Formation of Light-weight Low-density Materials via Gas Phase Aerosol Gelation

Christopher M. Sorensen, Rajan Dhaubhadel, Corey S. Gerving, and Amitabha Chakrabarti
Department of Physics, Kansas State University, Manhattan, Kansas, USA

ABSTRACT

We have demonstrated that gas phase explosive combustion can lead to nanoparticle aerosols with sufficiently large volume fraction to cause a volume spanning gel to form on the order of ten's of seconds. The term "aerosol gel" was coined to name these materials. So far we have made aerosol gels of carbon and silica. These aerosol gels are similar to well-known, liquid-phase, sol-gel synthesized aerogels.

INTRODUCTION

In the course of our fundamental studies to understand the physics of dense aerosols [1-4], we discovered a novel method to produce porous materials with high specific surface area and extremely low density [5, 6]. Our method involves the gelation of nanoparticles in the aerosol phase to yield a material that we have named an **"aerosol gel"**.

Unlike well known aerogel materials which begin with a liquid phase, sol-gel step, our aerosol gels are made in the gas phase. Simply said, a cloud of smoke in a volume gels or freezes to form a volume spanning, very light weight, porous body; truly "frozen smoke". The initial aerosol is composed of nanometer sized carbon or silica particles produced rapidly by exploding in a chamber any one of number precursor materials such as hydrocarbons or silane with an oxidizer, e.g. oxygen. The nanometer particles so produced aggregate and then gel on the order of ten's of seconds to form the aerosol gel. The materials we have made have densities as low as 2.5 mg/cc, roughly twice the density of air. The aerosol gel is a new material that has not been described before, and a patent for the production method and material has been awarded [6].

The current state of the art for manufacture of aerogel materials is the sol-gel/supercritical-drying method [7, 8]. Our gas phase aerosol gelation method is significantly different than this state-of-the-art and hence might therefore offer advantages because:

1) There is no need for a supercritical drying step as for aerogels, and

2) The aerosol gel method should be applicable to a greater variety of substances

Another interesting feature about our method is that during the detonation to quickly make the nanoparticle aerosol, the temperate inside the chamber reaches ca. 5000K during the 30m msec detonation as measured by a two-color pyrometer. This temperature is consistent with thermo-chemical calculations. It is also much hotter than typical flames which are on the order of ca. 2000K. Thus the particles have experienced both a very high temperature and a rapid cooling. Transmission Electron Microscope (TEM) pictures of the carbon aerosol gel show that the primary particles appear to be thin graphitic sheets and are more or less polygonal in structure. Subsequent test are indicating that these materials are a form of graphene. Such high temperatures and rapid quenches may lead to other novel formulations of matter for other materials.

THEORY

Any system of particles undergoing aggregation can form a gel if the combining particles do not coalesce (i.e., the particles stick at essentially point contacts rather than consume each other to form one) and if the time to reach the gel point is shorter than other time scales that can deter gel formation such as gravitational setting. Non-coalescence is necessary so that the aggregating particles will form a non-dense (ramified) fractal aggregate with fractal dimension, D, less than the spatial dimension, d. When D < d, the average cluster separation to cluster size ratio falls with time during aggregation until the separation equals the size. Then the clusters jam together to form a gel. This scenario describes the general features of all gelation phenomena, not just aerosol gels, from gelatin in water to hydrolysis and subsequent gelation of silica in solutions as precursors to aerogels.

A simple argument [5] can be used to calculate the approximate time it takes to gel as

$$t_{gel} = K^{-1} \frac{a^3}{f_v^{2.5}} \quad . \tag{1}$$

In Eq. (1) K is the aggregation constant obtained from kinetic theory, a is the primary particle radius and f_v is the volume fraction of solid material.

Equation (1) shows that if a is small and f_v is large, i.e., *if there is a lot of finely divided matter*, the system will gel fast. Moreover, the functionalities on a and f_v are very strong. In air at STP the aggregation constant $K = 3 \times 10^{-10}$ cm^3/s. Then for a volume fraction of 10^{-4} and a primary particle size of 10 nm, the gel time is predicted to be ca. 30 sec. This is fast enough to allow aerosols to gel.

The conditions for rapid gel formation, $f_v \geq 10^{-4}$ and $a \sim 10$nm, can be obtained with rapid, gas phase reaction. Any gas at STP if converted directly to a solid will yield a solid f_v of about 10^{-3} (recall that gases are about 1,000 times less dense than the condensed phase). Rapid reactions from the gas to the solid phase will drive the system deep into a supersaturated regime. Thus rapid and uniform nucleation to small particles will occur. This is what we did to form carbon and silica aerosol gels. It is reasonable to hypothesize that this can be done to create any solid chemical substance.

EXPERIMENT

Carbon Aerosol Gels.

To produce carbon aerosol gels a mixture of a hydrocarbon and oxygen in various proportions between the lower and upper explosive limits is introduced into a thick walled, 4 or 17 liter, aluminum chamber. Liquid fuels are introduced as micron sized liquid drop aerosols. Hydrocarbon to oxidizer ratios are adjusted to be "fuel rich" so that carbon is more likely to be produced instead of CO2. After exploding the fuel-oxygen mixture with an electric spark, the chamber can be opened to obtain a fluffy, dark black, volume spanning aerosol gel that often collapses to form a thick carbon layer on the inner surfaces of the chamber. The material is very light and elastic with a density as low as 2.5 mg/cc. Specific surface areas are on the order of

350 m^2/g. The aerosol gel can be compressed to densities as high as 300 mg/cc. Thermal gravimetric analysis showed no volatiles up to 600°C.

Carbon aerogels have been made by pyrolysis of resorcinol-formaldehyde aerogels in an inert atmosphere [11]. These materials have densities in the range 0.1 to 0.6 g/cc and specific surface areas of 400 to 1000 m^2/g, significantly higher than our aerosol gels.

Cluster morphology was determined from the TEM pictures by three different methods: correlation function, structure factor and perimeter analyses [9, 10]. When analyzed on the scale of the primary particle size ($2a$ ~50nm diameter) up to ca. 1 micron, the clusters were found to have a fractal dimension of 1.75±0.05 via all three analyses. Analysis of cluster morphology over length scales from ca. 1 micron to 50 microns with the perimeter analysis method, which is the only viable method when D>2, yielded a fractal dimension of $D = 2.6 \pm 0.2$ These results imply superaggregates with Diffusion Limited Cluster-Cluster Aggregate (DLCA) and percolation morphologies consistent with previous results for aerosol gelation in flames [2-4] and in our simulations [12, 13].

Silica Aerosol Gels.

Silica aerosol gels have been created in a similar manner with silane, SiH_4. Since silane is pyrophoric, there is no need for a spark. We used a system in which two reservoirs were filled with oxidizer and silane. These were connected via electronic valves to an evacuated 4L bomb. The valves were opened simultaneously so that the two gases rushed into and met in the bomb and exploded. Minutes later the 4L chamber was opened to find a light silica aerosol gel. Our silica aerosol gels have densities as low as 4mg/cc and surface areas as high as 400m^2/g.

We found that the primary particle size of the SiO_2 aerosol particles could be changed by changing the mass of an inert background gas. With no background gas present, a thin, white "paint" of silica was found on the inner walls of the explosion chamber. We concluded that after their creation in the explosive reaction of silane and oxygen the hot silica molecules moved ballistically in the absence of an inert background gas and "splashed" on the chamber walls. When nitrogen was used as a background gas, particles formed in the volume of the chamber and then subsequently aggregated to form a gel. It is reasonable to conclude that the role of the inert background gas was to remove the large kinetic energy of the hot silica molecules so that they could meet in the chamber and form particles. We found different results with use of different amounts of nitrogen as the background gas. This work is ongoing.

Silica aerogels have been studied extensively [7, 8, and 11] and their properties, such as specific surface area and mechanical strength, are at present quite superior to the silica aerosol gels that we have produced. However, the aerosol gelation method does have the advantage of not needing the supercritical drying step and the promise of control of the primary particle size. A significant quantity of future research will be needed to determine in what manner these new materials will be able to complement the current, aerogel state-of-the-art.

CONCLUSIONS

Under the right conditions, aerosols can gel. Such aerosol gels have properties that are similar to aerogels made via sol-gel processes and therefore hold similar technical promise.

ACKNOWLEDGMENTS

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