Critical Dynamics of the Sol-Gel Transition

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The dynamics of the sol-gel transition is probed by use of quasielastic light scattering. A type of critical dynamics is observed that is associated with a divergent friction, rather than a singularity in a thermodynamic quantity. Several novel effects are reported, including power-law time decay of the intensity autocorrelation function, critical slowing down of the average relaxation time, and observation of a fractal time set in the scattered field.

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A gelling solution at the sol-gel transition is a unique state of matter that is neither liquid nor solid, but rather is in transition between these states. For example, the viscosity of the *incipient* gel is infinite, but the modulus is zero. Recently we have come to appreciate the unusual dynamics of this transition state by using the technique of quasielastic light scattering[1] to probe the relaxation of density fluctuations of wave vector q by the autocorrelation function of the scattered intensity, $I(q,t) = \langle I(0)I(t)\rangle$. In many systems the decay of density fluctuations can be described by a single relaxation time (exponential time decay). More complex materials, such as polymeric melts near the glassy transition temperature, exhibit a spectrum of relaxation times that gives a "stretched" exponential decay, $\exp[-(t/\tau)^b]$ where $0<b<1$. Regardless of the form, all known $I(q,t)$ can be described by some characteristic time τ. In this paper we demonstrate that in a gelling solution the characteristic time diverges at the sol-gel transition. This observation is unexpected and must not be confused with the usual critical slowing down in second-order thermodynamic phase transitions, since scattered-intensity measurements show that the compressibility does not diverge at the gel point. The fact that a critical slowing down should *not* be observed in quasielastic light scattering at the gel point has been elaborated by de Gennes,[2] who points out that the longitudinal modes observed in a quasielastic light-scattering experiment should be insensitive to the formation of a weak gel phase.

The observation of an infinite characteristic time implies two possible modes of decay. First, the decay can be described by a function that is scaled by a divergent characteristic time, e.g., an exponential decay with $\tau \rightarrow \infty$. This is precisely the description of critical slowing down in second-order phase transitions. Second, the form of the decay can be *independent* of the time scale, at least on times short compared with the characteristic time. This is possible if the decay is described by a function that does not contain a time scale—a power law. In fact, we will show that at the gel point a decay of the form $I(q,t) \sim 1/t^{0.27}$ is observed over the experimentally accessible 5 decades in time. Before the gel point, this power-law decay is truncated by a stretched-exponential tail, at a certain divergent characteristic time. A simple description of these phenomena is proposed, and we show that the detected photons divide the time axis in a self-similar way (fractal time).

Silica gels were prepared in methanol from 1.0*M* tetramethoxysilicon (TMOS), 4.0*M* H_2O, and 0.1*M* NH_3OH base catalyst. To avoid dust contamination, preparation was conducted in a clean bench, and the final solutions were either filtered into scattering cells with 0.2μ polytetrafluoroethylene (PTFE) filters, or centrifuged for 15 min at 30000g. Quasielastic light-scattering measurements were made in the *homodyne* (self-beating) mode with an argon-ion laser at $\lambda = 457.9$ nm, and a 256-channel correlator. Very near the gel point, correlation functions were collected over an extensive relaxation-time regime by running at three delay times, 3.6×10^{-7}, 2.0×10^{-5}, and 1.3×10^{-3} s, and merging the data. A similar data-merging technique employing the two delay times 1.0×10^{-6} and 1.0×10^{-4} s was used to integrate $I(q,t)$ to obtain the average relaxation time. This integration was performed numerically, without recourse to curve-fitting techniques. The homodyne dynamic structure factor $S(q,t)$ was obtained by subtraction of the calculated incoherent baseline from $I(q,t)$ and normalization to unity at $t=0$. Gel points were determined by an attempt to dilute aliquots of the reacting mixture.[3]

Correlation functions taken prior to the sol-gel transition at roughly 10-min intervals, plotted logarithmically in Fig. 1, indicate an approach to power-law decay at t_{gel} ($\simeq 406$ min). In fact, at the gel point a correlation function taken over an extended relaxation-time domain (see Fig. 2) shows an initial exponential followed by ~ 5 decades of power-law decay with $S(q,t) \sim t^{-0.27\pm0.03}$. The initial exponential relaxation simply indicates a fastest observable decay in the system.

A critical plot (Fig. 3) of the *arithmetic* average relaxation time $\langle\tau\rangle$, obtained by numerical integration of $S(q,t)$ taken over a 4.4-decade time domain, shows the divergence $\langle\tau\rangle \sim \epsilon^{-1.9\pm0.1}$ (run-to-run uncertainty) where $\epsilon = |t_{\mathrm{gel}} - t|/t_{\mathrm{gel}}$. It is noteworthy that although

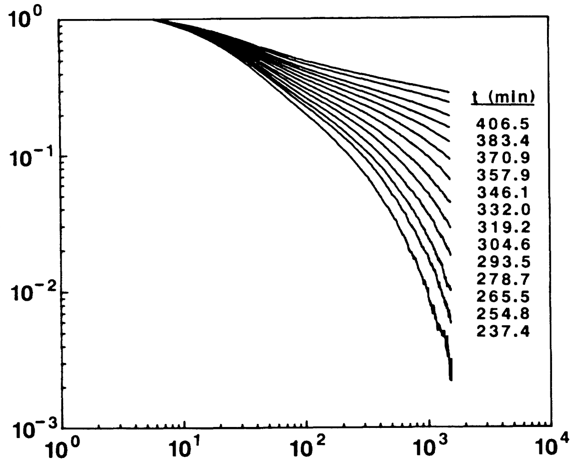

FIG. 1. Homodyne correlation functions plotted logarithmically for a gelling silica solution (gel point ~406 min). Near the gel point a power-law decay becomes evident.

$\langle\tau\rangle$ diverges, other characteristic times do not. For example, the characteristic time Γ^{-1} can be obtained from the initial relaxation rate $\Gamma = -d\ln S(q,t)/dt\,|_{t=0}$. This time is just the *harmonic* mean $\langle\tau^{-1}\rangle^{-1}$ of the relaxation spectrum, and since this average is sensitive to the fastest decays it does not diverge. Thus the critical dynamics observed near the sol-gel transition is qualitatively unlike that observed for thermodynamic phase transitions, where there is only a single characteristic time.

Our last observation (Fig. 4) is that the long-time tail is described by the stretched exponential $S(q,t) \sim \exp[-(t/\tau_z)^b]$ with $b = 0.65 \pm 0.05$. The inverse slope of these tails, τ_z, is the most strongly divergent (i.e., slowest) characteristic time in the system: Data supporting $\tau_z \sim \epsilon^{-2.5\pm0.1}$ are shown in Fig. 3. These correlation functions make a master curve when plotted against q^2t.

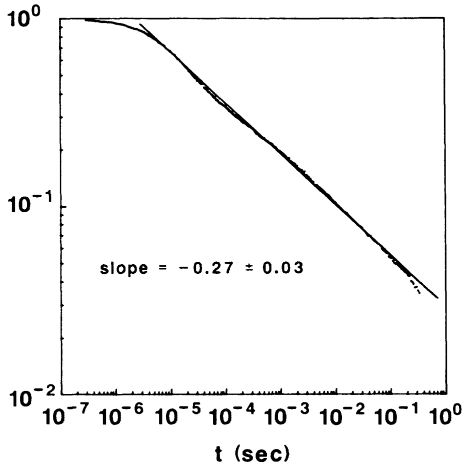

FIG. 2. At the gel point the homodyne correlation function shows power-law decay over 5 decades in time. The curvature at $t < 3$ μsec is due to a short-time cutoff in the relaxation spectrum.

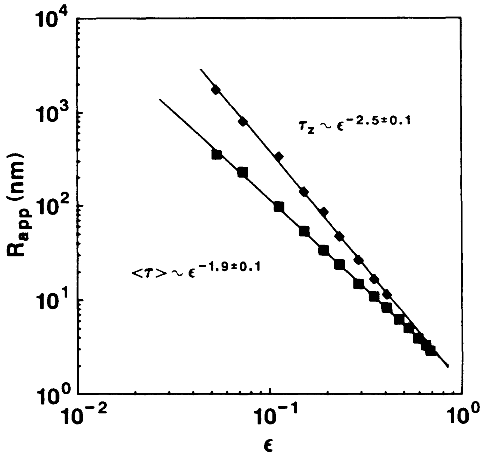

FIG. 3. The arithmetic-average relaxation time, obtained as the integral of the correlation function, shows the power-law divergence $\langle\tau\rangle \sim \epsilon^{-1.9\pm0.1}$, whereas the slowest decay time scales like $\tau_z \sim \epsilon^{-2.5\pm0.1}$. To remove the q dependence, these decay times are plotted as dynamic correlation lengths $R_{\mathrm{app}} \equiv (k_BT/6\pi\eta_0)q^2\langle\tau\rangle$.

A theory of the relaxation of density fluctuations in gelling solutions has to account for the power-law decay and stretched-exponential tail of $S(q,t)$; the divergence of $\langle\tau\rangle$ and τ_z, and nondivergence of Γ^{-1}; and the q^2t dependence of the correlation functions. A complete description of these phenomena would be complex, and so it is necessary to isolate the critical features. Generally, when a system is described by power laws, scaling methods can be used to simplify the problem.

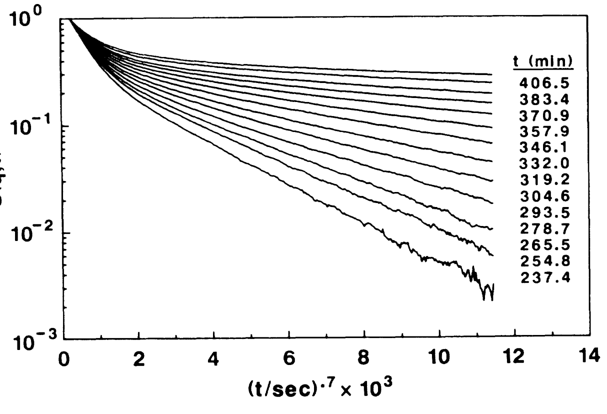

FIG. 4. The long-time tail of the correlation functions shown in Fig. 1 are well described by the stretched exponential $\exp[-(t/\tau_z)^{-0.65\pm0.05}]$ for $t \gg \tau_z$. Here τ_z is a decay time associated with a typical cluster.

Before proposing a description of these data, we briefly mention the connection to *fractal time,* a subject discussed by Mandelbrot.[4] The intensity autocorrelation function is just the density-density correlation function $\langle \rho(0)\rho(t)\rangle$ of the detected photons, since the intensity is the number of detected photons per unit time. For simplicity, imagine the time axis as a one-dimensional space, and replace each detected photon by a unit mass. Then we can easily visualize a disconnected mass fractal with a fractal dimension less than 1. For a fractal object the density-density correlation function is the power law $\langle \rho(0)\rho(r)\rangle \sim 1/r^{d-D}$, and so, observing that the dimension of time is $d=1$, for a fractal set on the time axis we expect the power-law decay $I(q,t)\sim 1/t^{1-D_p}$. Thus the fractal dimension of the detected photons is $D_p = 1-0.27=0.73$. Just as a mass fractal has no internal characteristic length, fractal time lacks an internal characteristic time: This is evidenced in the divergent times we observe.

The physical picture that we propose describes the relaxation of a density fluctuation as a sum of a normal cooperative diffusion component and an anomalous contribution due to the self-diffusion of clusters. Since the cooperative diffusion coefficient only contributes a fast relaxation and is not responsible for the unusual features we have observed, we will focus on the self-diffusion term. In order to understand the self-diffusion of a cluster, one must consider the structure of the incipient gel. The incipient gel is a self-similar distribution of fractal clusters of all sizes, from monomers to the infinite cluster. Self-similarity requires that the average separation distance S between clusters of radius $R\pm d\ln R$ be proportional to R, so that all clusters see the same environment, regardless of the size. Use of $S\sim 1/N(R)^{1/d}\sim R$ then gives the *number* distribution $N(R)d\ln R\sim R^{-d}\times d\ln R$, where d is the spatial dimension [$R^D\sim m$ then gives the well-known *hyperscaling* relation[5] $N(m)dm \sim m^{-1-d/D}dm$ for the mass distribution].

Consider a cluster of radius R attempting to diffuse in the incipient gel. Since branched polymers of comparable size cannot overlap, it is reasonable to describe the diffusion as Stokes-Einstein type, but in a medium with a *size-dependent* viscosity (i.e., the viscosity depends on the cluster size). In other words, we expect the diffusion coefficient of a cluster of radius R to be proportional to that of a sphere of radius R. On the time scale on which this cluster relaxes (moves a distance proportional to R) smaller clusters will have already relaxed, but much larger clusters will appear nearly stationary. Thus the smaller clusters form a fluid with a finite viscosity, embedded in a medium of essentially immobile clusters which form a tortuous system of caverns through which the cluster must diffuse. From self-similarity we recognize that the tortuosity is the same for all clusters, and simply reduces the diffusion coefficient by some fixed, radius-independent amount. Thus the central issue is the viscosity $\eta(R)$ of the fluid of clusters of radius less than R. If we note that the cutoff in the size distribution is the correlation length[5] ξ (the typical cluster radius), a fluid of viscosity $\eta(R)$ will be observed $\epsilon\sim R^{-1/\nu}$ beneath the gel point, where $\xi\sim\epsilon^{-\nu}$. Beneath the gel point the bulk viscosity diverges[6] like $\eta\sim\epsilon^{-k}$, and so the viscosity felt by a probe of radius R scales like $\eta(R)\sim R^{k/\nu}$. Use of the Stokes-Einstein formula $D_t(R)=kT/6\pi\eta R$ for the diffusion coefficient then gives $D_t(R)\sim 1/R^{1+k/\nu}$. (We obtain the same result if we assume that a probe larger than the correlation length feels the bulk viscosity, and a probe smaller than the correlation length feels a finite viscosity, i.e., *independent* of η since η diverges.)

To compute the observed quasielastic light-scattering behavior we must address a final point: Since the sol-gel transition is a connectivity divergence, not a thermodynamic phase transition, there are no singularities in the free energy and thus no divergence associated with the scattering from the *undiluted* incipient gel (experimentally this is indeed the case). Physically, this implies that the clusters neatly pack, so that the scattering from a single cluster is screened by the presence of the other clusters. In the absence of spatial correlations only the diagonal terms in $S(q)=(1/N^2)\sum\langle e^{iq(r_i-r_j)}\rangle$ contribute, and so the scattering from a cluster of mass m scales like $S(q)\sim m$, not $S(q)\sim m^2 f(qR)$. Our expression for the self-diffusion contribution to the structure factor is then

$$S_s(q,t)=\int_1^\infty mN(m)\exp(-q^2D_t t)\,dm. \tag{1}$$

Since the momentum transfer and time appear as the variable q^2t, a master curve will be obtained when plotting against this variable, in agreement with experiment.

Beneath the gel point the number distribution is $N(m)\sim m^{-1-d/D}e^{-m/M_z}$ where the exponential[5] truncates $N(m)$ at the *typical* cluster mass $M_z\sim\xi^D\sim\epsilon^{-\nu D}$. Using $D_t\sim 1/R^{1+k/\nu}$ and $D=d-\beta/\nu$, where $G\sim\epsilon^\beta$ is the gel fraction,[5] we obtain for the *heterodyne* correlation function $S_s(q,t)=S(q,t)^{1/2}$

$$S_s(q,t)\sim t^{-\beta/(\nu+k)},\quad \Gamma^{-1}<t<\tau_z, \tag{2a}$$

$$\langle\tau\rangle\sim\epsilon^{-(\nu+k-\beta)}, \tag{2b}$$

$$S_s(q,t)\sim\exp[-(t/\tau_z)^{D/(D+1)}],\quad t\gg\tau_z, \tag{2c}$$

$$\tau_z\sim 1/q^2D_z\sim\epsilon^{-\nu-k}. \tag{2d}$$

Ignoring any effect on prefactors, the exponents in Eqs. (2a)-(2d) apply to the homodyne structure factor if we replace β by 2β in (2a) and (2b). The stretched-exponential tail in (2c), obtained by the method of steepest descents, is due to the diffusion of clusters larger than the correlation length. These exponentially rare clusters feel the bulk viscosity, i.e., $D_t\sim\xi^{-k/\nu}R^{-1}$, and are thought to be lattice animals,[7] with $D=2$. The relaxation time in (2d) depends on the *z-average* diffusion coefficient $D_z\sim\xi^{-1-k/\nu}$ and so is due to the diffusion of a typical cluster of radius ξ. This slowest characteristic time diverges more strongly than $\langle\tau\rangle$, as seen in Fig. 3.

Equations (2a)-(2d) can be used to determine the gel fraction and viscosity exponents. Define the exponents ϕ and ψ through $S(q,t) \sim t^{-\phi}$ and $\langle\tau\rangle \sim \epsilon^{-\psi}$ and solve the homodyne version of (2a) and (2b) to obtain the expression $\beta = \phi\psi/2(1-\phi)$ for the gel-fraction exponent. Use of the experimental values $\phi = 0.27$ and $\psi = 1.9$ then gives $\beta = 0.35$, in good agreement with the percolation prediction of $\beta = 0.39$. To find k we use the *dilute-solution* experimental value[3] $\nu' = 1.35$ for TMOS and correct this for cluster swelling[3] to obtain the reaction-bath value $\nu = 1.35 \times 0.8 = 1.08$. Use of $k = \psi - \nu + \beta$ from (2b) then gives $k = 1.5$. This value is in good agreement with the viscosity measurements reported recently by Colby *et al.*[8] *for the base-catalyzed TMOS system,* which gave $k = 1.3$, but does not agree with the de Gennes prediction of $k = 0.7$, which is based on an analogy between the viscosity divergence and the divergence of conductivity in a superconductor-resistor network.[6,9] Substituting these exponents into (2d) we predict $\tau_z \sim \epsilon^{-2.6}$, in good agreement with our experimental observation $\tau_z \sim \epsilon^{-2.5 \pm 0.1}$. Finally, if the lattice-animal dimension $D = 2$ is used in (2c) we predict a long-time tail of the form $S(q,t) \sim \exp - (t/\tau_z)^{0.67}$, again in agreement with our observation of a stretched-exponential exponent of 0.65 ± 0.05.

In conclusion, we have observed a novel kind of critical dynamics near t_{gel} that is characterized by the presence of a power-law spectrum of relaxation times, with a longest time that diverges at t_{gel}. This spectrum gives rise to a power-law relaxation of the dynamic structure factor and to divergent characteristic time scales. A simple cluster diffusion model of the dynamics is proposed that relies on the concept of a size-dependent viscosity, the hyperscaling form of the size distribution, and the screening of the scattered intensity. From this cluster diffusion interpretation, we deduce the gel fraction exponent $\beta = 0.35$, the viscosity exponent $k = 1.5$, and find a stretched-exponential behavior consistent with the diffusion of exponentially rare lattice animals.

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