Hybrid superaggregate morphology as a result of aggregation in a cluster-dense aerosol

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From the digitized pictures of soot clusters formed after the explosion of a hydrocarbon gas mixed with oxygen, the cluster morphology was determined by two different methods: structure factor and perimeter analysis. We find a hybrid, superaggregate morphology characterized by a fractal dimension of $D \approx 1.8$ between the monomer size, ca. 50 nm, and 1 μm and $D \approx 2.6$ at larger length scales up to ~ 10 μm. The superaggregate morphology is a consequence of late-stage aggregation in a cluster-dense regime near a gel point.

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I. INTRODUCTION

Gels are usually a result of an aggregation process in which the solid material comes together to form ramified aggregates with a fractal dimension of less than 3 [1–3]. With such a dimensionality, the growing aggregates occupy a greater fraction of the available space with time and the system crosses over from cluster dilute to cluster dense. We define "dilute" and "dense" as when the ratio of the mean cluster nearest-neighbor separation to cluster size is large or small, respectively. Eventually the resulting aggregates completely fill the macroscopic volume in which they reside. The details of the evolution of the system from dilute to dense to gel have attracted considerable attention [4–11]. Gels are not only interesting from a fundamental point of view but also have significant practical applications [12].

The fractal morphology of aggregates formed via a diffusion-limited cluster aggregation (DLCA) process [13–15], which is cluster dilute, is now well established as having a mass fractal dimension of $D \approx 1.8$. On the other hand, the fractal nature of the gel itself is thought to be described by percolation theory which predicts a fractal dimension of $D=2.55$ for the gel network [16]. Previous simulations have given an indication of a crossover from the DLCA value of the fractal dimension to a larger value as the sol evolves from the cluster dilute case to the gel. Kolb and Herrmann [4] found 1.75 ± 0.07 as the fractal dimension of the clusters in two dimensions for a high-concentration system compared to 1.40 for the dilute situation in their computer simulations. Hasmy and Jullien [5] and Gimel *et al.* [6,7] both found a crossover from DLCA morphology for shorter length scales to percolation morphology for larger length scales with a concentration-dependent crossover length.

Our recent large-scale, three-dimensional, off-lattice computer simulations have shown that at the gel point the aggregates become so crowded that they percolate to form a $D \approx 2.6$ aggregate made up of $D \approx 1.8$ aggregates with an average size that we designate as $R_{g,G}$ [10]. We used the term *superaggregate* to mean such an aggregate of aggregates. The implication of this result is that near the gel point large clusters in the system have a short-range local structure described by a fractal dimension of 1.8 and a long-range overall structure described by a fractal dimension of 2.6. The ideal gel point radius of gyration, $R_{g,G}$, is a characteristic crossover length scale connecting the morphology of clusters at short and large length scales.

Experimental verification of this hybrid morphology of gelling clusters predicted by theory is limited at best. Simulations suggest a *universal* behavior; i.e., this should happen in any particulate system when it becomes dense and gels. Previous experiments by many groups on dense colloids have not seen the $D \approx 2.6$ superaggregates, perhaps due to fragmentation, reaction-limited kinetics, or gravitational settling due to the long gel time. There is, however, some indication of the formation of such superaggreates in a recent colloid experiment [11].

Aerosols, without significant solvent or hydrodynamic effects, are very clean systems, and one would expect them to be ideal model systems to compare with computer simulations. Soot aggregates in laminar diffusion flames can form a macroscopic gel network in the aerosol phase [17]. Subsequent studies of this flame showed soot clusters with a hybrid morphology having a fractal dimension of $D \approx 2.6$ for length scales between approximately 1 and 10 μm and a fractal dimension of $D \approx 1.8$ for length scales less than 1 μm down to the monomer size [18–20]. These experimental observations of superaggregates in laminar diffusion flames, although very useful, may still be affected by the complexity of the flames. A diffusion flame is a flowing system with both shear and thermophoretic forces. In addition, the laminar flame front becomes very narrow late in the flame, 100 μm or less. Thus, the mechanism for the formation of these superaggregates is uncertain. To determine the *universality* of the superaggregates one must avoid the complexity of the flame aerosol. This is done in our present work by creating aerosols in chambers and allowing them to aggregate in the three-dimensional volume.

II. EXPERIMENTS

A carbonaceous soot aerosol is formed in our experiment during the explosion of a mixture of a hydrocarbon and oxy-

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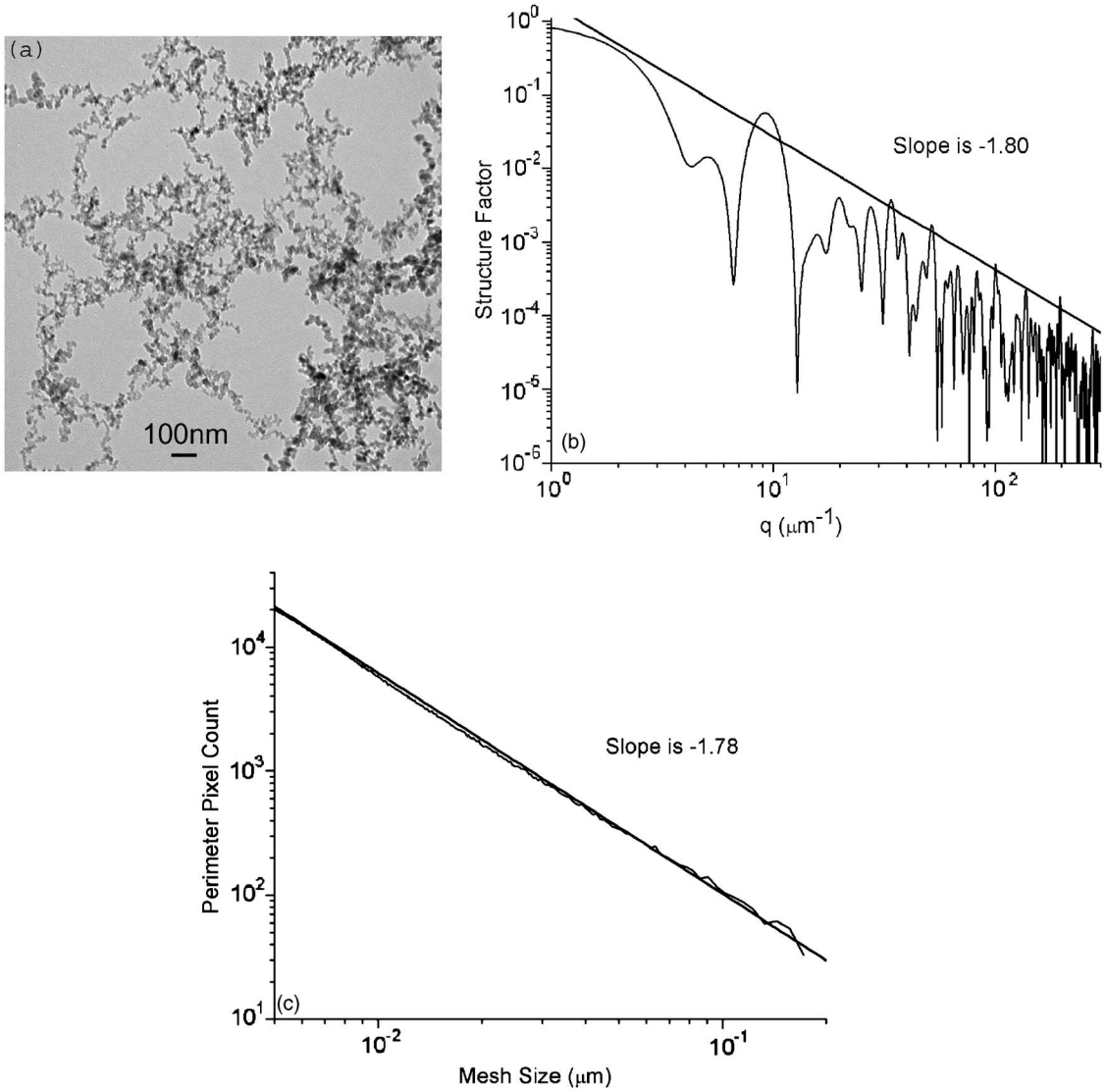

FIG. 1. (a) TEM picture of soot clusters (note the scale bar) and (b) structure factor of and (c) perimeter analyses of part (a). The fractal dimension measured is equal to the negative slope of either graph and is found to be ~1.8.

gen in a closed cylindrical chamber at atmospheric pressure. The explosion was carried out in either one of two different aluminum cylindrical chambers with different sizes. The larger chamber had a 23.9 cm internal diameter and a 37.1 cm height and hence a volume of 16.6 liters. The second chamber had a 12.5 cm internal diameter and a 31.5 cm height and hence a volume of 3.9 liters. Results were chamber independent. Acetylene (C_2H_2), ethylene (C_2H_4), and propane (C_3H_8) were used as gaseous hydrocarbon fuels.

With the hydrocarbon fuels at atmospheric pressure, we could potentially achieve solid carbon volume fractions greater than 10^{-4} (assuming all the hydrocarbon carbon becomes solid carbon). Nanometer-sized roughly spherical carbon particles with diameters of ca. 50 nm were produced rapidly during the explosion in a chamber. These particles aggregated over a period of about 15 sec proceeding from the cluster dilute to cluster dense condition and finally gelled.

After exploding the fuel-oxygen mixture, we waited for several minutes to allow all soot particles to deposit on the inner surface of the chamber. Then the chamber was opened to obtain a dark black fluffy carbon soot layer on the bottom, walls, and ceiling of the chamber. This soot layer on the bottom was about 2 cm thick for acetylene and $\leqslant$3 mm for other hydrocarbon fuels. From a broad perspective this soot is a result of an aerosol gelation process likely involving Brownian motion during the major growth period and then convection and gravitational settling.

III. AGGREGATE STRUCTURE DETERMINATION METHODS

Carbon soot aggregates were sampled on transmission electron microscope (TEM) grids and light microscope glass slides by inserting them in the chamber through a removable window and holding them horizontally for 30 sec, 3–6 min after the explosion. Soot clusters were deposited by gravitational settling on those grids and slides. Two-dimensional (2D) projection pictures of the 3D soot were produced by

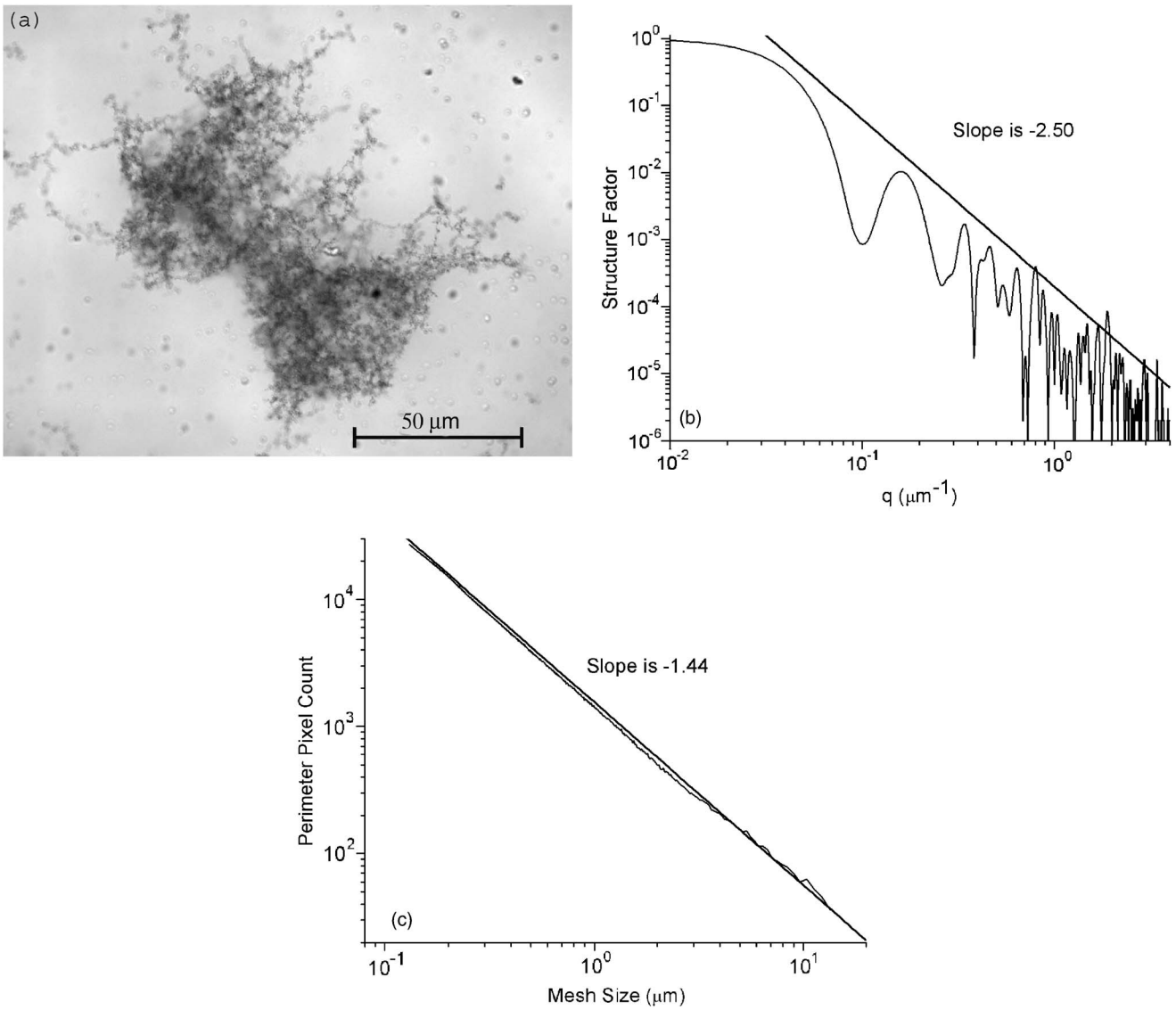

FIG. 2. (a) TEM picture of a large soot cluster (note the scale bar) and (b) structure factor of and (c) perimeter analyses of part (a). The fractal dimension is equal to the slope in the structure factor analysis. The perimeter analysis slope yields the perimeter fractal dimension, 1.44. The mass fractal dimension is found via Eq. (4) to be 2.42.

viewing under a TEM and a high-resolution high-magnification light microscope. These pictures were digitized to a binary format (the pixel is dark if there is material and white if there is none), and the cluster morphology was determined by two different methods: structure factor and perimeter analysis.

For fractal aggregates the structure factor $S(q)$ is given by [21]

$$S(q) = 1 \quad (qR_g < 1)$$
$$= C(qR_g)^{-D} \quad (qR_g > 1), \tag{1}$$

where q is the scattering wave vector, R_g is the radius of gyration of an aggregate, and C is a proportionality constant roughly equal to unity. $S(q)$ can be calculated for the digitized picture of the soot clusters using the formula

$$S(q) = N^{-2} \left| \sum_{i=1}^{N} e^{i\vec{q}\cdot\vec{r}_i} \right|^2, \tag{2}$$

where N is the total number of dark pixel points in the picture and $\vec{r}_i$ is the position vector of the ith dark pixel.

The perimeter analysis technique for finding the fractal dimension D (also called mass fractal dimension) of a three-dimensional fractal aggregate involves quantitative perimeter fractal dimension D_p analysis of the two-dimensional projection of a fractal aggregate. D_p describes the number $N(L)$ of square meshes of size L, each of which includes at least one pixel of the fractal aggregate perimeter when the digitized picture of the fractal aggregate is viewed under a grid. $N(L)$ and L are related to D_p as

$$N(L) = CL^{D_p}, \tag{3}$$

where C is a constant of proportionality. The slope of a doubly logarithmic regression of $N(L)$ against L is D_p.

Jullien and co-workers [22] found from computer simulations that, in the asymptotic limit of very large aggregates, the perimeter fractal dimension D_p is well defined and varies continuously with the mass fractal dimension of the three-dimensional aggregate. They proposed the following approximate formulas to account for this variation:

$$D_p = 1 + (3 - D)^{3/2}, \quad D \geqslant 2, \tag{4a}$$

$$D_p = D, \quad D < 2. \tag{4b}$$

We have confirmed the validity of the claim of Jullien *et al.* [Eq. (4)] by measuring D_p for two-dimensional projections of computer-simulated clusters with known fractal dimension. Thus we used Eq. (4) in the work reported here.

IV. RESULTS AND CONCLUSION

Two representative examples among the pictures used for the cluster morphology analysis are presented in Figs. 1 and 2. The structure factor and the perimeter analyses for a picture of the soot on the scale of about 1 μm down to the monomer size (20 nm) are shown in Fig. 1. The structure factor analysis measured the fractal dimension as 1.80 while the perimeter analysis gave 1.78, which is consistent. Likewise, Fig. 2 gives the structure factor and perimeter analyses for a picture of the soot in the scale from about 1 μm up to the cluster size (50 μm). The fractal dimension is 2.50 according to the structure factor analysis and 2.42 according to the perimeter analysis. Similar results were found with other pictures. The averages over all pictures are $D = 1.75 \pm 0.10$ from the monomer size length scale up to 1 μm and $D = 2.50 \pm 0.15$ in the cluster size length scale from 1 μm up to 50 μm.

In conclusion the cluster morphology of aerosol soot particles was determined from microscopic pictures using both structure factor and perimeter analyses. The soot clusters were found to have a hybrid morphology characterized by a fractal dimension of 1.75 ± 0.10 over scales from the monomer size of ca. 50 nm up to 1 μm and a fractal dimension of 2.50 ± 0.15 over length scales from ca. 1 μm to 50 μm via both methods of analysis. These results imply that aggregation in the cluster-dense regime yields a different morphology than the well-known cluster-dilute regime. These results also imply universality in superaggregates with hybrid DLCA and percolation morphologies consistent with previous results for gelation in simulations [10] and in flames [18–20].

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