Structure of Silica Gels

Fabio Ferri, B. J. Frisken, and David S. Cannell

Department of Physics, University of California, Santa Barbara, California 93106
(Received 26 August 1991)

The structure of silica hydrogels has been studied by elastic light scattering. Like colloidal silica gels and neutrally catalyzed aerogels, these gels show mass fractal behavior at length scales below a crossover length ξ and scatter like a spatially random distribution of fractal objects for length scales $> \xi$. Their fractal dimension D depends on ξ and, unlike the other gels for which $\xi \propto \phi^{1/(D-3)}$, ξ depends on both silica volume fraction ϕ and gelation conditions. However, all our data are consistent with the correlation function $\langle \delta\phi(0)\delta\phi(\mathbf{r})\rangle = A\phi^2 e^{-r/\xi}/(r/\xi)^{3-D}$, with $A = 1.8 \pm 0.13$.

Silica gels have been the object of many studies in recent years [1]. Interest in these materials is due in part to a variety of applications based on their fractal structure, remarkable porosity [2] (as much as 99.9% void space), and large surface area (600–800 m^2/g). Silica gels can be made by aggregation of colloidal silica (colloidal gels) or by the polymerization of silicon alkoxides in water (hydrogels) or in alcohol (alcogels). Alcogels can be hypercritically dried to obtain silica aerogels, which apparently retain the delicate fractal structure of the original alcogels. Aerogels find application as transparent insulators and particle detectors and also serve as precursors of certain glasses. Recently, a number of experiments have shown that these dilute structures have a profound effect on critical phenomena at the superfluid transition [3,4], the liquid-vapor transition [5], and the binary-fluid phase transition [6]. At the superfluid transition, the presence of aerogel reduces the transition temperature, as would be expected from finite-size scaling, but it also apparently increases the exponent ζ, which describes the temperature dependence of the superfluid density. Very recent work [4] shows that superfluid density data, taken over a range of pressures and for samples containing different density aerogels, are all consistent with $\zeta = 0.76$ ($\zeta_{\text{bulk}} = 0.67$), provided confluent singularities are included in fitting the data. In the case of the liquid-vapor transition of helium, Wong and Chan [5] found a drastically narrowed coexistence curve lying beneath, and on the high-density side of, the bulk coexistence curve. For the binary-liquid transition in lutidine-water, Frisken, Ferri, and Cannel [6] found that even gels occupying as little as 0.5% of the sample volume are capable of almost entirely masking or suppressing ordinary critical fluctuations, due to preferential adsorption of lutidine by silica. The boundary conditions imposed by a fractal silica network on a system undergoing a phase transition clearly lead to profound effects. Consequently, it is important to understand the structure of silica gels themselves as thoroughly as possible.

Previous scattering studies of colloidal gels [7] and neutrally catalyzed aerogels [8] have revealed that these two systems are remarkably similar. In both cases, the structure factor $S(q)$ is constant at low q and falls off as q^{-D} for values of the scattering wave vector $q > \xi^{-1}$, where D is the fractal dimension and ξ is a crossover length. Except for q values large enough to probe the dimensions of the individual units from which the gels are formed, the scattering is determined solely by D and this one length scale. For dilute colloidal gels, Dietler et al. [7] found $\xi \propto \phi^{1/(D-3)}$, with $D \simeq 2.1$, and this relationship was subsequently found to hold for denser neutrally catalyzed aerogels [8], with $D = 2.4$. The intensity and angular distribution of the observed scattering is consistent with a simple model where the gel structure is formed by placing mass fractal clusters of "size" ξ randomly throughout the sample volume with a number density $n \propto 1/\xi^3$. However, in order for the observed relationship between ξ and concentration to hold, the mass of the clusters must vary with ξ as $m(\xi) \propto \xi^D$, with the proportionality constant independent of concentration. The authors of Ref. [8] used the phrase "mutually self-similar" to describe such gels, and concluded that gels of a given type (e.g., neutrally catalyzed aerogels) cannot be distinguished from each other on the basis of measurements made at length scales $r \ll \xi$.

We have measured the static structure factor (Rayleigh factor) $S(q)$ for a number of undried silica hydrogels formed in solutions of different pH and spanning a wide range of silica volume fraction ϕ. Both the intensity and q dependence of $S(q)$ are very well described by the Fourier transform of the correlation function $g(r) = A\phi^2 e^{-r/\xi}/(r/\xi)^{3-D}$ with $A = 1.8 \pm 0.1$. To the best of our knowledge, this is the first absolute determination of $g(r)$ for any gel. We also find that the fractal dimension D depends on ξ, decreasing from ~ 2.3 for $\xi = 0.2$ μm to ~ 2.1 for $\xi > 2$ μm. As well, ξ is sensitive to pH and may be varied by more than a factor of 2 at fixed ϕ. Additional measurements on gels grown in methanol reveal similar sensitivity to pH. Since aerogels are made from alcogels, the relationship previously reported [8] between ξ and ϕ is almost certainly a consequence of the preparation method, and is not an intrinsic property of aerogels. Furthermore, neutrally catalyzed aerogels [8] are described by a correlation function of the same form as that given above. Consequently, it is clear that short-length-scale measurements can distinguish gels of different ξ un-
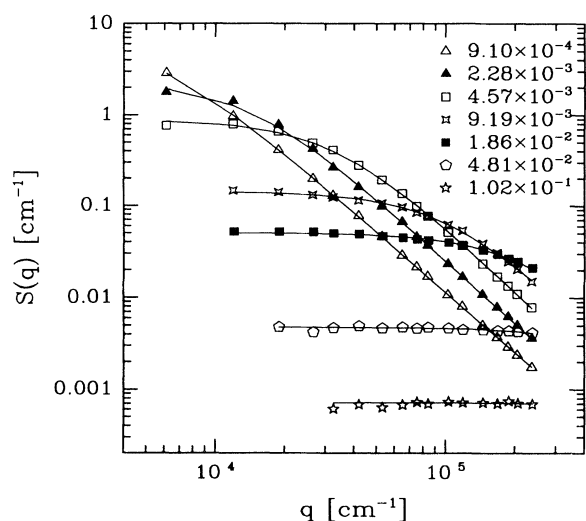
FIG. 1. Rayleigh factor as a function of wave vector for hydrogels of different silica volume fractions made in the pH range 5.7 ± 0.1. The continuous lines are the results of fitting the data with Eq. (1).

FIG. 2. Rayleigh factor as a function of wave vector for hydrogels of silica volume fraction 0.46×10^{-2} prepared with pH values in the range 5.34 to 6.34. The resulting gels exhibit values of ξ differing by more than a factor of 2. The continuous lines are the results of fitting the data with Eq. (1).

less $\phi^2 \xi^{3-D}$ is a constant, which is not the case for any known form of silica gel.

Gels with silica volume fraction in the range $0.091 \times 10^{-2} \leq \phi \leq 10.2 \times 10^{-2}$ were grown from solutions of $Si(OCH_3)_4$ (TMOS) in water using a two-step process [9]. The TMOS was first hydrolyzed by dissolving it in dilute HCl (pH 2.0) and stirring the solution for about 15 min. An equal volume of dilute NaOH (of appropriate pH) was then added to raise the pH of the final solution into the range $5.0 < pH < 6.4$; this step initiated the condensation reaction between the silica monomers. The solutions were then filtered through 0.22-μm filters into 4.72-mm-inner-diam glass scattering cells. Samples with $\phi \geq 0.46 \times 10^{-2}$ were allowed to gel at $20\,^\circ$C, and gels with $\phi \leq 0.23 \times 10^{-2}$ were gelled at $50\,^\circ$C. All gels were aged at least 10 times their gelation time before study. Gelling times varied from several minutes to weeks, depending on silica volume fraction and the pH of the final solution. Outside the pH range $5.0 \leq pH \leq 6.4$, gelling times became very large, typically of the order of months or longer for all silica volume fractions studied. The range of volume fractions investigated was also determined by gelation constraints; solutions with $\phi < 0.09 \times 10^{-2}$ did not gel regardless of pH and 10.2×10^{-2} is close to the largest volume fraction for which complete hydrolysis occurs.

The angular distribution of light ($\lambda = 6328$ Å) scattered by the gels was measured using an apparatus described previously [10]. The range of scattering wave vectors was 6.1×10^3 cm$^{-1} \leq q \leq 2.4 \times 10^5$ cm^{-1}, and the samples were rotated about their axes at 5 Hz during measurement, so as to average over many orientations. The Rayleigh factors $S(q)$ were determined in absolute
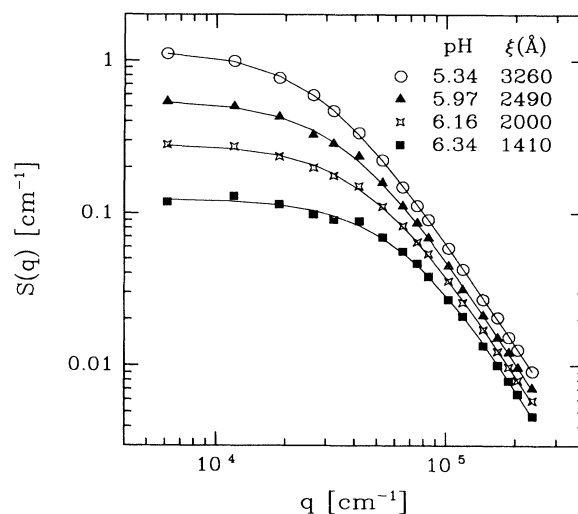
units (cm^{-1}) using toluene as a calibration standard. Small corrections for stray light were made by subtracting the scattering observed for sample tubes containing only water.

The data were well fitted by the form [11]

$$S(q) = \frac{S(0)}{[1 + q^2 \xi^2]^{(D-1)/2}} \frac{\sin[(D-1)\tan^{-1}(q\xi)]}{(D-1)q\xi}, \quad (1)$$

with deviations of a few percent. The adjustable parameters were $S(0)$, D, and ξ. Figure 1 shows data and fits for gels spanning the entire volume fraction range studied, where all samples were gelled at pH 5.7 ± 0.1. Figure 1 shows that both $S(0)$ and ξ increase strongly with decreasing volume fraction. However, neither $S(0)$ nor ξ is determined solely by volume fraction. Figure 2 shows data and fits for a series of 0.46×10^{-2} gels grown from solutions with $5.34 \leq pH \leq 6.34$. At fixed volume fraction, $S(0)$ varies by a factor of 10 and ξ by more than a factor of 2 over this range of pH.

The value of the fractal dimension D is also dependent on volume fraction and pH, but, to within our limited accuracy, seems to be uniquely related to ξ, as shown by Fig. 3. For large ξ, D approaches 2.1, consistent with reaction limited cluster aggregation. For smaller ξ, D rises; the results are consistent with the value $D = 2.4$ observed for aerogels [8] having ξ less than 300 Å. Based on these results, we fixed D at 2.30 for the gels with $\phi = 0.92 \times 10^{-2}$ and 2.35 for gels with $\phi = 1.86 \times 10^{-2}$. At these higher volume fractions, the results obtained for $S(0)$ and ξ were in fact very insensitive to the value assumed for D. Because of the limited q range of our apparatus, we were unable to extract values for ξ or D for gels hav-
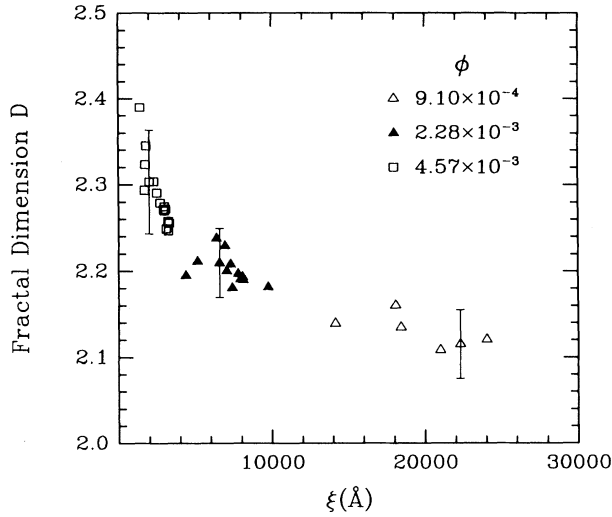
FIG. 3. Trend for the fractal dimension of hydrogels as a function of the crossover length. Typical error bars are also shown.

FIG. 4. Log-log plot of $S(0)/\phi^2\Gamma(D)$ vs crossover length for hydrogels. The data are consistent with a cubic dependence on ξ.

ing $\phi > 1.86 \times 10^{-2}$.

Despite the fact that $S(0)$, ξ, and D all vary with volume fraction and gelation conditions, they are related in a simple manner as shown by Fig. 4. This is a log-log plot of $S(0)/\phi^2\Gamma(D)$ vs ξ, and shows that all the data are consistent with

$$S(0) = B\Gamma(D)\phi^2\xi^3, \tag{2}$$

where $B = (1.4 \pm 0.1) \times 10^{18}$ cm^{-4}. Here $\Gamma(D)$ is the gamma function, which varies by less than 15% over the entire range of the data; it is included here only to simplify the correlation function. Equation (2) holds over two decades in the crossover length, with ξ ranging from 200 Å to 2 μm. This result is in accord with the simple model described above which predicts $S(0) \propto \phi^2\xi^3$, regardless of any relationship between ξ and ϕ.

We may use the results displayed in Fig. 4 to obtain the correlation function in absolute units. Since $S(q)$ is determined by fluctuations in the dielectric constant ϵ, which are caused almost solely by fluctuations in the local volume fraction of silica, we can write [12]

$$S(q) = (\pi^2/\lambda^4)(\partial\epsilon/\partial\phi)^2 \int e^{i\mathbf{q}\cdot\mathbf{r}} g(r) d^3r, \tag{3}$$

where $g(r) = \langle\delta\phi(0)\delta\phi(\mathbf{r})\rangle$, λ is the vacuum wavelength of the light, and $\partial\epsilon/\partial\phi = 0.32$ from the Lorentz-Lorenz relation. Using

$$g(r) = A\phi^2 \frac{e^{-r/\xi}}{(r/\xi)^{3-D}} \tag{4}$$

and Eq. (3), we obtain

$$S(0) = 4\pi A\Gamma(D)(\pi^2/\lambda^4)(\partial\epsilon/\partial\phi)^2\phi^2\xi^3. \tag{5}$$
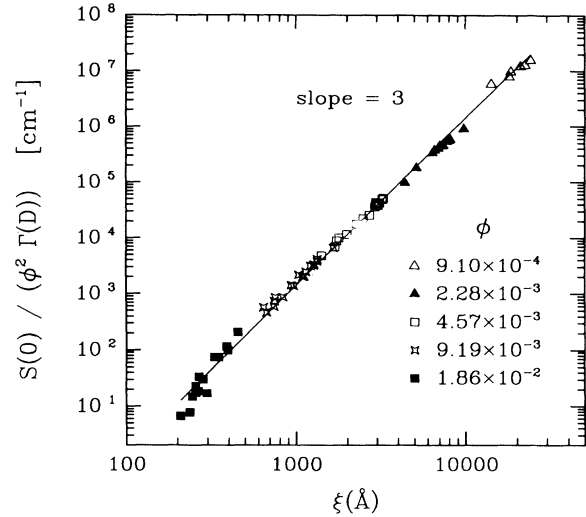
Comparing this to Eq. (2), we conclude that the fluctua-

tions in silica volume fraction for all our gels are well described by Eq. (4), with $A = 1.8 \pm 0.13$.

Of course $g(r)$ does not diverge at $r = 0$. It must approach a limiting value $\langle\delta\phi^2\rangle$, which is easily shown to be $\phi(1-\phi)$, regardless of the spatial distribution of silica. It is instructive to obtain a microscopic length scale by finding the value of r for which $g(r)$ reaches $\phi(1-\phi)$ for the various gels. The results (which are very sensitive to D) range from ~ 2 to ~ 10 Å for the hydrogels, which is not unreasonable considering that aerogels retain their fractal behavior even at scattering wave vectors as large as reciprocal angstroms. One would expect a larger value for colloidal gels which are formed by aggregation of silica spheres rather than grown from solution. To test this idea, we made several such gels from 70-Å-diam colloidal silica in $0.5M$ NaCl solutions. Their Rayleigh factors were well fitted by Eq. (1) and yielded a correlation function given by Eq. (4) with $A = 2.3 \pm 0.2$. The corresponding microscopic length scales ranged from 10 to 25 Å, clearly larger than the values for the hydrogels, but less than half the radius of the individual subunits.

There are striking similarities between various types of silica gels. Figure 5 is a plot of ξ vs ϕ for the hydrogels of this study and three other gels: the colloidal gels studied by Dietler et al. [7], the neutrally catalyzed aerogels studied by Vacher et al. [8], and methanol gels made using TMOS [13]. As may be seen, colloidal gels, aerogels, and hydrogels and methanol gels yielding the largest value of ξ for a given silica content have similar values of ξ for a given ϕ. Furthermore, all of these gels have structure factors of the forms given by Eqs. (1) and (2). Consequently, they all have correlation functions of the form given by Eq. (4), differing only in the value of A. This is very reminiscent of the correlation of order-parameter
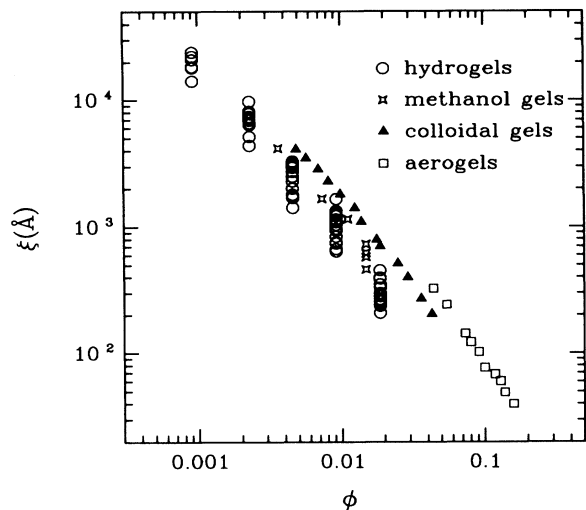
FIG. 5. Log-log plot of crossover length vs silica volume fraction for four different types of gels. The plot clearly shows that there is no unique correspondence between ξ and ϕ for hydrogels and methanol gels. However, when the largest values of ξ (for a given ϕ) are considered, all the gels are apparently very similar.

fluctuations near a 3D Ising critical point. In this case, $g(r) = Ce^{-r/\xi}/r^{1+\eta}$, and ξ diverges as the critical point is approached. There is, however, a very significant difference between the correlation function of the gels and that of a critical fluid. For a given critical system, C is a constant so that $g(r)$ is independent of ξ for $r \ll \xi$, which implies that the fluctuations observed at length scales $\ll \xi$ contain no information concerning ξ. This is not the case, however, for silica gels which are described by the correlation function of Eq. (4), since $\phi^2\xi^{3-D}$ is not constant.

[1] See, for example, Aerogels, edited by J. Fricke (Springer-Verlag, Berlin, 1986); Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing, edited by C. J. Brinker and G. W. Scherer (Academic, San Diego, 1990).

[2] L. W. Hrubesh, T. M. Tillotson, and J. F. Poco, in Better Ceramics Through Chemistry IV, edited by B. J. J. Zelinski, C. J. Brinker, D. E. Clark, and D. R. Ulrich, MRS Symposia Proceedings No. 180 (Materials Research Society, Pittsburgh, 1990), p. 315.

[3] M. H. W. Chan, K. I. Blum, S. Q. Murphy, G. K. S. Wong, and J. D. Reppy, Phys. Rev. Lett. 61, 1950 (1988); G. K. S. Wong, P. A. Crowell, H. A. Cho, and J. D. Reppy, Phys. Rev. Lett. 65, 2410 (1990).

[4] N. Mulders, R. Mehrotra, L. S. Goldner, and G. Ahlers, Phys. Rev. Lett. 67, 695 (1991).

[5] A. P. Y. Wong and M. H. W. Chan, Phys. Rev. Lett. 65, 2567 (1990).

[6] B. J. Frisken, F. Ferri, and D. S. Cannell, Phys. Rev. Lett. 66, 2754 (1991).

[7] G. Dietler, C. Aubert, D. S. Cannell, and P. Wiltzius, Phys. Rev. Lett. 57, 3117 (1986); 59, 246 (1987).

[8] R. Vacher, T. Woignier, J. Pelous, and E. Courtens, Phys. Rev. B 37, 6500 (1988).

[9] D. Avnir and V. R. Kaufman, J. Non-Cryst. Solids 92, 180 (1987); B. Cabane, M. Dubois, F. Lefaucheux, and M. C. Robert, J. Non-Cryst. Solids 119, 121 (1990).

[10] H. R. Haller, C. Destor, and D. S. Cannell, Rev. Sci. Instrum. 54, 973 (1983).

[11] S. K. Sinha, T. Freltoft, and J. Kjems, in Kinetics of Aggregation and Gelation, edited by F. Family and D. P. Landau (North-Holland, Amsterdam, 1984), p. 87.

[12] B. J. Berne and R. Pecora, Dynamic Light Scattering (Wiley, New York, 1976).

[13] These gels were also made in a two step process. In the first stage, TMOS was diluted by methanol to give the correct final concentration and water was added to this mixture in a molar ratio of 1:1 water to TMOS. After stirring, sufficient water was added to bring the final ratio to 8:1 and the pH was adjusted with NaOH solution to be between 7.0 and 8.5.