

Fractal geometry of vapor-phase aggregates

James E. Martin, Dale W. Schaefer, and Alan J. Hurd
Sandia National Laboratories, Albuquerque, New Mexico 87185
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Static and dynamic light scattering and small-angle x-ray scattering measurements are reported for vapor-phase aggregates of silica. From the static scattering data the fractal dimension is found to be $\sim 1.84 \pm 0.08$, in agreement with the prediction of the cluster-cluster aggregation model. The Rayleigh linewidth is found to vary as the 2.7 power of the momentum transfer for large momentum transfer.

In recent years it has become apparent that many random structures have power-law correlations in density. These long-range correlations are a manifestation of the dilation symmetry that many random structures possess, and imply a simple relation, $R^D \sim M$, between the particle radius R and the mass M . The exponent D is generally fractional and so is called the fractal dimension.¹ The enticing simplicity of this fractal geometry has spurred theoretical and experimental interest in random structures, and scientists are looking for systems which might express this peculiar dilation symmetry. For example, at this time it is known that spin lattices, percolation clusters, lattice animals, branched and linear polymers, and various models of kinetic aggregation possess dilation symmetry.² Still, it is sufficiently clear that experimental efforts lag behind theoretical results, so that much of the current understanding of fractal systems stems from simulations and analysis, rather than from a definitive body of experimental findings.

The concept of a fractal dimension has been particularly useful in the physics of aggregation, where it has been demonstrated that the complex morphology of *solution-grown* colloidal aggregates^{3,4} can be described in terms of fractal geometry. But solution-grown aggregates differ in two essential respects from *vapor-phase* aggregates. First, solution-grown aggregates are formed in a *hydrodynamic* regime where the friction factor of a cluster is proportional to its radius, or equivalently, the diffusion coefficient is proportional to $1/R$. Vapor-phase aggregates, which are produced in a flame (carbon black is a familiar example), are generally formed in a *nonhydrodynamic* regime, where the friction factor is proportional to the square of the cluster radius,⁵ so the cluster diffusion coefficient scales like $1/R^2$. In vapor-phase aggregation, then, the cluster diffusion coefficient is very sensitive to size, and only small clusters are effective diffusors. Second, solution-grown aggregates typically have a large, repulsive screened Coulomb interaction which tends to make the probability of sticking small. In the vapor-phase, however, thermal energies overwhelm repulsive barriers and the sticking probability is expected to be very high. As we shall see, these effects have important consequences on the fractal dimension of these aggregates.

In brief, vapor-phase aggregation is believed to occur in three stages; *coalescence* of particles, *aggregation* of parti-

cles, and *agglomeration* of aggregates.⁶ In the first stage, small spherical Brownian particles (which we will hereafter refer to as "monomers") produced by combustion collide and coalesce into larger spherical particles. The characteristic time for this process is $\eta R / \sigma$, where η and σ are the particle viscosity and surface tension, respectively.⁷ Thus as the particles grow and enter cooler portions of the flame, this characteristic time becomes very large and the coalescence remains largely incomplete. In this stage ramified aggregates are formed by the incomplete fusion of spherical particles. Finally, as the aggregates reach very cool portions of the flame collisions between aggregates lead to agglomerates—clusters of aggregates held together by relatively weak van der Waals forces.

In this paper we report x-ray and light scattering measurements of vapor-phase aggregates. In spite of electron microscopy studies which show ramified structures for gas-phase aggregates, we believe our study is the first to characterize the structure and dynamics of these aggregates. In their pioneering work, Forrest and Witten⁸ found fractal clusters in electron micrographs of smoke particles, but the relationship between the observed two-dimensional data and the precursor three-dimensional clusters is uncertain. As a prototypical system, we chose fumed silica (Cab-O-Sil, Cabot Corporation, Tuscola, IL) which is formed by burning silicon tetrachloride in a hydrogen flame. An important characteristic of this system is the extremely high *in situ* viscosity of silicon dioxide. Because of this high viscosity the characteristic coalescence time is very large even for small particles, leading to the formation of aggregates of very small monomers. The characteristic size of the monomers makes these aggregates ideal for light and x-ray scattering studies.

To prepare the scattering samples, Cab-O-Sil (we used M-5, HS-5, and EH-5) was freshly dispersed into either a water-surfactant or decanol-surfactant solution using an ultrasonic cell disruptor. Final concentrations were typically ~ 0.5 mg/ml. Although the exposure times were varied from ten minutes to three hours, it was found that the scattering data were insensitive to the dispersion time. These preparations were then filtered through Millipore filters with pore sizes ranging from 1 to 8 μm , and scattering measurements were made. The scattering data were found to be independent of the filter size. Static and dynamic light scattering measurements were made with

both a He-Ne laser ($\lambda=632.8$ nm) and an argon-ion laser operating at 457.9 nm. Small-angle x-ray scattering (SAXS) data were obtained at the National Center for Small Angle Research, Oak Ridge, TN, using a pinhole collimation camera coupled to a rotating anode, Cu- K_α source. The reported light scattering exponent is an average over 15 total samples, and the reported error is just the standard deviation of these measurements.

Before giving the experimental data it is useful to develop an intuitive understanding of the scattering process and to develop a general form of the intensity $I(q)$ as a function of the momentum transfer q . The relevant length scales are the reciprocal momentum transfer $1/q$, the radius of an aggregate R , and the size of a silica monomer a . Using these three lengths, a form of the scattering function can be obtained from scaling arguments. For simplicity we start with the large length scale cutoff and ignore the finite monomer size. In this case the scattered intensity from *single* fractal is of the form $M^2 f(qR)$ where $f(x)=1$ for $x \ll 1$ and $f(x) \sim x^\gamma$ for $x \gg 1$. Noting that the intensity scales like the mass for large x gives $\gamma = -D$ and $I \sim M^2/(qR)^D$ for $qR \gg 1$.⁹

To account for the small length scale cutoff ($qa \gg 1$) we write $I \sim M^2 f(qR)h(qa)$, where $h(x)=1$ for $x \ll 1$ and $h(x) \sim x^{\delta+D}$ for $x \gg 1$. Using $R^D \sim a^D N$, where N is the number of monomers in the fractal, gives

$$I \sim \frac{Nm^2}{(qa)^D} h(qa) \sim Na^D q^\delta,$$

where m is the mass of the monomers, which are presumed to be *surface* fractals of surface fractal dimension D_s .¹⁰ Here the scaling assumption is that the intensity for $qa \gg 1$ will simply be proportional to the number of monomers times the generalized surface area a^D , per monomer. The exponent δ is thus seen to be $D_s - 2d$, which gives $I \sim Nm^2/(qa)^{2d-D_s}$ for the large- q behavior of the scattering function. The behavior of these scaling functions can thus be summarized as

$$f(x) \sim \begin{cases} 1, & x \ll 1 \\ x^{-D}, & x \gg 1 \end{cases}$$

$$h(x) \sim \begin{cases} 1, & x \ll 1 \\ x^{D_s-2d+D}, & x \gg 1. \end{cases}$$

It is important to note that this product representation is not the usual factorization of the scattering function, and that $h(qa)$ does not have the interpretation of the monomer structure factor, but implicitly includes the large- q cutoff of the intermediate scattering regime. In order for $h(qa)$ to have the interpretation of a monomer structure factor we must add the term $1/N$ to the function $f(qR)$ (Refs. 11 and 12) to obtain $I \sim M^2[f(qR) + 1/N]h(qa)$, and the exponent for the function $h(qa)$ must be modified to $D_s - 2d$. This product form of the scattering function has the advantage of including the small length scale cutoff in a natural way, but it raises the practical problem of introducing another fitting parameter.

In the special case of fumed silica, where the monomers are hard spheres, the surface fractal dimension is just

$d-1$, so $I \sim q^{-4}$ for $qa \gg 1$. To apply this relation to a weakly polydisperse solution of fractals (specifically, we exclude gelation) it is necessary to express our result for the intensity in terms of average quantities. In terms of the concentration in mass per unit volume ρ , the weight averaged mass M_w , and the z -averaged radius R_z , the intensity is $I \sim \rho M_w f(qR_z)h(qa)$ with $f(x)$ and $h(x)$ still defined as above.

The combined small-angle x-ray and light scattering data for fumed silica (Cab-O-Sil M-5) are shown in Fig. 1. The fit to the data was obtained by using a product of modified Orstein-Zernike functions $(1+x^2/\gamma d)^{-\gamma}$, where 2γ was just D for the function $f(x)$ and $2d-D_s-D$ for the function $h(x)$. The entire scattering function was fit with $D=1.88$, $R_z=1250$ nm, and $a=13.5$ nm, so the fractal regime spans a reasonably broad two-decade length scale regime. The straight line in Fig. 1 has a slope of -1.88 to highlight the fractal regime of the scattering data. An average over all 15 scattering curves gave a fractal dimension of 1.84 ± 0.08 . As previously mentioned, scattering data were collected using both decanol and water as dispersing fluids. This allowed for a direct test of possible multiple scattering with a single cluster, since the optical contrast in the water-Cab-O-Sil dispersions was about 5.5 times the contrast in the decanol-Cab-O-Sil dispersions.¹³ Since no experimentally significant difference was found in these systems, we believe that multiple scattering was not a problem.

The light and x-ray scattering data are in *qualitative* agreement with the neutron scattering data reported by Sinha *et al.*¹⁴ for silica aggregates; in each of these experiments fractal scattering behavior was observed. A difference in the observed exponents (1.84 versus ~ 2.5) may be due to the different preparation schemes used in these experiments, or may be due to a difference in the silica aggregates themselves, pointing to a possible nonuniversality in the aggregation process.

On the other hand, the light scattering measurement of the fractal dimension agrees reasonably well with image analysis work of Forest and Witten.⁸ In their experiments, transmission electron micrographs of smoke particles deposited on surfaces were analyzed by two methods:

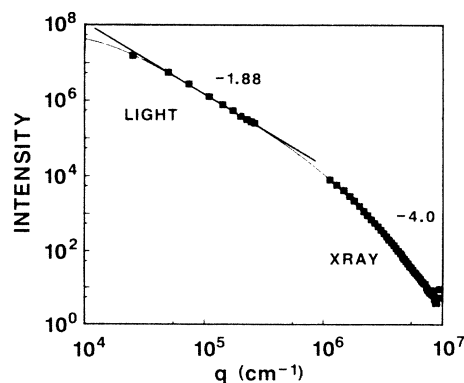


FIG. 1. Light and x-ray scattering data for Cab-O-Sil M-5 are combined to show the scattering function over six decades of intensity. The large- q (x-ray) data clearly demonstrate the crossover from fractal to nonfractal behavior.

“sandbox” scaling and the pair correlation function. The sandbox scaling method gave values in the range 1.85–1.90 for D when a correction-to-scaling term was included in their analysis. When the correction-to-scaling term was omitted, however, they obtained values of D which were smaller by ~ 0.3 . The pair correlation function values tended to lie between these extremes (1.55–1.90). However, although this agreement is encouraging it should be pointed out that the image analysis assumes that the clusters are simply projected onto the surface, without any additional distortion. Although this assumption is reasonable, these image analysis results should be accepted with this reservation.

The dynamic light scattering measurements made on the fumed-silica dispersions have a more complex interpretation than the static scattering data. These time-domain measurements probe the frequency broadening of the scattered light, and the result is expressed in terms of Γ , the Rayleigh linewidth. In thermal systems there are three diffusional line broadening mechanisms: translations, rotations, and configuration changes. In general, these contributions will give a very complex dependence of the line broadening on q , but in the special case of power-law polydispersity these complex details can be simply treated. The polydispersity function for a power-law distribution of sizes can be written as $N(m) \sim m^{-\tau} f(m/S)$, where S is a cutoff mass. For a system where τ is greater than 2 (percolation is prototypical) Martin and Ackerson¹⁵ find a very simple, universal $\Gamma \sim q^3$ result, provided that a certain dynamical scaling criterion is obeyed. The case $\tau < 2$ has been recently treated by Martin and Leyvraz¹⁶ under the same dynamical scaling assumption; the full results are summarized in Fig. 2.

The exponent ω in Fig. 2 gives the dependence of the linewidth on momentum transfer in the regime $qR \gg 1$ for a monodisperse solution, $\Gamma \sim q^{2+\omega}$, and the exponent α gives the dependence in the regime $qR_z \gg 1$ for a power-law polydisperse solution, $\Gamma \sim q^\alpha$. The exponent ω can be thought of as a measure of the contribution of internal modes to the dynamics. The case $\omega = 0$ corresponds to a system composed of rigid, roughly spherical particles whose dynamics are determined only by translational diffusion. On the other hand, completely flexible

systems, such as polymers, are characterized by $\omega = d - 2$. At the present time there are no calculations which interpolate between these rigid and flexible limits of ω .

As a matter of interest the exponent α has been calculated for two cases, strong hydrodynamic interactions, where the characteristic frequency, D_t/R^2 , scales like $1/R^d$, and weak hydrodynamic interactions, where the characteristic frequency scales like $1/R^{2+D}$. Of course in the real system hydrodynamic interactions are present and we need only concern ourselves with the lower curve in Fig. 2. It is observed that for $\tau < 2 - (d - 2 - \omega)/D$ the system acts as though it is monodisperse insofar as the dynamics are concerned. For $\tau > 2$ we obtain the universal $\Gamma \sim q^d$ gelation result, and in the region between these cutoffs the exponent α is given by $d - D(2 - \tau)$, a result which is independent of the monodisperse exponent ω . Likewise, it can be shown⁹ that the static scattering exponent (~ 1.84) is given by $D(3 - \tau)$ for $3 > \tau > 2$, but is given by the monodisperse result D for $\tau < 2$.

The line broadening data for fumed silica are shown in Fig. 3, where excellent power-law behavior is found in the experimental range of $30 \text{ nm} < 1/q < 300 \text{ nm}$. These linewidth data were obtained by the method of cumulants, as detailed previously.¹⁷ From the slope of these data we find $\Gamma \sim q^{2.7}$ for $qR \gg 1$, which is in agreement with previous measurements for solution-grown aggregates of colloidal silica.¹⁷ Since the linewidth exponent is less than 3 we are able to conclude that the polydispersity exponent is less than 2. And since τ is less than 2 we can conclude that the scattering exponent is the fractal dimension. The relation $\alpha = d - D(2 - \tau) = 2.7$ can be used to obtain $\tau = 1.86$. Now the critical reader will realize that this value of τ is really only an upper limit to the true value of τ , i.e., it is possible that internal modes in the monodisperse system scale like $q^{2.7}$ ($\omega = 0.7$). But even if we admit this possibility our interpretation of the scattering exponent as the fractal dimension remains intact.

The light scattering data lend support to the multiparticle diffusive aggregation model of Meakin¹⁸ and Kolb *et al.*¹⁹ In this model, aggregates diffuse according to $D_t \sim M^{-\alpha}$, and steadily grow via collisions with other aggregates. According to the scaling theory of Jullien *et al.*,²⁰ there are just two regimes in this aggregation model: *cluster-cluster* aggregation and *particle-cluster*

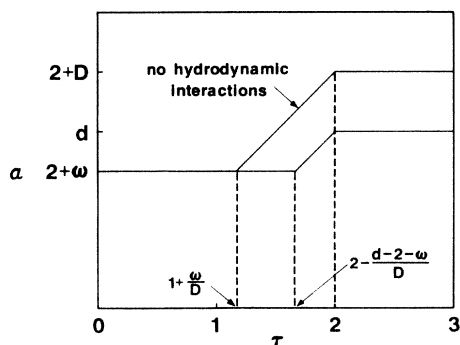


FIG. 2. The dependence of the linewidth exponent on the polydispersity exponent for the weak and strong hydrodynamic interaction limits ($\Gamma \sim q^\alpha$).

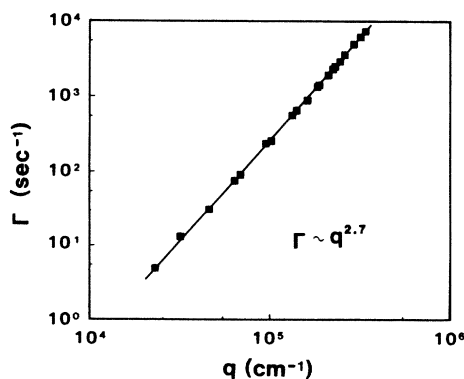


FIG. 3. The Rayleigh linewidth is plotted against the momentum transfer. Empirically, the linewidth scales like $q^{2.7}$.

(Witten-Sanders) aggregation. In three dimensions the cluster-cluster regime is defined by $\alpha < (D-1)/D$, where D is known from simulations^{12,13} to be ~ 1.78 . Particle-cluster aggregation occurs when $\alpha > (D-1)/D$ and gives a fractal dimension of ~ 2.5 . As noted previously, solution-grown aggregates are characterized by $\alpha = -D$ and so are well within the cluster-cluster regime. However, the observed fractal dimensions vary from ~ 1.8 to ~ 2.1 , the experimental variations possibly being due to a variation in cluster sticking probability. The primary effect of a low sticking probability is to increase the apparent fractal dimension to ~ 2 on small length scales. Thus, scattering experiments on finite-size samples would tend to overestimate the fractal dimension. Although vapor-phase aggregation corresponds to a smaller value of the diffusion exponent ($\alpha = -2D$), scaling would predict that vapor-phase aggregation is in the same universality class as colloidal aggregation, and a fractal dimension of

~ 1.8 is indeed what we find. This supports the universality thesis of Jullien *et al.*

In summary, the combined light and small-angle x-ray scattering measurements from fumed silica indicate a fractal dimension of 1.84 ± 0.08 , in accord with the 1.78 prediction of the cluster-cluster aggregation model. Dynamic light scattering measurements from this system indicate an apparent power-law dependence of the Rayleigh linewidth on the momentum transfer, giving an exponent of ~ 2.7 , in good agreement with previous observations for solution-grown aggregates of colloidal silica. From this linewidth exponent we are able to obtain an upper limit of 1.86 for the polydispersity exponent.

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the refractive index difference between the solvent and the scatterer. The refractive index of water is 1.334, the refractive index of decanol is ~ 1.437 and the refractive index of Cab-O-Sil is ~ 1.46 . So the optical contrast of water-Cab-O-Sil is ~ 5.5 times as great as the decanol-Cab-O-Sil system.

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