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POROSITY AND VARIATIONS IN MICROGRAVITY AEROGEL NANO-STRUCTURES
II. New Laser Speckle Characterization Methods

A.J. Hunt*[1], M.R. Ayers[2], L. Sibille[3], and D.D. Smith[4]

[1,2]E. O. Lawrence Berkeley National Laboratory, Berkeley, CA
[3,4]NASA, Marshall Space Flight Center

INTRODUCTION

The transition from sol to gel is a process that is critical to the properties of engineered nano-materials, but one with few available techniques for observing the dynamic processes occurring during the evolution of the gel network. Specifically, the observation of various cluster aggregation models[1], such as diffusion-limited and reaction-limited cluster growth can be quite difficult. This can be rather important as the actual aggregation model can dramatically influence the mechanical properties of gels, and is significantly affected by the presence of convective flows, or their absence in microgravity.

We have developed two new non-intrusive optical methods for observing the aggregation processes within gels in real time. These make use of the dynamic behavior of laser speckle patterns produced when an intense laser source is passed trough a gelling sol. The first method is a simplified time-correlation measurement, where the speckle pattern is observed using a CCD camera and information on the movement of the scattering objects is readily apparent. This approach is extremely sensitive to minute variations in the flow field as the observed speckle pattern is a diffraction-based image, and is therefore sensitive to motions within the sol on the order of the wavelength of the probing light. Additionally, this method has proven useful in determining a precise time for the gel-point, an event often difficult to measure.

Monitoring the evolution of contrast within the speckle field is another method that has proven useful for studying gelation. In this case, speckle contrast is dependent upon the size (correlation length) and number of scattering centers, increasing with increasing size, and decreasing with increasing numbers. The dynamic behavior of cluster growth in gels causes both of these to change simultaneously with time, the exact rate of which is determined by the specific aggregation model involved. Actual growth processes can now be observed, and the effects of varying gravity fields on the growth processes qualitatively described. Results on preliminary ground-based measurements have been obtained.

I. Experimental

Samples studied by these methods consisted of standard base-catalyzed (NH_3) tetraethyl-orthosilicate (teos) sols[2,3]. Fifteen mL of each sol was prepared and filtered through 0.45 μm PTFE filters immediately after mixing into glass scintillation vials. Laser radiation was provided by either a 50 mW diode laser (532 nm) or the 488 nm line of a 100 mW argon ion laser. Speckle patters were recorded using a Pulnix TM-1040 CCD camera (1024 x 1024 pixels, 10-bit ccd, 30 fps), and analyzed in real time with a standard PC running XCAP v 1.1 (Epix, Inc.) image analysis software. The sample vial and camera were placed in an acoustically quiet chamber to minimize interferences from ambient vibrations. Figure 1 gives a schematic of the experimental arrangement used to obtain specklegrams, an example of which appears in Figure 2.

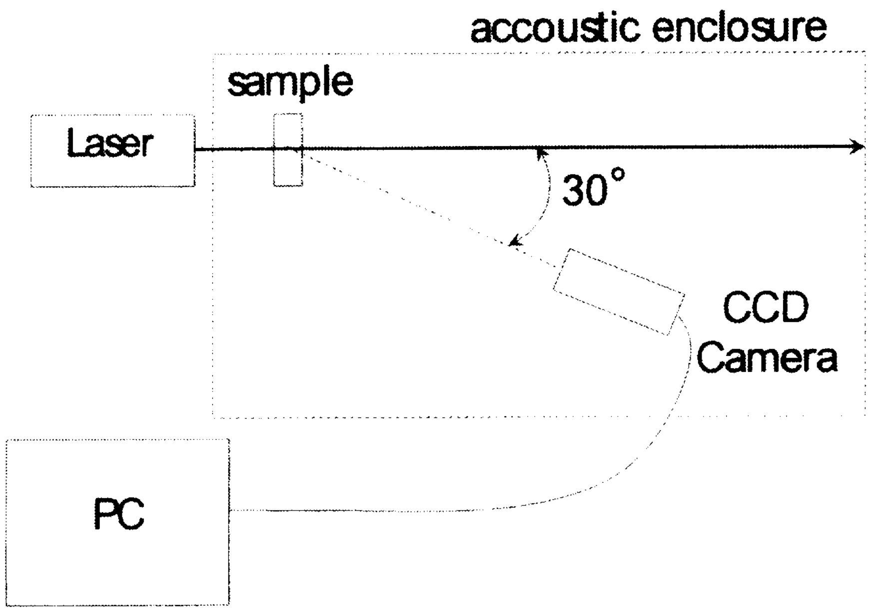

Figure 1. Schematic diagram of the dynamic laser speckle system.

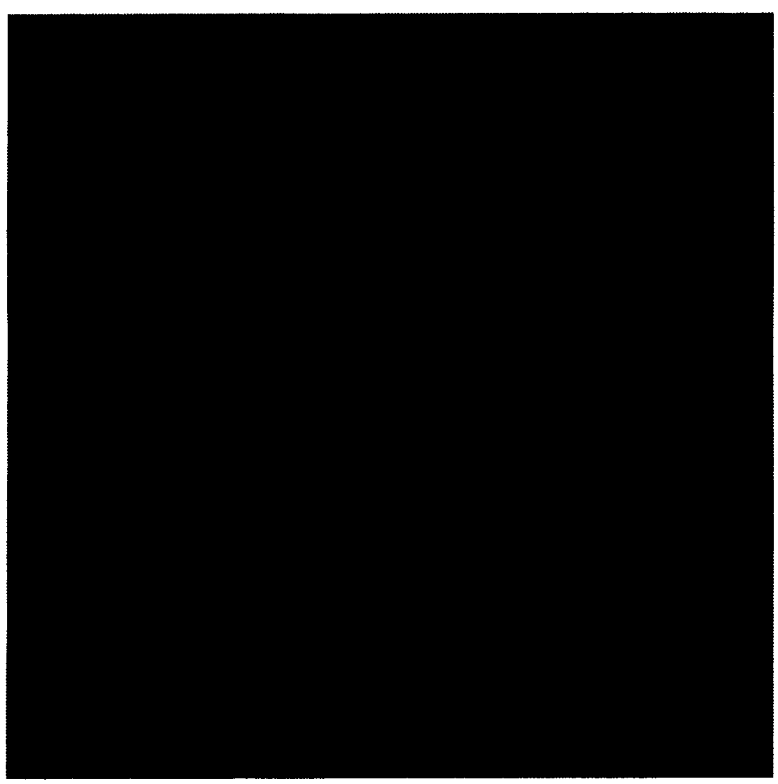

Figure 2. A typical specklegram for a silica sol.

II. Results and Discussion

Speckle methods have been used extensively to study the micro-scale properties of both static and dynamic systems[4]. However, in the case of dynamic systems, the use of speckle methods has most often been employed for systems in which the nature of the scattering centers remain fixed, such as the observation of small particles in a flowing fluid. In the case of the sol-to-gel transition, both the mobility of the scattering centers (silica particles) and their number and size, are changing simultaneously. We wish to learn as much as possible about both of these properties as sols evolve in normal and microgravity.

The mobility of silica particles in sols is conveniently monitored using speckle methods. The system we have developed measures both the total scattered light and a simplified 0.033 sec. correlation map (obtained by measuring the total intensity of a new image resulting from the absolute value of the difference of two adjacent frames) at 60 second intervals during the gelation process. Figure 3 gives a plot of the total scattering intensity versus time for a typical sol. The information available from such plots is rather limited, however. More information can be obtained from the correlation plot, shown in Figure 4, and the intensity-normalized correlation plot given in Figure 5. In Figure 4, a drastic decrease in particle mobility is observed at the gel point (marked by an arrow). The actual gel point is often difficult to detect using other methods. In the normalized plot, a decrease in particle mobility is observed prior to the gel point as aggregates of silica particles grow in size. The convective flow in the sol itself will also affect these correlation plots as the particle motion will be expected to be much lower under microgravity. The use of this system during parabolic flights may provide important information on the role of convective flows in gelation behavior.

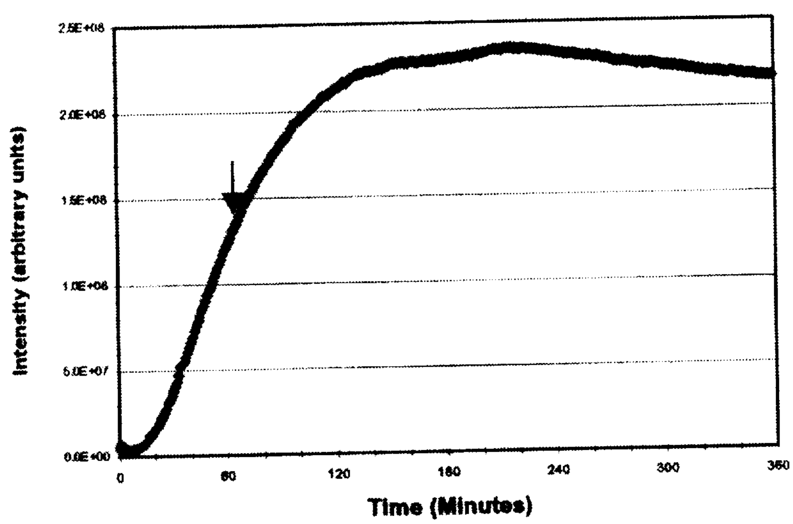

Figure 3. Plot of total scattering intensity versus time for a typical silica sol. The gel point is marked by an arrow.

The evolution of contrast in the specklegrams also provides important information on the aggregation process occurring in the sol. Speckle contrast has been widely used to measure surface roughness in a variety of systems [5-8]. In qualitative terms the contrast of a speckle image is :

$$\text{contrast} = \frac{\sigma_I}{\langle I \rangle} \propto \frac{(\text{size of scatterers})}{(\text{number of scatterers})}$$

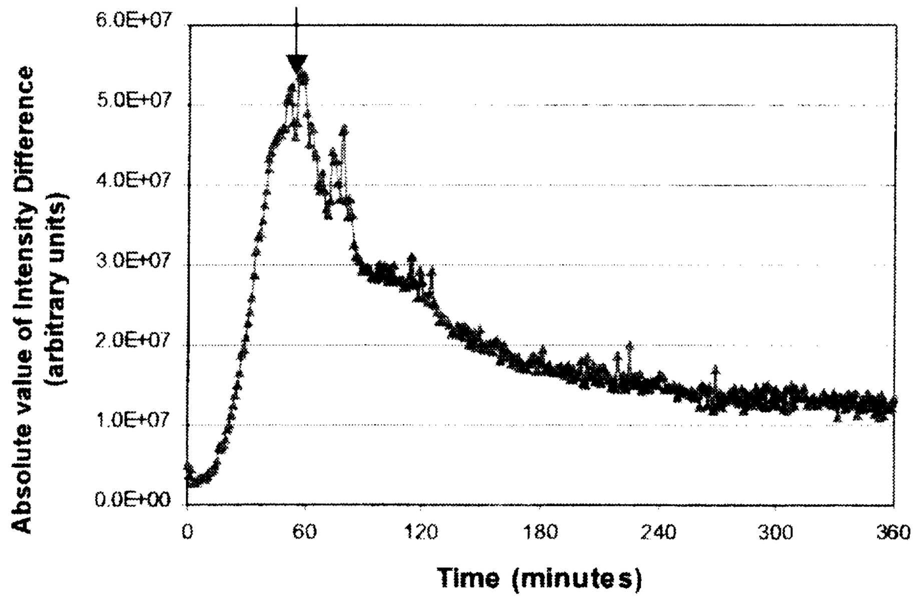

Figure 4. Plot of the 0.033 second correlation intensity versus time for the same sol as Figure 3. The gel point is marked by an arrow.

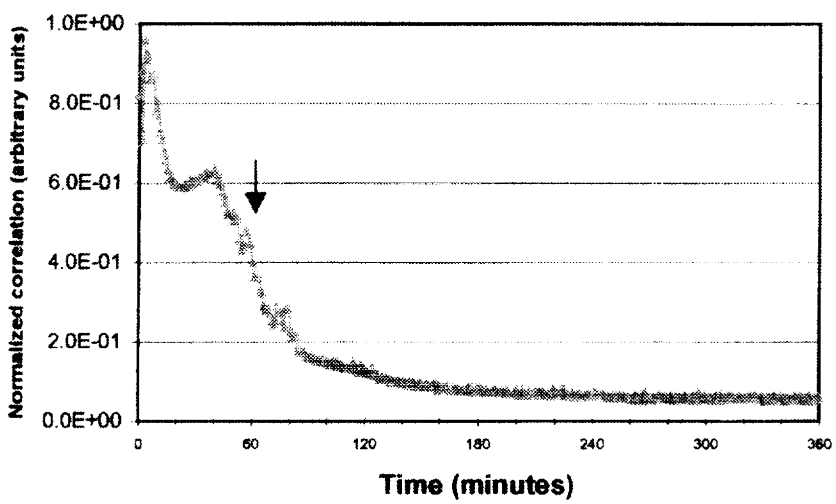

Figure 5. Intensity (total) normalized 0.033 second correlation plot for the same sol as Figure 3. The gel point is marked by an arrow.

Where σ_I is the standard deviation of the image intensity, and I is the intensity. In general, small numbers of large scatterers will produce the maximum image contrast, while large numbers of small scatterers, the minimum. As sols evolve towards the gel point, the size of scatterers increase and their numbers decrease. The rate and magnitude of these changes depend intimately on the specific aggregation mode employed by the sol. The evolution of contrast versus time for various silica sols appears in Figures 6 and 7.

A clear pattern of particle growth is apparent. The contrast of the speckle image decreases as the sol evolves, to a minimum ranging between 0.4-0.7 times the gel time. From there the speckle contrast increases, reaching its maximum shortly after the gel point. This shows a change in the particle growth behavior, from an increasing number of small particles at the beginning of the process, to the onset of aggregation and the growth of fewer, but larger particles. Variation of teos

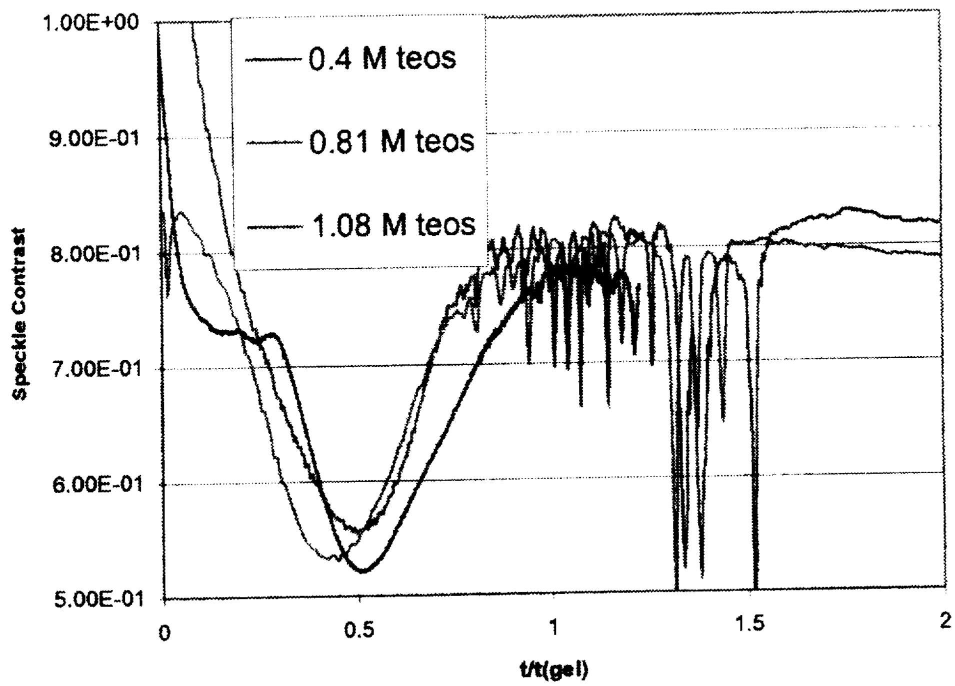

Figure 6. Speckle contrast versus time (normalized to gel time) for various teos concentrations.

concentration (Figure 6) does not result in any significant change in the onset of the aggregation phase. Similarly the variation of water content in the sol also does not alter this behavior. However, adjusting the amount of ammonia present (the determining factor in colloidal stability) significantly affects the onset of aggregation. Higher levels of ammonia delay the start of aggregation to late in the gelation process, as seen in Figure 7.

Earlier flight experiments on silica sols have shown a definite effect of gravity on their aggregation behavior. This new technique may prove useful in observing these changes during future flight experiments.

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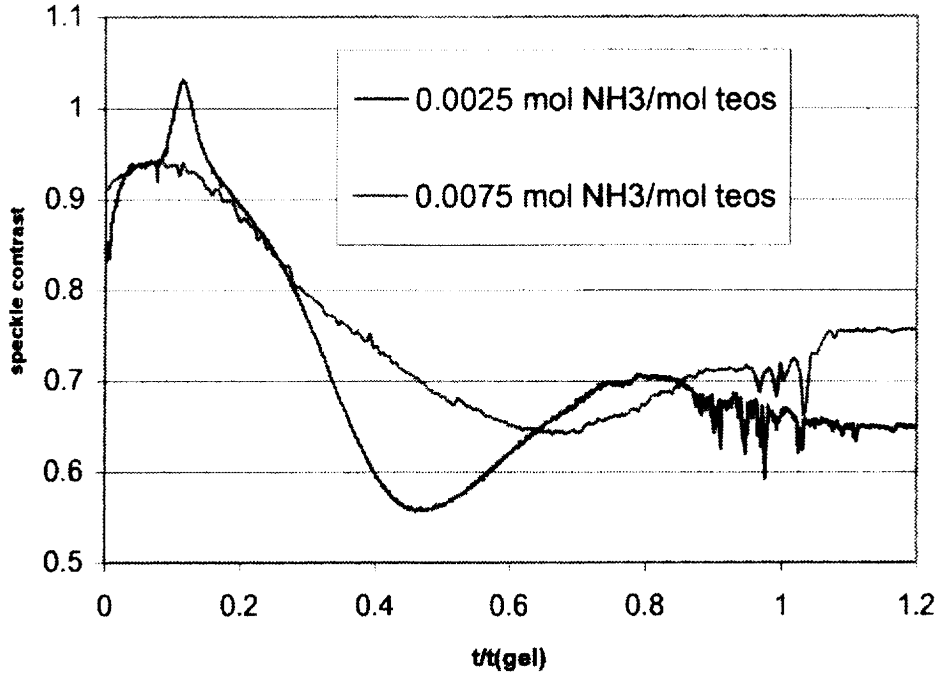

Figure 7. Speckle contrast versus time (normalized to gel time) for two NH_3 to teos ratios.