Diffusion of fractal aggregates in the free molecular regime

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We use static and dynamic light scattering to determine how the diffusion coefficient of a fractal aggregate in the free molecular regime depends on its morphological properties. Our system is a carbonaceous flame soot aerosol containing fractal aggregates with $D_f = 1.8$. We find that the Epstein equation for the diffusion coefficient holds with an effective mobility radius given by $R_m = 0.99aN^{0.43}$, where N is the number of monomers per aggregate and a is the monomer radius. This result is quantitatively explained as due to the projectional area of the aggregate which includes monomer-monomer screening.

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I. INTRODUCTION

Dispersed phase particulate systems, colloids and aerosols, are a common and important part of both our living and technical environments. It is now well established that random aggregation in these systems leads to clusters of particles that are well described by fractal concepts [1,2]. In a fractal aggregate many of the physical properties are related to the size of the aggregate by power laws. The most common expression of this fact is the manner in which the cluster radius of gyration R_g scales with the cluster size, measured by the number of monomers per cluster N, as $R_g \sim N^{1/D_f}$ where D_f is the fractal dimension. Now that the fractal nature of these aggregates is established, we ask how other important physical parameters scale with N.

In this paper we report a study of the diffusion coefficient of fractal aggregates in the free molecular regime. This regime is defined by $\mathrm{Kn} \gg 1$, where Kn is the Knudsen number which for a spherical particle is the ratio of the mean free path of the medium molecules to the particle radius [3]. This is an important problem since diffusion is a fundamental transport mechanism, and it determines aggregation kinetics; hence the properties of the aggregate size distribution. A considerable amount of previous work has been devoted to understanding the diffusion coefficient for fractal aggregates in the continuum regime, $\mathrm{Kn} \simeq 0$ [4–9]. In particular, Wiltzius [6] found a Stoke-Einstein relation, $D = kT/6\pi\eta R_H$ where η is the medium viscosity, held with a hydrodynamic radius given by $R_H = \beta R_g$ with $\beta \simeq 0.95$ when the measurements were properly corrected for polydispersity [7]. The proportionality to R_g can be understood physically since the fluid, when $\mathrm{Kn} \simeq 0$, does not freely drain from the interior of the aggregate despite the porosity of the fractal.

The physics of diffusion in the other extreme, $\mathrm{Kn} \gg 1$, is very different. For a spherical particle of radius R the Epstein equation holds [3],

$$D = \frac{k_B T}{f} = \frac{3}{8\rho R^2 \delta} \left[\frac{k_B T m}{2\pi} \right]^{1/2} . \qquad (1)$$

Here f is the friction coefficient, ρ the medium mass density, m the medium molecular mass, and $\delta = (1 + \pi\alpha/8)$ where $0 \leq \alpha \leq 1$ is the acccommodation coefficient. The $f \sim R^2$ dependence is due to collisions of the gas molecules with the particle. Since $\mathrm{Kn} > 1$, these molecules travel in straight lines relative to R; hence the momentum transfer is proportional to the projectional area of the particle. This is unlike the $f \sim R$ dependence due to hydrodynamic flow when $\mathrm{Kn} \simeq 0$. In view of the Stokes-Einstein relation, still valid for fractal aggregates when $\mathrm{Kn} \simeq 0$, and because of the differences in the mechanism of diffusion in the two Kn regimes, it is interesting to ask if Eq. (1) still holds for fractal aggregates in the free molecular regime. If so, how does the effective radius of the aggregate compare to R_g, or better, how does it scale with N?

Here we present diffusion coefficient measurements on fractal carbonaceous soot aggregates with $D_f \simeq 1.8$. We have recently developed an ability to use light scattering to perform a complete *in situ* characterization of the morphology of fractal aggregates [10–13]; thus we can quantify the dependence of diffusion on the aggregate morphology in an unprecedented manner. We will show that Eq. (1) still holds and then define a mobility radius R_m by replacing R with R_m. We find R_m scales with N in a way to imply that the drag depends on the projectional area of the cluster. However, some screening of monomers by other monomers occurs; hence this projectional area is not linearly proportional to N, but rather the proportionality is sublinear. Furthermore, unlike when $\mathrm{Kn} \simeq 0$, R_m is not proportional to R_g.

II. EXPERIMENTAL METHODS

Our experimental methods involve both static and dynamic light scattering [(SLS) and (DLS)] measurements on fractal soot clusters in a flame. The flame is premixed CH_4/O_2 supported on a cooled, porous frit burner. Above a thin (~ 1 mm) reaction zone, a high temperature soot aerosol exists in the flame with the only significant change being due to aggregation; hence mean aggregate size increases with height above the burner. Our past work [10–13] has well characterized this system both optically and with electron microscopy to show that

diffusion limited cluster aggregation (DLCA) -type fractals with $D_f = 1.79 \pm 0.1$ occur in the flame aerosol.

Our light scattering uses an argon ion laser operating at $\lambda = 488$ nm as a source. Light scattered from and transmitted through the flame are both detected. The SLS technique consists of two parts. (i) A static structure factor measurement is featured [10,12] wherein the scattered intensity $I(q)$ is measured as a function of scattering wave factor $q = 4\pi\lambda^{-1}\sin\theta/2$, which is varied by changing the scattering angle θ. $I(q)$ is proportional to the static structure factor. This yields R_g, the sole variable when $qR_g \lesssim 1$, by a Guinier analysis. The fractal dimension is determined by a fit to the static structure factor for a fractal aggregate with R_g as an input parameter. The static structure factor we use is $S(x) = \exp(-x^2/D_f) \, _1F_1(\frac{3}{2} - D_f/2, \frac{3}{2}; x^2/D_f)$ where $_1F_1$ is the confluent hypergeometric series and where $x = qR_g$. We have shown [12] how this results from an aggregate with a density correlation function with a Gaussian cutoff and is the most accurate fractal aggregate structure factor. (ii) A scattering-extinction measurement is featured [11,14] wherein the absolute scattered intensity at $qR_g < 1$ ($\theta \lesssim 20°$) obtained by calibration with gases of a known Rayleigh ratio is compared to the extinction coefficient measured by the transmitted intensity. This method relies on soot's complex index of refraction. Then for small particles (relative to λ) scattering and extinction are proportional to nN^2a^6 and nNa^3, respectively, where n is the soot number density, N is the number of monomers per cluster, and a is the monomer radius. The proportionality constants are known functions of soot's refractive index, which is adequately described by $1.6 - 0.6i$. Hence a ratio of these two measurements eliminates n and yields $R_{SE}^3 = a^3N$ where R_{SE} is the "scattering-extinction" radius, which is the radius of a volume equivalent sphere. Given all this and the scaling relation

$$N = k_0(R_g/a)^{D_f} , \qquad (2)$$

with $k_0 = 1.2 \pm 0.1$, which was obtained from our TEM analysis [15(a)] and DLCA simulations [15(b)], we see that knowledge of R_g, R_{SE}, D_f, and k_0 allows one to solve for N and a. Thus a complete in situ characterization of a fractal soot aggregate in terms of R_g, D_f, N, and a can be accomplished [11]. We have recently verified this procedure by comparison to electron micrograph analysis [13].

DLS measurements were accomplished by connecting the scattering photomultiplier tube (PMT) to an ALV5000 digital correlator, which calculates the intensity autocorrelation function of the scattered light. Typical scattering angles were $5° \leq \theta \leq 20°$ to ensure that the correlation time due to diffusion is both significantly longer than PMT afterpulsing effects (~ 1 μsec) and shorter than beam transit terms (~ 100 μsec) due to the flowing aerosol [16]. These small angles also eliminate effects of rotational diffusion on the intensity autocorrelation function [17]. A two-cumulant fit is performed and from the first cumulant the diffusion coefficient D is measured.

To determine R_m from D we use Eq. (1), which is good for $Kn \gg 1$. To a good approximation $Kn \gg 1$ holds for our soot aggregates since for our flame the gas mean free path was ~ 330 nm, and our measured R_m values were 20 to 70 nm. Thus if we use R_m in the Kn calculation, we obtain $4 \leq Kn \leq 16$. For this range the empirical Cunningham corrected Stokes-Einstein equation [3], which is good for all Kn, yields values of D that are at most (when $Kn=4$) 10% different than those obtained from the Epstein equation (1). Thus the error in R_m incurred by using (1) would be at most 5%, within other experimental errors. Furthermore, in calculating R_m from D with (1) we used $\alpha = 0.91$, which yields equivalent values for D in the limit $Kn \to \infty$ for both Epstein and Cunningham formulas. Other quantities needed are temperature, which was determined by optical pyrometry, and the average molecular mass m of the flame medium, which was calculated from measured concentrations of chemical constituents extracted from the flame [18,19].

III. RESULTS

The measured values of R_g, R_{SE}, and R_m are shown in Fig. 1. Not only are they different physical quantities, but they are different weighted averaged over the size distribution of the soot clusters [7,11,13] as well. That is, they are related to different moments of the distribution and hence are not directly comparable. If the size distribution $n(N)$ is known, a mean size $\langle N \rangle$ can be defined and the measured R values can be converted to R values for the same mean size. The conversion involves knowing to which moments the R values are related. At small scattering angles, such that $qR_g < 1$, the scattered intensity for a cluster goes as N^2; hence one can show that $R_g \sim M_{2+2/D_f}/M_2$, $R_{SE} \sim M_2/M_1$, and $R_m \sim M_2/M_{2-2x}$ where $M_i = \int N^i n(N)dN$ is the ith moment of the distri-
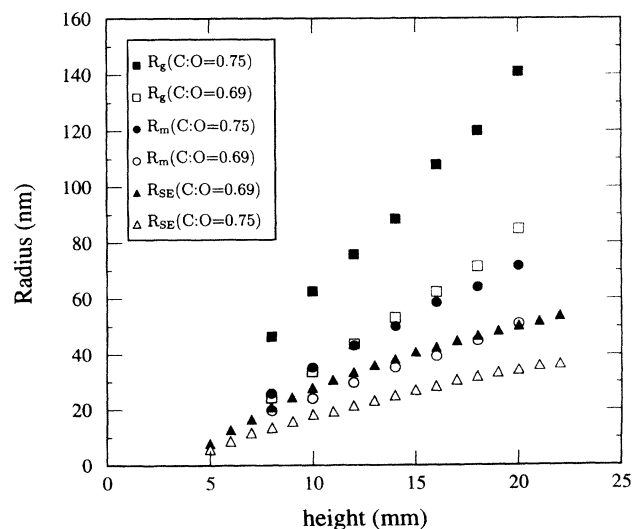

FIG. 1. The various radii as a function of height above burner. The reaction zone is at 4–5 mm. C:O is the atomic carbon to oxygen ratio for the premixed flame. R_m was calculated for $\alpha = 0.91$.

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bution. The value x is defined by $R_m \sim N^x$ and is as yet unknown, so correction of the measured R_m values to R_m for the mean size cannot be done yet. Therefore our analysis of R_m will be performed in two steps. First we will compare the measured values of R_m and N under the assumption of a monodisperse distribution of clusters all of size N. This will yield an accurate value of x. Then we will correct for polydispersity [11] to find the mean size $\langle N \rangle$ and with this x find R_m for this mean size. To do this we assume the size distribution is given by the scaling distribution [20],

$$n(N)=M_1\langle N \rangle^{-2}\phi(u) , \tag{3a}$$

$$\phi(u)=u^{-\tau}e^{-cu} , \tag{3b}$$

$$u=N/\langle N \rangle . \tag{3c}$$

In Eqs. (3) we will define the mean size as $\langle N \rangle = M_1/M_0$. We take the value of $\tau=0.2$, which we have measured with both a DLS cummulant technique [21,22] and a different SLS method [22]. This value is theoretically reasonable since $\tau=\frac{1}{6}$ for solid spheres when $\mathrm{Kn}>1$ [3,23]. This scaling size distribution function has been found to describe the soot size distribution quite well [23].

Analysis of the measured R_m as a function of N yielded $x=0.43$. Using this we corrected the measured values of R_m to R_m for a cluster of mean size. We determined R_g and R_{SE} for the same mean size and then calculated $\langle N \rangle$ and the monomer radius a via our SLS analysis.

Figure 2 shows R_m/a for a cluster of mean size as a function of mean size on a log-log plot. The graph implies

$$R_m=\beta a N^x , \tag{4}$$

with fit values of $\beta=0.99\pm0.02$ and $x=0.43\pm0.03$. The value of β is a function of the assumed accommodation coefficient and for $0\leq\alpha\leq1$ can be written as

$\beta=1.15(1+\pi\alpha/8)^{-1/2}$ so that $0.98\leq\beta\leq1.15$. The fact the β is near unity, especially for $\beta(\alpha=0.92)=0.99$ shows that our experiment yields the expected limit when $N\to1$, which is $R_m=a$, the spherical monomer size. The actual uncertainty in β will be larger than that implied by the fit if we consider the uncertainties in various input parameters that affect the a and N measurements [11]. These parameters are k_0, D_f, and the soot index of refraction [11]. The errors in β due to the uncertainties of each parameter are 3.6%, 4.4% , and 6.4%, respectively. Therefore the total error in β is about 8%; thus $\beta=0.99\pm0.08$.

The exponent $x=0.43$ has important physical implications. First of all, since $D_f=1.79\pm0.1$, $R_g\sim N^{1/D_f}\sim N^{0.56}$. Thus R_m is not proportional to R_g, contrary to the continuum regime when $\mathrm{Kn}\simeq0$. This is demonstrated graphically in Fig. 3 where R_m/R_g for mean size $\langle N \rangle$ is plotted versus $\langle N \rangle$. Whereas R_m/R_g is in the vicinity of unity, a definite nonconstancy is seen. Note that for $N=1$ the ratio R_m/R_g for a spherical particle should be $(\frac{5}{3})^{1/2}=1.29$, and the data are consistent with this limit.

The meaning of $x=0.43$ can be understood if we consider how momentum is transferred from the gas to the aggregate. When $\mathrm{Kn}>1$ the gas molecules move in straight lines relative to the size of the aggregate. To transfer momentum they must hit the aggregate, and the probability of a hit is proportional to the projectional area of the aggregate. Thus we expect the drag to be proportional to the projectional area. This is what Rogak, Flagan, and Nguyen [24] found when they compared projected areas of clusters in electron micrographs to mobility measured with an electrostatic classifier for aggregates in the transition regime. For a large $D_f<2$ aggregate, one would at first estimate the projectional area to be proportional to the number of monomers per aggregate; hence the drag on an N aggregate would be N times the drag on a monomer $f_N=Nf_1$. This would yield $R_m=aN^{0.5}$. On second thought, however, one realizes for finite aggregates that screening of monomers by other monomers occurs, hence the exponent x should be less than 0.5, as we observe.
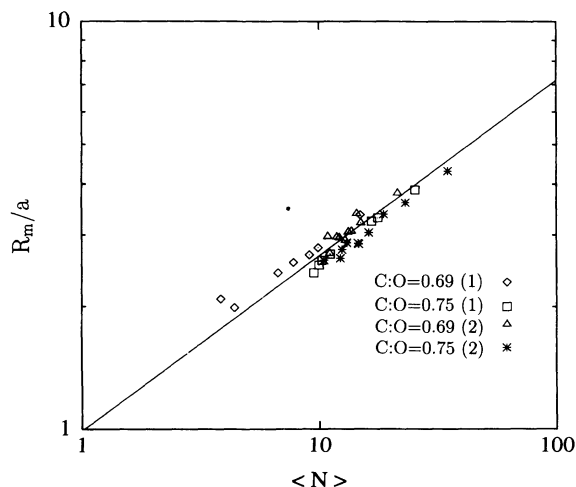

FIG. 2. Mobility radius of the mean size cluster normalized by the monomer radius versus mean size (average number of monomers per cluster) for four different experimental runs (C:O is the atomic carbon to oxygen ratio for the flame). R_m was calculated for $\alpha=0.91$. Line is best fit with $R_m=0.99aN^{0.43}$.
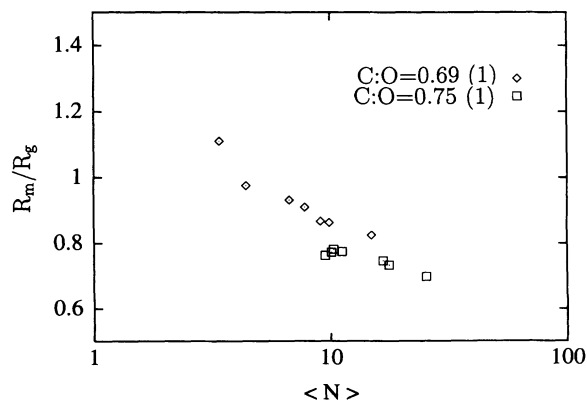

FIG. 3. Ratio of the mobility radius and radius of gyration of the mean size particle versus mean size for two different experimental runs. R_m was calculated for $\alpha=0.91$.

This argument can be quantified. Electron micrographs of three-dimensional clusters result in a two-dimensional picture as the straight line trajectories of the electrons project the cluster onto the photographic film. Thus the same monomer-monomer screening phenomenon occurs in electron micrography as in the gas-aggregate momentum transfer. For small clusters a number of earlier workers [25–27] have found the projected area to obey $A \propto N^{0.87 \text{to} 0.92}$ for electron micrography. Since $R_m^2 \sim A$, this implies $x = 0.43$ to 0.46. Meaking, Donn, and Mulholland [28] studied screening in computer generated aggregates, and our analysis of their data yields $x = 0.45$ for $N < 100$ clusters. In recent work with electron micrography on the same soot system used here, we [13] found $A \propto N^{0.82 \text{to} 0.92}$ to imply $x = 0.41$ to 0.46.

The value of x can also be obtained from the result of Schmidt-Ott [29], who used electrostatic classifiers to measure the mobility radii of gas-phase Ag clusters before and after "tempering." The clusters after tempering collapsed into a compact structure whose radii were volume equivalent sphere radii R_v. Combination of the before (R_m) and after $(R_v \sim N^{1/3})$ radii yielded $D_f \simeq 2.18$ assuming $N \sim R_m^{D_f}$. This result is somewhat confusing since the value is much higher than the known range, $1.6 \leq D_f \leq 1.9$, for DLCA clusters. The problem lies in a failure to realize that mobility radius is not a "static" radius R_s as Schmidt-Ott defined correctly in Eq. (1) of [29], $N \sim R_s^{D_f}$. Another way of saying this is that R_m is not proportional to R_g in the free molecular regime, as seen in Fig. 3; hence it is wrong to assume $N \sim R_m^{D_f}$. On the other hand, from this we can obtain $R_m \sim N^{1/2.18} \sim N^{0.46}$, i.e., $x = 0.46$, which is in excellent agreement with our light scattering result.

IV. CONCLUSION

We conclude that fractal aggregate diffusion in the free molecular regime obeys the Epstein equation with an effective radius determined by the projectional area of the cluster. This projectional area has a sublinear dependence on the number of monomers per aggregate because some monomer-monomer screening occurs. We expect this screening effect to be less important for larger aggregates, but computer simulations [28] imply some significant screening even for very large aggregates.

ACKNOWLEDGMENTS

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