An ultra-small-angle neutron scattering study of the restructuring of sheared colloidal silica gels

LETTER TO THE EDITOR

An ultra-small-angle neutron scattering study of the restructuring of sheared colloidal silica gels*

C D Muzny†§, B D Butler†, H J M Hanley† and M Agamalian‡∥

† National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80303, USA
‡ Spallation Neutron Source, Oak Ridge National Laboratory, USA

Abstract. Neutron scattering curves for a sheared colloidal silica gel were measured using a Bonse–Hart ultra-small-angle neutron scattering instrument. When they are combined with data taken from a conventional small-angle neutron scattering instrument, the accessible scattering vector range extends over approximately four orders of magnitude: $3 \times 10^{-4} < q \ (\text{nm}^{-1}) < 3$. A peak in the scattering data is observed at $q = 2.7 \times 10^{-3} \ \text{nm}^{-1}$ corresponding to a correlation length of 2.3 μm. The scattering curves show an approximate power-law behaviour with an exponent of -2.9 over the range $4 \times 10^{-3} < q \ (\text{nm}^{-1}) < 4 \times 10^{-2}$. These results are compared with our previously reported observation that an unsheared sample yields a correlation length of only $\sim$20 nm with no observable power-law regime. The present data confirm that shear stresses induce a structural densification in gelling colloidal silica systems.

This letter reports results obtained from the ultra-small-angle neutron scattering (USANS) instrument at Oak Ridge National Laboratory that extend to low-q conventional SANS data obtained from gelling colloidal silica [1]. Here q is the scattering wavevector: $q = (4\pi/\lambda) \sin(\theta)$ with 2θ the scattering angle and λ the neutron wavelength. In the previous work [1], we measured simultaneously the viscosity and the neutron scattering curve $I(q)$ of the silica system as functions of time after gel initiation. We demonstrated, figure 1, that when the specimen is subjected to a constant shear rate, the viscosity first increases after gel initiation, peaks at a shear-rate-independent threshold, and then declines asymptotically to about one-tenth of the peak value. While shearing, the intensity rose slowly with time at low q, but increased abruptly at around the moment at which the viscosity reached its maximum value; $I(q)$ continued to rise to an effective plateau value at a time when the viscosity approached its asymptotic limit. According to the discussion in [1], the maximum in the viscosity, coupled with the marked variation of $I(q)$, arises from a shear-induced densification transition in the growing clusters of colloidal silica. It was noted that the system gels when the shear is removed, but that the scattered intensity remains approximately unchanged. Here, the very low-q range of the USANS camera allows us to estimate the cluster correlation length of this final sheared gel and to determine its power-law exponent.

The gel precursor was an aqueous suspension of colloidal silica spheres with a mean diameter of 7 nm, estimated polydispersity of 20%, at a volume fraction of 30% and a pH $\sim$ 10 [2]. Gelation was initiated by adding concentrated HCl until the pH fell to 8.0 [1].
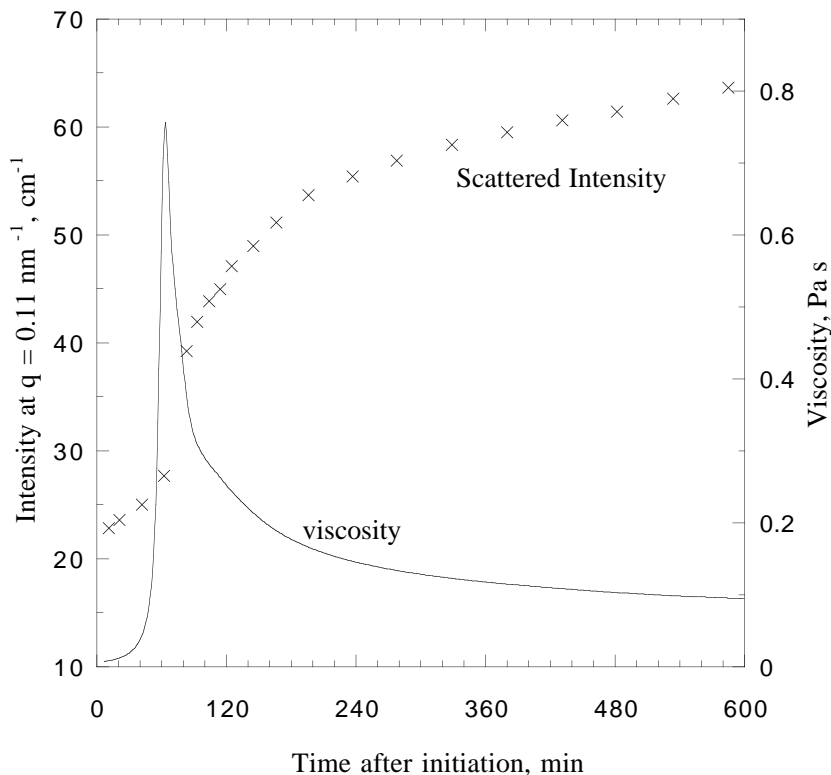
Figure 1. Viscosity and scattered intensity at $q = 0.11$ nm^{-1} for a gelling colloidal silica sample sheared at a rate of 500 s^{-1}. Note the abrupt increase in scattering corresponding to the peak in sample viscosity [1].

After this initiation, the sample was placed immediately in a Couette cell and sheared at a constant rate of 500 s^{-1}. The viscosity behaviour mirrored that shown in figure 1 with a peak corresponding to a shear stress of 350 Pa s after 30 min of shearing. After 12 h, the sample was removed from the shearing cell and placed in a rectangular quartz cuvette with a 2 mm path length and allowed to gel. This final sheared gel was then placed in the sample chamber of the USANS instrument.

The Bonse–Hart [3] USANS facility at the Oak Ridge National Laboratory (ORNL) has been recently modified to reduce a parasitic scattering from the Si channel-cut monochromator and analyser crystals [4, 5]. As a result, the signal-to-noise ratio is improved by over three orders of magnitude. The minimum acceptable scattering vector of the ORNL USANS instrument is $q_{min} \sim 2 \times 10^{-4}$ nm^{-1}, which corresponds to a maximum resolvable real-space dimension of $2\pi/q_{min} \sim 30$ μm. In our experiment, data were collected with the angular step $1.0''$ in the range $3.0'' < 2\theta < 150.0''$, which corresponds to the q-range $3.5 \times 10^{-4} < q$ (nm^{-1}) $< 2 \times 10^{-2}$ given that the wavelength of the primary beam is 0.259 nm. The raw USANS data were corrected for the transmission, detector background, time, and sample thickness as described in [4].

The USANS measured intensities were checked for multiple scattering—estimated to be 5%—and corrected for slit smearing (i.e. transferred to point geometry) using a given model function applied to the instrument resolution function and incorporating the SANS data to

allow for a proper extrapolation of the scattering to higher wavevectors. Least-squares fits using several standard models, including those due to Sinha *et al* [6], Sabine and Bertram [7], and one based on a polydisperse form factor, were unsatisfactory. In fact, a best fit was obtained from an empirical expression proposed by Butler *et al* [8] to scale the scattered intensities from unsheared gels generated at pH < 8. The expression has the form

$$S_1(q) = \left[\frac{\alpha}{1-\alpha} + 2\left(\frac{q\xi}{2\pi}\right)^{d_f} \right] \bigg/ \left[\frac{1}{1-\alpha} + \left(\frac{q\xi}{2\pi}\right)^{2d_f} \right] \tag{1}$$

which describes a scattering curve with a $q = 0$ limit of α, a correlation peak of unit height at $q/2\pi = 1/\xi$, and an asymptotic power-law behaviour with an exponent of $-d_f$. To obtain a fit of the combined USANS and SANS data, we incorporated equation (1) into a general expression for $I(q)$:

$$I(q) = I_0 S_1(q) + S_2(q) F_{\text{polydisperse}}^2(q), \tag{2}$$

where I_0 is an amplitude, S_2 is a liquid-like structure factor fitted to the SANS data to within the experimental error, and $F_{\text{polydisperse}}^2$ is the polydisperse form factor for the precursor system of 7 nm silica spheres.

Figure 2 shows the desmeared USANS data plotted with the SANS data. Included is the fit of equation (2) with parameters $I_0 = 4050$, $\xi = 2300$ nm, $\alpha = 0.73$, and $d_f = 2.92$.
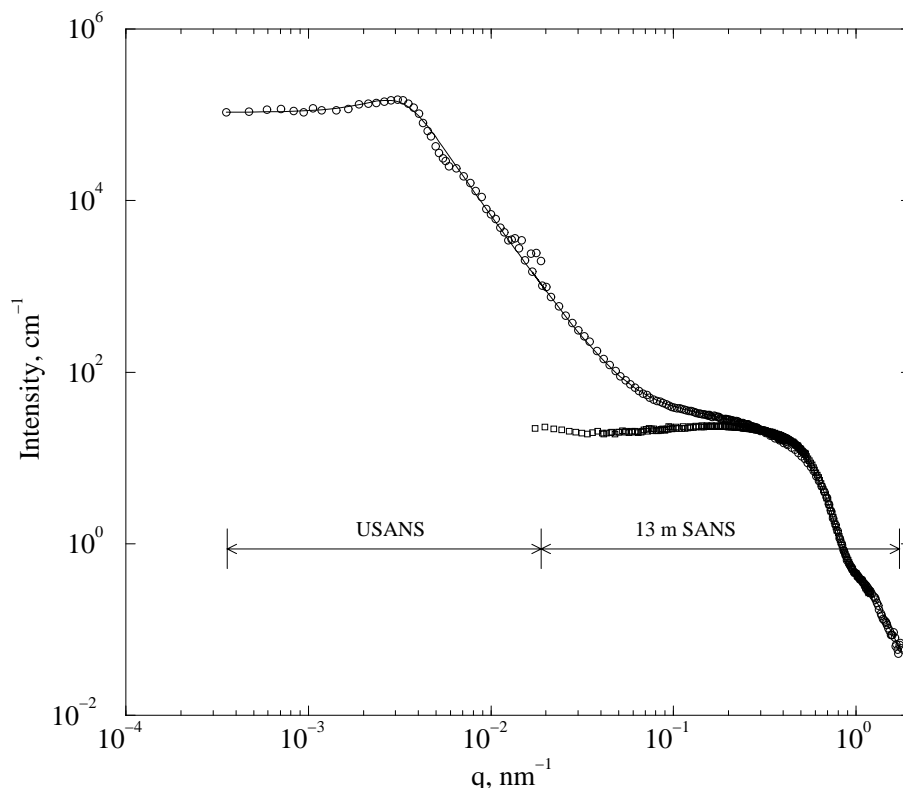
Figure 2. Scattering from a colloidal silica gel when subjected to a shear during gelation (open circles) and when unsheared (open squares). Data above $q = 0.015$ nm^{-1} were taken on a conventional 13 m SANS instrument. The low-q data are from USANS. The solid curve is the functional form of equation (2) used to desmear the measured USANS data.

That the effect of shear on gelation is pronounced is demonstrated unquestionably by the fourfold order-of-magnitude difference in the low-q scattering intensity between the sheared and unsheared gels, and the appearance of the peak at $q \sim 4 \times 10^{-3}$ nm^{-1}. We identify the peak with cluster–cluster correlations of about 2.3 μm, equation (1). Compare this estimate with cluster sizes of $\sim$20 nm characteristic of the unsheared gel [1].

Finally, figure 2 illustrates how the power-law slope $d_f \sim 2.9$ (equation (1)) associated with the sheared gel contrasts with the low-q intensity plateau of the unsheared gel. Since we have shown in reference [1] that the fractal dimension of the system immediately before gelling is about 1.4, this result confirms the hypothesis that the viscosity peak, figure 1, is indeed the consequence of a shear-induced cluster densification transition.

References

[1] Hanley H J M, Butler B D, Muzny C D, Straty G C, Bartlett J and Drabarek E 1999 *J. Phys.: Condens. Matter* **11** 1369
[2] Ludox SM-30 from DuPont Corporation. The trade name is noted to allow the experiment to be repeated exactly. (Use of this material does not imply an endorsement by NIST.)
[3] Bonse U and Hart M 1965 *Appl. Phys. Lett.* **7** 238
[4] Agamalian M, Wignall G D and Triolo R 1997 *J. Appl. Crystallogr.* **30** 345
[5] Agamalian M, Christen D K, Drews A R, Glinka C J, Matsuoka H and Wignall G D 1998 *J. Appl. Crystallogr.* **31** 235
[6] Sinha S K, Freltoft T and Kjems J 1984 *Kinetics of Aggregation and Gelation* ed F Family and D P Landau (Amsterdam: North Holland) p 87
[7] Sabine T M and Bertram W K 1999 *Acta Crystallogr.* A **55** 500
[8] Butler B D, Muzny C D and Hanley H J M 1999 *Int. J. Thermophys.* **20** 35
    Butler B D, Muzny C D and Hanley H J M 1996 *J. Phys.: Condens. Matter* **8** 9457