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Surface and mass fractals in vapor-phase aggregates

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Several types of fumed-silica aggregates with differing surface areas were studied over a wide range of spatial resolution by employing both light and neutron scattering. At intermediate length scales, between 100 and 1000 Å, the aggregates are mass fractals with $D_m \approx 1.7-2.0$, in basic agreement with simulations of aggregating clusters. At short length scales below 100 Å where the nature of the surfaces of the primary particles dominates the scattering, some of the samples appear to be fractally rough. In particular, a higher surface area seems to be correlated not with smaller primary particles in the aggregates, as previously assumed, but with fractally rough surfaces having D_s as high as 2.5. These may be the first materials discovered to have both mass and surface fractal structure.

Silica soot formed in a flame, or "fumed" silica, has long been popular[1-4] as a model system for studying the formation and structure of fractal aerosol aggregates.[5] This recent attention is well deserved from both a scientific and a technological view. As a result of its widespread use as a high-purity inert filler and as a high-surface-area material, large quantities of fumed silica are commercially produced with several values of specific surface areas under such trade names as Cab-O-Sil (Cabot Corporation, P.O. Box 188, Tuscola, Illinois 61953). From the standpoint of processing science, an incremental improvement in understanding the formation of these powders may lead to profitable improvements in their production. From a physicist's view, fumed-silica particles are relics from the aggregation process, encoded with information about the gas-phase environment in which they were formed. Indeed, the effort to understand aerosol aggregation[5,6] and fumed silica in particular[4,7] led to the discovery of fractal structure in aggregates[6] that spawned a new field of physics.

Most of the recent attention is focused on the *mass* correlations within clusters and addresses issues such as why they are fractal. In addition, there are conditions under which the *distribution* of cluster sizes is fractal (power law), depending largely on cluster mobilities and, hence, the environment (vapor or liquid phase). Our measurements pertaining to the mass correlations show no apparent surprises, although the interpretation of our data requires certain assumptions about the cluster-size distribution. (The unique properties of the cluster mobility in vapor environments and its effects on the cluster-size distribution are discussed in the following paragraphs.) Of more novel interest, however, are the surprising characteristics we discovered about the *surfaces* internal to the clusters: Our scattering data strongly suggest that the surfaces are fractally rough. Again, the interpretation requires certain reasonable assumptions about the size distribution of the "primary particles," which are the basic units making up the cluster. The important implication is that the specific surface area, which is the area available for catalytic coatings, for example, is at least partially determined by this roughness and not entirely by primary-particle size, as has been assumed. The origin of the surface texture is beyond the scope of this paper, unfortunately, because of a lack of specific (proprietary) information about the production of high-surface-area fumed silica.

The diffusion of small particles in an aerosol is controlled by kinetic, rather than continuum, gas behavior: When the mean free path of a gas molecule is large compared to the size of a particle, the diffusion constant of that particle is inversely proportional to the *square* of its radius, in contrast to continuum behavior where the diffusion constant is simply inversely proportional to the radius (the Stokes law). Hence, the collision frequency between sufficiently small airborne clusters is more strongly dependent on radius than in continuum systems, such as colloids.[8] The random path of such a small cluster is similar to that of a large gas molecule, having extended ballistic trajectories between collisions. Eventually, when the cluster size exceeds the gas mean free path (approximately 500 Å in a flame), the diffusive path becomes controlled by continuum behavior and the Stokes law prevails.[7]

In an aggregating system, the type of diffusive path affects the shape and evolution of the cluster-size distribution. Simulations suggest[8] that the cluster-size distribution is sharply peaked ("quasimonodisperse") when the small clusters diffuse sufficiently rapidly compared to the large clusters; otherwise it decays monotonically, possibly by a power law. If γ defines the dependence of the diffusion constant on the cluster radius through $D_0 \sim R^{-\gamma}$, the crossover between the quasimonodisperse and power-law regimes happens to be near $\gamma = 1$ (Stokes law). Measurements in aerosols generally exhibit a peak,[9] as expected since $\gamma > 1$; we expect this to be the case for fumed silica with $\gamma \approx 2$. To be able to assume quasimonodispersity simplifies the interpretation of the scattering data because then the fractal scattering cannot be confused with polydispersity.

The cluster geometry is not as sensitive to the diffusivity, however. Cluster-cluster simulations have shown that the aggregate structure is fractal, regardless of the particle trajectory, and that the fractal dimension is approximately $D_m \approx 1.8$ if the diffusion of smaller species is faster than that of larger species.[10]

In this report we combine the results of light scattering and small-angle neutron scattering (SANS) to achieve a wide spatial resolution range that spans the primary particle size and the cluster size. These data provide us with information about both the early and late stages of growth. In contrast to our previous study[1] of Cab-O-Sil M-5, which focused primarily on the aggregate mass, we have studied two additional grades, EH-5 and HS-5, that have higher specific surface area in order to explore differences owing to surface structure.

Although many of the manufacturing details of Cab-O-Sil are proprietary, all grades are formed by the combustion of silicon tetrachloride. The nucleation of molten silica droplets, called "primary particles," is thought to be essentially instantaneous[6] with the onset of combustion. From the nucleation point on, the temperature history largely determines the specific surface area of the final product. If the particles are allowed to cool slowly, the yield is a powder with a low specific surface area σ (e.g., Cab-O-Sil M-5, $\sigma = 200\ \mathrm{m^2/g}$) and, if cooled rapidly, a high surface area is obtained (e.g., Cab-O-Sil EH-5, $\sigma = 390\ \mathrm{m^2/g}$).

Previous work has implicated the coalescence rate of the primary particles, which is controlled by a highly-temperature-sensitive viscosity, for the surface-area differences.[6,7] That is, the inviscid droplets coalesce upon colliding, thereby lowering the surface-to-volume ratio in the low-surface-area powders, whereas the cool particles aggregate together without coalescence in the high-surface-area powders. Under the assumption that the primary particles are smooth spheres, this scenario is consistent with radii calculated from the Brunaver-Emmet-Teller (BET) gas-adsorption isotherm (see Table I).

Our results indicate that the smooth-particle assumption may not be correct. From small-angle neutron scattering, we find that the typical primary particle size is the same for all three Cab-O-Sil grades studied here but that the surface roughness varies. It may be that thermal stresses cause surface irregularities during rapid cooling. Unfortunately, we have not yet obtained high-resolution electron micrographs to document this surface roughness independently.

Our light scattering samples were prepared by dispersing 0.2 g of dry Cab-O-Sil powder in 30 $\mathrm{cm^3}$ of either decanol or 0.1% aqueous sodium lauryl sulfate solution using 10 min of ultrasonification at 150 W. The resulting suspensions were diluted to less than 1 mg/ml and filtered (8 μm) into the light scattering cell. Scattering was performed with vertical-vertical polarization between scattering angles of $\theta = 10°$ and 135° using either an argon-ion laser operating at 4579 Å or a helium-neon laser at 6328 Å. The scattering wave vector $q[=(4\pi n/\lambda)\sin(\theta/2)$, where n is the index, θ is the scattering angle, and λ is the wavelength] covered 0.0002 to 0.004 $\mathrm{Å}^{-1}$ depending on the solvent and wavelength. No significant differences between different solvents were found. A background of pure solvent was subtracted and a correction made for the size of the illuminated volume seen by the detector as a function of angle.

In the neutron scattering, performed at Oak Ridge National Laboratories, dry samples were loosely packed (density ≈ 30 mg/ml) into 2-mm-path-length cells and run at $\lambda = 4.75$ Å ($\Delta\lambda/\lambda = 0.05$) with sample-to-detector distances of 3 and 18 m. The intensities, which were recorded on a two-dimensional detector, were rotationally averaged about the transmitted beam and background corrected with an empty-cell curve. The 3-m geometry spanned $q = 0.01$–$0.2\ \mathrm{Å}^{-1}$, while the 18-m geometry covered 0.001–0.02 $\mathrm{Å}^{-1}$. Calibration of the neutron intensity, which was performed against a water standard for the 3-m and against an aluminum standard for the 18-m geometry, yielded absolute scattering intensities that matched to within 10% in the region of q where the data overlap. Each sample was also run in an contrast-matching H_2O-D_2O mixture to assess the scattering from closed pores. No significant scattering was found under these conditions, hence no closed porosity exists. The manufacturer also reports no significant porosity using BET gas-adsorption analysis.

Packing clusters together, however loosely, presumably distorts or destroys the information about the cluster size in a scattering experiment. It is possible to estimate how closely packed the clusters are in comparison to their characteristic size, which we discuss later. In any case, the length scale relevant to the cluster size was covered by the light-scattering experiments in which the clusters were well dispersed.

To combine the light scattering and the two neutron scattering curves for each sample, the data were scaled in intensity in order to yield smooth curves for analysis (by matching logarithmic derivatives). Duplicate data below

TABLE I. Scattering results for three grades of Cab-O-Sil. The BET radius for the primary particles was calculated by assuming smooth spheres and using the gas-adsorption specific surface area provided by the manufacturer (Ref. 5). The other parameters are from fitting the scattering data with Eq. (2). The mass fractal dimension designated with * was found by fitting with the form used in Ref. 2. A pessimistic error bar is given for each column.

Grade	BET surface area ($\mathrm{m^2/g}$)	Radius of gyration BET r_g (Å)	Radius of gyration Primary r_g (Å)	Radius of gyration Cluster R_g (Å)	Fractal dimension Surface D_s	Fractal dimension Mass D_m	Fractal dimension Mass D_m^*
M-5	200	53	95.5	8700	2.00	1.91	2.03
	±25	±7	±2.5	±1700	±0.10	±0.10	±0.10
HS-5	325	33	86.7	4000	2.28	1.84	2.00
EH-5	390	27	82.5	3520	2.54	1.81	1.94

and above the point where matching was done were removed so as not to emphasize the weighting there. The resulting curves are plotted in Fig. 1 where, in the interest of clarity, not all of the data points are shown (although all were used in the fitting analysis) and the curves have been displaced.

The scattering curves have the general form we expect for colloidal aggregates. There are two breaks in the log-log plots, corresponding to the two important lengths in the system, the radius of gyration r_g for the primary particles and R_g for the clusters. Between these crossovers there is a slope given by the fractal dimension of the clusters D_m, and above the highest crossover there is a slope related to the surface fractal dimension D_s of the primary particles. If the particles are smooth, the slope would be -4 (Porod's law) corresponding to a two-dimensional surface, and if the particles are fractally rough then the slope would be between -3 and -4.[11]

More quantitatively, the scattered intensity should have the following regions:[2]

$$\begin{aligned} I &\sim 1 - q^2R_g^2/3 + \cdots, \quad q \ll R_g^{-1} \\ &\sim q^{-D_m}(1 - q^2r_g^2/3 + \cdots), \quad R_g^{-1} \ll q \ll r_g^{-1} \qquad (1) \\ &\sim q^{-(6-D_s)}, \quad r_g^{-1} \ll q \, . \end{aligned}$$

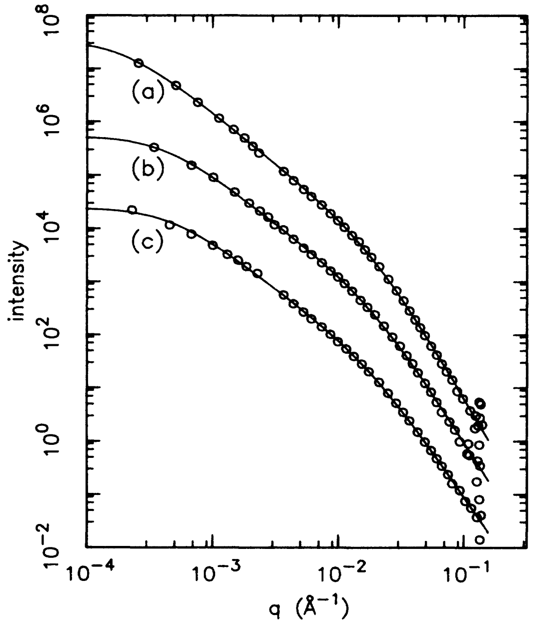

FIG. 1. Combined light scattering and SANS curves for vapor-phase silica aggregates. The light scattering data cover the small-q regime, the 18-m SANS covers the intermediate-q regime, and the large-q regime is covered by the 3-m SANS data. Three grades of Cab-O-Sil were studied, (a) M-5, (b) HS-5, and (c) EH-5, which differ in specific surface area. The important differences and similarities between the three samples are at large q, where the asymptotic slope is steepest for M-5 (the powder with the lowest surface area), and shallowest for EH-5 (with the highest surface area) but the crossover "knee" is at virtually the same position for all three. These features indicate that the primary particles are nearly the same size but differ in *surface roughness* from one grade to the next.

A nonlinear least-squares fit was made to a modified Ornstein-Zernike form, identical to that used in Ref. 1 but with an extra free parameter η for the exponent characterizing the primary-particle surfaces,

$$I = I_0 \frac{1}{(1+\beta^2q^2)^\alpha} \frac{1}{(1+\delta^2q^2)^\eta} \, . \qquad (2)$$

Thus, there are four free parameters in addition to the amplitude I_0: β is related to the cluster size, δ to the primary-particle size, α to the mass fractal dimension, and η to the surface fractal dimension. This equation has the asymptotic forms we desire and the advantage of calculational simplicity. The data for $q < r_g^{-1}$ were also fit to a formula containing a single exponential crossover function[2] for R_g^{-1} with essentially the same results for the fractal dimension. (For $D_m = 2$, these two methods of analysis are identical.) It should be possible to fit the data with appropriate polydisperse distributions while fixing one or two of the above fractal dimensions. Hence our interpretation is not unique.

The results are tabulated in Table I. Expansions of Eq. (2) for small, intermediate, and large q make it possible to relate the fit parameters to the physical parameters in Eq. (1),

$$\begin{aligned} R_g^2 &= 3\alpha\beta \, , \\ D_m &= 2\alpha \, , \\ D_s &= 6 - 2(\alpha+\eta) \, , \\ r_g^2 &= 3\eta\delta^2 \, . \end{aligned} \qquad (3)$$

Since the high-q crossover falls in the midst of the neutron data and is spanned by ample points on either side (in contrast to the low-q crossover), we are more confident in the parameter δ than in β. The conclusions we draw are based mainly on δ.

The mass fractal dimension was found to be $D_m = 1.7-2.0$, consistent with our previous measurements on M-5 using light and small-angle x-ray scattering.[1] This range covers the simulation results for cluster-cluster diffusion-limited and reaction-limited aggregation,[10] but we cannot confidently claim the presence or absence of either of these two limiting behaviors. The fractal dimension agrees fairly well with the neutron scattering results by others[2] for dispersed or loosely packed dry samples.[2] It does not agree with results from compacted samples[2] ($D_m \approx 2.5$) or with preliminary *in situ* results ($D_m = 1.5$).[3]

We do not believe that the packing of our neutron samples has substantially influenced the measured D_m because the packing was as loose as possible. By estimating the ratio of the radius of gyration to the cluster separation, this packing problem can be assessed. According to the manufacturer, the loose-packed density of Cab-O-Sil is 0.03 g/cm^3 and the typical cluster has 10^3 monomers; then a back-of-the-envelope calculation shows that the cluster separation is 5–10 times the radius of gyration. Since the data have fairly uniform slopes above $q = R_g^{-1}$, there seems to be no evidence of packing influence in the critical region.

Our most interesting observations concern the primary particles. We see first of all that the primary particle size is relatively constant for the three grades of Cab-O-Sil, even though the surface area σ differs by a factor of nearly 2 from its highest value to its lowest. Moreover, the surface fractal dimension of the primary particles increases with σ, as shown in Fig. 2. The product $(\frac{5}{27})^{1/2}\rho r_g \sigma$, where $\rho = 2.20$ g/cm^3 is the density of silica, would be 1.0 if the primary particles were all smooth spheres, and it would at least be constant for all three samples if the surface area were accounted for by only the primary particle radius; we get 1.81, 2.67, and 3.05 for M-5, HS-5, and EH-5, respectively. That these numbers are greater than unity reflects the fact that the primary particle volume is larger than would be expected for monolayer coverage on a smooth, nonporous particle in the BET gas-adsorption measurements of σ.

It appears from this evidence that coalescence is not as important as the development of surface roughness in determining surface area. That is not to say that coalescence and sintering is unimportant in the formation of Cab-O-Sil (particularly for the very low-area *L* grades), only that another process may account for the difference between the grades under study.

An equivalent interpretation of our scattering data is that there is polydispersity in the primary particles. Power-law polydispersity can lead to noninteger scattering exponents[12] and high surface areas. However, since the thermodynamic evidence indicates that nucleation occurs in a single burst,[6] the primary particles would be expected to be reasonably uniform in mass.

In summary, our combined results from light scattering and small-angle neutron scattering on fumed silica show that the aggregates are fractal on two levels. They are mass fractals for large length scales, owing to the aggregation of the primary particles, and surface fractals for small length scales at the level of surface irregularities on the primary particles. We believe that the high surface areas of EH-5 and HS-5 are at least partially explained by the surface roughness.

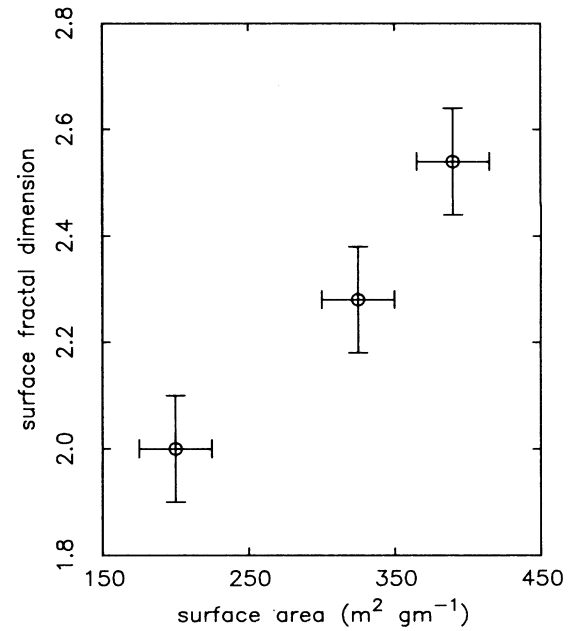

FIG. 2. Surface fractal dimension as a function of specific surface area.

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