

Aerogelation in a Flame Soot Aerosol

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Evidence is given for gelation in a flame soot aerosol. The aggregation rate is more than 2 orders of magnitude greater than expected from the Smoluchowski equation with a cluster-cluster aggregation kernel. The breakdown of this equation occurs when aggregate crowding becomes significant. [S0031-9007(98)05371-X]

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The sol-gel transition in colloidal and polymeric liquid solutions is a common and important phenomenon in Nature and for the creation of materials of practical value [1,2]. In this Letter, we report the first example of gelation in an aerosol of freely aggregating clusters. To date, gelation has been observed only in the liquid state although there is one example of aerogelation induced by an applied electric field [3]. The aerosol studied here is soot in an acetylene diffusion flame, and the gelation is responsible for the creation of unusually large soot clusters.

Our results are significant not only for their novelty but also because they allow for a more quantitative study of gelation kinetics than heretofore achieved. In a particle suspension, cluster-cluster aggregation proceeds gelation, which can occur with sufficient particle density or time. The cluster-cluster aggregation kinetics, which can be either diffusion limited (DLCA) or reaction limited (RLCA), are governed by the Smoluchowski equation. This equation in its simplest form (for a monodisperse system of particles) is given by

$$dn/dt = -Kn^2, \quad (1)$$

where K is the aggregation kernel which specifies the aggregation rate and n is the cluster number density. The equation is based on the assumption of uncorrelated, binary collisions, as indicated by the n^2 term. A problem arises in that the kinetic aggregation model based on the unsimplified Smoluchowski equation predicts that both DLCA and RLCA have nongelling kernels; hence, a particle suspension should not gel [1,2,4]. This prediction is contrary to experimental fact. This conundrum can be addressed by studying the soot aerosol. An aerosol is simpler than liquid colloidal systems because there are no solvent effects which can yield an aggregation rate which is difficult to quantify theoretically. In this work, we measured the aggregation rate of the soot clusters formed by the aerogelation process and found it to be more than 2 orders of magnitude faster than that predicted for simple DLCA, a prediction which we have previously verified for a dilute system of soot aerosol fractal aggregates [5]. We find that the enhanced aggregation rate is associated with when the ramified aggregates fill all of the available space. This implies that aggregate crowding causes the kinetics to cross over from kinetics governed by the Smoluchowski equation (i.e., this equation becomes invalid) to an as yet

undescribed gelation kinetics, and thereby explains why gelation can occur in particulate systems that begin their aggregation as either DLCA or RLCA. This space filling occurs at the transitions from small, submicron soot clusters to soot of essentially macroscopic dimensions, a transition anticipated theoretically by Lushnikov [6] as being not accounted for by the Smoluchowski theory. Also, of practical importance is that this is the first report of soot cluster formation via a pathway other than the usually DLCA kinetics. However, this new gelation pathway with its greatly enhanced kinetics may be important in combustion systems in which *local* soot volume fractions are large.

Carbonaceous soot is a common by-product of fossil fuel combustion and, as such, is a major atmospheric pollutant [7]. Typically, soot is composed of ramified aggregates of roughly spherical monomers or primary particles with radii on the order of $a = 10\text{--}30$ nm. Each aggregate has $N = 1\text{--}100$'s of primary particles to yield an overall size (radius of gyration) of $R_g = 50\text{--}500$ nm. A great body of evidence now exists that establishes that these soot clusters are fractal aggregates [8] and, thus, describable by

$$N = k_0(R_g/a)^D, \quad (2)$$

where $D \simeq 1.8$ is the fractal dimension and k_0 is a pre-factor of order unity. The fractal dimension is consistent with that expected for a DLCA process [9,10].

The experiment described here consisted of a simple diffusion burner composed of a 0.9 cm i.d. brass tube through which acetylene could be passed at variable flow rate. The flame that was ignited above this tube burned in the ambient air with various screen buffers to stabilize the flow. The flame was bright yellow-white at its base but cooled with increasing height above burner h to a dull orange and then a black, narrow laminar flowing soot aerosol by $h \simeq 8$ cm, depending somewhat on flow rate. An argon ion laser operating at $\lambda = 514.5$ nm was directed through the flame. The turbidity of the flame was measured with one photomultiplier tube, and the scattered light intensity at various angles was measured with another, to yield an optical structure factor measurement. Direct observation of the very large soot in the flame was performed using a 10 power photomicroscope with an object distance of 15 cm. The flame was backlit by a 1.5 μ s xenon flashlamp shining on a white background behind the flame. This lamp

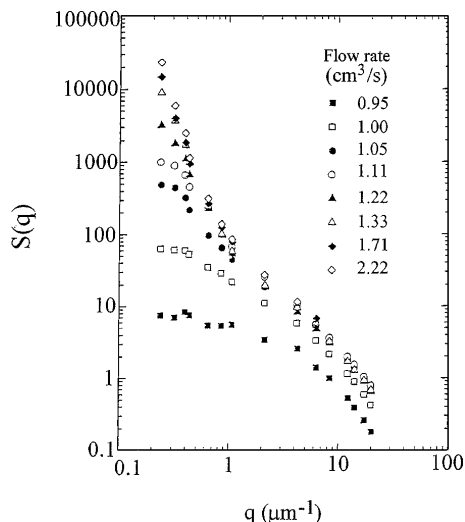


FIG. 1. Structure factors measured at a height above burner of 10 cm for various acetylene flow rates.

was triggered by the flash accessory of a 35 mm camera that was part of the photomicroscope.

Figure 1 shows the optical structure factor [11,12] for various acetylene flow rates at $h = 10$ cm. At low flow rates, a typical structure factor $S(q)$ is seen indicating soot clusters of ca. $0.5 \mu\text{m}$ and a fractal dimension of 1.8. With increasing flow rate, however, a drastic increase in scattered intensity is seen at low q while the feature representing the $0.5 \mu\text{m}$ clusters changes only slightly. This feature indicates a second phase with characteristic dimensions greater than $5 \mu\text{m}$, the inverse of our smallest experimental q value. Thus, light scattering indicates the presence of two soot phases: one submicron, typical of mass fractal soot, and one "supersoot" phase that develops quickly with flow rate after a threshold is reached.

Since the supersoot phase was so large, it could be studied *in situ* with microsecond photomicroscopy. Typical results are shown in Fig. 2. Figure 2(a) shows an unresolved soot aerosol when the acetylene flow rate is $0.83 \text{ cm}^3/\text{s}$. This is the submicron soot aerosol. At a flow rate of $1.7 \text{ cm}^3/\text{s}$, however, Fig. 2(b) shows large soot clusters on the order of $10 \mu\text{m}$ superimposed upon the submicron soot phase background. At the yet larger flow rate of $3.4 \text{ cm}^3/\text{s}$, Fig. 2(c) shows that there are many large, essentially touching, supersoot clusters superimposed on the submicron phase background as a web of interconnected clusters. This apparent interconnection is not an artifact of the 2D projection of the photograph because, as we shall see below, the supersoot resides in a thin annulus in the flame. These photographs corroborate the light scattering results that two soot aerosol phases exist in the flames. Apparently, the structure in Fig. 2(c) is very fragile because the rising, laminar flowing aerosol eventually breaks into turbulence, and the soot that results is millimeter sized. Most importantly, Fig. 2(c) is direct and positive evidence of a soot gel in the flame.

In previous work, we collected soot samples from the flame for *ex situ* analysis [8]. The sampling device is similar to a device originally developed by Dobbins and Megaridis [13]. The probe consisted of a thin blade of metal that could carry either a transmission electron microscope grid or an optical microscope glass slide. The probe was inserted into the flame for a residence time of 50 msec either vertically, so that the soot was collected by thermophoresis, or horizontally, so that the larger soot could also be collected via impaction. Figure 3 shows an example of the soot collected, and this photograph demonstrates once again the two-phase nature of the soot aerosol. Our previous work found the morphologies of each phase to be the same in that each had $D = 1.8$ and $k_0 \approx 1.7$. The

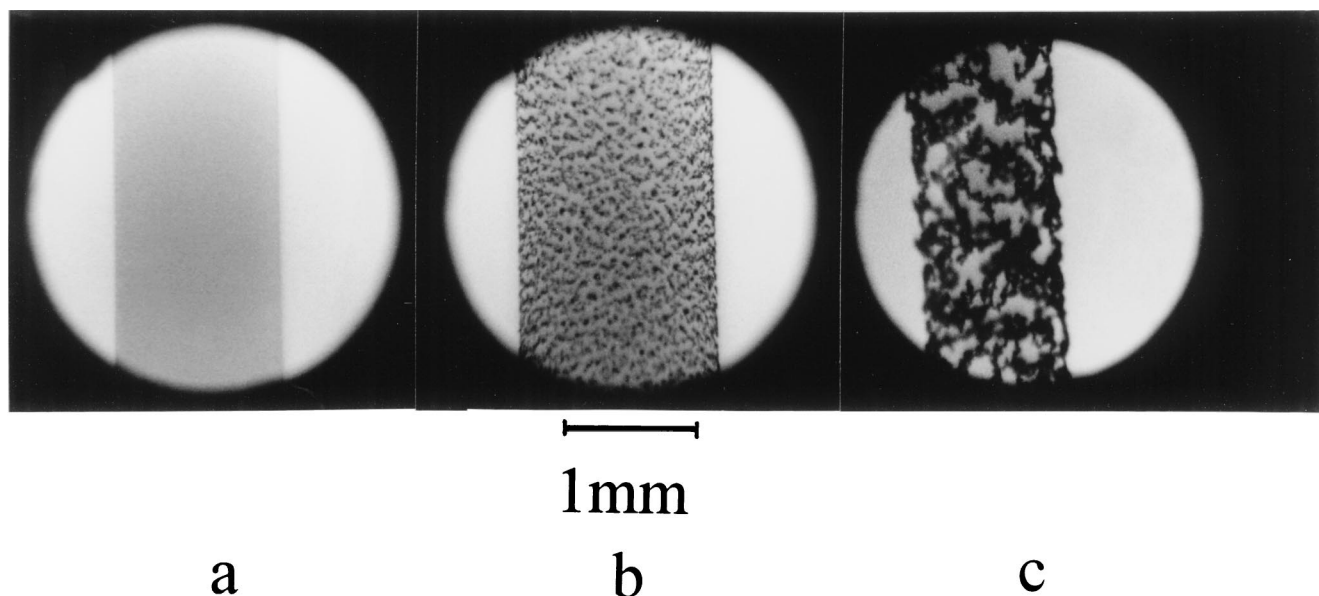


FIG. 2. Microsecond photographs of soot aerosol at a height above burner of 10 cm for acetylene flow rates of (a) $0.83 \text{ cm}^3/\text{s}$, (b) $1.7 \text{ cm}^3/\text{s}$, and (c) $3.4 \text{ cm}^3/\text{s}$.

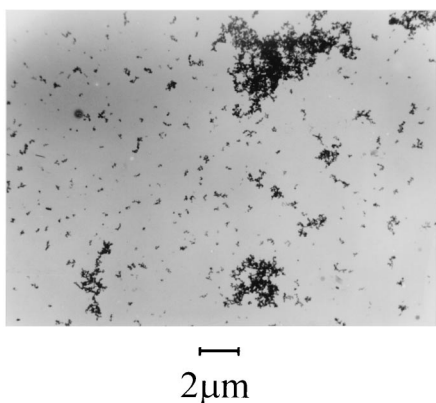


FIG. 3. Electron microscope picture of soot collected from the aerosol at a height above burner of 4 cm and acetylene flow rate of $1.1 \text{ cm}^3/\text{s}$.

primary particle size was constant at $a = 23 \pm 3 \text{ nm}$ for all of the samples implying that the chemistry which causes the primary particles to grow was effectively completed and not a factor in the subsequent aggregation kinetics.

Since the fractal dimension of the soot particles is less than the spatial dimension, when the aggregation proceeds to a certain *critical size*, the soot clusters will fill the entire volume, the clusters will touch, and the aerosol will gel. This occurs approximately when the monomer number density of the clusters equals the overall monomer number density of the system. We assume for simplicity that the clusters are monodisperse and spherical with a perimeter radius $R = \sqrt{(D+2)/D} R_g$ [14]. Then, using Eq. (2) and the soot volume fraction $f_v = 4\pi n N a^3/3$, the critical radius of gyration is

$$R_{g,c} = a \{ [(D+2)/D]^3 k_0^{-1} f_v \}^{1/(D-3)}. \quad (3)$$

To determine $R_{g,c}$, the soot volume fraction must be measured. This was done by measuring both the incident and transmitted intensities and calculating the turbidity τ of the flame from

$$I_T = I_0 e^{-\tau x}, \quad (4)$$

where x is the optical path length in the flame. Flame profile measurements showed a thin soot annulus surrounding a relatively empty, cylindrical core. The width of the annular region at a height above burner of 4 cm was measured to be $1.0 \pm 0.2 \text{ mm}$ to imply $x = 2.0 \pm 0.4 \text{ mm}$.

The turbidity is related to the extinction cross section by [15]

$$\tau = n \sigma_{\text{sca}} + n \sigma_{\text{abs}}. \quad (5)$$

In Eq. (5), n is the number density of clusters in the flame, and σ_{sca} and σ_{abs} are the scattering and absorption cross sections, respectively. For fractal clusters with $D < 2$, these are given by [15]

$$\sigma_{\text{sca}} = \frac{8}{3} \pi N^2 k^4 a^6 F(m), \quad (6a)$$

$$\sigma_{\text{abs}} = -4\pi N k a^3 E(m). \quad (6b)$$

In Eqs. (6), $k = 2\pi/\lambda$, $F(m) = |(m^2 - 1)/(m^2 + 2)|^2$, and $E(m) = \text{Im}[(m^2 - 1)/(m^2 + 2)]$, where m is the soot refractive index. Here, we take the often used value

of $m = 1.57 - i0.56$ [16]. Since m is complex, a typical approximation in soot studies is to use the fact that $a \ll \lambda$, hence $\sigma_{\text{abs}} \gg \sigma_{\text{sca}}$, thus

$$\tau \approx 3k f_v E(m). \quad (7)$$

This approximation is good as long as the clusters are not too big, an approximation which obviously is invalid for the supersoot phase. Hence, we shall use Eq. (7) only up to the threshold of supersoot production.

The results shown in Fig. 4 show that the soot volume fraction increases with acetylene flow rate to 1×10^{-4} at the threshold of supersoot production at a height $h = 4 \text{ cm}$. This is more than 2 orders of magnitude larger than f_v values typically measured in flames using other, more saturated fuels.

We now use Eq. (3) to calculate the critical cluster size. For $a = 23 \text{ nm}$, $D = 1.8$, $k_0 = 1.7$, and $f_v = 10^{-4}$, we find $R_{g,c} \approx 10 \mu$. This value is very comparable to the size of the supersoot fraction observed in the flame, and, hence, the implication is that the supersoot is formed via a gelation process.

This relatively large density or packing of the soot clusters implies that the Smoluchowski equation, which can be used to describe aggregation in the dilute limit, may not be valid for the supersoot aggregation kinetics. Unlike previous liquid phase aggregate gelation studies, we can measure the aggregation rate without concern for the effects of the solvent, as described above. This allows us to make a direct comparison to theory. Moreover, our recent measurements [5] have substantiated the theory for a premixed methane flame soot aerosol with DLCA fractal clusters of $D = 1.8$. An aggregation rate of $K_0 = 1.0$ to $1.8 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ was found. This was in good agreement with theory in the Knudsen number range $\text{Kn} \approx 10$, where the Knudsen number is the ratio of the suspending gas mean free path to the cluster size. Thus, we can have confidence in the theoretical prediction for larger clusters, hence smaller Kn , that the aggregation rate should be $K_0 (\text{Kn} \rightarrow 0) = 1.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ if Smoluchowski kinetics is valid. We now compare this value to a semi-quantitative measurement of the aggregation rate that leads

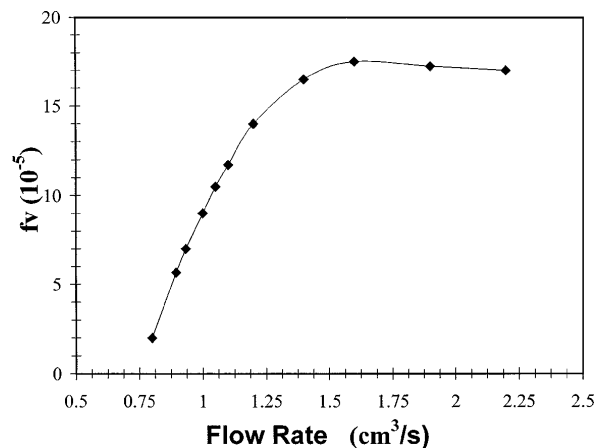


FIG. 4. Soot volume fraction at a height above burner of 4 cm as a function of acetylene flow rate.

to the formation of the supersoot. The time is based on the hot gas flow rate of ~ 40 cm/s and the height above burner where the supersoot first appears, $h = 4.0$ cm. Thus, $t = 0.1$ s. A primary particle radius $a = 23$ nm and a soot volume fraction of 10^{-4} implies an initial number density of primary particles $n = 2.1 \times 10^{12}$ cm $^{-3}$. The supersoot at $h = 4.0$ cm has $R_g \approx 10\mu$; thus, by Eq. (2), with $D = 1.8$ and $k_0 = 1.7$, $N = 9.5 \times 10^4$. One can then calculate the density of clusters as $n(\text{clusters}) = 2.1 \times 10^7$ cm $^{-3}$. Equation (1) implies $K = d(1/n)/dt$, which, using the values above, yields $K = 4.6 \times 10^{-7}$ cm $^{-3}$ s $^{-1}$.

Although this is a semiquantitative result, it differs significantly (a factor of 460 greater, which is well beyond our uncertainty) from the value expected for Brownian aggregation in the $\text{Kn} \rightarrow 0$ regime governed by the Smoluchowski equation. Our conclusion is that kinetics of supersoot formation, thus, the kinetics of cluster gelation, is faster than that described by the Smoluchowski equation. It is reasonable to propose that the reason for the enhanced kinetics is due to the fact that the clusters are filling all of the available space. In such a situation, the Smoluchowski equation, valid in the dilute limit, must break down because the conditions for its validity, which are uncorrelated, binary collisions, cannot hold in the crowded aggregate system.

Recently, Brunner *et al.* [17], in a study of a liquid phase sol-gel transition for clusters, saw a distinct increase in the aggregation rate at a point where the clusters were approaching the critical radius for complete space filling. Although they could not compare (and, in fact, did not measure) their aggregation rate to that expected for pure, Brownian DLCA (because of solvent effects), their results and ours are in unison with regard to the enhanced rate due to cluster packing. In simulation work, Hasmy and Jullien [18] also saw the effective aggregation rate increase as either the monomer density or the run time increased, both of which lead to aggregate crowding. Some previous gel simulation work [3,18,19], but not all [20], has shown clusters with fractal dimension significantly greater than that expected from cluster-cluster aggregation, in some cases approaching the spatial dimension. This is in contrast to our supersoot clusters for which we have found $D = 1.8$, in good agreement with DLCA. These simulations show D increasing with volume fraction, and one may infer from these works that, when the volume fraction is less than $\sim 10^{-2}$, the DLCA fractal dimension is obtained. This agrees with our results.

The two-phase nature of our system is an indication of the initial inhomogeneity of the flame and supports the gelation picture. The chemical reactions leading to primary particle production and the subsequent aggregation occur in the annular flame front centered on the centerline of the flame. In a cylindrical diffusion flame at small h , the primary particle number density is a strongly peaked function of radial position. Smoluchowski kinetics, which should govern the aggregation early in the flame because the initial primary particle densities are far from filling

or packing the volume, is proportional to density squared. Thus, the denser regions grow large clusters quicker. The fairly catastrophic appearance of supersoot with flow rate implies that at some critical value of the density, which would reside at some thin annular region within the complete annular flame front, the Smoluchowski kinetics can create clusters large enough and growing fast enough so that the even faster gelation kinetics can occur. Thus, one part of the soot aerosol runs away from the rest creating the two-phase aerosol. Remarkably, the great difference between the two phases downstream is a consequence of an initially small difference in monomer density upstream.

In conclusion, we have presented evidence for gelation in an aerosol of soot. The large soot clusters formed by gelation result from kinetics that cannot be described by the Smoluchowski equation which is invalidated by aggregate crowding.

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- [1] *Kinetics of Aggregation and Gelation*, edited by F. Family and D. P. Landau (North-Holland, Amsterdam, 1984).
 - [2] C. J. Brinker and G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing* (Academic, Boston, 1990).
 - [3] A. A. Lushnikov, A. E. Negin, and A. V. Pakhomov, *Chem. Phys. Lett.* **175**, 138 (1990).
 - [4] M. Kolb and H. Hermann, *J. Phys. A* **18**, L435 (1985).
 - [5] C. Oh and C. M. Sorensen, *J. Aerosol Sci.* **28**, 973 (1997).
 - [6] A. A. Lushnikov, *J. Colloid Interface Sci.* **65**, 276 (1978).
 - [7] *Particulate Carbon Formation During Combustion*, edited by D. C. Siegla and G. W. Smith (Plenum, New York, 1981).
 - [8] C. M. Sorensen and G. D. Feke, *Aerosol Sci. Technol.* **25**, 328 (1996).
 - [9] P. Meakin, *Phys. Rev. Lett.* **51**, 1119 (1983).
 - [10] M. Kolb, R. Botet, and R. Jullien, *Phys. Rev. Lett.* **51**, 1123 (1983).
 - [11] S. Gangopadhyay, I. Elminyaw, and C. M. Sorensen, *Appl. Opt.* **30**, 4859 (1991).
 - [12] C. M. Sorensen, J. Cai, and N. Lu, *Appl. Opt.* **31**, 6547 (1992).
 - [13] R. A. Dobbins and C. M. Megaridis, *Langmuir* **3**, 254 (1987).
 - [14] C. Oh and C. M. Sorensen, *J. Colloid Interface Sci.* **93**, 17 (1997).
 - [15] C. M. Sorensen, in *Handbook of Surface and Colloid Chemistry*, edited by K. S. Birdi (CRC Press, Boca Raton, FL, 1997), p. 533.
 - [16] W. H. Dalzell and A. F. Sarofim, *J. Heat Transfer* **100**, 104 (1969).
 - [17] R. Brunner, S. Gall, W. Wilke, and M. Zrinyi, *Physica (Amsterdam)* **239A**, 477 (1997).
 - [18] A. Hasmy and R. Jullien, *J. Non-Cryst. Solids* **186**, 342 (1995).
 - [19] A. Hasmy and R. Jullien, *Phys. Rev. E* **53**, 1789 (1996).
 - [20] A. Hasmy, E. Anglaret, M. Foret, J. Pelous, and R. Jullien, *Phys. Rev. B* **50**, 6006 (1994).