)^2}{\sigma^2} \right). \]  

Equation [3] was used to calculate the normalized scattered intensity from an ensemble of clusters with fractal dimension \( D_s = 1.75 \), typical of DLCA clusters. The single cluster structure factor was that due to a Gaussian cutoff, Eq. [8]. Both the ZOLD and the scaling distribution were used with a series of different width parameters, \sigma and \nu, respectively. The intensity was inverted to I(D_s)/I(q),

\[ n(N) = M_{\nu} \, \Phi(q) \]  

\[ \Phi(q) = a_0 \, q^{-\nu} \, e^{-\lambda q^2} \]  

\[ x = N/s. \]  

\[ \text{In Eq. [10], } x = M_{\nu}/M, \text{ a mean size, } \alpha = 1 - \lambda, \text{ and } \Gamma \text{ is the Gamma function. The effective width parameter is } \lambda \text{, and the bigger } \lambda \text{ the broader the distribution. Equations [10] are good only for the large tail of the distribution (} x \gg 1). \text{ This is all we need for light scattering, however, since the scattering weights the large } x \text{ tail. This is seen in Eq. [3] and } \alpha \text{ due to the } a_0 \text{ term. In fact it's all we can get from light scattering which is biased to the small } x \text{ part of the distribution.} \]

Both these distributions have various attributes. The ZOLD is intuitively reasonable and is popular in the engineering community. It can be used to describe nearly any ensemble of particles or clusters. It can also be a good job of approximating the self-preserving size distributions that result from aggregation. The scaling distribution is an exact description of the self-preserving size distributions and \lambda is the aggregation kernel homogeneity. The apparent disadvantage of having the wrong small size limit is unimportant since essentially all of the mass \alpha in our case, all of the light scattered is due to the large size part. This approach is popular in the physics literature. We have preferred the scaling distribution because it accurately describes moments higher than the second which become important for interpreting light scattering measurements (5), for example Eq. [6] shows \( \langle \mathbf{r}^2 \rangle \sim M_{\nu}/M_{\nu} \) for \( D_s = 2 \). In describing self-preservation distributions, the two distributions yield identical first and second moments when

\[ (2 - \lambda)/(1 - \lambda) = \exp(\ln \sigma^2), \]

for \( \lambda < 1. \) This rough equivalence will be seen in our results below.
plotted versus \((qR_p)^2\) and the results are shown in Figs. 2 and 3.

Figures 2 and 3 readily show that the curvature (or lack of it) in these graphs is a function of the distribution width when \(qR_p > 1\). Note how inclusion of a finite width drastically lessens the curvature compared to the monodisperse case (Fig. 2). Data for scattering from a soot aerosol at two different heights above the burner of a C/O = 0.75 premixed CH\(_4\)/O\(_2\) flame are also shown in these figures and one can see a measurement of the width as either \(\lambda = 0.2 \pm 0.3\) or \(\sigma = 2.3 \pm 0.3\). These two values roughly fit with Eq. (11). When \(qR_p < 1\), all the curves lie together as expected for the Guinier regime.

Thus we propose the following method for measurement of mean size and size distribution width for an aerosol or colloid. Relative intensity is measured as a function of wave factor \(q\) at several \(q\) values, most conveniently by changing the scattering angle. The fractal dimension is either determined from the large \(q\), power law behavior (5), other more external means (1), or assumed from the possibly known aggregation kinetics. Plot \(I(q)/I(0)\) versus \(q^2\); the limiting \(q \to 0\) slope yields \(1/3 (R_g^2)\) via the Guinier equation, and the data can be accurately extrapolated to \(q = 0\) to yield \(I(0)/I(0)\). Replot as \(I(q)/I(0)\) versus \((qR_p)^2\) and compare the data to the curves in Figs. 2 and 3 as easily calculated by Eq. (3). Read off the value of the width parameter. Appendix A describes the mathematical detail in calculating Eq. (3) for a given \(R_g\).

Perhaps the greatest asset of this method is its simplicity. Problems arise, however, in the sensitivity of these curves to other factors in the single cluster structure factor, the fractal dimension \(D_g\) and the cutoff function. These problems are analogous to spherical shape effects for noncluster particles in the earlier work (9-11). We illustrate these sensitivities next.

Figure 4 shows \(I(q)/I(0)\) versus \((qR_p)^2\) for a scaling distribution with \(\lambda = 0\) and a Gaussian cutoff structure factor with various \(D_g\). We see the curvature in these graphs is sensitive to \(D_g\). Fortunately, \(D_g\) is readily measurable. Com-
The slope of $I(0)/I(q)$ versus $q^2$ is $(R_g^2)^{-3/2}$ where $(R_g^2)$ is given by Eq. [5]. The monomer ratio in [5] is related to the mean sizes of the scaling distribution to yield

$$(R_g^2) = \int_0^{\infty} q^2 \psi(q) R(q)^2 dq$$

$$(\xi + a + 2 + 2D_2)/(\Gamma(a + 2).$$

Similarly for the ZOOL distribution,

$$(R_g^2) = N^2 \pi \int_0^{\infty} q^2 \psi(q) R(q)^2 dq$$

Thus the mean size $a$ is most probable size $R_0$ can be found from the $R_g$ measurement.

To calculate the curves in Figs. 2-5, either Eq. [A1] or [A2] is inverted to obtain $a$ or $R_0$. Since Eq. [3] is used with the dimensions variable $x = N \xi + \alpha$. Upon substitution all the constants in Eqs. [A1] and [A2], such as $\mu_0$, $\alpha$, and $D_2$, cancel out. The structure factor becomes the function $S(q)(R_g^2)^{-3/2}$, where $(R_g^2)$ was from the Guinier measurement. The result from [3] is thus not dependent upon the various unknown constants and can be played versus $q/(R_g^2)$, namely $\psi(q)$, in Figs. 2-5.

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