Comment on "Structure of Silica Gels"

In a recent Letter [1] Ferri, Frisken, and Cannell (FFC) measured the wave vector dependent scattered light intensity, $I(q)$, from silica hydrogels to show mass fractal behavior for length scales less than a crossover length ξ with fractal dimension D. Two important results were (1) an absolute determination of the correlation function as having an exponential cutoff, $g(r) \sim \exp[-(r/\xi)]/(r/\xi)^{3-D}$, and (2) D depended on ξ. This Comment demonstrates that these conclusions are not the only ones consistent with the data, and offers alternatives which describe the data better.

Given the aggregating cluster nature of the precursor gel, we propose to model the gel as an ensemble of clusters with a size distribution that scales with a single length ξ_0. We assume "optical screening" of small clusters possibly trapped within large clusters is not significant because cluster density is a function of cluster size; hence small dense clusters would stand out against the low density, large cluster's background. Furthermore, viewing the gel as an ensemble of clusters is supported by the scaling of the initial volume fraction with the gel correlation length, $\phi_0 \sim \xi^{D-3}$, found earlier [2]. Then the scattered light is given by

$$I(x) = B \int \xi^{2D} S(q\xi) n(\xi/\xi_0) d\xi \,, \tag{1}$$

where $x = q\xi_0$, $S(q\xi)$ is the static structure factor for a single cluster dependent on the cluster correlation function cutoff, and B ensures $I(0)=1$. With (1), one can imagine a two-dimensional space of possibilities involving different combinations of $S(q)$ and $n(\xi)$ to yield a given experimental intensity, $I(q)$ [3].

We have calculated $I(x)$ from Eq. (1) using a scaling size distribution [4] $n(\xi/\xi_0) \sim \xi^{-D\tau} \exp(-\xi/\xi_0)^D$ with $\tau = 1.5$ and an $S(q)$ derived [3] from a Gaussian cutoff correlation function, $g(r) \sim \exp[-(r/\xi)^2]/(r/\xi)^{3-D}$. We call this $I(G, \tau = 1.5)$. Our choice for $n(\xi/\xi_0)$ was motivated by earlier work of Cannell and co-workers [2] on colloidal gels and current understanding of the size distribution in aggregating systems [4,5]. This $I(q)$ is nearly identical (within 1%) to that calculated with $S(q)$ obtained from an exponentially cut off $g(r)$ with length scale ξ, i.e., that used by FFC. This implies that a fit of the data to $I(G, \tau = 1.5)$ would have yielded an equally satisfactory fit. To demonstrate this we simulated data with $D = 2.1$ by calculating $I(G, \tau = 1.5)$ over a broad range of x and fit these data in the same manner as FFC, i.e., varying ξ_0 and D with an exponentially cut off $S(q)$. The fit was excellent with an identical ξ_0 and $D = 2.15$.

The choice of S and n may not be unique. If we simulate data for $D = 2.1$, a Gaussian cluster structure factor, and a scaling distribution with $\tau = 0$, the dependence of D on ξ seen in Fig. 3 of FFC can be recreated. To simulate their fits for the various experimental values of ξ_{exp} we fit the data over several ranges of x corresponding to $x_{min} = q_{min}\xi_0$ to $x_{max} = q_{max}\xi_0$ where now $\xi_0 = \xi_{exp}$ and q_{min} and q_{max} are the actual minimum and maximum values of q used in the experiment (6.1×10^3 cm^{-1} and 2.4×10^5 cm^{-1}). Again the FFC fit used an exponential $S(q)$, and D and ξ_0 were allowed to vary. This shows what their fit would yield if the gel was described by a Gaussian cutoff and a scaling distribution with $\tau = 0$.

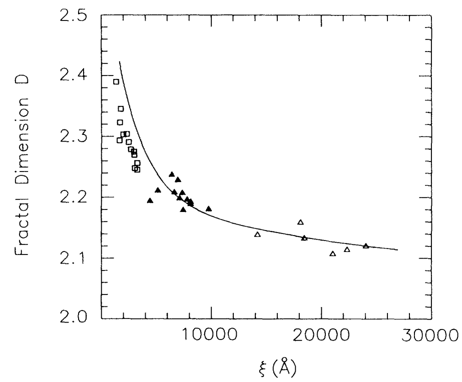

FIG. 1. Data of FFC compared to inferred D vs ξ from simulation (line).

Our result is the solid line in Fig. 1 which recreates their Fig. 3. D varies with ξ despite the fact that the simulation had constant $D = 2.1$. Since the line passes through the data, the obvious inference is that if their data had been fitted with our cluster model using a Gaussian cutoff $S(q)$ and $\tau = 0$ scaling polydispersity *no* dependence of D on ξ would have been obtained.

We remark that it would be valuable for the FFC data to be fit first in the Guinier regime, $q\xi < 1$, where ξ is the only fit parameter and which would yield ξ independent of morphology and model, and then hold this ξ constant while fitting to all the data with D the only variable.

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