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Small-angle neutron-scattering study of dense sheared silica gels

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Small-angle neutron-scattering (SANS) shearing experiments on dense colloidal silica suspensions in a H_2O-D_2O medium are reported for the wave vector range $0.03<Q(nm^{-1})<0.8$, at volume fractions $\phi=0.1$, 0.12, 0.18, 0.24, and 0.3. For the unsheared gels, apparent fractal structures were observed at the lower volume fractions, and a small maximum at a Q corresponding to a contact particle morphology was apparent at all volume fractions. A fractal dimension $d=1.60\pm0.05$ was estimated for $\phi=0.10$ and 0.12 by fitting the power law behavior of the structure factor. Shear induces an apparent fractal domain into the dense gels and enhances the contact particle structure.

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The flow properties of a sheared non-Newtonian [1] fluid depend on the applied shear rate γ, as is well known. Shear, however, also affects the equation of state, the thermodynamic properties, and the stability criteria [2], so a sheared system will have phase behavior which is perturbed or even different from its counterpart in isolation [3]. Since gelation is a phase change, a shear applied to the precursor or sol will influence the final gel structure. Moreover, its effect on a reaction limited gelation process of nanometer particulate matter, with reaction times of the order of seconds, should be detectable in the laboratory. Simulation studies [4] suggest that non-Newtonian characteristics are observed in a fluid if the dimensionless product $\tau\gamma>0.01$, where τ is defined conveniently as the Maxwell relaxation time ($\tau=\eta/G$, with η the viscosity and G the shear modulus). Experiments to probe non-Newtonian behavior using colloidal suspensions [5], whose relaxation times are of the order of milliseconds, are consistent with this criteria.

The objective, therefore, of this paper is investigate the effect of shear on gelation [6]. Results from a small-angle neutron-scattering (SANS) study on aqueous silica suspensions are reported. In addition, we present structure data on gels that are, to our knowledge, more dense than those probed by radiation up to now [7–13]; relatively high volume fractions ϕ are required because our previous experiments [14] have indicated that the effect of shear on the structure of a colloidal suspension appears to be negligible if $\phi\leq0.15$.

The study was carried out with colloidal silica on the 30-m SANS instruments at the National Institute of Standards and Technology (NIST) Cold Neutron Research Facility. The first series of experiments measured the scattered intensities from ungelled suspensions of volume fractions $\phi=0.1$, 0.12, 0.18, 0.24, and 0.30, prepared in an aqueous medium from a stock solution of Ludox, TM-50, silica particles [15] of nominal diameter, $\sigma=22$ nm. To maximize intensity while minimizing multiple scattering, most suspensions were prepared in a H_2O-D_2O(30%) medium. To check on the effect of multiple scattering, additional suspensions at $\phi=0.1$ were made up with solvents containing 22% and 50% D_2O. It turned out that the behavior of the measured intensities from all the $\phi=0.1$ suspensions was essentially identical. A given suspension was placed in a quartz cell of path length 1 mm and the spectrometer configured to a wavelength $\lambda=0.6$ nm and sample-to-detector distances of 15, 13, 8, 5, and 2 m. Scattered intensities $I(Q)$ were recorded as two-dimensional images. In Cartesian coordinates, the neutron beam is incident along the y axis and the detector is in the x-z plane. $I(Q)$ was circularly averaged at a given wave vector Q [$Q=(4\pi/\lambda)\sin\theta/2$, where λ is the incident neutron wavelength, and θ the scattering angle], corrected for the cell background and detector variation and put on an absolute scale. The single particle form factor data were measured from a suspension at $\phi=0.0025$ and the result checked against a theoretical polydisperse form factor modified to account for detector smearing [16]. On the basis of this comparison, and from a Guinier plot of the low-Q data, the particle diameter was estimated to be $\sigma=24$ nm with a polydispersity of 15%. Structure factors at a given volume fraction were calculated by dividing the intensity data at that fraction by the form factor, taking into account all scaling terms [17].

Gelation was induced by adjusting the pH of the suspensions to 5.8 ± 0.1 with $0.1M$ HCl, with NaCl added to give a solution of $0.4M$ NaCl. The gel at $\phi=0.30$, and an alternative gel at $\phi=0.24$, were prepared without salt. Intensities were measured from the gelled samples in the quartz cells, and the data analyzed as before. The gelation process, assumed complete when the intensity was independent of time, took from 6 h for the dense suspension to 12 h for the dilute. The progression from sol to gel at $\phi=0.1$ was monitored by measuring the intensities at 10 min intervals after gelation initiation for 3 h, then hourly for a further 9 h.

For the shear studies, the SANS instrument was configured at 13 m and 8 m at a wavelength of 0.6 nm with the NIST 1 mm gap width Couette shearing cell [14,18] in the sample holder position. (In our coordinate system with the incident beam along the y direction, the flow velocity $\mathbf{u}$ is along the x direction, and the shear rate is defined as $\gamma=\partial u_x/\partial y$.) A gelation-initiated sample was loaded into the

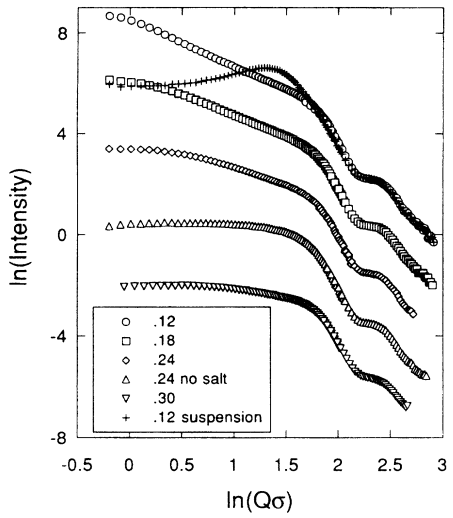

FIG. 1. Logarithmic plot of the scattered intensities $I(Q)$ of the unsheared colloidal silica gels at several volume fractions ϕ as a function of $Q\sigma$, where σ is the diameter of the colloidal silica particle, $\sigma=24$ nm. The curve for the suspension at $\phi=0.12$ is shown for comparison. Gelation was induced by lowering the suspension pH and by adding NaCl, unless otherwise stated. The plots are offset for clarity.

Couette cell, subjected to a shear rate of $\gamma=4500\ s^{-1}$, and the intensity recorded. A sector average of the sheared intensities in the x-z plane of the detector showed possible anisotropy at the higher volume fractions. This, however, was very weak [19] and the data were circularly averaged and reduced following the procedure for the unsheared suspensions and gels. Intensities were measured at regular intervals until the scattering pattern from the shearing system was time independent. At this point the shear was removed and the intensity remeasured. Only very small relaxation was noted; in effect, the intensity did not change significantly.

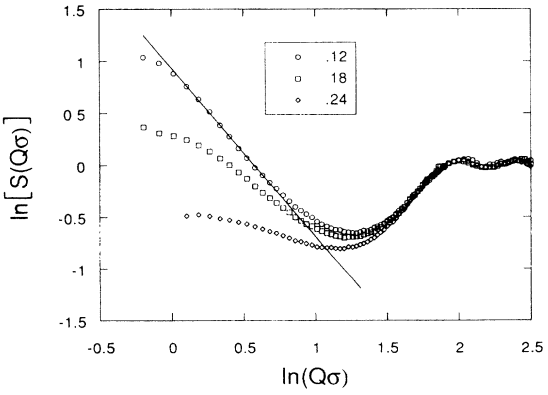

FIG. 2. Structure factors $S(Q)$ for three unsheared gels. Note the signature of a long range correlation at low $Q\sigma$, with an apparent fractal dimension at $\phi=0.12$ of $d=1.60$. Note the absence of the typical suspension peak, which would appear between about $Q\sigma\approx4$ and 6, depending on the volume fraction.

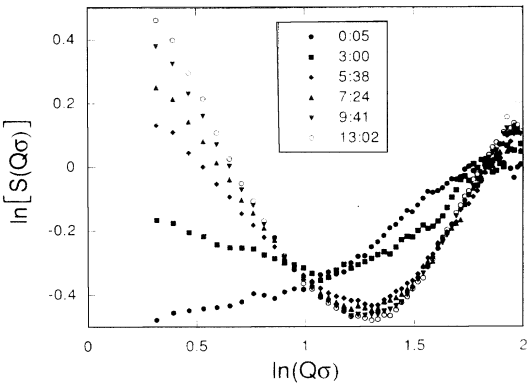

FIG. 3. The variation of $S(Q)$ with time (h:min) after gelation initiation for the $\phi=0.10$ sample.

Figures 1–3 display the main features of the unsheared gels. The scattering intensities from the gels at $\phi=0.12$, 0.18, 0.24 (with and without salt), and 0.30 are shown in Fig. 1 with an intensity for the ungelled suspension at $\phi=0.12$ for comparison. The structure factors for gels at $\phi=0.12$, 0.18, and 0.24 are plotted in Fig. 2. Figure 3 plots the variation of $S(Q)$ with time for $\phi=0.1$. Comments on these diagrams are as follows. Figures 1 and 2 demonstrate that the intensities essentially superimpose at high Q and reflect single particle scattering. We thus conclude that the basic unit of the gelling system (a Ludox particle of diameter 24 nm) remains unchanged during gelation. Figures 1–3 show that the characteristic major peak of the suspension is eliminated in the gel, and Fig. 2 displays the concurrent formation of a weak peak at $Q\sigma\approx2\pi$. A peak at this position is a signature of particles in contact. A gel-induced peak at high values of $Q\sigma$ has not, to our knowledge, been reported before.

The linear, power law, portions of the logarithmic curves for $\phi\leq0.24$ are consistent with a fractal structure [7–12] in our system, as is the change in the structure factor as the gelation proceeds [20]; see Fig. 3. However, based on the variation of $S(Q)$ with Q at $\phi=0.10$ and 0.12, the apparent fractal dimension $d=1.60\pm0.05$. This value is lower than the dimension of 2.1 estimated from the reaction limited cluster-cluster model [7,8], and significantly lower than the dimension of about 2.4 assigned to similar silica gels at lower, but comparable, volume fractions [12]. It should be pointed out, however, that if we were to estimate a dimension from the intensity plots, as is usually done, $d=1.94\pm0.03$. This dimension is still somewhat low and, furthermore, the dimension from the intensity plots decreases as ϕ increases ($d\approx1.64$ at $\phi=0.18$ and $d\approx1.36$ at $\phi=0.24$), which was not anticipated [9].

A more detailed analysis of the fractal nature of our gels is not attempted at this time because the SANS experiments do not cover wave vectors low enough to determine quantitatively the fractal cluster correlation length, ζ at low ϕ. Ferri, Frisken, and Cannell [9] stress how the fractal dimension depends on the correlation length, which in turn depends on the volume fraction and on the mechanism of gelation. That the gelation mechanism plays a substantial role

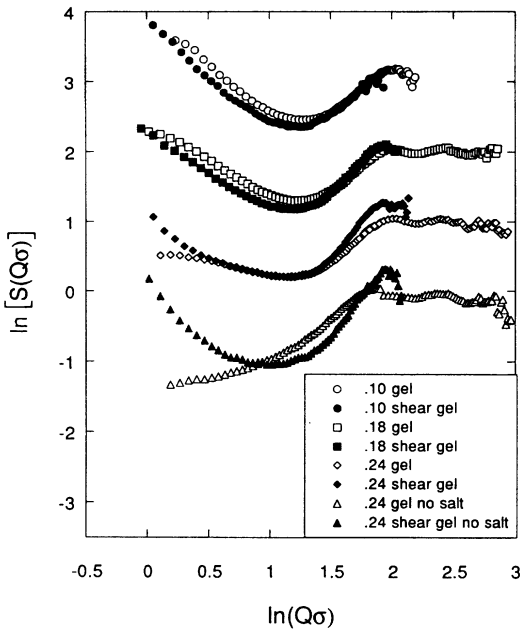

FIG. 4. The effect of shear. Structure factors for sheared ($\gamma=4500\ s^{-1}$) and unsheared gels at several volume fractions. Shear: (i) appears to extend the range of the long range correlation to lower $Q\sigma$ for the lower volume fractions, (ii) induces a long range correlation into the dense gel, and (iii) enhances the peak at $Q\sigma\approx 2\pi$. The plots are offset for clarity.

is very clear from our work. Figure 1 shows, for example, how the low-Q intensity differs for the two gel variants at $\phi=0.24$, one prepared with salt, the other not. In short, the interpretation of our fractal dimensions is an open question. Nevertheless, $\zeta/\sigma>5$ from the extent of the linear plot at $\phi=0.12$. Further, the curves suggest a correlation length would decrease as ϕ increases, as it should [10,12,21].

Figure 4 summarizes the results from the shear experiments. Plotted are the structure factors for the sheared systems at $\gamma=4500\ s^{-1}$ along with $S(Q)$ of the unsheared gel for comparison. At $\phi=0.10$ and 0.18, we notice that the fractal slopes of the sheared and unsheared gelled system are comparable, but the fractal region is extended to lower Q under shear. There is also a small but definite enhancement of the peak at $Q\sigma\approx 2\pi$. Substantial differences in the curves are seen at the higher volume fraction; shear has induced a long range correlation in the gel at $\phi=0.24$ (and at $\phi=0.3$, not shown [22]). The action of the shear has retarded the tendency of this dense suspension to form an amorphous gel and possibly allowed fractal clumps to form.

The time dependence of the gelation under a constant shear of $4500\ s^{-1}$ was found to parallel that for the gelation of the isolated system. We also investigated the dependence of the final gel structure at $\phi=0.24$ on the steady shear rate: specifically at $\gamma=45$, 450, and $4500\ s^{-1}$. As expected, the low-Q structure factor varied progressively between that of the isolated pattern and the fractal pattern at the highest shear.

Overall, our results confirm the picture of the unsheared silica particulate gel as a filamentary structure in which the particles are essentially in contact, provided the volume fraction of the precursor sol is not too high. Above a certain volume fraction, about $\phi=0.24$ in our case, the gel has no distinct structure that can be detected with the SANS equipment. Under shear, however, the filamentary nature of the gel is enhanced, even at the high volume fractions. Computer simulations, based on the assumption that gel formation and spinodal composition in the gas-solid part of the phase diagram have points of similarity, support this interpretation and show that shear promotes the formation of an extended gel network. The simulations are planned to be discussed in another paper [23].

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