

Universal Aging Features in the Restructuring of Fractal Colloidal Gels

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We use multispeckle dynamic light scattering to measure the dynamic structure factor, $f(q, \tau)$, of gels formed by aggregation of colloids. Although the gel is an elastic solid, $f(q, \tau)$ nearly completely decays on long time scales, with an unusual form, $f(q, \tau) \sim \exp\{-(\tau/\tau_f)^\mu\}$, with $\mu \approx 1.5$ and with $\tau_f \propto q^{-1}$. A model for restructuring of the gel with aging correctly accounts for this behavior. Aging leads to a dramatic increase in τ_f ; however, all data can be scaled on a single master curve, with τ_f asymptotically growing linearly with age. This behavior is strikingly similar to that predicted for aging in disordered glassy systems, offering convincing proof of the universality of these concepts.

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Disordered systems far from equilibrium typically relax very slowly; as a result, response functions that characterize equilibrium material properties behave in a highly unusual way. If the response functions are measured over a relatively short period of time, they sample quasiequilibrium properties over the measurement period; however, they can vary substantially if they are measured at a different time, as the material will have relaxed, or aged, to a new state. Often, the decay time of correlation functions depends on the waiting time after the system is first quenched, t_w , reflecting the aging of the material, and complicating considerably the study of its properties. However, aging effects are predicted to exhibit some surprisingly universal features: the dynamics of the system slow down with age, but response functions can nevertheless be scaled onto a single master curve [1–3]. The physical picture that underlies these predictions is that the system becomes trapped in a local minimum of some generic energy landscape, with the time to escape from the deepest local minimum dominating the response functions; this time is ultimately a significant fraction of t_w , leading to the observed aging phenomena. The effects of aging on response functions, such as the viscoelasticity, have been studied extensively [1]; however, the consequences of aging on the dynamic structure factor, which is the most direct measure of aging effects, have been explored almost exclusively in theoretical [3] and simulation [2] work on disordered glassy samples. While there have been some studies of aging in colloidal glasses [4], there is a dearth of experiments to directly test these concepts on structural relaxation, and to test their generality and applicability to other materials.

In this Letter, we present the results of an investigation of aging of colloidal gels. There are suggestions that colloidal gelation can exhibit similarities to the colloidal glass transition [5]; here we show that colloidal gels exhibit aging behavior similar to that predicted for glassy samples. We measure ultra-low-angle static and dynamic light scattering (SLS and DLS, respectively) at

many scattering vectors simultaneously, spanning almost two decades: $100 \text{ cm}^{-1} < q < 7000 \text{ cm}^{-1}$ [6]. For DLS, we take advantage of the multispeckle technique [6] to reduce the measurement time to the longest delay in the dynamic structure factor $f(q, \tau)$, a factor 10^3 to 10^4 less than that required in a traditional experiment; this allows “snapshots” of the dynamics to be taken, thereby directly probing the aging. We find that $f(q, \tau)$ initially decays by only a few percent to a plateau, as expected for a gel whose vibrational modes are thermally excited [7]. However, on time scales of several hours, a complete decay of $f(q, \tau)$ is observed; strikingly, this final decay is faster than exponential. In addition, the dynamics strongly depend on the age of the gel t_w , with the characteristic relaxation time τ_f increasing by more than 2 orders of magnitude as the sample ages. However, τ_f asymptotically becomes nearly linear with t_w , and all the data can be scaled onto a single master curve; this is exactly as expected within the universal picture for aging. We present a model, based on restructuring of the gel due to shrinkage, that correctly accounts for this unusual behavior. These experiments offer the first direct, full characterization of the evolution of the structure of an aging material, and provide convincing support of the validity and generality of many of the universal features predicted.

The gels are prepared by aggregating polystyrene colloids of radius $a = 10.5 \text{ nm}$, at volume fractions $10^{-4} < \varphi < 10^{-3}$. They are suspended in a buoyancy-matching mixture of H_2O and D_2O [8], to prevent the collapse of the tenuous network due to gravity. Aggregation is induced by adding MgCl_2 to a final concentration of 16 mM. In Fig. 1 we show the time evolution of the scattered intensity $I(q)$, after initiating the aggregation of a sample with $\varphi = 4.8 \times 10^{-4}$. From the high- q behavior of $I(q)$ we determine a fractal dimension $d_f = 1.82$ immediately after gelation, consistent with diffusion-limited cluster aggregation (DLCA) [9]. The characteristic peak in the scattering at small q is due to the relatively monodisperse size distribution of clusters near gelation [8]; at early times, the shift

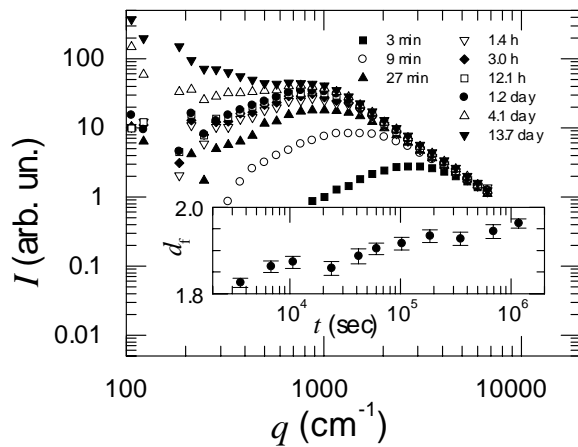


FIG. 1. Static scattered intensity time evolution for a colloidal gel with $\varphi = 4.8 \times 10^{-4}$. Curves are labeled by the time elapsed after initiating the aggregation. Inset: Time dependence of the fractal dimension. Gelation occurred at $t \approx 6000$ sec.

to smaller q and the increase in the height of the peak reflect the growth of the clusters. After about 2 h, the static light scattering stops evolving in time, indicating that a space-filling network of interconnected fractal clusters has been formed. The peak position q_{\max} is related to the radius R_c of the clusters forming the gel by $q_{\max} \approx 1/R_c$. The static light scattering from this gelled structure exhibits little change over several tens of hours: the peak position is fixed and only a small growth of the intensity for $q < q_{\max}$ and a slight increase in d_f are observed (see inset of Fig. 1). Remarkably, however, after several days, the very low- q intensity increases by a factor of 10, and the peak almost disappears, as shown by the last two data sets in Fig. 1. The increase in d_f suggests that the gel becomes more compact [10]. Eventually, this compaction is accompanied by the development of inhomogeneities on large length scales, resulting in the large increase in scattered intensity observed at very low q . Indeed, “lumpy” regions are clearly visible by eye at the later stages.

To follow the aging of the network, we use DLS to probe the gel dynamics near the peak in the structure factor. Typical results are shown in Fig. 2, where we plot $f(q, \tau)$ for a gel with $\varphi = 5 \times 10^{-4}$, measured 67 hours after gelation. We define $t_w = 0$ by the gelation time, determined from the time of the arrest in the shift of the peak of the static light scattering. The $f(q, \tau)$ exhibit an initial decay to a very high plateau that extends for more than two decades in τ . However, despite the solidlike rheological behavior of the gel [7,11], at very long times, the data exhibit an unexpected final decay, even at scattering vectors comparable to q_{\max} , indicating that the dynamics extend to length scales up to R_c . Interestingly, very little change in the structure is detected by SLS on time scales comparable to the relaxation times measured by DLS. The shape of the correlation functions is quite unusual: their decay is faster than exponential, and they depend on the product $q\tau$. We show this by plotting the final decay of

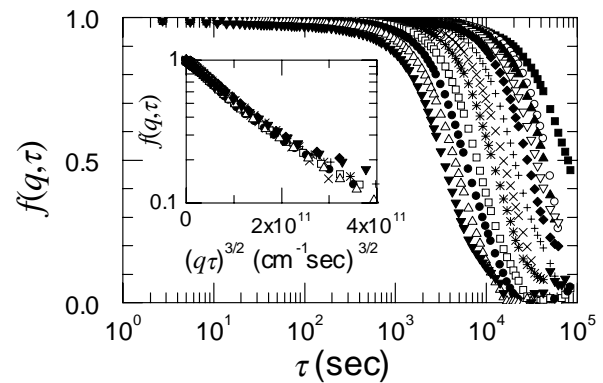


FIG. 2. Dynamic structure factors $f(q, \tau)$ for a colloidal gel with $\varphi = 5 \times 10^{-4}$. From right to left, q varies from 249 cm^{-1} to 6745 cm^{-1} . Inset: $f(q, \tau)$ vs $(q\tau)^{3/2}$, for $q > q_{\max}$.

$f(q, \tau)$, for all $q \geq q_{\max}$, logarithmically as a function of $(q\tau)^\mu$, with $\mu \approx \frac{3}{2}$. As shown in the inset of Fig. 2, all the data scale together on a straight line; therefore, for large τ , $f(q, \tau) \propto \exp[-(\tau/\tau_f)^{3/2}]$. A similar stretched exponential form also describes the data for $q < q_{\max}$, although the quality of the data is not as good. The q dependence of τ_f can be determined by plotting τ_f/τ_{\max} , where $\tau_{\max} = \tau_f(q_{\max})$, as a function of the scaled scattering vector q/q_{\max} . As shown in Fig. 3, all the data for different times and φ collapse onto a single curve, allowing a precise determination of the behavior. We find $\tau_f \propto q^{-1}$ for $q > q_{\max}$, as implied by the scaling shown in Fig. 2, with a much weaker dependence for $q < q_{\max}$. The limited frame rate of the charge-coupled device (CCD) and the height of the plateau, which is close to unity at the lower q , do not allow us to study the short time behavior of $f(q, \tau)$ in detail. Nevertheless, analysis of data for gels at lower concentrations, where the plateau is lower, shows that the initial decay rate scales as q^2 , and the plateau height varies as $\exp(-q^2\delta^2/6)$, where δ is the φ -dependent maximum excursion of a particle in the network, due to thermal excitation of elastic modes [7].

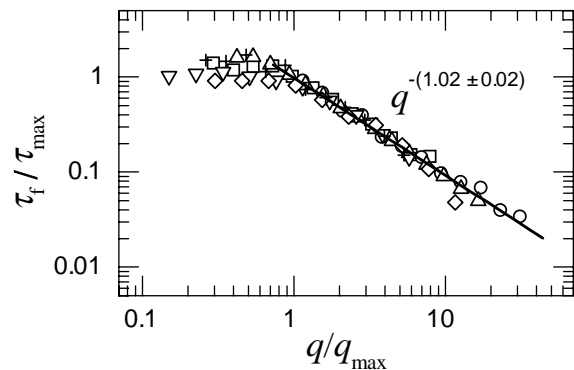


FIG. 3. Scaled final decay time of the dynamic structure factor, τ_f/τ_{\max} [$\tau_{\max} = \tau(q_{\max})$], as a function of scaled scattering vector q/q_{\max} , for colloidal gels with $10^{-4} < \varphi < 10^{-3}$. The line is a power law fit of the data for $q > q_{\max}$.

The evolution in the static light scattering from the gel is accompanied by a dramatic slowdown of the dynamics with sample age, as shown in Fig. 4, where we plot $f(q, \tau)$ for a single scattering vector, $q = 6756 \text{ cm}^{-1}$, but for different ages, for a sample with $\varphi = 4.8 \times 10^{-4}$. Similar behavior is observed for all scattering vectors, with the q dependence of τ_f preserved throughout the aging. The relaxation time increases by more than 2 orders of magnitude, while the plateau preceding the final decay of $f(q, \tau)$ becomes flatter and its height increases; this suggests that G' is increasing with age as a result of the restructuring [1,7]. However, the shape of the decay of $f(q, \tau)$ remains essentially the same; indeed, data for different t_w can be scaled onto a single master curve by plotting $f(q, \tau)$ as a function of τ/τ_f , as shown in the inset of Fig. 5. This behavior is characteristic of the universal picture for aging [2,3]. To further investigate this aging, we show the evolution of τ_f with t_w in a logarithmic plot in Fig. 5. Initially, τ_f grows nearly exponentially, while for large t_w the growth rate decreases, ultimately becoming approximately linear, $\tau_f \sim t_w^\nu$, with $\nu = 0.9 \pm 0.1$. This behavior is also characteristic of the universal picture for aging. Thus, these results confirm that the model for aging applies to colloidal gels, and that the universal features predicted are observed experimentally.

Interestingly, a temporary but pronounced decrease in τ_f is observed at long times, indicated by the arrow in Fig. 5; this behavior is reproducible, and corresponds to the first appearance of large inhomogeneities in the sample. This suggests that the restructuring on large length scales is accompanied by the breaking of intercluster bonds, temporarily weakening the network and increasing the decay rate. We note that a similar weakening may also trigger the macroscopic collapse observed for non-buoyancy-matched gels [12].

Any model for the physical mechanism responsible for this aging must correctly account for the unusual q and τ dependence of the data. The q^{-1} dependence of τ_f rules out diffusive motion and suggests instead

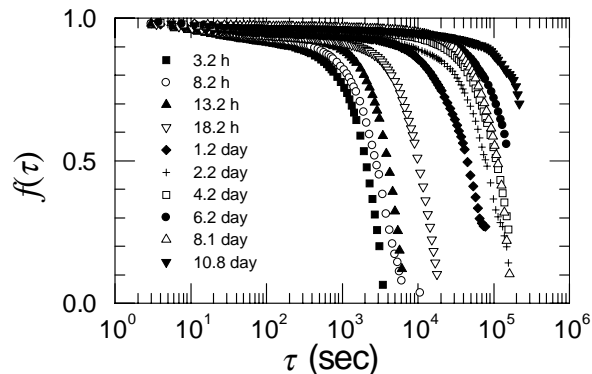


FIG. 4. Time evolution of the dynamic structure factor at $q = 6756 \text{ cm}^{-1}$ for a sample with $\varphi = 4.8 \times 10^{-4}$. Curves are labeled by the gel age t_w .

that a drift mechanism is responsible for the decorrelation of the scattered light, with a drift velocity $v \sim (q\tau_f)^{-1} \approx 5 \times 10^{-8} \text{ cm sec}^{-1}$ immediately after gelation. However, we found no differences in the decay for samples more poorly buoyancy matched and for wave vectors parallel or perpendicular to the direction of gravity; thus, we rule out sedimentation. We also rule out propagation of phonons in the solid network; the resultant elastic modulus, $G' = v^2/\rho \sim 10^{-15} \text{ dyne/cm}^2$, is many orders of magnitude less than the measured value of $G' \sim 10^{-3} \text{ dyne/cm}^2$, obtained from the plateau of $f(q, \tau)$ [7] and from mechanical measurements on similar structures [11]. Finally, thermally induced formation of new bonds, or breaking of old bonds in the network would result in a random process of rare, uncorrelated events, which would lead to an exponential decay, and thus must also be ruled out. Thus, a new mechanism is required to correctly explain the observed dynamics.

To account for the unusual q and τ dependence of $f(q, \tau)$, we introduce a new model for the dynamics based on the syneresis of the gel, the shrinking commonly observed for polymer gels when the solvent quality becomes poorer and incipient phase separation ensues [13]. Syneresis would cause the gel to shrink continuously and uniformly with time; however, adhesion to the cell walls prevents macroscopic shrinking. Instead, the gel shrinks locally and its inhomogeneity results in random regions of higher deformation; because the gel is elastic, there is a displacement field around each of these deformations. These inhomogeneities can then be regarded as localized forces that deform the network. Since no external net force is applied, each inhomogeneity acts as a force dipole. Thus, the displacement field ΔR a distance r from

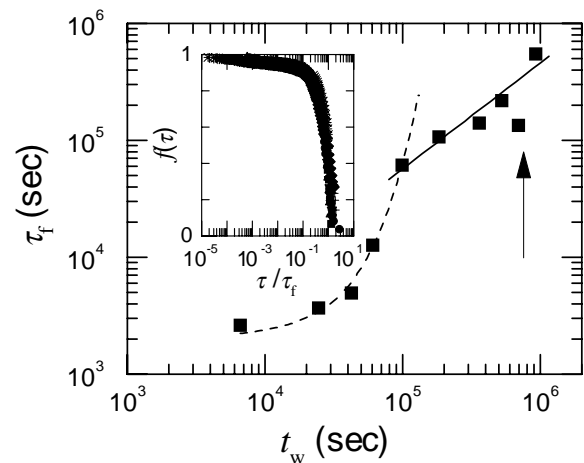


FIG. 5. Age dependence of τ_f from the data of Fig. 4. The dotted line is the fit of an exponential growth to the data for $t_w < 10^5 \text{ s}$. The straight line is a power-law fit of the late stage, yielding an exponent of 0.9 ± 0.1 . The arrow indicates the temporary decrease in the relaxation time discussed in the text. This point was not included in the fit. Inset: Scaling of the data of Fig. 4

an inhomogeneity of size ξ falls off one power of r faster than that due to a point force [14], namely as r^{-2} . We take ΔR to be proportional to the strain $e(\tau)$ which would have occurred in a time τ if the sample were allowed to shrink macroscopically,

$$\Delta R \sim e(\tau)\xi^3/r^2 \sim e(\tau)R_c^3/r^2, \quad (1)$$

for $r \gg \xi$, and where we have set $\xi = R_c$, since the fractal gel is inhomogeneous up to R_c and it is the largest inhomogeneity that will dominate. To evaluate the effect of the displacement field on the measured correlation function, we calculate the fraction of particles in the gel that contribute scattering with time *correlated* intensity after a delay τ ; these are scatterers for which the displacement is less than q^{-1} . Particles close to an inhomogeneity will have moved, and thus not have contributed correlated scattering; therefore only particles a distance from the closest inhomogeneity larger than a threshold value r_{\min} , such that $\Delta R < q^{-1}$, can contribute, giving

$$r_{\min} = [e(\tau)qR_c^3]^{1/2}. \quad (2)$$

We assume that the inhomogeneities are randomly distributed with number concentration c , assumed to be low, so that the probability $P(r_{\min})$ for an arbitrary point of the gel to be at a distance larger than r_{\min} from any inhomogeneity is

$$P(r_{\min}) = \exp[-cr_{\min}^3] = \exp\{-c[R_c^3e(\tau)q]^{3/2}\}, \quad (3)$$

and $f(q, \tau) \propto P(r_{\min})$. Finally, we assume that the strain increases linearly in time, $e(\tau) = \alpha\tau$, giving $f(q, \tau) \propto \exp[-(\tau/\tau_f)^{3/2}]$, with $\tau_f = c^{-2/3}(R_c^3\alpha q)^{-1} \sim q^{-1}$. This form correctly captures both the q and the τ dependence of the measured dynamic structure factor for $q > q_{\max}$. For $q \leq q_{\max}$, the length scale of motion required to cause decorrelation becomes longer than R_c ; this requires the particles to be close to the inhomogeneity, where the far-field dipole approximation is no longer valid, presumably accounting for the observed change in behavior.

Qualitative support for this picture is provided by the experimental observation that samples prepared in round cells which are gently spun, thereby detaching the gel from the cell wall without breaking it, do indeed exhibit syneresis, shrinking by a factor of at least 2 in length scale. By contrast, undisturbed samples do not shrink macroscopically, due to the adhesion of the gel to the cell walls. On a microscopic level, the origin of the syneresis is most likely the sintering of aggregated particles, due to the strong van der Waals attraction acting on the relatively soft polystyrene colloids. Electron microscopy confirms that freshly

aggregated particles retain their individuality, while the particles in aged samples are fused together, resulting in a pronounced decrease in their center-to-center separation.

The observation of the age dependence of the dynamics in colloidal gels confirms that the underlying physics does provide a very general description of these effects which should be applicable to a wide variety of materials. The analogies between the aging of colloidal gels and that of many glassy materials are intriguing [5]; more experiments are required to test the generality of these aging phenomena. However, gelation for most colloidal particles is disrupted by gravitational collapse [12]; thus microgravity experiments are required to study the aging of gels made from most other colloidal materials [15].

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