

Internal Dynamics and Elasticity of Fractal Colloidal Gels

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The dynamic structure factor of fractal colloidal gels is shown to exhibit a stretched exponential decay to a finite plateau with an exponent of about 0.7. The value of the plateau depends on both initial particle volume fraction ϕ_0 and scattering wave vector. We show that this behavior results from the contribution of internal elastic modes of many length scales, and present a model which accounts for the data. From the observed plateau we determine that the very small elastic modulus scales as $G \sim \phi_0^{3.9}$, in agreement with predictions, and with direct mechanical measurements. [S0031-9007(97)05169-7]

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Colloidal aggregates form fascinating structures; despite the apparent disorder of their shape, they possess a remarkable degree of symmetry, and can be well described as fractals [1]. This scale invariance has facilitated the description of their structure and its relationship to the kinetics of their formation [2]. One of the unique features of a fractal structure is that its density decreases as its size grows; as a result, colloidal aggregates ultimately gel to form a very weak solid, comprised of a connected, disordered network that fills all space [3–5]. If the aggregation is predominantly diffusion limited, the average clusters that form the gel are surprisingly uniform in size, resulting in a strong peak in the static light scattering intensity at low angles [3,5]. By contrast, if the aggregation is reaction limited, the large polydispersity in the cluster size precludes the low angle scattering peak [4]. Suspensions with exceedingly low initial particle volume fraction ϕ_0 can gel, provided buoyancy matched particles are used to avoid sedimentation. The resultant solid is a very interesting material; although it is a highly disordered network, the scale invariant structure is nevertheless well determined. This makes colloidal gels ideal models for the study of the internal dynamics and related mechanical properties of disordered networks in general. Unfortunately, however, such gels are so weak that it is very difficult to measure their properties with mechanical techniques.

In this Letter, we overcome this experimental limitation by using dynamic light scattering (DLS) to measure the internal dynamics of fractal colloidal gels, and develop a model that allows us to determine their mechanical properties. We show that colloidal gels exhibit unusual behavior. At early times the dynamics appear as anomalous or “stretched” diffusion with an exponent independent of scattering wave vector q or initial particle volume fraction ϕ_0 ; this is in sharp contrast with polymer gels, where stretched diffusive behavior is observed only after an initial regime of simple exponential decay [6,7]. For colloidal gels, it is still possible to define an effective diffusion coefficient, which scales as q^{-2} ; this is in sharp contrast with DLS from internal motions of polymers,

where a q^{-3} behavior is expected [8]. For colloidal gels formed from higher ϕ_0 , the dynamics saturate at a plateau whose value depends on q . We develop a local-mode analysis which sums all contributions to the motion and correctly accounts for all the unusual behavior. Moreover, this model enables us to use light scattering to determine the very weak elastic modulus of the gel G . The value so determined is in excellent accord with that measured by traditional mechanical means for gels with high ϕ_0 , while the measured scaling $G \sim \phi_0^{3.9}$ is in excellent accord with theoretical expectations.

Our gels are formed from polystyrene colloidal particles of radius $a = 9.5$ nm, suspended in a buoyancy-matching mixture of H₂O and D₂O [3,5]. Aggregation is initiated by the addition of MgCl₂ to a final concentration of 6 mM, and is allowed to proceed for several days to ensure complete gelation. We study very weak networks, $1.0 \times 10^{-4} \leq \phi_0 \leq 5.0 \times 10^{-3}$. The gels appear homogeneous; however, gentle shaking of the sample is enough to destroy the gel, causing large cracks in the structure. Static light scattering confirms the cluster structure has a fractal dimension of $d_f \approx 1.9$, intermediate between diffusion- and reaction-limited cluster aggregation [9]. We use DLS to determine the dynamic structure factor $f(q, t)$, properly correcting the data with the average scattered intensity to determine the true ensemble average for more concentrated gels, where the dynamics are not ergodic [10]. Because the clusters are constrained by the network, the preponderance of the contribution of translational and rotational diffusion is eliminated, and DLS is sensitive to internal dynamics of the clusters.

Typical results are shown in Fig. 1, where we plot $f(q, t)$ for three gels of varying ϕ_0 and for three values of q . In all cases, the smallest q is still larger than that of the peak observed with static scattering, ensuring that we measure the dynamics within the fractal clusters that make up the gel. For larger ϕ_0 , the dynamics are highly arrested, with $f(q, t)$ decaying to a plateau. As shown in Fig. 1(a), for the stiffest gel, with $\phi_0 = 5.0 \times 10^{-3}$, the height of this plateau exceeds 0.85 even at correlation times beyond 100 s. Moreover, as shown in the inset,

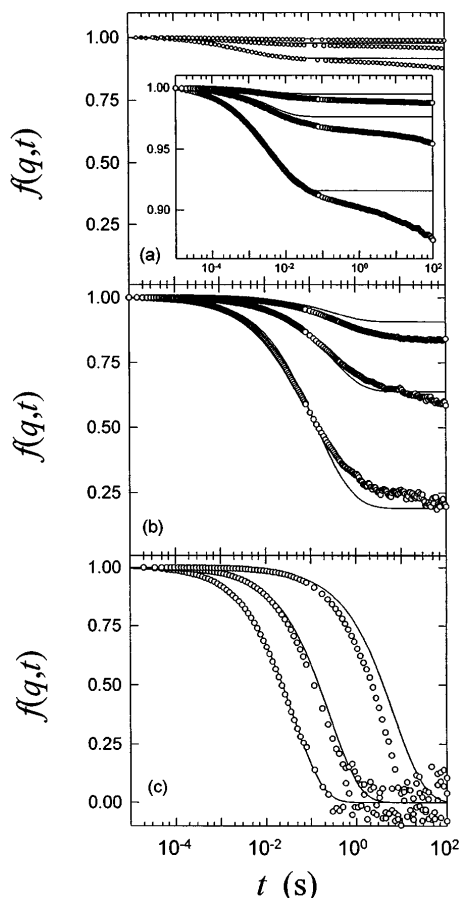


FIG. 1. Dynamic structure factors $f(q, t)$ of fractal colloidal gels for different ϕ_0 and q ; (a) $\phi_0 = 5.0 \times 10^{-3}$, and $q = 4.1, 8.7,$ and $16.7 \mu\text{m}^{-1}$ from top to bottom; smooth curves are theoretical fits yielding $\delta^2 = 1.9 \times 10^{-3} \mu\text{m}^2$ and $\tau = 3.9 \times 10^{-3} \text{ s}$; (b) $\phi_0 = 1.5 \times 10^{-3}$; $q = 4.1, 8.7,$ and $16.7 \mu\text{m}^{-1}$; $\delta^2 = 3.5 \times 10^{-2} \mu\text{m}^2$, $\tau = 0.36 \text{ s}$; and (c) $\phi_0 = 1.7 \times 10^{-4}$; $q = 4.1, 12.1,$ and $22.3 \mu\text{m}^{-1}$; $\delta^2 = 13 \mu\text{m}^2$, $\tau = 1850 \text{ s}$.

the plateau height decreases markedly with increasing q . Similar behavior is observed with decreasing ϕ_0 , except the plateau height decreases, as shown in Fig. 1(b), for $\phi_0 = 1.5 \times 10^{-3}$. By contrast, for gels with the lowest ϕ_0 , $f(q, t)$ decays completely at all q , as shown in Fig. 1(c) for $\phi_0 = 1.7 \times 10^{-4}$.

The characteristic time scales of the decay of $f(q, t)$ also vary dramatically with ϕ_0 . At the higher ϕ_0 , when the decay is arrested, the decay time is essentially independent of q . By contrast, at the lowest ϕ_0 , the characteristic decay time is a strong function of q , decreasing by two decades as q increases from 4.1 to $22.3 \mu\text{m}^{-1}$. Furthermore, in all cases, the decay of $f(q, t)$ is not exponential, but instead extends over several decades in time. This behavior is most evident when the data are plotted semilogarithmically; the initial logarithmic slope, or first cumulant, diverges even at the very earliest time scales. Instead, the data are well described by a stretched exponential. Furthermore, for

lower ϕ_0 the data exhibit a striking scaling behavior, as shown in Fig. 2, where we plot $f(q, t)$ logarithmically as a function of the dimensionless parameter $D_p q^2 t^p$. The data for all q scale onto a straight line. The exponent, chosen to give the best linear behavior for all the data, is $p = 0.66$. This behavior contrasts sharply with DLS from fractal aggregates before they gel, where translational and rotational diffusion combine to produce correlation functions with well-defined first cumulants [11]. The q^2 dependence allows us to define an effective diffusion coefficient D_p , provided we use the stretched time t^p . This highly unusual behavior is in sharp contrast with that observed with DLS from internal motion of polymers, where the decay time typically exhibits a q^{-3} behavior; a factor of q^{-2} arising from diffusive relaxation, and an additional factor of q^{-1} arising because the scattering vector sets the length scale of relaxations probed [8]. Thus, the dynamics of colloidal gels are significantly different than any previous observations.

To understand this highly unusual behavior, we consider a simple physical picture of the scattering from colloidal gels. Because of the disordered structure, DLS probes the dynamics of segments of the gel with a length scale of $\xi \sim q^{-1}$, measuring their mean square displacement $\langle \Delta r_\xi^2(t) \rangle$ through $f(q, t) = \exp\{-q^2 \langle \Delta r_\xi^2(t) \rangle / 6\}$. However, the excursion of each segment is constrained because it is attached to the rest of the gel. For gels with high ϕ_0 , the maximum excursion will be less than q^{-1} and the scattering will not be ergodic leading to the arrested decay observed in the correlation function. By

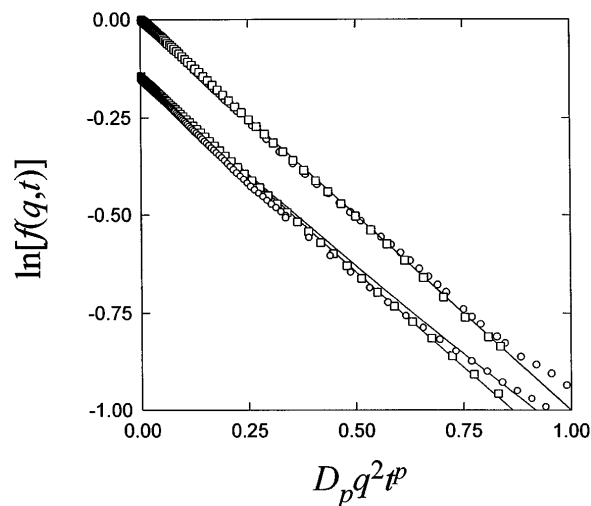


FIG. 2. Scaling of the dynamic structure factors of dilute fractal gels showing stretched-exponential dynamics occur down to the earliest delay times. The smooth curves are computed from Eq. (4); D_p is defined by $\delta^2 / 6\tau^p$ with $p = 0.66$. Upper data and curves: $\phi_0 = 1.0 \times 10^{-4}$; $q = 8.2 \mu\text{m}^{-1}$ (circles) and $q = 15.8 \mu\text{m}^{-1}$ (squares); $\delta^2 = 55 \mu\text{m}^2$, $\tau = 1.4 \times 10^4 \text{ s}$. Lower data (offset for clarity): $\phi_0 = 7.0 \times 10^{-4}$; $q = 10.8 \mu\text{m}^{-1}$ (circles) and $q = 22.3 \mu\text{m}^{-1}$ (squares); $\delta^2 = 0.30 \mu\text{m}^2$, $\tau = 6.1 \text{ s}$.

contrast, for gels with lower ϕ_0 , the maximum excursion will be greater than q^{-1} and the scattering will appear ergodic, leading to a complete decay of the correlation function. Because of these constraints, their full excursion must reflect the elasticity of the gel.

The motion of each segment of length ξ results not only from thermal fluctuations of the segment itself, but also from the thermal motion from any larger segment to which it is attached within the cluster. The fluctuations can, in principle, be calculated through analysis of the normal modes of the fractal. However, normal modes extend across the whole cluster whereas, because of the fluid, all fluctuations are overdamped, and hence localized to a length s ; thus, we must sum over the localized modes of all lengths greater than ξ to determine $\langle \Delta r_{\xi}^2(t) \rangle$. To do so, we take the contribution of a mode of length s as

$$\langle \Delta r_{\xi}^2(t) \rangle_s = \frac{2k_B T}{n(s)\kappa(s)} \{1 - e^{-t/\tau(s)}\}. \quad (1)$$

Here the fluctuation is constrained to a maximum amplitude, and relaxes exponentially with a size-dependent time scale $\tau(s)$. The amplitude of this localized mode depends on its spring constant $\kappa(s)$, which is size dependent for a fractal object, reflecting the fact that a stretching motion of an aggregate causes the chainlike structure to unbind, rather than stretch [12,13]. The spring constant is given by $\kappa(s) = \kappa_0(a/s)^\beta$, where κ_0 is the spring constant of a bond between two particles within the cluster. As s increases, $\kappa(s)$ decreases, reflecting the greater floppiness at larger length scales. The elasticity exponent is $\beta = 2 + d_B$, where d_B is the bond dimension [14]. The value of β reflects the propensity for loops within the aggregate; as the number of loops increases, the cluster will be less floppy [13]. For diffusion-limited clusters, computer simulations suggest $d_B \approx 1.1$ [14] and we use this value here. The amplitude of the localized fluctuation is determined by equipartition; each normal mode has $k_B T$ of energy. However, a normal mode extends over the whole cluster, while $\langle \Delta r_{\xi}^2(t) \rangle_s$ reflects the motion due to a localized mode; thus the fraction of the mode energy localized within the region of size s is reduced by the number of regions of this size, $n(s) = N_c(a/s)^{d_f}$, where N_c is the number of particles in the average cluster. Finally, the time constant is determined by viscous relaxation $\tau(s) = 6\pi\eta s/\kappa(s)$, where η is the viscosity of the fluid; the scaling is $\tau(s) = \tau_0(s/a)^{\beta+1}$, where $\tau_0 = 6\pi\eta a/\kappa_0$ is the relaxation time for the motion of a single particle. The longest relaxation time is that of the cluster $\tau_c = \tau_0(R_c/a)^{\beta+1}$. Integrating over fluctuations of all lengths using the density of modes $-dn(s)/ds$, we have

$$\langle \Delta r_{\xi}^2(t) \rangle = 2d_f k_B T \int_{\xi}^{R_c} \frac{ds}{s\kappa(s)} \{1 - e^{-t/\tau(s)}\}. \quad (2)$$

The lower limit of the integral is $\xi = q^{-1}$; this can be extended to zero since motion on shorter length scales

has an exceedingly small amplitude, thus contributing a negligible amount to the integral.

Equation (2) can be evaluated analytically, yielding an expression with a sum of complete and incomplete gamma functions; in the limit of short times, $\langle \Delta r_{\xi}^2(t) \rangle \sim (t/\tau)^p$, with $p = \beta/(\beta + 1) \approx 0.76$, consistent with the stretched-exponential behavior observed. However, to compare to our data, which extend over the full range of decay, it is more convenient to evaluate it numerically and note that the result is well approximated by

$$\langle \Delta r_{\xi}^2(t) \rangle = \delta^2 [1 - e^{-(t/\tau)^p}], \quad (3)$$

where $\delta^2 = 2d_f k_B T (R_c/a)^\beta / \beta \kappa_0$. We adjust $\tau = b\tau_c$ and p for the best accuracy and find $b = 0.35$ and $p = 0.70$. This form exhibits the expected behavior, increasing like t^p at short times and attaining a plateau at long times. The hierarchy of fluctuations on all length scales leads to the stretched exponential decay. Both the characteristic relaxation time and the maximum mean square displacement are determined by the average clusters of size R_c ; thus the floppiest and slowest modes dominate the behavior and characterize the dynamics of the gel. By contrast, the slow modes make only a small contribution to the motion at short times, resulting in the apparent q^2 dependence of the initial decay of the correlation function. Finally, as ϕ_0 increases, the gels become more rigid and δ^2 decreases, leading to the arrested decay.

We fit all the data for each concentration using Eq. (3) to obtain the optimum values of p , δ^2 , and τ ; the fits are shown by the solid lines in Figs. 1 and 2. While not in perfect agreement, the fits do capture the behavior remarkably well given that the same fitting parameters are used for all q for each value of ϕ_0 . We find that a single exponent describes all the data, with $p = 0.66$, in good agreement with the expected value of 0.70. In Fig. 3 we plot the ϕ_0 dependence of δ^2 (open symbols) and τ (solid symbols). Values represented by circles apply to more concentrated gels where the arrested decay of $f(q, t)$ is observable and both δ^2 and τ can be obtained from the fit. For the more dilute gels, the exponentially small plateau cannot be resolved; we therefore assign δ^2 from an extrapolation of its values at higher ϕ_0 , and fit for τ ; the values so obtained are shown as solid squares in Fig. 3, yielding an excellent continuation of the trend set by the concentrated gels. The open squares show those values assigned to δ^2 by extrapolation of the high- ϕ_0 trend. A power-law behavior is observed for both δ^2 and τ ; the solid lines in Fig. 3 are fits to the data, given by $\delta^2 = c_1 \phi_0^{-2.7}$ and $\tau = c_2 \phi_0^{-3.9}$ with $c_1 = 1.1 \times 10^{-9} \mu\text{m}^2$ and $c_2 = 3.5 \times 10^{-12} \text{ s}$. The ratio of these quantities provides a consistency check; it provides an estimate of the average cluster size, yielding $R_c = 0.3a\phi_0^{-1.2}$. This result is in good accord with the prediction $R_c = a\phi_0^{-1/(3-d_f)} = a\phi_0^{-1.1}$ obtained by assuming gelation occurs when the average cluster size grows to uniformly fill space; it is also

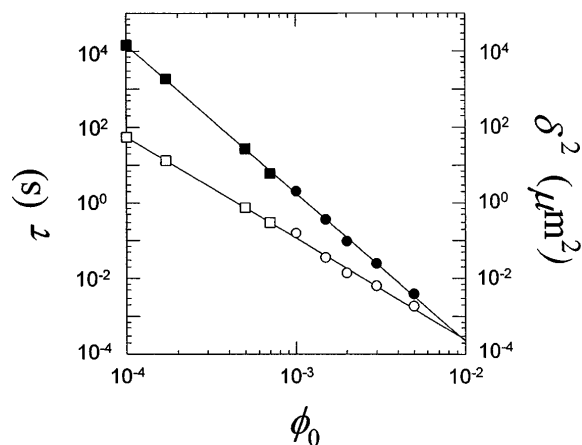


FIG. 3. The parameters δ^2 (open symbols) and τ (closed symbols) as functions of ϕ_0 . Circles: both parameters are adjusted in fits of Eq. (4) to measured $f(q, t)$. Squares: only τ is adjusted while δ^2 is assigned by extrapolation of the fit to the data.

in good agreement with the value determined from the peak in the small angle scattering [3,5].

This model also provides an estimate of the elastic modulus G of the gel; it is determined by the spring constant of the largest clusters $G = \kappa(R_c)/R_c = \kappa_0 a^\beta R_c^{-1-\beta}$. Therefore, the scaling of the modulus with ϕ_0 has the same exponent as τ^{-1} and is given by $G = c_3 \phi_0^{3.9}$, where $c_3 = 1.6 \times 10^{10}$ dyn/cm². The predicted [3,5] scaling of the modulus is $G \sim \phi_0^{-(1+\beta)/(d_f-3)}$, yielding an exponent of 3.7, in excellent accord with the measured value of 3.9. Moreover, the magnitude of the modulus measured by light scattering is also in excellent accord with that measured mechanically with a rheometer for gels with sufficiently high ϕ_0 ; we measure $G = 100$ dyn/cm² for a gel with $\phi_0 = 9.0 \times 10^{-3}$, which compares well with the value of 160 dyn/cm² determined from the light scattering. By comparison, colloidal gels at much higher volume fractions have shear moduli that scale as $G \sim \phi_0^\nu$, with $\nu = 3.5 \pm 0.2$ for diffusion-limited cluster aggregation and $\nu = 4.5 \pm 0.5$ for reaction-limited cluster aggregation [15]; these exponents are consistent with ours.

Finally we note that the data for the lower ϕ_0 gels appear ergodic when the system itself should be nonergodic if the motion of the segment is constrained by the gel. However, we cannot unambiguously determine whether these systems are truly gels solely by light scattering measurements, since the hallmark of a solid is nonergodic motion, while the scattering appears ergodic. Unambiguous confirmation of a solid gel would require collecting scattering data at even lower q to observe nonergodic behavior.

While all the measurements presented here apply directly to colloidal gels, we expect similar behavior to pertain for other random networks. In particular, the elas-

tic modulus of networks of semiflexible actin are anomalously large; moreover the mean square displacement of probe particles within them exhibits a stretched exponential behavior, with an exponent of 0.75 [16], which is exactly what we would predict at short times for linear chains with $d_B = 1$. We note that the exponent measured in our experiments is smaller because we fit the data over the full range of its decay. Thus, it is likely that the origin of the dynamics is the same for colloidal gels and actin networks. More generally, our results represent a method for using light scattering to measure the rheological properties of a complex material. Previous examples relied on a uniform distribution of probe particles [17]; the results here generalize this to the strongly correlated colloidal particles in a gel. However, the basic physics is the same; by probing the response to thermal fluctuations, the elastic modulus is determined.

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