POST-FLAME SOOT

by

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I. INTRODUCTION

We have used an acetylene diffusion flame to create carbonaceous soot. The soot has been physically collected from all portions of the flame and the post-flame regime. Inspection of the soot was performed with both transmission electron and optical microscopy. We measure soot cluster radius of gyration and show that these clusters retain their fractal morphology over nearly four orders of magnitude in size. The average fractal dimension is $D_f \approx 1.80$ consistent with Diffusion Limited Cluster Aggregation (DLCA). We also give evidence that the kinetics of growth when the soot clusters are on the order of 1mm may be a gelation mechanism.

II. EXPERIMENTAL METHODS AND RESULTS

A. The Flame

The burner arrangement was simply a 1.0 cm I.D. brass tube with a screen cap. Acetylene passed through this tube at a flow rate of 3.2 cm^3/sec., hence an average flow velocity of 4.1 cm/s. The flame burned in still air. The flame front was roughly 0.3 cm above the tube and was at lowest heights above the burner, h, yellow-white then diminishing through yellow, orange, dull orange, and finally black at h=8cm. The flow remained laminar until h≈15 cm.

B. Soot Sampling

1. Thermophoretic Sampling and TEM Analysis

Copper electron microscope grids with Formvar coating were placed on our "frog-tongue" probe device [1] designed after Dobbins and Megaridis [2]. This injects the grids into the flame for a residence time of 15msec. Grids were injected at a variety of heights above burner between 1.7 to 25.4cm. TEM micrographs at 14600X were taken and enlarged to 29200X. Figure 1 shows examples. These photographs were scanned into a PC in 16 levels of gray. This was converted to a binary format. Calibration of pixels to real sizes was performed. Programs were written to calculate projectional area and radius of gyration. Hundreds of clusters were analyzed. This whole analysis is similar to that which we have used earlier [1]. The average monomer radius was a=23nm (radius).

Figure 1 shows micrographs of the soot with scales that differ by 2 1/2 orders of magnitude. Despite this difference, the morphology of the clusters is similar to imply the scale invariance of fractals.

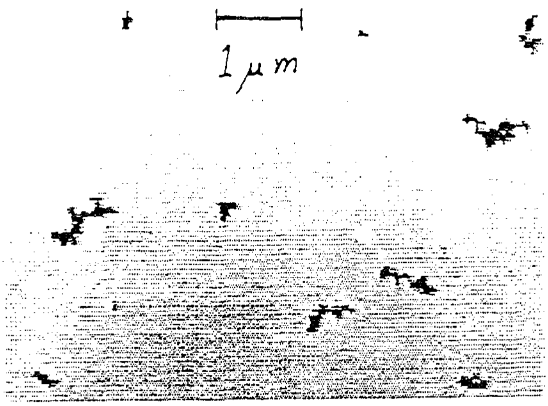

Fig. 1a TEM photograph of thermophoretically sampled soot at a height of h=7.6cm.

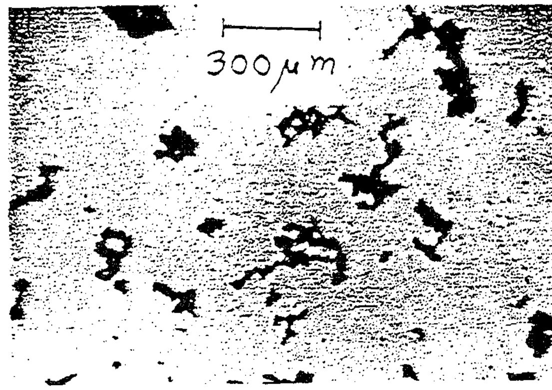

Fig. 1b Optical photograph of impaction sampled soot at a height of h=7.6cm.

Our analysis involved calculating the radius of gyration, R_g, of the digitized micrographs with a computer and determining the projected area of the cluster, A_c, from which the number of monomers per cluster was calculated using

$$N = (A_c/A_m)^{\alpha} \quad (1)$$

where α=1.09. The N vs. R_g for an ensemble of clusters was graphed on a double log plot to yield straight lines, indicating fractals and adherence to

$$N = k_o(R_g/a)^{D_f} \quad (2)$$

where D_f is the fractal dimension and a is the monomer radius determined from the higher power (20800x) TEM micrographs. Both the TEM and optically viewed clusters yielded essentially the same D_f, but, to our surprise, drastically different values of k_o; averages of k_o=1.77 for the TEM samples and k_o=24.3 for the optical samples.

The cause of the discrepancy was due to the fact that the monomers were not resolved in the low power, optically viewed pictures. Because of this, a pixel, which represents the resolution limit of the micrograph, will contain many monomers. The number of monomers in a pixel determines whether the pixel will be dark or bright; only the dark pixels will be included in the analysis for N. To account for this one must use the fractal nature of the monomeric particle arrangement and the ratio of effective pixel size to monomer size. The mathematical details of this correction are described in a paper we have submitted for publication [3]. The correction factor we derive is 0.12.

This correction applied to the average uncorrected k_o(unc.) in Table 2, below, for the optical clusters yields k_o=2.9±1.0. This value is considerably larger than the TEM value of 1.77±0.35 but still within experimental error.

Table 1
D_f and k_o for Soot Clusters Sampled by Thermophoresis and Viewed by TEM

Height Above Burner	D_f	k_o
5.7cm	1.92	1.36
7.6	1.77	2.00
9.5	1.82	1.69
11.4	1.79	1.73
15.2	2.01	1.42
25.4	1.71	2.39
Average	1.84±0.11	1.77±0.35

Table 2
D_f, Uncorrected k_o, and k_o Corrected for the Nonresolved Monomer at the Viewing Magnification, for Soot Clusters Sampled by Impaction and Viewed Optically

Height Above Burner	D_f	k_o(unc.)	k_o
5.7	1.68	37.8	4.53
7.6	1.75	25.9	3.10
9.5	1.78	21.1	2.53
11.4	1.77	21.8	2.62
17.8	1.82	15.1	1.81
Average	1.76±0.05	24.3±8.5	2.92±1.0

Tables 1 and 2 show our results and Fig. 2, which plots N vs. R_g, demonstrates the large range of similarity. These results are important because they study soot two orders of magnitude larger (in R_g) than any previous work. They establish that the same morphology holds from clusters of a few monomers up to clusters of 100 million monomers! Both D_f and k_o, which we measured over this vast range of sizes, are key variables for future optical and kinetic characterization. Finally, our results strongly imply that Diffusion Limited Cluster Aggregation (DLCA) is the kinetics of formation upto this large size range.

Our results also suggest a remarkable possibility that the clusters may grow so large that they will eventually touch or overlap in the aerosol phase. This will occur because the fractal dimension of the clusters, ~1.8, is less than the spatial dimension of the aerosol, 3. Thus as the clusters grow their relative separation decreases. To see this we calculate $d_{sep,c}/2R_g$ where $d_{sep,c}$ is the average separation between clusters (this is a rough, order of magnitude calculation). The volume fraction is given by

$$f_v = \left(\frac{d_m}{d_{sep,m}}\right)^3 \qquad (3)$$

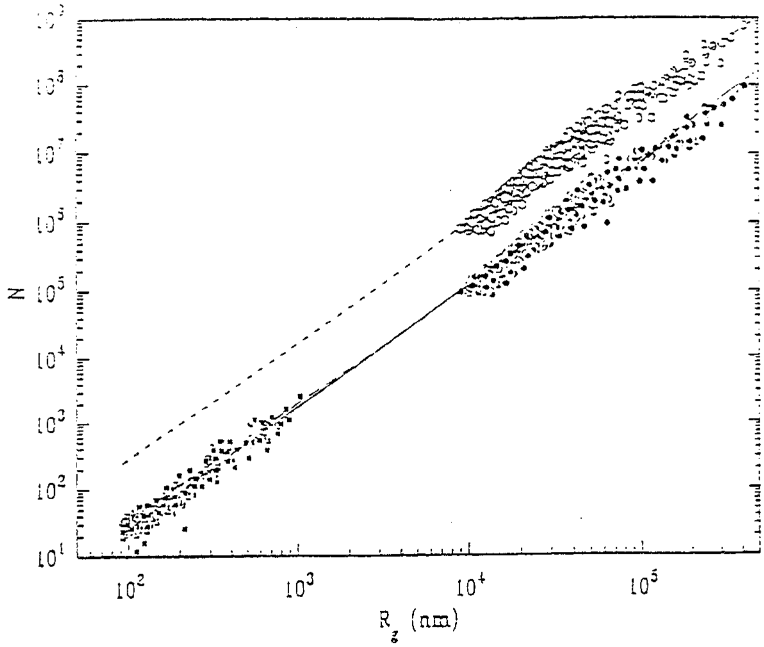

Fig. 2 Number of monomers per cluster versus cluster radius of gyration for both thermophoretically sampled, TEM viewed soot (closed squares) and impaction sampled, optically viewed soot (circles). This is a composite plot of all soot obtained at all heights above burner. For the optically viewed soot the open circles are uncorrected, the closed circles are corrected by multiplying by 0.12. The lines are fits to Eq.(2) which yield D_f=1.84 and k_o=1.73 for the squares and D_f=1.78 and k_o=2.44 for the closed circles.

where d_m=dia. of monomer, $d_{sep,m}$=ave. separation of monomers. The total volume of the aerosol is

$$V_T = N_m \, d_{sep,m}^3 \; . \tag{4}$$

Here N_m=number of monomers in the flame. For clusters the same total volume is

$$V_T = N_c \, d_{sep,c}^3 \tag{5}$$

where N_c=number of clusters. We also need

$$N \sim (R_g/a)^{D_f} \tag{6}$$

where N is the ave. number of monomers per cluster and $2a=d_m$. Now to calculate $d_{sep,c}/2R_g$ first set V_T=V_T, i.e., Eq.(4) equal Eq.(5)

$$N_c \, d_{sep,c}^3 = N_m \, d_{sep,m}^3 \; . \tag{7}$$

Then use $N_c = N_m/N$ so

$$d^3_{sep,c} = N\, d^3_{sep,m} \tag{8}$$

Now use Eqs.(3) and (6) to find

$$d^3_{sep,c} = 8R_g^{D_f}\, a^{3-D_f}\, f_v^{-1} \tag{9}$$

to yield

$$\frac{d_{sep,c}}{2R_g} = (R_g/a)^{\frac{D_f-3}{3}}\, f_v^{-1/3}\ . \tag{10}$$

We have used Eq.(10) to calculate $d_{sep,c}/2R_g$ for $f_v = 10^{-5}$, $D_f = 1.8$, and a=25nm, very typical values. The results are shown in Fig. 3.

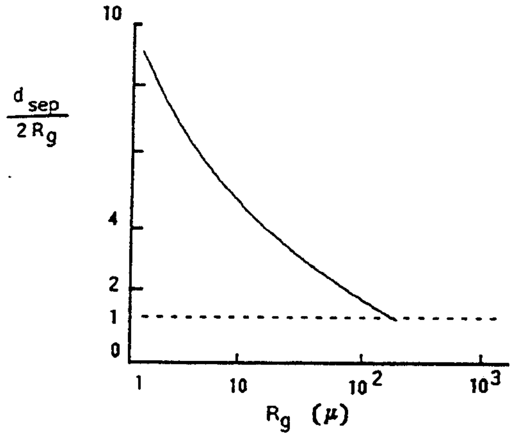

Fig. 3 Average cluster separation divided by cluster diameter versus cluster radius for a soot aerosol with $f_v = 10^{-5}$, monomer radius a=25nm, and fractal dimension $D_f = 1.75$.

Figure 3 shows the average separation distance becomes comparable to the cluster diameter when the cluster R_g is ~250μm for $f_v \approx 10^{-5}$. Soot of this size and larger was obtained from the upper regions of our flame. Thus it is conceivable that the DLCA kinetics expected at low soot cluster densities and implied by the fractal dimension of $D_f \approx 1.8$ might give way to some other kinetics higher up; kinetics similar to gelation kinetics.

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REFERENCES

1. J. Cai, N. Lu and C.M. Sorensen, Langmuir 9, 2861 (1993).
2. R.A. Dobbins and C.M. Megaridis, Langumir 3, 254 (1987).
3. C.M. Sorensen and G.D. Feke, submitted to Combustion and Flame.