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Analysis of Fractal Cluster Morphology Parameters: Structural Coefficient and Density Autocorrelation Function Cutoff

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Electron micrograph images of fractal soot clusters obtained from a premixed CH_4/O_2 flame are analyzed for two, somewhat neglected, morphological parameters: the structural coefficient k_0 in $N = k_0(R_g/a)^{D_f}$ and the perimeter cutoff function $h(x)$ of the cluster density autocorrelation function. We find for our fractal aggregates that $k_0 = 1.23 \pm 0.07$ and $h(x)$ is well described by a Gaussian or overlapping spheres model.

Key Words: fractal clusters; morphology; soot.

1. INTRODUCTION

The process of aggregation in colloids and aerosols leads to random aggregates of small primary particles. These aggregates have been shown to be describable by a fractal morphology (1–3); that is, the number of monomers per aggregate N scales with the radius of gyration R_g as

$$N = k_0\left(\frac{R_g}{a}\right)^{D_f}, \qquad [1]$$

where k_0 is a structural coefficient, a is the monomer radius, and D_f is the fractal dimension of the aggregate. Such a fractal description of the seemingly random structure brought about a major breakthrough in the study of aggregation phenomena. Much effort has been spent in studying the fractal dimension, which is of great importance in ramified aggregate morphology. A less well-studied parameter is the structural coefficient k_0. So far there is no general agreement as to the value of k_0, which is essential to fully characterize the morphology, nor have there been any systematic studies regarding the dependence of k_0 on the aggregation process.

We first realized the importance of k_0 during our light scattering studies of fractal soot aggregates, wherein we argued that k_0 can be determined by the $N \to 1$ limit of Eq. [1] (4). Computer simulations provide a means by which k_0 may be determined. Wu and Friedlander (WF) (5) gathered previously published simulation data and found k_0 ranged from 1.05 to 1.59 for diffusion limited cluster aggregation (DLCA) clusters and $k_0 \sim 1.3$ for these clusters in the free molecular regime, i.e., when the cluster radius is much less than the medium gas molecule mean free path. Another value for simulated smoke clusters was reported by Mountain and Mulholland (6), who gave $k_0 = 1.55$. Experimental methods of determining k_0 are also possible through transmission electron microscopy (TEM) or light scattering (7, 8). Puri *et al.* (7) reported from TEM analysis that $k_f \simeq 9.0$ and $D_f \simeq 1.4$, where $k_f = 2^{D_f}k_0$, since monomer diameter was used in their formula while we used monomer radius. With $D_f \simeq 1.4$, one finds $k_0 = 3.4$. Köylü and Faeth obtained $k_f = 8.1$ and $D_f = 1.82$ from their optical measurement (8), which gives $k_0 \simeq 2.3$. Both of these values are much bigger than those from simulations.

Another important morphological parameter is the cutoff function for the cluster density autocorrelation function $g(r)$, which is a power law function of the position variable r as a consequence of the scaling in Eq. [1],

$$g(r) \sim r^{D_f-d}, \qquad [2]$$

where d is the spatial dimension. The Fourier transform of this function gives the optical structure factor $S(q)$ for the scattered intensity, assuming that there is no intracluster multiple scattering. Here $q = 4\pi\lambda^{-1}\sin\theta/2$ is the magnitude of the scattering wave vector. The structure factor $S(q)$ also displays a scaling behavior for $qR_g \gg 1$ as

$$S(q) \sim q^{-D_f}, \qquad [3]$$

which signifies a fractal structure and is often used to determine the fractal dimension.

Equation [3] is very useful if sufficiently large q data are available and all that is desired is D_f. On the other hand, the complete expression for $S(q)$ for all q is necessary for analysis of data limited to $qR_g \leqslant 5$, since the asymptotic nature displayed in Eq. [3] is no longer present. The manner in which $S(q)$ transforms from the Rayleigh regime, where it is a constant, to the behavior in Eq. [3], i.e., the range $0 \leqslant qR_g \leqslant 5$, is determined by the large r behavior of $g(r)$.

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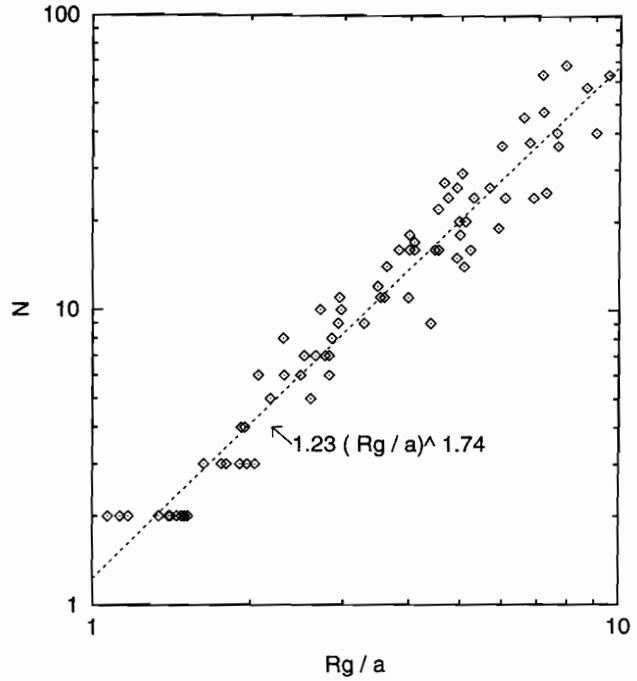

FIG. 1. Plot of N versus R_g/a for an ensemble of 92 clusters. The fit line slope gives $D_f = 1.74 \pm 0.04$ and the intercept yields $k_0 = 1.23 \pm 0.07$.

of the soot cluster by an algorithm similar to that in Samson *et al.* (22). From the $g(r)$, D_f was determined and used in the calculation of $h(r)$.

Figure 2 shows the cutoff function for four of the largest soot clusters. We have found that the projection into two dimensions has little effect for large clusters (18), so the two-shade format was used here.

Also plotted on the graph are the exponential cutoff function

$$h(r/\xi) = e^{-r/\xi}, \qquad [9]$$

where

$$\xi^2 = \frac{2}{D_f(D_f+1)} R_g^2; \qquad [10]$$

the Gaussian cutoff function

$$h(r/\xi) = e^{-(r/\xi)^2}, \qquad [11]$$

with

$$\xi^2 = \frac{4}{D_f} R_g^2; \qquad [12]$$

and the OS cutoff function

$$h(r/\xi) = (1 + x/4)(1 - x/2)^2, \qquad [13]$$

where $x = r/\xi$ and

$$\xi^2 = \frac{(D_f+2)(D_f+5)}{2D_f(D_f+1)} R_g^2; \qquad [14]$$

all for $D_f = 1.75$.

4. DISCUSSION AND CONCLUSION

Our measured value of $k_0 = 1.23 \pm 0.07$ from the TEM analysis is in good agreement with those from computer simulations listed in WF ($k_0 \sim 1.3$) and those obtained in this lab ($k_0 = 1.2 \pm 0.1$) (to be published), but it is much smaller than the experimental results of Puri *et al.* (7) and Köylü and Faeth (8). We do not know the reason for this discrepancy. Since this value, as determined from an ensemble of clusters, is an average, it may depend on the size range from which it is determined.

In earlier work (15) we used light scattering data fitted to various structure factors derived from different forms of the cutoff function in order to obtain D_f and found that the exponential cutoff function performed badly and by no means could yield results compatible with D_f as reported from previous experiments and simulations for a flame system. We remark that this structure factor is well represented by the so-called Fisher–Burford form. On the other hand,

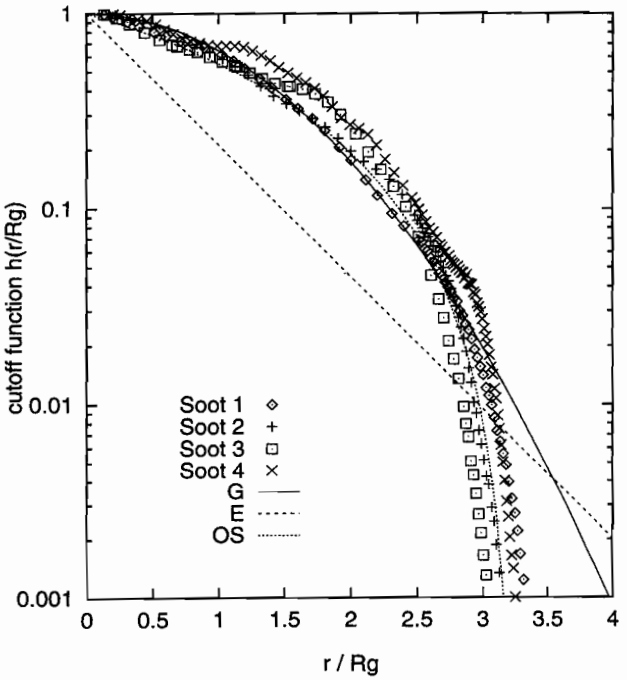

FIG. 2. Plot of the cutoff function $h(x)$ for the four largest clusters and of the exponential (E), Gaussian (G), and overlapping spheres (OS) cutoff functions. The cutoff functions of the soot clusters are in excellent agreement with the Gaussian and the OS cutoff functions.

the Gaussian cutoff function did a good job of fitting the data when polydispersity was included. It is clearly seen that the soot cutoff functions from TEM analysis agree very well with the Gaussian cutoff function up to $r = 3R_g$. No agreement with the exponential cutoff function is seen. The OS cutoff function yields the best comparison, dropping to zero at about the same r/R_g value as that of the soot cutoff. Therefore this result lends further support to our light scattering result that the exponential cutoff function is not sharp enough to do an adequate job in describing the cluster perimeter cutoff and a structure factor similar to the one derived from the OS or Gaussian cutoff function is the appropriate one for soot clusters.

We note that for $r \geqslant 3R_g$ the soot cutoff functions from TEM analysis begin to fall much more sharply than the Gaussian cutoff function. This should be so for a real cluster since the cutoff function goes to zero at $r = l_{max}$, where l_{max} is the maximum length of the cluster. Our data gave $l_{max} = 3.18$–$3.52\ R_g$, with an average of $l_{max} = 3.33R_g$. For $D_f = 1.75$, the OS cutoff function falls to zero at $l_{max} = 3.24R_g$, which agrees well with the soot particles. Although the Gaussian cutoff function will not go to zero until ∞, the extra tail is small and only adds a negligible uncertainty to the derived structure factor. From a physical point of view, the OS cutoff best describes the cluster. However, it is more difficult to use in performing a fit since it does not yield an analytical form for the structure factor for a noninteger D_f. From a calculation point of view, the Gaussian cutoff is preferred because it yields an analytical structure factor (15) which is about the same as the OS structure factor.

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