Relaxations in Gels: Analogies to α and β Relaxations in Glasses

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We present dynamic light scattering data which show that aqueous gelatin gels display a power-law relaxation to a nonergodic background. In the pregel sol this power law is terminated by a stretched exponential which restores ergodicity and which has a q dependent characteristic time proportional to the viscosity. The power-law exponent is q dependent and related to a characteristic length in the gel. Except for the q dependences these behaviors are similar to the α and β relaxation behavior in glasses. It is proposed that the different q dependences of the gels and glasses is a result of different characteristic length scales.

Relaxation phenomena in amorphous systems, gels and glasses, is an area of current active interest [1–3]. In glasses, these phenomena have held a long and abiding interest which has intensified lately due to the advent of the mode coupling theory (MCT) of the glass transition [4–7]. MCT predicts two relaxations for glassy systems which have been identified as the α and β relaxations long known to be present [8]. Under the guidance of MCT, the picture that has developed, and is substantiated by experiment [9–12], is that below the glass transition temperature only a power-law β relaxation to a nonergodic background exists [9–11]. Above T_g, the strongly temperature-dependent α relaxation restores ergodicity to the long time part of the β relaxation via a stretched exponential decay.

Gel systems have been less extensively studied. For some time it has been recognized that an exponential relaxation occurs that can be described as due to thermally excited density fluctuations that are dissipated via continuum mechanics [13]. It was thought that only this so-called gel mode exists. Recent dynamic light scattering (DLS) measurements on both colloidal and polymeric gels have shown a second, power-law relaxation after the gel mode [14–16]. Also recently, Joosten and co-workers [17,18] have shown that polymeric chemical gels are nonergodic whereas the sol is ergodic.

Of course, a number of obvious similarities exist between glasses and gels: both are amorphous solids, for physical gels both can be reversibly melted, and both are a result of some sort of physical arrest of the molecular motion. Thus it is not unreasonable to ask if other similarities exist if we look closer at the physics of these systems.

The purpose of this Letter is twofold. First we present DLS data which show that gelatin gels have a power-law relaxation to a nonergodic background. The power-law exponent is q dependent and hence yields a length scale which is comparable to the screening length of the gel. Furthermore, we show that in the pregel sol ergodicity is restored by a stretched exponential decay. With this new knowledge, we then make comparisons between gels and

similar results for glass systems to propose these relaxations are analogous to the β and α relaxations, respectively, found in a glass. The analogy is imperfect for light scattering measurements for both systems because our gel relaxations show q dependences, whereas the glass relaxations do not. Recent quasielastic neutron scattering data on glasses, however, show the same q dependence as do our gel data. Since light and neutron scattering operate at significantly different length scales, we propose that an important difference between glasses and gels lies in a characteristic length scale of the system.

Gelatin (300 bloom, Aldrich, $M_w = 1.2 \times 10^5$) solutions, which form physical, i.e., thermally reversible gels, were made up by weight in purified water. The solutions were carefully filtered through 0.22 μm filters, heated to 45°C for ~1 h in 1 cm^2 cuvettes, and then quenched to 25°C where set gels formed. After a 2-d equilibration period, dynamic light scattering was performed using a multitau, ALV-5000 digital correlator. Care was taken to ensure good spatial coherence on the detecting photocathode by imaging with a lens the scattering volume onto a 100 μm pinhole 50 cm in front of the cathode and ensuring the incident laser light (Ar$^+$, $\lambda = 514.5$ nm) was in the TEM$_{00}$ mode [19,20]. Scattering from polystyrene microspheres showed our coherence factor to be 0.94 (1.0 is perfect).

The desired experimental quantity is the dynamic structure factor which is related through a Fourier transform to the space-time density correlation function of the system. A problem arises in both gels and glasses in that as structural arrest sets in, the system may no longer be ergodic. Correlators determine time average correlations of the scattered light which for a nonergodic system will not be equal to the ensemble average. This problem was first recognized and addressed by Pusey and van Megen [19] who described in detail how to extract the dynamic structure factor from time averaged correlation data from a nonergodic system. Guided by their work, we have developed an alternative scheme [21] which yields the following results.

As stressed by Pusey and van Megen, the scattered light field from a nonergodic medium will have two parts,

$$E(q,t) = E_F(q,t) + E_c(q) , \qquad (1)$$

where E_F is the fluctuating component due to localized motion and E_c is a constant component scattered from the structurally arrested fraction. Our approach treats E_c as a local oscillator for E_F and uses the standard theory of heterodyne detection. The correlator measures the time average intensity correlation function $\langle I(0) \times I(t) \rangle_T$. The time-averaged, normalized correlation function is $g_T^{(2)}(t) = \langle I(0)I(t) \rangle_T / \langle I \rangle_T^2$, and we define $\phi(t) = g_T^{(2)}(t) - 1$. The dynamic structure factor of the fluctuating field (ergodic) is $f_F(q,t) = \langle E_F(0)E_F(t) \rangle / \langle E_F^2 \rangle$. One can then show [21] that

$$f_F(q,t) = \frac{[\phi(t) + 1 - \sigma]^{1/2} - (1 - \sigma)^{1/2}}{1 - (1 - \sigma)^{1/2}} , \qquad (2)$$

where $\sigma = \phi(0)$ parametrizes the nonergodicity and is related to the relative strength of the static scattering [21]. This result also recently has been obtained by Joosten, McCarthy, and Pusey [18]. For $\sigma \ll 1$, $f_F(q,t) \simeq \phi/\sigma$. Equation (2) allows the correlator-measured, time-averaged $\phi(t)$ to be converted to the fluctuating component dynamic structure factor regardless of the degree of ergodicity.

An alternative but equivalent approach is to once again measure $g_T^{(2)}(t)$ and extract the normalized, time-averaged, field correlation $f_{tot}(t)$ of the total field, Eq. (1), with a generalized Siegert relation [21]

$$g_T^{(2)}(t) = \sigma + |f_{tot}(t)|^2 . \qquad (3)$$

Then the fluctuating field correlation function is

$$f_F(q,t) = \frac{f_{tot}(t) - f_{tot}(\infty)}{1 - f_{tot}(\infty)} . \qquad (4)$$

In a nonergodic system $f_{tot}(\infty) \neq 0$ while $f_F(\infty) = 0$.

We are now ready to describe our data. Figure 1 shows $f_{tot}(q,t)$ measured for a 3% gelatin gel at 90° scattering angle and $T = 25°C$. A nondecaying component is clearly shown as f_{tot} levels off at a plateau with

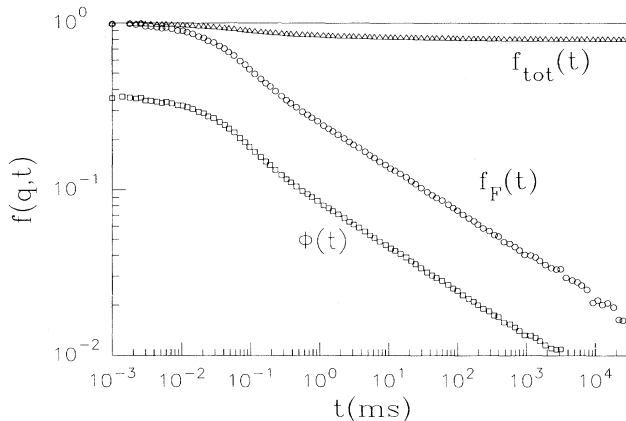$f_{tot}(\infty) = 0.80$. Hence the gel is nonergodic. $f_F(q,t)$ can now be calculated using Eq. (4). Alternatively, we use Eq. (2) with the measured $\phi(t)$ and σ. The two methods yield the same result within experimental error. Figure 1 contains both $\phi(t)$ and $f_F(q,t)$, and one sees $f_F \simeq \phi/\sigma$ to a good accuracy.

Removal of the nonergodic background, $f_{tot}(\infty) = 0.80$, leaves two distinct decays in the fluctuating part: an initial exponential decay followed by a startling power law spanning five decades in time. It is reasonable to assign the exponential part to the gel mode [13]. The power law is relatively new; recent work on gelling systems has shown power-law behavior, but the important result here is that Fig. 1 demonstrates explicitly that the gel relaxes to its nonergodic background with this power-law decay.

We find the exponent of the power law to be both wave vector and concentration dependent. Figure 2 shows the wave vector dependence. Writing the power law as t^{-a}, we find $a = l^2 q^2$, where the proportionality constant l must have units of length. This is consistent with our earlier work on the pregel sol phase of the same system [16]. Furthermore, the l values extracted from $l = q^{-1} a^{1/2}$ are on the order of 100 Å and decrease with gelatin concentration consistent with the manner reported previously [16].

The power-law relaxation to a nonergodic background in the set gel is very similar to the β relaxation in glasses. Both recent experiment and MCT of the glass transition have seen or predicted this exact same behavior for glasses below the glass transition. MCT, however, does not predict a q dependency for the exponent. The experiments on glasses have not tested for this.

The dynamic structure factor obtained from a DLS experiment can be interpreted as the result of diffusional motion. Thus one can show $f_F(q,t) \propto \exp[-q^2 \langle r^2 \rangle]$, where $\langle r^2 \rangle$ is the time-dependent mean-squared displacement of the scatterers. Comparison of this to our experimental result, $f_F(q,t) \propto t^{-a}$ with $a = l^2 q^2$, and assuming Gaussian diffusion leads to the empirical conclusion

$$\langle r^2 \rangle = l^2 \ln(t/t_0) . \qquad (5)$$

FIG. 1. Plot of $f_F(t)$, $\phi(t)$, and $f_{tot}(t)$ for a 3% gelatin gel.
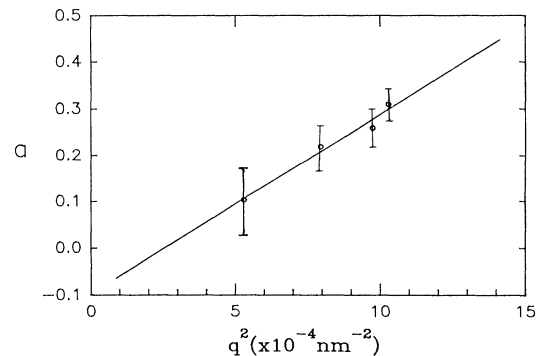

FIG. 2. Power-law exponent a vs q for a 3% gelatin gel.

We proposed [16] that Eq. (5) was due to motion of polymer segments constrained to cages along the reptation tube of the molecules. Hence the dynamic screening length was the relevant length scale and, in fact, l behaves like it. Thus our physical picture for the set gel is one in which polymer segments may move but are ultimately constrained to frozen cages so this relaxation is nonergodic. This same physical picture, that in some manner the diffusing entities in a glass are contained in cages thus inhibiting full ergodic motion, is that currently used by MCT to explain the β relaxation in glasses.

The analogy can be carried further if we melt the gel or glass. In a gel above the gel point or in the quenched pregel liquidlike sol, we found [16] the power-law decay is terminated by a stretched exponential decay. Figure 3 gives new data of this sort obtained with the ALV 5000 correlator, which was not available for our previous work. We found values of $\sigma = \phi(0) = 0.92$, very close to the calibrated value, thus indicating the stretched exponential relaxation restores ergodicity to the sol system. In a glass above the glass transition the same behavior is seen. This similarity is further strengthened by the fact that we found [16] the relaxation time of the stretched exponential scales linearly with the solution viscosity, identical to the behavior found in glasses [9,10]. In the glass case this longer time, stretched exponential decay is called the α relaxation, which MCT ascribes to the relaxation of the cages.

Once again, however, the analogy fails with the q dependence. In glasses light scattering shows the α relaxation to be q independent. On the other hand, our gel work showed a strong q dependence for the characteristic time of the stretched exponential above the gel point. We again argue from an empirical viewpoint that this implies Gaussian diffusion scatterers with
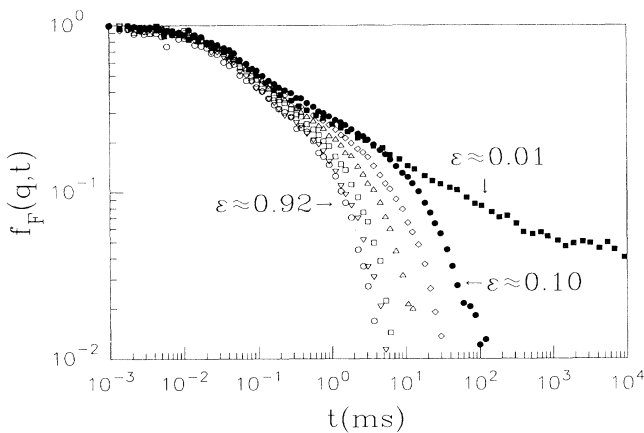
$$\langle r^2 \rangle = Dt^b . \tag{6}$$

FIG. 3. Behavior of $f_F(q,t)$ for a 3% gelatin sol quenched from 45 °C to 27 °C as a function of reduced time, $\epsilon = (t_{gel} - t)t_{gel}^{-1}$, from the gel point.

Equation (6) has a theoretical basis. For $b < 1$ it is anomalous diffusion due to random walk on a fractal lattice [22], and such a lattice is expected near the percolation or gel point [23]. This model gave an excellent description of our previous gel data [16].

We summarize on this point: Both gels and glasses have a power-law relaxation to a nonergodic background (β relaxation) below the glass or gel transition. Above the transition, there is further relaxation of this background to ergodicity via a stretched exponential (α relaxation) with characteristic time proportional to the viscosity. The q dependences, however, in each case do not match.

Recently Colmenero et al. [24] have used quasielastic neutron scattering to measure the dynamic structure factor of three glasses. They found a q dependent, stretched exponential α relaxation for $0.4 \leq q \leq 5$ Å^{-1}. Furthermore, the q dependency was well described by an anomalous diffusion model identical to Eq. (6); i.e., the neutron scattering q dependence for glasses is the same as the light scattering q dependence for our gel. (Similar q dependences in neutron scattering have also been seen by Bartsch et al. for a molecular glass [25].) This suggests the difference between gels and glasses may be one of length scale. The q range of neutrons is 10^2 to 10^3 greater than that of light; hence it probes at a much smaller length scale than light. The relevant length scale in the gel, the dynamic screening length, is on the order of 100 Å, whereas the intermolecular distance between molecules in a glass is a few angstroms. In other words, the cages may be much bigger in gels than in glasses. Recalling that the glass α relaxation measured with light scattering is q independent, we conclude that α relaxation q dependences may only be seen when $ql \gtrsim 1$, where l describes the cage scale. This speculation adheres to data known so far, and suggests the direction for future experiments.

In summary, we have found a power-law relaxation to a nonergodic background in set gelatin gels, the exponent of which is q dependent. In the sol phase this power law is terminated by a stretched exponential which restores ergodicity. This behavior is very similar to the α and β relaxations observed in glasses and predicted by MCT. The light scattering q dependences of these relaxations, however, do not match between gels and glasses, but the neutron scattering q dependence for glasses does match the light scattering q dependence for gels for the α relaxation. This may be due to differences in length scales in these systems.

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