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1999 J. Phys.: Condens. Matter 11 1369

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# Shear-induced restructuring of concentrated colloidal silica gels\*

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Received 5 October 1998, in final form 30 November 1998

**Abstract.** The viscometric properties and structure of concentrated sheared colloidal gels, formed at a pH = 8 from a commercial aqueous sol of 7 nm diameter silica particles, were investigated. As the system gels under a constant shear rate, the viscosity first increases, then peaks when the shear stress reaches a shear-rate-independent threshold value of about 350 Pa, and finally decreases asymptotically to approximately one tenth the peak value. This low-viscosity state can apparently be held indefinitely by maintaining the shear, but the system gels once the shear is removed. The structural origins of this viscometric behaviour were studied using *in situ* small-angle neutron scattering (SANS). An abrupt change in the character of the SANS intensity was observed at the time corresponding to the peak in the viscosity. Samples of the gelling system were extracted and diluted at various times after gel initiation. Effective hydrodynamic diameters of these extractants were estimated by dynamic light scattering, and their Guinier diameters were estimated by SANS when appropriate. We conclude that the drop in viscosity corresponds to a structural densification of growing clusters of the colloidal particles, and that this transformation occurs once the critical stress is reached.

## 1. Introduction

Aggregation (flocculation or gelation) may be initiated in a stable suspension of charged colloidal silica particles by changing the chemical environment. Flocculation, commonly observed when salt is added to the suspension at low particle densities, is characterized by the formation of particulate clusters with a density different from the initial sol. A floc will, therefore, separate from the solvent through gravitational settling or centrifugation. Gelation usually occurs at higher densities when an acid is added to the suspension, and is the growth of a continuous network of clusters, with a macroscopic density identical to that of the initial suspension, that will eventually span the system's container. Furthermore, in contrast to a system that flocs, the colloidal gel has a divergent viscosity and behaves as an elastic solid, even though it is structurally bicontinuous, having a silica skeleton which is penetrated completely by the solvent. Radiation scattering experiments on gels often show a power-law rise in scattered intensity toward lower wavevectors  $q$  according to the relation  $I(q) \sim q^{-d_f}$ . Because of a connection with theories on fractal aggregation, this scattering behaviour is

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frequently interpreted as arriving from fractal objects of dimension  $d_f$ , which contain a power-law distribution of pore sizes and are characterized by length scales  $\zeta \sim 2\pi/q$  which range from the size of the colloidal particles ( $\sim 5\text{--}50$  nm) to about  $1\ \mu\text{m}$  [1].

It is technologically important in the context of sol–gel processing, and scientifically rewarding, to investigate how the structure of the gel relates to its macroscopic physical properties [2]. It is especially interesting to investigate how the structure might be tailored to suit a particular application by manipulating the gelation environment as the reaction proceeds from the precursor sol or suspension to the final gel. In fact, the object of this paper is to establish a connection between the viscometric behaviour of a sheared gelling colloidal system and its structure by performing simultaneous viscometry and SANS measurements. Studies on sheared aggregating systems are not very common, and those reported have largely been restricted to the viscometry of flocs [3]. In 1994, however, SANS experiments, carried out with gelling colloidal silica, sheared in a constant rate Couette cell [4], indicated that the system's structure can be altered when a modest shear is applied during the gelation reaction [5]. Specifically, for concentrated colloidal suspensions (volume fractions  $\phi$  greater than  $\sim 0.15$ ), we showed that shear causes a marked increases in the scattering at low angles. This work is extended substantially in this paper. Recently, we have modified a commercial rheometer to couple with a SANS spectrometer [6]. Since the SANS intensities and the viscometric properties of a sample can be measured *simultaneously*, it is now possible to record the scattered intensity as a function of time concurrent with the shear viscosity coefficient  $\eta$  and/or the shear stress.

Thus, the focus of this paper is to report SANS scattering intensities from concentrated aqueous suspensions of colloidal silica as they gel when subjected to a constant shear rate, and to correlate the results with Couette cell viscometric data measured simultaneously. The rheological measurements are supported by independent data taken from the rheometer configured with different cells, and by the results obtained from another rheometer set up in a cone and plate configuration. The discussion is augmented by dynamic light scattering results.

## 2. Experiment

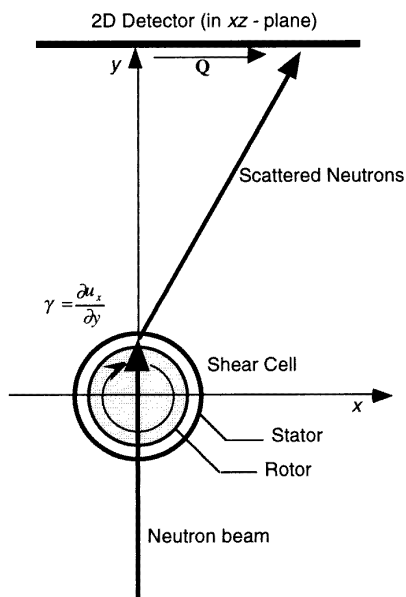
All gels were prepared from a stock aqueous suspension of commercial grade Ludox SM-30 silica at  $\text{pH} = 9.8$  [7]. The spheres were designated by the manufacturer to have a nominal diameter  $\sigma = 7$  nm with an estimated 20% polydispersity. The suspension consisted of 31 mass%  $\text{SiO}_2$  (corresponding to a volume fraction  $\phi = 0.17$ ) with a suspension density of  $1.215\ \text{g cm}^{-3}$ .

Gels can be formed conveniently from this sol by lowering the pH to values between about 4.5 to 8.5, but, depending on pH, the time of gelation varies from minutes to days. Here we found that the system gelling at  $\text{pH} \approx 8$  was convenient for our experiments because an unsheared system gelled at this pH in about an hour (defining loosely the gelling time as the time taken for the viscosity to diverge), which gave sufficient time to perform several SANS measurements during the reaction. Accordingly, in a typical experiment, the suspension was filtered through a  $0.45\ \mu\text{m}$  membrane to remove any large aggregates, and gelation was initiated by adding concentrated HCl to the filtrate. Specifically,  $250 \pm 1\ \mu\text{l}$  of HCl ( $5.030\ \text{mol dm}^{-3}$ ,  $\rho = 1.082\ \text{g cm}^{-3}$ ) were added to 12.15 g of the filtered sol ( $10.0\ \text{cm}^3$ ), and the resulting mixture was vigorously agitated for approximately 30 s. The pH of this gelling mixture was measured to be  $8.00 \pm 0.02$ .

The SANS component of the simultaneous SANS/viscosity experiments was performed on the 30 m SANS NG7 spectrometer of the NIST Center for Neutron Research configured

with an incident neutron wavelength  $\lambda = 0.6$  nm and using sample–detector distances of 4.0 and 13.55 m. The instrument's 2D position sensitive detector was offset by 0.25 m to increase the accessible wavevector range  $0.02 < q < 1.45$  nm<sup>-1</sup>. Here, the wavevector  $q = (4\pi/\lambda) \sin(\theta/2)$ , where  $\theta$  is the angle between the incident and scattered neutron beams and  $\lambda$  is the incident neutron wavelength. The scattered intensities  $I(q, t)$  were measured as a function of time  $t$  from gelation initiation: that is, the time at which the acid was added to the sol suspension. Since all measured scattering patterns were isotropic,  $I(q, t)$  was azimuthally averaged. Corrections to the intensity were made for empty cell and solvent scattering in the usual way, and the corrected data were placed on an absolute scale by normalizing to the intensity of water [8].

The viscometric components of the experiments were carried out using a commercial constant stress rheometer with a modified Couette cell and with software written so that the rheometric controls and viscometric output could be coordinated with the instrumentation of the SANS spectrometer [6]. Figure 1 shows schematically the cell arrangement and beam path for the apparatus set up in the Couette geometry shearing mode. In Cartesian coordinates, the beam is incident along the  $y$ -axis and  $I(q, t)$  is measured as a function  $q$  with the SANS detector in the  $xz$ -plane when subjected to a constant applied shear rate  $\gamma = du_x/dy$ , where the flow velocity of the sample  $u_x$  is in the  $x$ -direction. The sample (approximately 7 ml in volume) was contained in the 1 mm annular gap between an inner cylinder (rotor) and a stationary outer cup (stator) both manufactured from quartz to minimize cell scattering. The cell was jacketed and thermostatted at  $298 \pm 0.01$  K and sealed with a cap to prevent evaporation.



**Figure 1.** Beam path through the rheometer modified for SANS experiments.

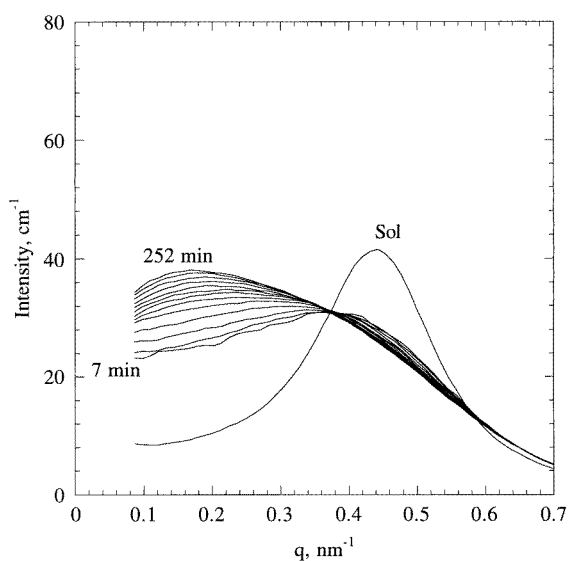
The SANS and viscometric measurements were combined. Immediately after gel initiation, the sample was placed into the Couette cell, already set up in the SANS beam path, and the rheometer was programmed to subject the sample to a constant shear rate and to record the shear viscosity and the shear stress as functions of time. The corresponding SANS intensities were collected and averaged over 5 min intervals for the duration of the experiment, typically 10 h. Results were obtained for a gelling system subjected to constant shear rates of 0 (i.e. the system is unsheared), 244, 500, 533 and 1645 s<sup>-1</sup>.

In addition to these measurements, a separate study of the viscometric properties was performed using a rheometer configured in the cone-and-plate geometry. The apparatus employed a 60 mm diameter stainless steel lower plate with a  $1^\circ$  angle conical rotor. The lower plate was thermostatted at 298 K by water circulating in an integrated compressor cooling circuit, and the sample temperature was monitored using a platinum resistance element. A solvent trap minimized evaporation from the gel during these measurements.

### 3. Results

#### 3.1. Unsheared gel

Figure 2 displays how the SANS intensities evolve from the silica system as gelling takes place at zero shear. It is seen that the intensity from the sol peaks at  $q_{max} \approx 0.45 \text{ nm}^{-1}$ , which is the consequence of the positional correlations between the colloidal particles spaced about  $l = 2\pi/q_{max} \sim 14 \text{ nm}$  apart. This particle–particle separation peak disappears at very early times after gel initiation, because the added HCl screens the Coulomb forces between the charged colloidal spheres, hence decreasing their effective interaction diameter and their effective volume fraction, and allowing the particles to cluster. The gelling states are thus characterized by the onset of particle clustering and the appearance of a cluster–cluster correlation peak. As time progresses and the system coarsens, the clusters grow and this peak moves toward lower wavevectors. The evolution of the SANS intensities in this wavevector range effectively ceases after approximately 4 h. The cluster–cluster correlation peak at this time is at  $q \approx 0.18 \text{ nm}^{-1}$ , which corresponds to a separation distance of  $\sim 35 \text{ nm}$ , that is, only a few particle diameters.

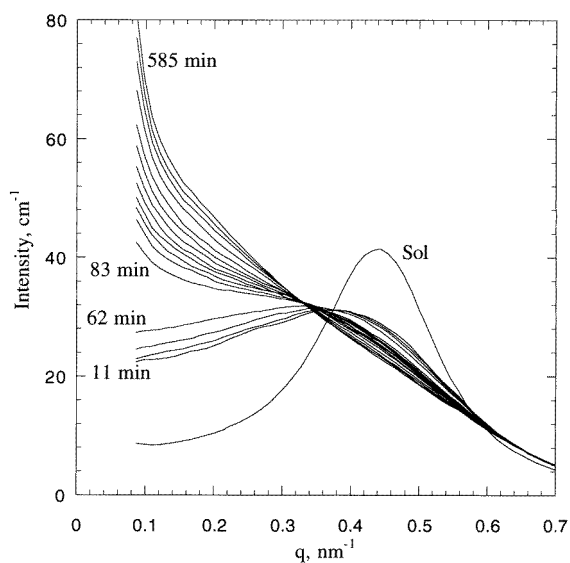


**Figure 2.** SANS intensities as a function of time after gel initiation for an unsheared system; 4 m SANS data.

The viscosity of the ‘unsheared’ system was measured every 30 s by running the rheometer in constant stress mode at a low stress ( $\sim 0.1 \text{ Pa}$ ). Technically, the system is under shear but, by changing the magnitude of this low stress, we verified that minimal shearing did not affect the structure of the sol. The time variation of the viscosity, which diverges after about 80 min indicating the gel time, can thus be confidently interpreted as that from an unsheared system.

### 3.2. Sheared gel

The small-angle scattering intensities from a gel sheared *in situ* at a constant rate of  $500 \text{ s}^{-1}$  is shown in figure 3; similar patterns were obtained from the runs at other applied shears. Compare with figure 2 for the unsheared system. The scattered intensities for time after initiation up to approximately 1 h are very similar. After about 1 h, however, they deviate markedly—at low wavevectors the intensity in figure 3 rises abruptly: it is apparent that shear has induced a structural transformation at length scales greater than about 25 nm. Figure 4 gives the viscosity measured concurrently with the scattered intensities at 30 s intervals. The differences between the sheared and unsheared samples are obvious. In the early stages, the increase in viscosity of the sheared sample parallels that observed for the unsheared system, albeit at a somewhat accelerated pace. The viscosity of the sheared system then reaches a maximum at a time  $t_m$  corresponding roughly to the time it takes for the unsheared system to gel. The maximum, however, is followed by a sudden drop in viscosity, and the viscosity then diminishes until it reaches an asymptotic value of about one-tenth its peak value. Furthermore, the maximum is clearly correlated with an abrupt change in the scattering behaviour, as can be seen when the data of figure 3 are cross-plotted at  $q = 0.11$ .

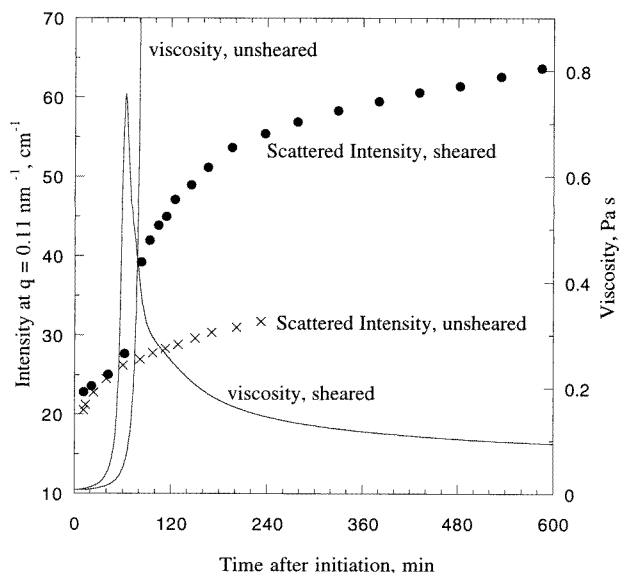


**Figure 3.** SANS intensities as a function of time after gel initiation for a system experiencing an applied constant shear rate of  $500 \text{ s}^{-1}$ ; 4 m SANS data.

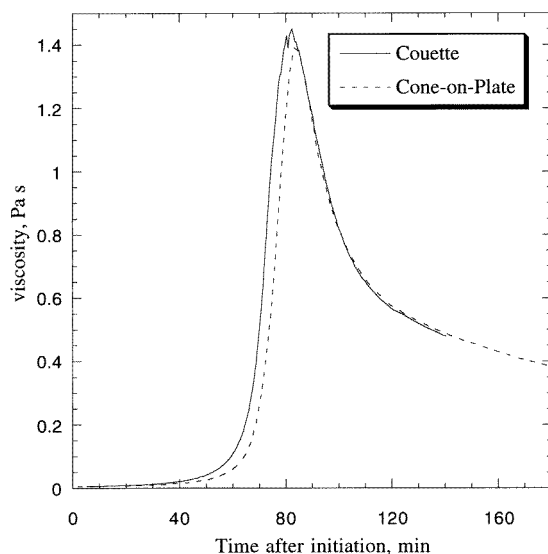
The low-angle scattering continues to increase after  $t_m$ , but this change slows with time until after  $\sim 10$  h the scattering intensity becomes approximately time independent. Interestingly, if the shear is removed after this time the sample gels in about 1 h (similar to an unsheared suspension) yet no further change in the SANS data is observed.

### 3.3. Rheometric data

The behavioural pattern of the viscosity for the shearing system was not expected. It must be emphasized that the material in the cell at the end of the experiment is *not* a 'broken' gel, or a gel that has separated from the container walls due to the high shear stress near the gel point (as we might suspect [9]), but rather is a *fluid whose viscoelastic properties have been somehow altered by the application of the shear*. Moreover, all evidence indicates that the results reflect changes in the material properties of the gelling silica and are not artifacts of the experiments

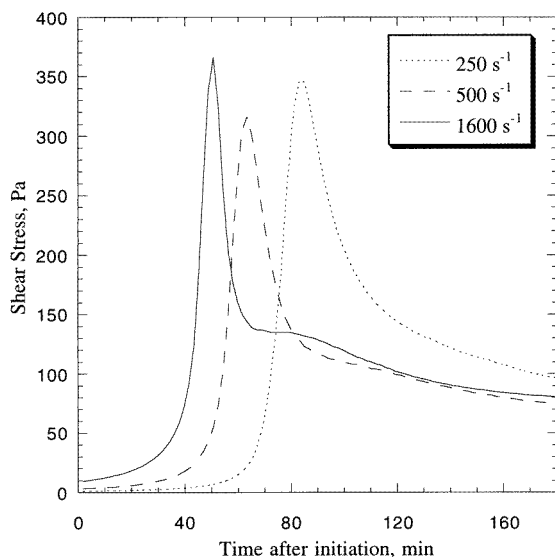


**Figure 4.** Comparison of how the SANS intensity at  $q = 0.11 \text{ nm}^{-1}$  varies with the viscosity as a function of time after gel initiation for the sheared and unsheared system.



**Figure 5.** Comparison of two shear cell configurations on the measurement of the viscosity as a function of time after gel initiation. These data were both collected using a constant shear rate of  $250 \text{ s}^{-1}$ .

itself. For instance, the pattern does not depend on the shear rate applied, and the results do not depend on the configuration of the cell; Couette cells runs were carried out with the cells set at different gap widths and with the stator and rotor reversed. Furthermore, and significantly, the quantitative behaviour of the viscosity does not depend on the type of cell used. Figure 5, for example, is a typical plot that compares the viscosity from the system sheared at  $250 \text{ s}^{-1}$  from a rheometer set up in Couette geometry with a different rheometer in the cone-and-plate configuration. The values of the peak viscosities are very close, and there is only a very small difference in the time taken to reach the maximum. This time is, however, very sensitive to the sample preparation, the pH and, to a lesser extent, the temperature. Overall, for a given set of initial conditions, we estimate that the time taken to reach the viscosity maximum and the value of the maximum itself are both repeatable within 5%.



**Figure 6.** Measured shear stress as a function of time after gel initiation for three samples sheared at different rates. Note, that as the shear rate increases the time taken to reach the peak (critical) shear stress decreases.

Figure 6 plots the stress-versus-time curves at three shear rates for gelling silica in the cone-and-plate apparatus and shows that the time taken to reach the peak is inversely related to the applied shear rate, but the figure also exhibits one of the key observations of this work. It is seen that the maxima in the viscosity coefficients achieved at all three shears correspond to a stress of around 350 Pa. Equivalent results were obtained from the Couette rheometer at these shear rates, and from both the Couette and cone-and-plate at other applied shears for the system at  $\phi = 0.17$  gelling at  $\text{pH} = 8$ . This association of a maximum viscosity with an approximately constant stress has also been checked for samples gelled at several values of  $\text{pH} < 8$ , and for samples at other precursor volume fractions. In short, we surmise that, to a first approximation, *a peak in the viscosity coefficient and a concomitant enhancement in the low- $q$  scattering pattern occurs only when a shear-rate-independent critical stress is reached in the gelling sample* [10].

#### 4. Discussion

Other workers have reported interesting consequences of the effect of shear on a gelling system. For example Rueb and Zukoski [11] discussed how shear influences the structure of gels formed from octadecyl silica sols in an organic solvent, and Cabane and coauthors investigated the shear influenced gelation of polyethylene oxide silica sols in water [12]; the light-scattering work of Verduin *et al* on stearyl-coated silica spheres is additionally relevant [13]. It should be pointed out, however, that these authors studied physically reversible gels, whereas the colloidal silica system considered in this paper is generally regarded to form a chemically irreversible gel; clearly, however, the viscosity evidence refutes this. As already noted, the effect of steady and oscillatory shear on the aggregation and breakup of flocs formed from dilute sols has also been examined [3], but again we stress that the results reported in this paper are from a concentrated sol of particulates which forms a bicontinuous material, not a floc, which spans the container, does not phase separate and is transparent.

The key experimental observations from the concentrated colloidal silica system are as follows:



(1) Under zero-shear conditions, the viscosity increases as a function of time after gel initiation and then diverges when the gel becomes solid—a well known result. By contrast, under a constant applied shear rate, the gelling system's viscosity increases initially but, at a time  $t_m$ , it reaches a maximum. For times greater than  $t_m$ , it decreases to an asymptotic value that is higher than that of the initial sol, but lower than the peak value. Hence, throughout the shear-influenced gelation reaction, the system remains fluid. On removing the shear, the viscosity increases and the gel sets to a microscopically homogeneous solid.

(2) The viscosity at its maximum, and the corresponding time  $t_m$ , is a function of the applied shear rate, but the shear stress corresponding to this maximum is relatively independent of the shear rate. A critical shear stress is thus observed.

(3) The viscosity behaviour can be directly correlated with the gelling system's structure by noting the differences in the low- $q$  behaviour of the SANS scattered intensity  $I(q, t)$  between gels formed at zero shear and gels formed under a constant shear rate. In general,  $I(q, t)$  increases at low wave vectors as the gelation reaction proceeds, but the increase is enhanced substantially when gelation occurs in the presence of an applied shear, due largely to a discontinuous jump at  $t_m$ . The values of  $I(q, t)$  for unsheared and sheared gelling systems are essentially identical if  $t < t_m$ . Thus, the shear-induced enhancement in the intensity is observed only when  $t > t_m$ . Furthermore, once the shear is removed, and the sample is allowed to gel, this enhanced scattering at low  $q$  does not change. That is, the shear has permanently altered the structure at the length scales probed by this study, but has not altered the sample characteristics such that a gelation reaction cannot proceed when the shear is removed.

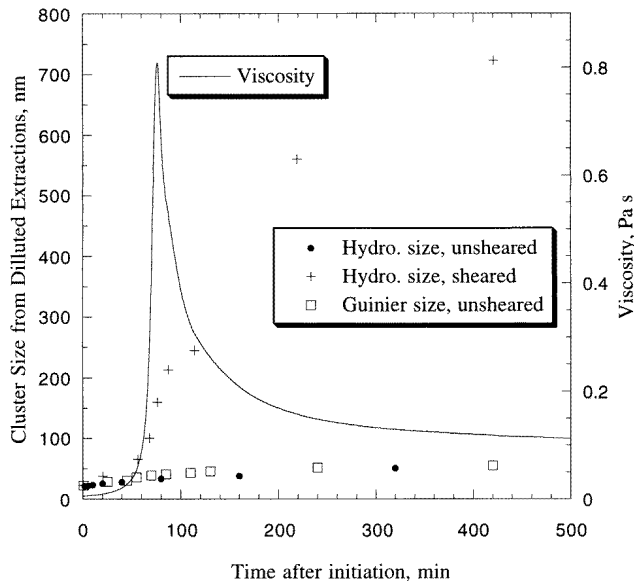
What is the origin of the interesting viscometric behaviour? We can rule out two superficial causes. First, it is unlikely that there can be any shear-induced change in the interaction potential between clusters. Secondly, the effects of viscous heating are small. A possible rate of change in the temperature from viscous heating can be estimated, assuming no heat loss through the cell walls, from the relation  $\Delta\dot{T} = (\eta\dot{\gamma})\gamma V/C_v$  where  $V$  is the sample volume and  $C_v$  the specific heat at constant volume. The highest applied shear considered in our experiments was  $1645\text{ s}^{-1}$  and this corresponded to a stress  $\eta\dot{\gamma} \sim 350\text{ Pa}$  at  $t_m$ . At this condition we estimate a worst case  $\Delta\dot{T}$  to be  $\sim 5 \times 10^{-4}\text{ K s}^{-1}$ , which would result in a temperature increase of  $\sim 2.5\text{ K}$  after 5000 s. Such a rise in temperature might account for a small variation in  $t_m$ , but is too small to influence the behaviour of the viscosity. This calculation is consistent with direct measurements of the cell temperature which were made for some of the Couette experiments by placing a thermocouple on the exterior wall of the stator. The temperature was observed to increase by about 1 K throughout a run. Further, the temperature was recorded in the cone-and-plate experiments. Given the thermostatted mean temperature of 298 K, it was observed that the maximum temperature increment was 2 K.

Authors have argued that clusters can fragment when a critical stress is reached [14], but this possibility seems questionable given the evidence. We would expect the viscosity to plateau at the critical stress not to peak as is observed. In addition, we would anticipate that the corresponding SANS intensities would fall and shift to higher wave vectors should clusters disintegrate; on the contrary  $I(q, t)$  jumps at the lowest wavevectors at time  $t_m$ .

Nevertheless, since the chance that fragmentation occurs could not be eliminated unambiguously, we performed additional scattering experiments to reinforce the evidence against it: namely, a small amount,  $50\ \mu\text{l}$ , of gel was extracted from the Couette cell at selected times after gel initiation, and each extractant added to 10 ml of deionized water. These diluted extractants were sealed in conventional SANS cells and their intensities measured to yield effective cluster Guinier radii of gyration  $R_g$  [15] where  $R_g^2 = (3/5)R^2$  for spherical objects with radii  $R$ , or an effective size of  $2R$ .

In addition, effective hydrodynamic diameters of the clusters in the extractants were determined by dynamic light scattering (DLS) [16]. The DLS apparatus incorporated an Ar-ion laser operating at  $\lambda = 488$  nm, and data were taken at a scattering angle  $\theta = 90^\circ$  using a log-time autocorrelator. Approximate hydrodynamic sizes were obtained by fitting the autocorrelation function to a simple exponential decay. Thus it was assumed that the gel clusters are approximately spherical with a diffusion coefficient  $D = kT/6\pi R\eta'$ , where  $k$  is Boltzmann's constant and  $\eta'$  is the viscosity of the medium. The effective hydrodynamic size is  $2R$ . More sophisticated models verified that the distribution of cluster sizes were unimodal.

Effective hydrodynamic cluster sizes for the unsheared gel and for a gel sheared at  $533 \text{ s}^{-1}$  are shown in figure 7, together with the variation of the sheared gel's viscosity with time. At early times, both for the sheared and unsheared gel, the cluster sizes increase, as we would expect for an aggregating system. The clusters from the sheared gel expand more rapidly, however. This result was predicted from a computer simulation study of a shear influenced coarsening system [17]. As the peak in the viscosity is approached, the cluster expansion accelerates. The clusters, however, do not contract at times greater than  $t_m$ . In fact, the clusters appear to continue to grow long after the viscosity falls, and reach an apparent asymptotic size far in excess of the equivalent cluster diameter from an unsheared gel. Guinier diameters of the growing clusters were also estimated from SANS data taken from the diluted samples. Results for the unsheared samples are also plotted in figure 7 and are in agreement with the hydrodynamic size estimates. This is also true at early times for the sheared samples, but, it was not possible to estimate the sizes from SANS data near and after the observed peak in viscosity because the sizes exceeded the range of the instrument. In summary, the results of the dilution experiments rule out the possibility that the drop in viscosity at times greater than  $t_m$  occur because clusters fragment.



**Figure 7.** Cluster sizes measured using dynamic light scattering and SANS Guinier analysis on extracted samples, diluted by a factor of 200, as a function of time since gel initiation. The variation of the viscosity when a constant shear of  $533 \text{ s}^{-1}$  is applied is shown for reference.

The data are best explained if it is assumed that the gelling clusters instead densify when a critical shear is reached. Densification will reduce the effective volume fraction of the clusters which, in turn, will cause the viscosity to fall. A fractal argument supports this hypothesis:

We define a reduced cluster size,  $\xi$ , by  $\xi = R_c/r_p$  where  $R_c$  is the cluster radius and  $r_p$  is the radius of the colloidal silica particles. Let  $N_e$  be the number of particles in a cluster:  $N_e = \xi^{d_f}$  where  $d_f$  is the fractal dimension of the clusters. Noting that, at the gel point, the effective volume occupied by the clusters is the volume of the system, it can be easily shown that [18]

$$\xi_{gel} = \phi^{-1/(3-d_f)} \quad (1)$$

where  $\xi_{gel}$  is the cluster size at gelation and  $\phi$  is the silica volume fraction of the precursor suspension. The effective volume fraction  $\Phi$  occupied by the growing fractal clusters written in terms of the cluster size  $\xi$  is

$$\Phi = \phi \xi^{3-d_f} \quad (2)$$

where we have defined  $\Phi \equiv 1$  at the gel point.

For the sheared gelling system, we relate the variation of the viscosity to the variation of  $\Phi$ . This can be done simply and conveniently through an empirical expression proposed by Mooney [19, 20] for the viscosity of aggregates in a suspending fluid:

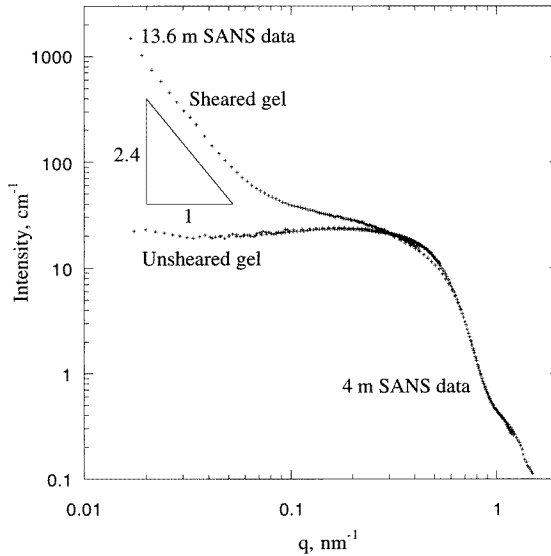
$$\eta_r = \exp \left[ \frac{k_e \Phi}{1 - S\Phi} \right]. \quad (3)$$

Here  $\eta_r$  is the viscosity of the solution with respect to that of the suspending fluid, and  $k_e$  and  $S$  are parameters. Equation (3) will reduce the Einstein equation for the viscosity of a dilute suspension in the single-sphere limit when  $k_e = 2.5$ . Here we set  $S = 1/\Phi_{gel}$ , or  $S = 1$  so that the viscosity will diverge at the gel point. The viscosity of the system is thus expressed as a function of the effective volume fraction occupied by the clusters. The volume fraction can, in turn, be expressed in terms of the cluster size and fractal dimension by equation (2), but a structural transformation consistent with the densification of fractal clusters at  $t_m$  will be associated with an increase in  $d_f$ .

For times less than  $t_m$ ,  $d_f$  cannot be estimated from a power-law slope of the measured SANS intensity because the clusters in this concentrated system are only a few times the size of the colloidal particles as evidenced by the location of the low-angle cluster-cluster correlation peak [21]. This fact is made clearer in figure 8 which shows the scattering for the unsheared gel on a log-log plot where it can be seen that there is no place that a power-law slope (even one corrected for the particle form-factor) could be fitted to yield  $d_f$ .

Alternatively,  $d_f$  can be evaluated from a scaling analysis of the evolution of the cluster-cluster correlation peak [22, 23] but, unfortunately, this analysis fails for the system at pH = 8, probably because the correlation peak only evolves over a short period of time. Scaling analyses, however, do yield accurate fractal dimensions for the same 7 nm colloidal silica system when gelation is initiated at lower values of pH. In systems ranging from a pH of 5 to 7 [23] we have found  $d_f \approx 1.4$  and to be relatively insensitive to the pH. We thus use  $d_f = 1.4$  for times less than  $t_m$  for the system here.

At times greater than  $t_m$ , we estimate  $d_f = 2.4$  from the power-law slope of the scattered intensity measured with the SANS spectrometer set at 13 m (figure 8). This value is consistent with the  $d_f$  reported by Reub and Zukoski [11] for their coated silica precursors. There is, however, no evidence of enhanced particle-particle contact in the scattering at  $q \sim 0.9 \text{ nm}^{-1}$  which might be expected when the clusters densify. Possibly, however, the clusters, even with  $d_f = 2.4$ , are not near enough to their close-packed density to have a substantial impact on this region of the scattering curve.



**Figure 8.** The measured SANS intensity at two different detector settings for an unsheared gel and for a gel made from a sample sheared at  $500 \text{ s}^{-1}$  that was well into the asymptotic regime,  $\sim 10 \text{ h}$  after initiation. The low- $q$  region of the sheared gel data shows power-law scattering behaviour indicative of a fractal structure with  $d_f = 2.4$ .

A rough estimate of the volume fraction change due to densification across the viscosity maximum can now be made. The ratio of volume fractions at times immediately after and before  $t_m$  is simply  $\Phi_2/\Phi_1 = (\xi_2/\xi_1)^3$ . Assuming that the number of particles in a cluster remains the same during this structural change, the ratio can be written

$$\Phi_2/\Phi_1 = \xi_1^{3((d_{f1}/d_{f2})-1)}. \quad (4)$$

An estimate of  $\xi_1$  follows from equation (1) by recognizing that at time  $t_m$ ,  $\xi_1 \approx \xi_{gel}$ . The result is  $\xi_1 \approx 3$ , consistent with this experimental hydrodynamic size estimate, whence, using the appropriate values of  $d_f$ , we obtain  $\Phi_2/\Phi_1 \approx 0.25$ . Inspection of equation (3) indicates that this drop in volume fractions will cause a substantial drop in the viscosity, as observed experimentally.

For the system gelling under shear, the experimental hydrodynamic clusters expand for times greater than  $t_m$ , rather than contract as predicted by the densification argument. There is, however, a plausible explanation for the apparent contradiction. The extracted gel clusters could swell on contact with the deionized water [24].

We conclude this paper with two remarks. First, the literature is ambiguous as to whether reversible or irreversible gels are formed from uncoated colloidal silica. It is, nevertheless, very often assumed that the gels are irreversibly bonded due to the formation of interparticle siloxane bonds [25]. It would be impossible, however, to explain our data if this were true because both the shear-induced densification and the probable swelling of clusters upon contact with deionized water would not be allowed if the silica particles were covalently bonded. It seems, therefore, that the bonds between the colloidal silica particles, in solution, are far more pliable than is often assumed and are likely the much weaker van der Waals or hydrogen bonds.

Second, we remark on the technological implications of the results presented here. As far as we are aware, it was not previously known that a silica sol, which has had its pH altered so as to initiate gelation, could be held indefinitely in the fluid state by the application of a

constant shear without irreversibly altering its ability to later form a gel. Apparently, there are no irreversible chemical reactions that prevent the normal formation of a gel once this shear is removed. This implies that production of materials using the sol–gel process might be accomplished by a continuous process instead of the currently used batch process mode—a fact that might have technological importance. It is, therefore, important to understand the structural changes that take place in the asymptotic regime that may impact a gel made from this presheared sol.

### Acknowledgments

The work was funded in part by a grant from the Office of Basic Energy Sciences, Division of Engineering and Geosciences, US Department of Energy. The SANS experiments were carried out at the NIST Center for Neutron Research. We are grateful to Bill Roberts of Du Pont, and to Jim Woolfrey of ANSTO for their support and encouragement throughout this project. H Hanley also thanks the staff of the Materials and Physics Divisions of ANSTO for their hospitality during his stay there.

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