Dynamic structure factor scaling in dense gelling silica suspensions

B D Butler, C D Muzny and H J M Hanley

Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, CO 80303, USA

Abstract. Small-angle neutron scattering data from dense (30% by mass) gelling 7 nm colloidal silica spheres are presented. The coarsening process that occurs during gelation exhibits temporal self-similarity, and the time-dependent structure factor obeys the dynamic scaling relation $S(q, t) \sim q_m^{-d_f}(t)\tilde{S}(q/q_m(t))$. Here, q is the scattered wavevector, $q_m(t)$ is the location of the low-angle peak in $S(q, t)$, $\tilde{S}(x)$ is a time-independent characteristic structure function which has a maximum at $x = 1$, and d_f is the fractal dimension. Connections between the silica gelation and spinodal decomposition in a simple fluid are reviewed.

1. Introduction

Structural studies on dilute gels have proven to be very rich and rewarding from many viewpoints, especially in the context of the gel's behaviour as a fractal object [1]. Data on the structure of dense gels (mass fractions greater than 5%), however, are scarce and, in any case, we have pointed out that the fractal analysis applied routinely to interpreting the scattering from dilute gels is unlikely to be appropriate when one wishes to understand the behaviour of a dense gel [2]. For instance, the well known power-law variation $S(q) \sim q^{-d_f}$ of the structure factor $S(q)$ with the wavevector q, where d_f is a fractal dimension, only makes sense, and the fractal dimension only has meaning, when the length scales probed are simultaneously much larger than the size of the individual particles and much smaller than the characteristic size of the fractal aggregates. This condition cannot normally be satisfied in a dense gel. Hence, an alternative and more general approach to interpreting the growth mechanism is needed. In fact it has been pointed out that the fractal dimension characterizing a coarsening process can be obtained from an analysis of the time evolution of $S(q)$ [2–6]. In this short paper, we present small-angle neutron scattering (SANS) data taken from dense colloidal silica gels that support this supposition.

2. SANS data from colloidal silica

The system of interest is a gel of colloidal silica spheres of diameter $\sigma = 7$ nm. The precursors were suspensions in an H_2O medium at several volume fractions ϕ, where $\phi \geqslant 10\%$. SANS experiments were carried out on the samples using the 30 m spectrometer at the NIST Cold Neutron Research Facility. The scattered intensities, $I(q)$—proportional to the scattering cross section $d\Sigma/d\Omega$—were measured as a function of q where $q = (4\pi/\lambda)\sin(\theta/2)$; λ is the incident wavelength and θ is the scattering angle.
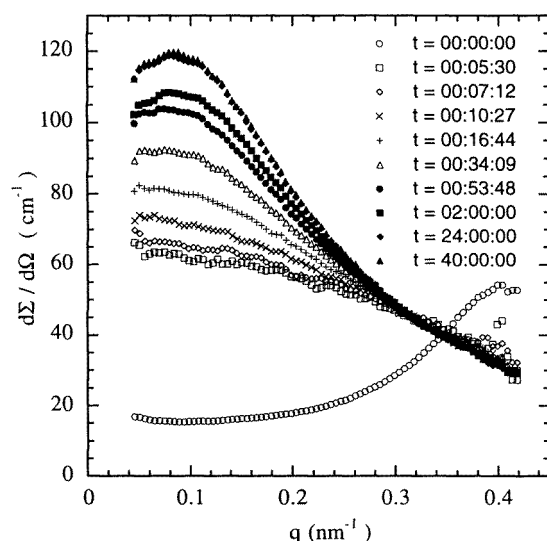
Figure 1. Measured neutron scattering cross section as a function of time since initiation for a $\phi = 0.13$, 7 nm diameter suspension of colloidal silica. Concentrated HCl was added to lower the pH to 6.7 and initiate gelation.

Results were obtained from the initial suspensions, from the final gels, and from the gelling system as a function of time. Full details will be published elsewhere; selected results are as follows.

Figure 1 displays scattering cross sections for the system at $\phi = 0.13$. Gelation was initiated in the suspension by adding concentrated HCl until the pH was lowered from 9.8 to approximately 6.7. After the acid was added, the solution was loaded immediately into a quartz cell with a 1 mm path length and placed in the neutron beam. The first measurements, designated 00:05:30 in the figure, were initiated approximately 5 min after the loading. The scattering intensity was then followed as a function of time by making, sequentially, measurements throughout a period of 55 min. In addition 30 min duration measurements were made at 2 h, 24 h, and 40 h after the reaction had begun. Plots of these intensities as a function of time are shown. Scattering from the suspension (labelled $t = 00:00:00$) is also presented.

The curve for the suspension shows a characteristic peak at the largest wavevectors; this peak reflects an average colloidal particle separation distance of about 16 nm. Immediately after gel initiation, however, this particle–particle separation peak disappears because the addition of HCl to the medium destroys the long-range repulsion between the silica particles, causing them to approach each other, coalesce, and form a cluster. Hence, a particle–particle contact peak will develop and be located near $q\sigma/2\pi \approx 1$ (not shown). The disappearance of the 16 nm separation peak, however, is counterbalanced by a marked increase in scattering at low q, indicating the onset of clustering. As time progresses, the low-q scattering continues to increase as the clusters coarsen. At later times, a peak at approximately $q \approx 0.09$ nm^{-1} indicates the presence of cluster–cluster correlations [7]. As the gelation evolves, analysis indicates that this peak moves to lower q and grows in height, reflecting increasing cluster separation distances and an increase in the number of particles contained in an average cluster. Similar results were obtained from other 7 nm and 24 nm silica suspensions and
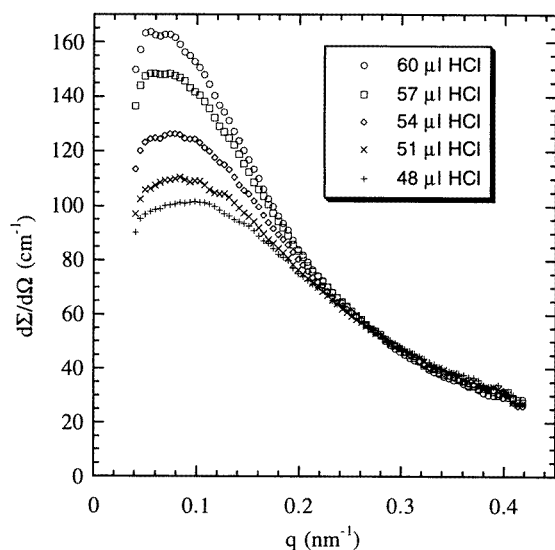
Figure 2. Measured neutron scattering cross sections from five different samples in which gelation was initiated by the addition of various amounts of HCl. All curves were measured approximately 10 h after gel initiation after which the cross sections are independent of time.

gels at volume fractions $\phi < 0.18$; in general, the low-q rise in the scattering was not observed from gels with silica volume fractions above 0.18 [8].

Figure 2 displays the scattering cross sections of five samples, each after 10 h had passed, prepared from the same precursor stock suspension, but gelled by adding different amounts of HCl (that is, by altering the initiating pH). The sample with the lowest pH of 5.2 (60 μl HCl per 3 ml of solution) peaks at the smallest q while the one with the highest pH of 6.8 (48 μl HCl) has a maximum at the largest q. Each of the five gels, therefore, is characterized by a different length scale. Figure 2 is similar in form to figure 1, but the separation of the low-q correlation peaks is more noticeable and the movement of the peak to lower q-values is more clear. Each of the curves of figure 2 corresponds to an end point of a set of curves similar to those shown in figure 1.

3. Computer simulation: dynamic scaling

Many features of unstable colloidal systems can be described in terms of the nucleation and growth or spinodal decomposition theories developed for simple liquids and alloys. We have, in particular, noted the conceptual similarity between gelation and the decomposition, and subsequent cluster growth, following a quench from a conventional fluid [2, 4]. In this context the effect of the sudden destruction of the repulsive potential of a stable silica particle when the pH of a suspension is lowered is equated (loosely) to the effect of a rapid drop in temperature. Specifically, in reference [2] we discussed the evolution of a simulated two-dimensional Lennard-Jones system that was quenched from above the critical temperature to a state point inside the spinodal and monitored the structure factor as a function of the wavevector and time. The system was characterized by the onset and subsequent development of a peak in $S(q, t)$ at small q, as we subsequently observed in the gelation experiments depicted here by figures 1 and 2. The peak results from the spatial
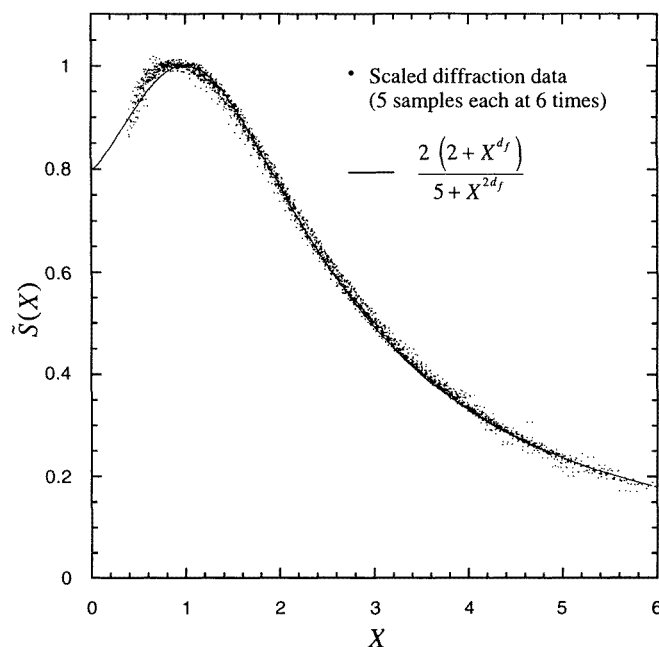
Figure 3. Scattering cross sections (small dots) taken at various times during gel formation from five samples with different amounts of HCl initiator added (see the text). The data were all scaled using $d_f = 1.4$. The vertical axis was divided by $4.12 \times 10^{-7} \mathrm{nm}^{-(1+d_f)}$ to facilitate comparison with the characteristic structure function equation (3) (the solid line).

correlations between growing particle clusters formed after the quench. Most importantly, we found that the coarsening proceeded in such a way that the structure at early times was similar to the structure at later times, except for a simple change in length scale. This temporal self-similarity implied that the structure factor must scale, and a straightforward argument that allows for mass fractal cluster growth leads to the scaling relation, first discussed in [3],

$$S(q, t) \sim q_m(t)^{-d_f} \tilde{S}(q/q_m(t)) \tag{1}$$

where $q_m(t)$ is the location of the low-angle peak in $S(q, t)$, $\tilde{S}(x)$ is a time-independent characteristic structure function, and d_f is the fractal dimension. For our simulation we found $d_f = 1.85$.

When equation (1) is applied to the silica data represented by figures 1 and 2 (and several other diffraction scans taken as functions of time), we find that using the dimension $d_f = 1.4 \pm 0.1$, the equation correlates 30 data sets almost perfectly; see figure 3. In this figure all data, except those measured at the earliest times (where we suspect the gels had not yet reached the coarsening regime), are shown. It must be emphasized that there were no independent adjustments to the vertical axes of the curves; the only variable parameter is d_f.

We propose a form for the structure function $\tilde{S}(X)$:

$$\tilde{S}(X) = \frac{2(2 + X^{d_f})}{5 + X^{2d_f}}. \tag{2}$$

This expression is similar in outline to Furukawa's relation [9] which does not fit our

data but does describe accurately structure factors from computer-simulated coarsening [2], coarsening in an Al–Zn alloy [10], and the phase separation of polymer/colloidal systems [5]. Note that function (2) peaks at $X = 1$ for all values of d_f, has a nonzero low-q limit, and is consistent with the form of a fractal object at large wavevectors. The function is shown as the solid curve in figure 3 and one sees it fits the scaled data remarkably well. We emphasize again that all the data and the curve of figure 3 are scaled with only the one parameter, d_f.

We conclude with the remark that, although characteristic fractal power-law slopes are often extracted from scattering intensities from dilute gel samples [1], the apparent fractal dimension obtained by measurement of a power-law slope from a dense gel is suspect because the cluster correlation peak will, in general, interfere. For instance, measurements of the power-law slopes from the scattering curves presented in figures 1 and 2 would indicate that the fractal dimension depends on both the time following gel initiation and on the pH of the solution. This is not the case since a fit of equation (1) gives $d_f = 1.4$ for all samples (figure 3).

Acknowledgments

References

[1] For example,
Martin J E and Hurd A J 1987 *J. Appl. Crystallogr.* **20** 61
Schaefer D W, Martin J E, Wiltzius P and Cannell D S 1984 *Phys. Rev. Lett.* **52** 2371
Dietler G, Aubert C, Cannell D S and Wiltzius P 1986 *Phys. Rev. Lett.* **57** 3117
[2] Butler B D, Hansen D, Evans D J and Hanley H J M 1996 *Phys. Rev.* B **53** 2450
[3] Carpineti M and Giglio M 1992 *Phys. Rev. Lett.* **68** 3327
[4] Butler B D, Hanley H J M, Hansen D and Evans D J 1995 *Phys. Rev. Lett.* **44** 4468
[5] Poon W C K, Pirie A D and Pusey P N 1995 *J. Chem. Soc. Faraday Discuss.* **101** 65
[6] Earnshaw J C and Robinson D J 1995 *Physica* A **214** 23
[7] It is interesting to note that the mechanical properties of the system suggest that a gel network, sufficiently strong to support its own weight, had formed after approximately 20 min. But the low-q peak continues to grow long after this apparent gel-point.
[8] When shear is applied during gelation of the higher-density samples, however, this power-law increase of $S(q, t)$ returns;
Muzny C D, Straty G C and Hanley H J M 1994 *Phys. Rev.* E **50** R675
[9] Furukawa H 1985 *Adv. Phys.* **34** 703
[10] Komura S, Osamura K, Fujii H and Takeda T 1985 *Phys. Rev.* B **31** 1278