PHYSICAL REVIEW E, VOLUME 63, 051402

Dynamic structure of thermoreversible colloidal gels of adhesive spheres

Michael J. Solomon* and Priya Varadan
Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109-2136

(Received 18 September 2000; published 17 April 2001)

The dynamic structure factor $f(q,t)$ of suspensions of adhesive colloidal spheres has been characterized as a function of temperature over the volume fraction range $0.010<\phi<0.075$. Below a critical temperature that is volume fraction dependent, the suspensions underwent an abrupt, reversible transition in dynamic structure. Below their gel points suspensions became nonergodic, and the time decay of $f(q,t)$ was arrested by as many as five decades. Static light scattering demonstrated that the adhesive spheres formed a fractal cluster gel structure. A recent model of the dynamics of fractal clusters [A. H. Krall and D. A. Weitz, Phys. Rev. Lett. **80**, 778 (1998)] was applied to extract the temperature and volume fraction dependence of the characteristic decay times of $f(q,t)$. Immediately above the gel temperature a single stretched exponential decay of $f(q,t)$ was observed. The temperature dependence of the decay time was $\tau_\alpha \sim \varepsilon^{-1.15\pm0.06}$, where $\varepsilon=(T-T_{\mathrm{gel}})/T_{\mathrm{gel}}$, and T_{gel} is the gelation temperature. The argument of the stretched exponential decay p decreased monotonically as the temperature was lowered toward the gel point, until, at gelation, $p\sim 0.5$. Below the gel temperature, an initial stretched exponential decay of $f(q,t)$ was followed by a plateau. Finally, at long times, an additional exponential decay of the gel $f(q,t)$ was observed. By applying the fractal cluster dynamics model, it was found that the initial decay time, $\tau_\beta \sim \varepsilon^{-1.00\pm0.07}$. The plateau in $f(q,t)$ was due to an upper bound of the mean-squared displacement of gel segments, denoted δ^2. The typical magnitude of δ^2 was not much greater than the square of the particle radius. The data showed $\delta^2 \sim \varepsilon^{-1.05\pm0.07}$. The additional exponential decay at long times, τ_γ, depended only weakly on ε. Its dependence on the scattering vector was $\tau_\gamma \sim q^{-0.53\pm0.06}$. The argument of the stretched exponential decay of the gel $f(q,t)$ and volume fraction dependence of τ_β and δ^2 indicate that the spatial scaling of the gel compliance is consistent with the gel network bonds possessing angular rigidity. The ε dependence of the characteristic times τ_α and τ_β could not be fully explained by the fractal cluster dynamics model. The long time decay of $f(q,t)$ exhibited behavior that differed from that recently reported for dilute gels of aqueous colloidal polystyrene [Cipelletti *et al.*, Phys. Rev. Lett. **84**, 2275 (2000)]. We hypothesize that the long-time decay in $f(q,t)$ of the gels studied here is due to rare bond disaggregation processes that occur because of the relatively weak interaction between the adhesive spheres ($\Delta E_{\mathrm{min}}/kT \sim 10$) of the thermoreversible gel.

DOI: 10.1103/PhysRevE.63.051402 PACS number(s): 82.70.Gg, 61.20.Lc, 82.70.Dd, 61.43.Hv

I. INTRODUCTION

Colloidal particulate suspensions with amorphous structure may exhibit an abrupt transition in dynamics as the solid volume fraction is increased or as the interparticle potential is varied. Qualitatively, the transition, often called gelation, is from liquidlike to solidlike dynamics. Its onset is a sensitive and poorly characterized function of static structure and interparticle interactions. Technologically, colloidal gelation is relevant to the chemical processing of ceramics and the fabrication of particulate coatings [1]. Moreover, understanding colloidal gel dynamics is a preliminary step in explaining the unusual rheological properties of gels such as solidlike linear viscoelasticity and the existence of an apparent yield stress.

The origin of gelation is of fundamental interest because of its possible relationship to glass or frustrated phase transitions. Comparison to the glass transition arose because gelation involves an abrupt slowing down of dynamics in systems that maintain amorphous structure [2]. The role of phase behavior has been debated, because was conjectured that gelation is triggered by a phase transition, such as spinodal decomposition, that does not proceed to completion because of strong interparticle interactions that trap the material in a nonequilibrium state [3,4]. The slowing down of dynamics that accompanies gelation is observable, for example, as an arrested decay of the autocorrelation function of particle concentration fluctuations [5,6]. Gelled suspensions display nonergodicity and an apparent low frequency plateau of the dynamic mechanical storage modulus.

Dynamic transitions have been observed in suspensions of hard spheres [6], depletion flocculated colloids [4], dilute aqueous suspensions of colloidal polystyrene [5,7,8], suspensions of adhesive spheres [3,9–12], and dispersions of deionized laponite [13,14]. For colloidal hard spheres, the dynamical transition at $\phi=0.58$ has been likened to the glass transition. The ensemble averaged autocorrelation function of particle concentration fluctuations has been modeled by mode coupling theory in the vicinity of the glass transition [6]. Recent direct visualization of hard sphere colloidal dynamics characterized the role of cooperative dynamics in mediating particle displacements in regions above and below the glass transition volume fraction [15,16].

While the colloidal hard sphere glass transition is reached by increasing volume fraction, gelation may also be induced by manipulating the strength and range of attractive interparticle interactions. For example, dilute, density matched, sus-

---

*Email address: mjsolo@umich.edu

pensions of aqueous colloidal polystyrene aggregate to form gels upon the addition of divalent electrolyte [7,8]. Upon gelation, the time decay of the dynamic structure factor is retarded by many orders of magnitude [5]. The full decay of dynamic structure is achieved only at very long times by an aging process that is thought to involve syneresis [17].

Another system that gels due to attractive particle interactions is sterically stabilized colloidal silica that has been dispersed in a liquid that poorly solvates the grafted chains [18]. For aliphatic grafted species, example solvents are hexadecane, benzene, decalin, and tetradecane. Since the solvent-grafted chain interaction is temperature dependent, the interparticle potential is also a function of temperature. As the temperature is decreased, the solvent quality deteriorates, and a net attractive interparticle interaction results. This interaction has been modeled by the Baxter adhesive sphere model, which includes a single parameter τ_b [19]. The Baxter interaction parameter τ_b has been quantitatively related to temperature for various adhesive-sphere–solvent systems [3,20]. Experimentally, as the temperature of the adhesive sphere suspensions is decreased, a stable gel is formed. It has been hypothesized that the observed transition is a consequence of percolation [11], freezing of the stabilizing layers [21], a frustrated gas-solid phase transition [3], or a dynamic instability explainable by mode coupling theory [2].

Suspensions of adhesive hard spheres are an excellent system for the study of gelation, because the interparticle potential is well characterized and the transition is reversible. Since the strength of the attractive potential can be varied continuously and reversibly, the divergent scaling of characteristic times in the vicinity of the gelation transition can be measured in a way previously accomplished only for colloidal hard spheres.

We report a characterization of the dynamic structure of thermoreversible gels of adhesive spheres in the vicinity of the gel point. The dynamic structure factor, which quantifies the normalized autocorrelation function of particle density fluctuations, was measured by means of photon correlation spectroscopy. Suspensions of colloidal silica, sterically stabilized by surface grafted octadecyl aliphatic chains, formed gels below a critical temperature in the solvent hexadecane. The temperature of the reversible transition was a function of volume fraction. At high volume fraction ($\phi > 0.01$) the structure of the gels was sufficiently rigid and the particle size sufficiently small that gravitationally induced collapse of the gel occurred only very slowly (e.g., $t > 1$ week for $\phi = 0.035$). Because of the approximate refractive index matching of silica and hexadecane, scattering studies could be conducted up to a very high volume fraction ($\phi \sim 0.12$). This extended the range of study possible by light scattering beyond that of aqueous polystyrene gels, where multiple scattering precludes measurements much above $\phi \sim 10^{-3}$. Previous studies of this system demonstrated that the interparticle interaction can be modeled by the Baxter adhesive sphere potential, and that the gel curve, determined by the onset of solidlike linear viscoelasticity, is coincident neither with the percolation, spinodal decomposition, nor gas-solid coexistence curves [3]. In fact, as opposed to the organophilic silica-benzene system studied by Verduin and Dhont [10], the silica-hexadecance system apparently does not exhibit any experimental evidence of phase separation, since only gelation is observed as the temperature or volume fraction is varied.

The extraction of characteristic decay times from the dynamic structure factor of colloidal gels was facilitated by the recent report of a model of fractal cluster dynamics [5]. The model, which computes the average mean-squared displacement of gel segments due to thermal excitation of the elastic modes of a fractal cluster, predicts a time decay of $f(q,t)$, given the cluster radius, fractal dimension and segmental elasticity of the gel. The Krall-Weitz model provides a useful means to characterize gel dynamics systematically as a function of the strength of the interparticle potential.

In this study, we report measurements of the static structure factor $S(q)$ of the organophilic silica as functions of temperature and volume fraction. As the temperature is varied above the gel point, $S(q)$ displays a behavior consistent with an approach to the spinodal curve; however, as the temperature is decreased further, gelation occurs instead of phase separation. Below the gel temperature, the structure of the gel is consistent with fractal clusters that fill space in a way that is volume fraction dependent. The dynamic structure factor $f(q,t)$ was characterized by photon correlation spectroscopy in the vicinity of the gelation transition at a number of volume fractions. Above the gel point, $f(q,t)$ exhibited a stretched exponential decay with characteristic times that were remarkably temperature dependent. Below the gelation temperature a region of arrested structural decay was encountered. The arrested decay persisted for a time interval that depended on the proximity to the gel temperature. At long times, an additional decay of $f(q,t)$ was observed. This decay was attributed to rare, thermally induced, bond breaking processes.

II. METHODS AND MATERIALS CHARACTERIZATION

A. Organophilic colloidal silica

Colloidal silica was synthesized by the Stober method [22] according to the correlation of Bugosh and Zukoski [23]. Octadecyl aliphatic chains were then grafted to the colloid surface by the method of Ref. [24]. The radius of the resulting colloids was $a = 40$ nm (by dynamic light scattering). The standard deviation in the particle radius was 4 nm (by scanning electron microscopy). The silica density $\rho = 1.8\ \mathrm{g/cm^3}$ was used for the calculation of the suspension volume fraction [23]. Suspensions were prepared in hexadecane ($\rho = 0.773\ \mathrm{g/cm^3}$, $n = 1.434$) by vortex mixing of the warm ($T \sim 60\,°\mathrm{C}$) mixture.

B. Static and dynamic light scattering

The static structure factor $S(q)$ of the suspensions was measured by means of small and wide-angle light scattering. The small-angle light scattering device was based on the design of Cumming *et al.* [25]. The wavelength of the incident radiation was $\lambda_o = 0.633\ \mu\mathrm{m}$ and the scattering vector, q, was varied from $0.50\ \mu\mathrm{m}^{-1} < q < 4.9\ \mu\mathrm{m}^{-1}$. The size of the scattering volume was approximately 0.66 mm^3. Temperature was controlled to ±0.5 °C. Additional details of the device are reported elsewhere [26]. Wide-angle static light scattering was conducted on an ALV (Langen, Germany) compact goniometer system. The incident wavelength was $\lambda_o = 0.488\ \mu\text{m}$ and the scattering vector was varied from $3.8\ \mu\text{m}^{-1} < q < 35.6\ \mu\text{m}^{-1}$. The temperature was controlled to ±0.02 °C. The scattering volume was estimated to be $0.0020\ \text{mm}^3$ at $\theta = 90°$.

For nonergodic gels, the time-averaged intensity $\langle I \rangle^t$ does not necessarily equal the ensemble-averaged intensity, $\langle I \rangle^e$. Because of the small scattering volume of the wide-angle device, ensemble-averaged measurements were collected by interrogating the intensity within many scattering volumes ($n > 100$). $S(q)$ (in arbitrary units), was extracted from the data via the proportionality $I(q) \propto \phi P(q) S(q)$ where $P(q)$ is the particle form factor and ϕ is the volume fraction.

The intermediate scattering function, or dynamic structure factor, $f(q,t)$ was measured by means of photon correlation spectroscopy. The function $f(q,t)$ represents the normalized autocorrelation function of particle density fluctuations. The compact goniometer system described above was used in conjunction with a multitau correlator (ALV-5000E) (Langen, Germany). The minimum delay time of the correlator was 0.2 μs. The time-averaged normalized intensity autocorrelation function, $g_2^t(q,t) = G_2^t(q,t)/\langle I(q) \rangle^2 = \langle I(q,t) I(q,0) \rangle / \langle I(q) \rangle^2$ was measured. The superscript denotes a time-averaged quantity. Due to nonergodicity, for colloidal gels $g_2^t(q,t) \neq g_2^e(q,t)$, and the usual Siegert relationship $g_2(q,t) = 1 + \beta [f(q,t)]^2$ cannot be used to extract $f(q,t)$ from $g_2^t(q,t)$. Here the coherence factor β increases with the ratio of the speckle size to the detector area, and has a magnitude between zero and 1. Pusey and van Megen developed a method for extracting $f(q,t)$ from $g_2^t(q,t)$ for nonergodic samples, provided that the particulate scatterers undergo only limited Brownian displacements about a fixed position [27]. In such instances $f(q,t)$ may be obtained from a single measurement of $g_2^t(q,t)$, and a determination of the ratio $\langle I(q) \rangle^t / \langle I(q) \rangle^e$. The superscripts again denote time and ensemble averages, respectively.

Alternatively, $f(q,t)$ may be directly measured by collecting the time-averaged unnormalized intensity autocorrelation $G_2^t(q,t)$ at an ensemble of uncorrelated locations, averaging the results and applying the Siegert relationship directly [6]. Figure 1 shows $f(q,t)$ obtained by the two methods for a typical organophilic silica-hexadecane gel ($n = 10$ for the direct method). In light of the good agreement, $f(q,t)$ was determined by the method of Pusey and van Megen for all nonergodic samples. Correlation functions were collected for a duration that was 200 times longer than the largest reported delay time.

Care was taken to apply a consistent temperature history to all samples studied. Samples were maintained at $T = 60\ °\text{C}$ for 15 min, at which time they were transferred to the scattering device which was maintained at the test temperature. The specimen was allowed to equilibrate for 15 min before the initiation of a measurement.

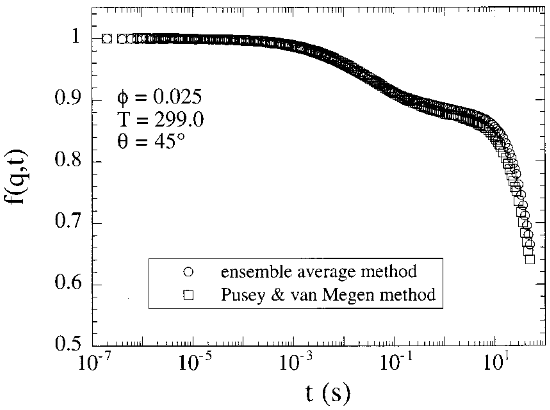


FIG. 1. Comparison between the Pusey–van Megen method [27] and the direct method of measuring $f(q,t)$ of nonergodic suspensions.

C. Characterization of static structure factor $S(q)$

Figure 2 reports wide angle light scattering measurements of $S(q)$ in the immediate vicinity of the gelation temperature. Proximity to this critical temperature is quantified by $\varepsilon = (T - T_{\text{gel}})/T_{\text{gel}}$. Since all the temperatures probed fall within a range that is comparable to the minimum limit of temperature stability in the small-angle light scattering device, measurements in this geometry were not pursued. No time evolution in the scattering intensity was observed at any temperature. From these data the absence of phase separation was concluded. Figure 2 demonstrates that as temperature decreases toward the gel point, large changes in $S(q)$ occur. Below a critical temperature, we find that $\langle I(q) \rangle^t \neq \langle I(q) \rangle^e$. This observation coincides with significant changes in the dynamic structure factor (cf. Sec. III). Below the gelation temperature little further effect of temperature on $S(q)$ is observed. Above the gelation temperature, the data are con-

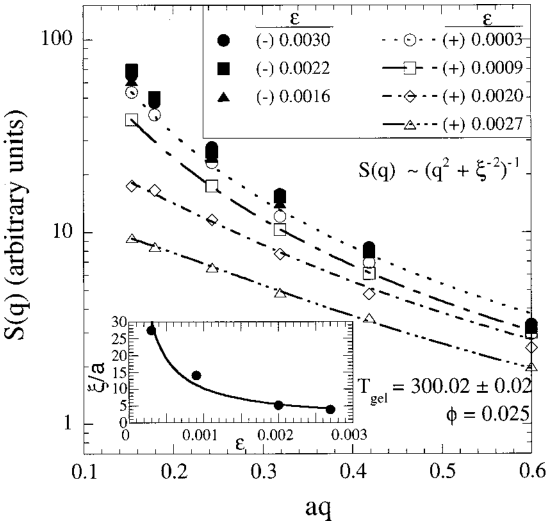
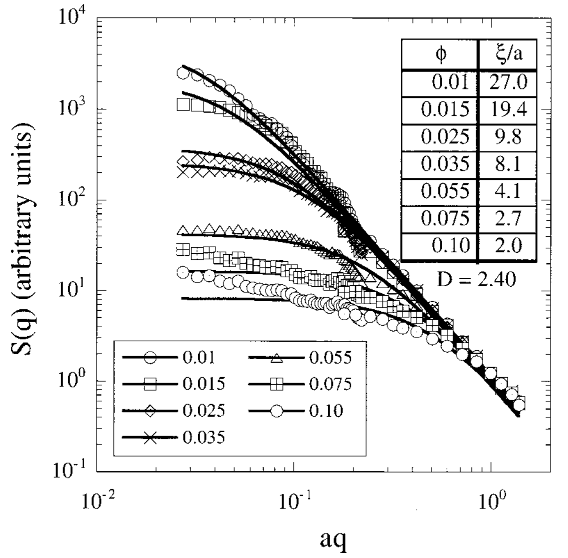


FIG. 2. Temperature dependence of the static structure factor $S(q)$ in the vicinity of the gel temperature. Filled symbols indicate nonergodic samples. Here $\varepsilon = (T - T_{\text{gel}})/T_{\text{gel}}$. The curves are fits to the scaling $S(q) \sim (q^2 + \xi^{-2})^{-1}$, where ξ is a phenomenological correlation length. The variation of ξ in the fluid phase is plotted in the inset figure. The curve is a power-law fit to the four datum points in the fluid phase.



ϕ	ξ/a
0.01	27.0
0.015	19.4
0.025	9.8
0.035	8.1
0.055	4.1
0.075	2.7
0.10	2.0

FIG. 3. Volume fraction dependence of the static structure factor $S(q)$ below the gelation temperature. The table lists model parameters extracted from fits to Eq. (1).

sistent with the scaling $S(q)\sim(q^2+\xi^{-2})^{-1}$, where ξ is a phenomenological correlation length (cf. Fig. 2, inset). Such a behavior has been taken as evidence of an approach to the spinodal curve in organophilic silica-benzene adhesive sphere suspensions [10]. However, for the silica-hexadecane system, gelation (loss of ergodicity), rather than spinodal decomposition, is observed as the temperature is decreased below the transition temperature.

Combined wide and small angle light scattering studies of $S(q)$ at a number of volume fractions are reported in Fig. 3. The two sets of data were scaled by equating the measurement of each instrument at a value of the dimensionless scattering vector, $aq=0.205$. While the resulting arbitrary scale of $S(q)$ precludes an interpretation of its absolute magnitude, the shape of the scattering curves includes structural information that can be deduced by model comparison. We find that a structure represented by the pair distribution function $g(r)=A\exp(-r/\xi)r^{d-3}$ is consistent with the experimental measurements. Here ξ is a cluster radius, and d is the fractal dimension. The corresponding expression for the structure factor is [28]

$$S(q)=\left(\frac{S(0)}{[1+(q\xi)^2]^{(d-1)/2}}\right)\frac{\sin(d-1)\tan^{-1}(q\xi)}{(d-1)d\xi}. \qquad (1)$$

The data of Fig. 3 were fit to Eq. (1). Although the region of fractal scaling is certainly limited for the measurements at the highest volume fraction, we find $d=2.4$, independent of volume fraction. The error in d, as estimated by analysis of the fit sensitivity and residuals, is ±10%. Consideration of the region of overlap between the small and wide-angle light scattering data suggests that the small-angle device underreports the scattering at the highest angles probed by the instrument ($aq>0.2$); however, exclusion of these data from the fits to Eq. (1) changed d and ξ by less than 5%.

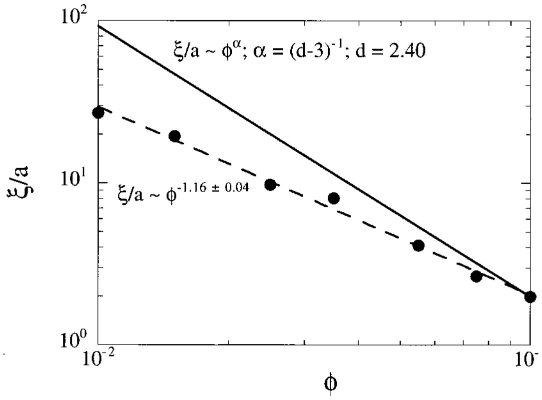


FIG. 4. Volume fraction dependence of the nondimensional cluster radius, ξ/a. The filled symbols are from fits to experimental data, which show a power-law scaling $\xi/a\sim\phi^{-1.16\pm0.04}$. The additional curve shows the predicted scaling for fractal clusters with fractal dimension, $d=2.4$, that are distributed independent of volume fraction.

The volume fraction dependence of the cluster radius, ξ, is plotted in Fig. 4. Assuming that the fractal clusters fill space in a way that is independent of volume fraction, the scaling $\xi/a\sim\phi^{1/(d-3)}$ relates the two model parameters ξ and d. This scaling, referenced to the experimental data at $\phi=0.10$, is plotted for comparison in Fig. 4.

III. RESULTS

The effect of temperature on the intermediate scattering function, or dynamic structure factor, $f(q,t)$ is plotted in Fig. 5 for $\phi=0.055$. Figure 5 shows the remarkable sensitivity of the dynamic structure to temperature (interparticle potential). At $T=301.94\pm0.02$ K, the longest decay time of the structure increases by orders of magnitude, and the sample undergoes an ergodicity transition. At lower temperatures a

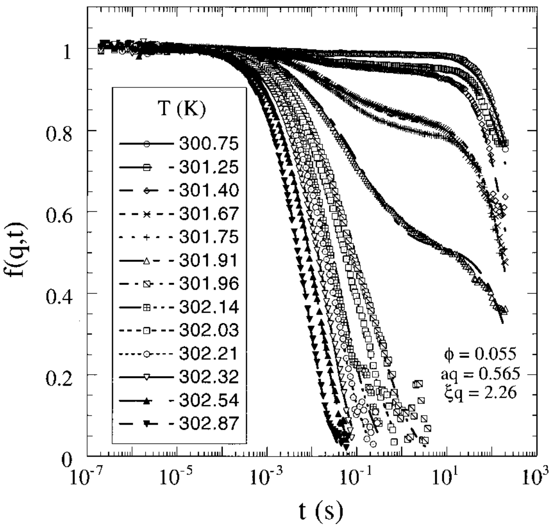


FIG. 5. Temperature dependence of the dynamic structure factor $f(q,t)$ for adhesive spheres with $\phi=0.055$. Fits are for Eq. (2) above the gel temperature and Eq. (5) below the gelation temperature.

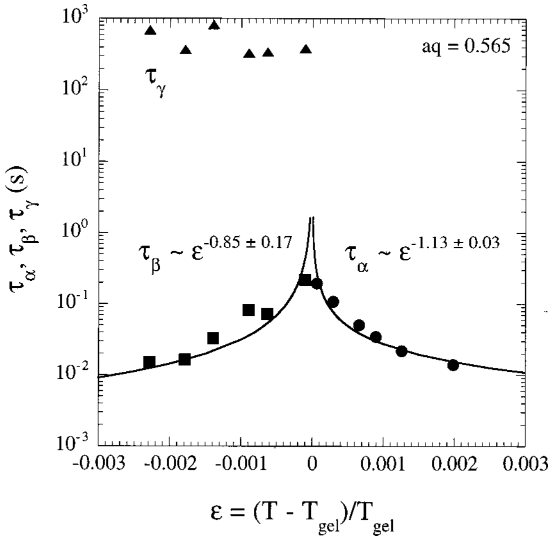


FIG. 6. ε dependence of the characteristic times τ_α, τ_β, and τ_γ for the data of Fig. 5.

plateau in $f(q,t)$ is observed at intermediate times. The plateau, which at the lowest temperatures persists for more than five decades, and is followed by a final decay, of which only the initial region can be resolved within the experimental duration. We find that the temperature of the transition in $f(q,t)$ is independent of the scattering vector q. The effect of temperature on $f(q,t)$, depicted in Fig. 5, is typical of the volume fraction range $0.01 < \phi < 0.1$, although the transition temperature is itself a function of ϕ. For example, $T_{\text{gel}} = 296.7\,\text{K}$ for $\phi = 0.01$, while $T_{\text{gel}} = 302.6\,\text{K}$ for $\phi = 0.10$.

Characteristic decay times and structural features may be extracted from the measurements plotted in Fig. 5 by application of models of the dynamics of the gel structure. The modeling of the data above the gelation temperature is described first. An account of the modeling below the gel point follows.

Above the gelation temperature, the decay of $f(q,t)$ is consistent with the stretched exponential form

$$f(q,t) = \exp[-(t/\tau_\alpha)^p], \tag{2}$$

where τ_α is a characteristic decay time, and p is the argument of the stretched exponential. This expression for $f(q,t)$ was previously applied to low-volume fraction gels of colloidal polystyrene [5]. We find that the stretched exponential decay is essential to describe the data above T_{gel}, since in the vicinity of the gelation temperature $f(q,t)$ lacks a well-defined first cumulant (data not shown). Of particular interest is the dependence of τ_α on the dimensionless temperature difference $\varepsilon = (T - T_{\text{gel}})/T_{\text{gel}}$. The data are plotted as part of Fig. 6. For $\phi = 0.055$, we find $\tau_\alpha \sim \varepsilon^{-1.13 \pm 0.03}$. The ε dependence of the parameter p will be discussed later.

Below the gelation temperature the decay of $f(q,t)$ is more complex. Three regimes of behavior are observed. An initial decay in $f(q,t)$ is followed by a plateau at intermediate times. An additional decay at long times is observed. A recently reported model of the internal elasticity of colloidal fractal clusters is applicable to the first two regimes [5]. The dynamic structure factor is related to the mean squared displacement $\langle \Delta r_\zeta^2 \rangle$, of gel segments of length scale $\zeta \sim q^{-1}$ by

$$f(q,t) = \exp[-q^2 \langle \Delta r_\zeta^2(t) \rangle / 6]. \tag{3}$$

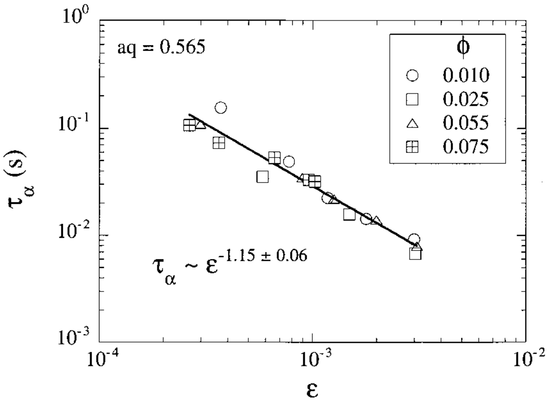


FIG. 7. ε dependence of the characteristic time τ_α for $0.010 < \phi < 0.075$.

Krall and Weitz [5] found that the thermal excitation of normal modes of the fractal cluster leads to expressions for $\langle \Delta r_\zeta^2 \rangle$ of the general form

$$\langle \Delta r_\zeta^2 \rangle = \delta^2 [1 - \exp(-t/\tau_\beta)^p] \tag{4}$$

Here τ_β is a characteristic decay time, and δ^2 is the characteristic maximum mean squared displacement of the fractal cluster segments. The second decay at long times was not reported by Krall and Weitz. We determine this decay to be exponential with characteristic decay time τ_γ. Consequently, we fit the complete $f(q,t)$ dependence below the gelation temperature by the expression

$$f(q,t) = \exp\left(-\frac{(q\delta)^2}{6} [1 - \exp(-t/\tau_\beta)^p] \right) \exp(-t/\tau_\gamma). \tag{5}$$

Empirically, we determine $p \sim 0.5$ independent of temperature for $T < T_{\text{gel}}$, and we maintain this parameter constant throughout. Equation (5), with $p = 0.5$, adequately models the $f(q,t)$ data for $T < T_{\text{gel}}$, as is shown in Fig. 5.

In the gel regime, the characteristic times τ_β and τ_γ determine the onset of the first and second decays, respectively. For $\phi = 0.055$ the ε-dependence of these quantities is plotted in Fig. 6. From Fig. 6, $\tau_\beta \sim \varepsilon^{-0.85 \pm 0.17}$ for $\phi = 0.055$. The dependence of τ_γ on ε is not readily apparent from the figure, so we refrain from assigning a functional dependence to τ_γ. The parameter δ^2 determines the value of $f(q,t)$ that corresponds to the intermediate plateau. The ε dependence of δ^2 will be considered subsequently.

To characterize the dynamic structure of the thermoreversible gels more completely, the temperature dependence of $f(q,t)$ at three other volume fractions was studied ($\phi = 0.010$, 0.025, and 0.075). Model parameters were extracted from the data by means of Eqs. (2) and (5). Results are reported in Figs. 7–10.

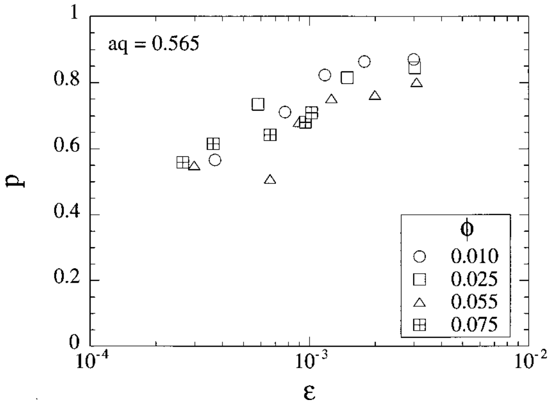


FIG. 8. ε dependence of the argument of the stretched exponential p above the gelation temperature.

The dependence of τ_α on ε is plotted in Fig. 7. Analyzing the data at all volume fractions yields $\tau_\alpha \sim \varepsilon^{-1.15\pm0.06}$. Figure 7 shows that to within the error of the power law fit, the ε dependence of τ_α is not a function of volume fraction. For $T > T_{\mathrm{gel}}$, the other model parameter is p, which characterizes the stretched exponential decay. The ε dependence of p is plotted in Fig. 8. Although the dependence has not been correlated, Fig. 8 shows that p decreases monotonically as the gel point is approached. Just above the gel temperature, $p \sim 0.5$, and this value persists, invariant of temperature, as the temperature is decreased through the gel point into the gel regime.

Unlike the behavior for $T > T_{\mathrm{gel}}$, that was shown in Figs. 7 and 8, below the gelation temperature model parameters depend upon the volume fraction. In Fig. 9 the ε dependence of τ_β is reported. (Here, and for other plots of data below the gelation temperature, $\varepsilon = |T - T_{\mathrm{gel}}|/T_{\mathrm{gel}}$.) To correlate the ε dependence of τ_β while still accommodating the implicit volume fraction dependence, a master curve was generated by normalizing data for each volume fraction by $\tau_\beta(\varepsilon = 0.001)$. By this method we find $\tau_\beta/\tau_\beta(\varepsilon = 0.001) \sim \varepsilon^{-1.00\pm0.07}$. To within its error this exponent is independent of volume fraction. The particular choice of $\varepsilon = 0.001$ for the volume fraction normalization is not crucial; the change in the power law exponent for a different choice is less than the error of the exponent. The volume fraction dependence of $\tau_\beta(\varepsilon = 0.001)$ used in constructing Fig. 9 is plotted in the figure's inset. Over the somewhat narrow interval probed, $0.01 < \phi < 0.075$, $\tau_\beta(\varepsilon = 0.001) \sim \phi^{-1.81\pm0.01}$.

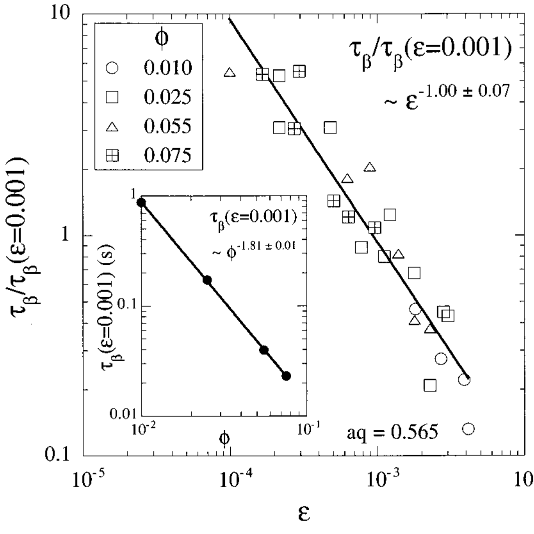


FIG. 9. ε dependence of the normalized characteristic time $\tau_\beta/\tau_\beta(\varepsilon = 0.001)$ for $0.010 < \phi < 0.075$. The volume fraction dependence of $\tau_\beta(\varepsilon = 0.001)$ is plotted in the inset. Here, and in Figs. 10 and 11, since $T < T_{\mathrm{gel}}$, $\varepsilon = |T - T_{\mathrm{gel}}|/T_{\mathrm{gel}}$.

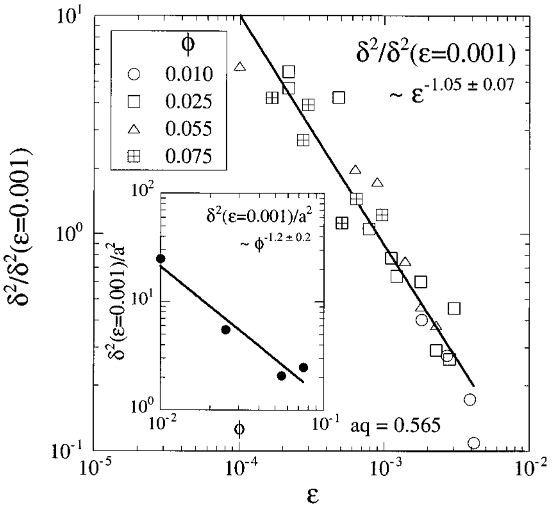


FIG. 10. ε dependence of the normalized maximum mean squared displacement of fluctuations of order q^{-1}, $\delta^2/\delta^2(\varepsilon = 0.001)$ for $0.010 < \phi < 0.075$. The volume fraction dependence of $\delta^2(\varepsilon = 0.001)$ is plotted in the inset.

The maximum mean squared displacement of gel segements, δ^2, which sets the value of $f(q,t)$ at the intermediate plateau, was also determined. The ε dependence of δ^2 (at $aq = 0.565$) for the volume fractions studied is shown in Fig. 10. As was the case for τ_β, δ^2 exhibits a volume fraction dependence that is accounted for by nondimensionalization with $\delta^2(\varepsilon = 0.001)$. Consequently, we find $\delta^2/\delta^2(\varepsilon = 0.001) \sim \varepsilon^{-1.05\pm0.07}$. The inset of Fig. 10 shows the volume fraction dependence of $\delta^2(\varepsilon = 0.001)$. Here $\delta^2(\varepsilon = 0.001) \sim \phi^{-1.2\pm0.2}$.

It is of interest to investigate the q dependence of the relaxation of dynamic structure, particularly with regards to the final exponential decay observed for all samples. Figure 11 plots the q dependence of $f(q,t)$ for a thermoreversible gel with $\phi = 0.055$ and $\varepsilon = 0.001$ (i.e., $T < T_{\mathrm{gel}}$). The fits are for Eq. (5), with $p = 0.50$. Analogous studies were conducted for $\phi = 0.010$, 0.025, and 0.075. Over the volume fraction and scattering vector range ($0.15 < aq < 1.41$) investigated the model parameters τ_β and δ^2 are approximately independent of scattering vector ($\tau_\beta \sim q^{0.1}$ and $\delta^2 \sim q^{-0.2}$). These observations provide further support for the applicability of the Krall-Weitz fractal cluster dynamics model to describe the initial decay of $f(q,t)$ for the thermoreversible gel system. The long-time exponential decay of $f(q,t)$ is governed by τ_γ. The scattering vector dependence of this quantity is shown in Fig. 12. We find that scaling $\tau_\gamma/\tau_\gamma(\xi q = 1)$ versus ξq generates a master curve, independent of volume fraction

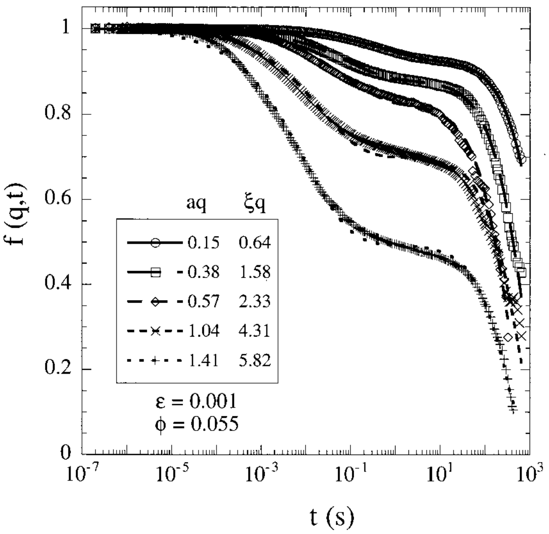


FIG. 11. q dependence of $f(q,t)$ for $\varepsilon=0.001$ and $\phi=0.055$. Curves are fits to Eq. (5).

and ε. Recall that ξ is the ϕ-dependent cluster size of the thermoreversible gel. From Fig. 12, $\tau_\gamma/\tau_\gamma(\xi q=1) \sim \xi q^{-0.53\pm0.06}$ for $\xi q>1$. The particular choices of nondimensionalization and fit interval were chosen to facilitate comparison to the recent report of Cipelletti *et al.* for dilute gels of aqueous colloidal polystyrene [17].

IV. DISCUSSION

This study of dynamic structure has demonstrated the complex decay of particle density fluctuations that occurs in thermoreversible colloidal gels. The system, which undergoes an abrupt dynamical transition at a critical temperature, consists of colloidal particles whose potential interactions are well modeled by the adhesive sphere model of Baxter. We first discuss features of the static structure salient to the dynamic behavior. We then consider the temperature and volume fraction dependence of characteristic times extracted from photon correlation spectroscopy of the colloidal gels by application of the model of Krall and Weitz, modified to account for the long-time behavior of $f(q,t)$. We discuss the divergence of characteristic times in the vicinity of the gel point in light of the structure and potential interactions of the system. The behavior of the thermoreversible gels is compared to recent studies of the dynamic structure factor of dilute, density matched aqueous polystyrene gels.

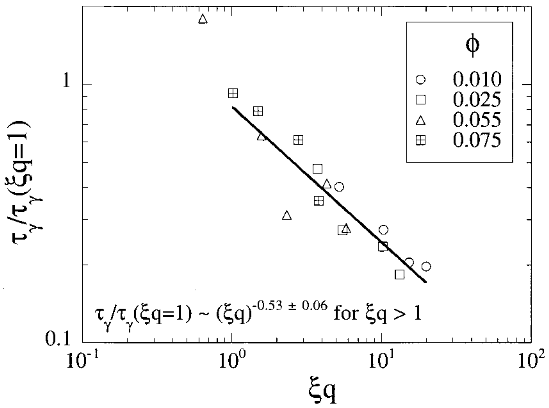


FIG. 12. q dependence of the characteristic time τ_γ, plotted according to the scaling suggested by Cipelletti *et al.* [17].

For thermoreversible gels, above the gel temperature, the static structure factor $S(q)$ changed continuously with temperature. Just above the gel point, a phenomenological correlation length ξ increased dramatically. The q dependence of the structure factor was consistent with an approach to the spinodal curve, in agreement with observations for other adhesive sphere dispersions. Although over the temperature interval studied a phenomenological correlation length ξ, obeyed a power law scaling, the studies at very low q and very small ε that would be required to determine if ξ truly diverged at the gel point were not conducted. Instead of such a divergence, it is possible that the fluid phase ξ grows to some critical value, at which point an ergodicity transition occurs. The correlation length present at the transition would then persist into the gel phase, since little change in $S(q)$ was observed as the temperature was decreased below the gel point. The data plotted in the inset of Fig. 2 are not sufficient to resolve the issue, since the correlation lengths extracted for the fluid and gel phases cannot be compared quantitatively. [The former were obtained from the Ornstein-Zernike equation, while the latter were from Eq. (1).] Thus the conclusions that can be drawn from Fig. 2 are limited: (1) The behavior of the adhesive sphere $S(q)$ in the fluid phase above the gel point is consistent with an approach to the spinodal curve. (2) For reasons that are not understood, at the critical temperature the adhesive spheres gel rather than phase separate.

The gel phase $S(q)$ was consistent with the fractal cluster model of Ref. [28], except at the highest volume fractions. The fractal dimension of the system, $d=2.4$, was large relative to other systems, particularly dilute aqueous colloidal polystyrene gels formed by addition of divalent electrolyte, for which diffusion-limited aggregation ($d=1.8$) has been reported [7,8]. The difference between the fractal dimension of the two gel systems is most likely explained by their different aggregation mechanisms. In the dilute gels of aqueous polystyrene, strong aggregation due to van der Waals interactions ($\Delta U_{\min}/kT, >1000$) occurs when the repulsive electrical double layer is destabilized by the addition of divalent electrolyte. The aggregation is strong and irreversible. However, adhesive spheres gel according to a mechanism that, although poorly understood, has some correspondence to spinodal decomposition, and results in only weak, reversible aggregation between colloids ($\Delta U_{\min}/kT<10$) [29,30].

Additional structural differences between thermoreversible and dilute aqueous polystryrene gels can be inferred from Fig. 4. It has been reported that fractal clusters of the latter fill space in a way that is independent of volume fraction [7,8]. This is not the case for the adhesive sphere gels, as demonstrated by the different scaling of the two curves plotted in Fig. 4. For the organophilic silica-hexadecane thermoreversible gels, the effective volume fraction (based on the cluster radius, ξ), varies by about a factor of 2 from the lowest volume fraction to the highest. This difference could conceivably be due to differences in the volume fraction range studied for the two systems (aqueous polystyrene gels: $\phi \sim 10^{-4}-10^{-3}$; thermoreversible gels: $\phi \sim 10^{-2}-10^{-1}$). Cluster polydispersity might play a role, particularly since the characteristic peak in $S(q)$ observed for dilute gels of monodisperse clusters is not apparent for the adhesive sphere gels. The ±10% error in the characterization of the fractal dimension d could also be relevant, since the slope of the curve plotted in Fig. 4 is a sensitive function of d. Alternatively, the observations of Fig. 4 might again signify real differences between the gelation mechanisms of the two systems.

The characterization of $S(q)$ establishes the fractal cluster structure as a plausible basis from which to interpret the dynamics of thermoreversible gels. Because the potential interaction of the adhesive colloidal spheres is sensitive to temperature, and because temperature can be precisely controlled during photon correlation spectroscopy, these suspensions are a good model system with which to study colloidal gelation. Above the gel temperature, the dynamic structure, $f(q,t)$, which characterized the decay of particle density correlations, exhibited a single, stretched exponential decay. Below the gel temperature, the decay was more complex. An initial, stretched exponential decay of $f(q,t)$ was arrested at a plateau value that persisted for as long as five decades in time. At a later time, $f(q,t)$ again decayed exponentially. The two-stage decay is a persistent feature of the thermoreversible gel dynamic structure factor below the gelation temperature. Possible artifactual origins of the long-time decay related to laser stability, temperature stability, and sedimentation have been considered by the authors. It has been concluded that each inadequately explains the observed behavior.

The argument of the stretched exponential relaxation, p, of $f(q,t)$ contains implicit information about the hierarchy of intracluster elastic modes that contributes to the decay of density correlations in the gel. The Krall-Weitz model of fractal cluster dynamics relates the stretched exponential relaxation of $f(q,t)$ to the length-scale-dependent bond spring constant $\kappa(s)$, where s is the length scale of an elastic mode. Because theory and simulation suggest that the fractal cluster is more compliant on longer length scales, $\kappa(s) \sim s^{-\beta}$ where β is the elasticity exponent. In the Krall-Weitz model the argument of the stretched exponential and the elasticity exponent are related by $p = \beta/(\beta+1)$. From computer simulation of clusters formed by diffusion-limited aggregation, $\beta \sim 3.1$ [31]. For dilute aqueous polystyrene gels, $p = 0.7$, and thus $\beta = 2.3$ [5].

The suspensions studied here exhibit an ε dependence of p above the gel temperature. Over the temperature range studied p decreased from about 0.8 to 0.5, independent of volume fraction. Below the gel point, $p = 0.5$ independent of ϕ and ε. Thus, for the thermoreversible colloidal gels, we find $\beta = 1.0$, a value that is significantly lower than that of the dilute aqueous polystyrene gels. This result is a central conclusion of our study, and demonstrates the remarkable differences in dynamic structure between these two types of colloidal gels.

A recent computer simulation of gel networks with particle-particle bonds possessing angular rigidity found $\beta \sim 1.1-1.3$ [32]. (For example, a trimer aggregate is a simple structure with angular rigidity. Singly connected particle pairs with bonds that transmit only central forces possess no angular rigidity.) This exponent is far smaller than for diffusion-limited aggregation, and demonstrates that the inclusion of particle-particle bonds with angular rigidity renders the structure less compliant on longer length scales. Thus the discrepancy between the elasticity exponent β of the thermoreversible colloidal gels and aqueous polystyrene gels is potentially explained by the angular rigidity of local structure.

Possible explanations for differences in the angular rigidity of the thermoreversible and dilute aqueous polystyrene gels are as follows. First, the greater ϕ of the thermoreversible gels may present greater opportunities for the formation of multiparticulate structures that are angularly rigid. Second, the enhanced surface roughness of the inorganic silica particles relative to the polystyrene colloids may cause a locking of aggregated particles with resultant noncentral forces and angular rigidity. Third, thermoreversible gels form by a mechanism that has some similarities to spinodal decomposition while aqueous polystyrene gels form by a kinetically controlled aggregation mechanism. The former case results in gels of a greater fractal dimension. The denser thermoreversible gels may again have more multiconnected and, therefore, angularly rigid regions.

Finally, we note that the approach to gelation as the temperature is decreased in thermoreversible gels appears to be accompanied by an increase in bond angular rigidity. This is demonstrated in Fig. 8, where the elasticity exponent decreases as the temperature is decreased toward the gel point. The effect saturates at gelation, where $\beta = 1.0$.

The above inferences about the elasticity exponent derived from experimental observations of p are consistent with the volume fraction dependence of the model parameters τ_β and δ^2. While for dilute aqueous polystyrene gels the reported scalings are $\tau_\beta \sim \phi^{-3.9}$ and $\delta^2 \sim \phi^{-2.7}$ [5], the exponents are significantly smaller for thermoreversible gels: $\tau_\beta \sim \phi^{-1.8}$ and $\delta^2 \sim \phi^{-1.2}$ (cf. the insets of Figs. 9 and 10). This discrepancy is explained by differences in cluster compliance. For fractal clusters $\tau_\beta \sim \xi^{(1+\beta)}$ and $\delta^2 \sim \xi^{\beta}$, where ξ is the cluster radius [5]. For thermoreversible gels, from Fig. 4, $\xi \sim \phi^{-1.16}$. Using this scaling and the previously characterized $\beta = 1.0$, the small scaling exponents of the adhesive sphere gels are predicted.

Although the success of the Krall-Weitz model of fractal cluster dynamics in modeling the initial and intermediate behavior of the adhesive sphere gels is remarkable, the interpretation of the data in this way is not unambiguous. Recalling again that static light scattering studies show the static correlation length $\xi \sim \phi^{-1.16 \pm 0.04}$, we note, however, that the Krall-Weitz model provides an alternative estimate of a (dynamic) correlation length, $R_c \sim \tau_\beta / \delta^2 \sim \phi^{-0.6 \pm 0.21}$. If the magnitudes of τ_β and δ^2 were solely determined by the normal modes of the fractal clusters, the two scalings would be congruent. The lack of agreement points to the possibility of additional mechanisms of cooperative dynamics in the adhesive sphere gels. Another potential origin of the discrepancy is the limited range over which the volume fraction scalings were collected. Alternatively, the clusters formed at the higher volume fractions studied may be too small (c.f. the inset table of Fig. 3) to exhibit fractal scaling.

The divergence of characteristic times at the gel point is reminiscent of the behavior at the colloidal hard sphere glass transition. For hard spheres, as the glass transition is approached from the fluid side, the mode coupling theoretical prediction of the divergence exponent of τ_α is -2.58. In the amorphous glass, the α relaxation is quenched while the β relaxation persists. The mode coupling prediction of the exponent for τ_β is -1.66 [33]. The analogous experimental scalings for the thermoreversible gels are $\tau_\alpha \sim \varepsilon^{-1.15}$ and $\tau_\beta \sim \varepsilon^{-1.00}$. A prediction of these exponents for the adhesive sphere suspensions, perhaps by means of mode coupling theory, awaits further theoretical development (see, however, recent reports in Refs. [2], [34]). Here we briefly consider the ε scaling of characteristic times in light of the fractal cluster model of gel dynamics.

Specifically, if the characteristic times τ_α and τ_β scale with the cluster relaxation time, as is implied by Eqs. (2) and (5) and the model of Krall and Weitz, then $\tau_\alpha \sim \tau_\beta \sim \tau_0(\xi/a)^{\beta+1}$, with $\beta = 1.0$ for thermoreversible gels. Here τ_0 is the relaxation time arising due to the viscous damping of a single bond with spring constant κ_0. Due to the apparent approach to the spinodal curve (cf. Fig. 2) observed above the gel point, $\xi \sim \varepsilon^{-1/2}$ (mean-field behavior) might be expected in this region, approximately, as has been observed for the organophilic silica/benzene system [10]. Thus the increase in cluster size that occurs as the gel point is approached from above provides one possible explanation for the ε dependence of the divergence of τ_α. However, we note that this simple explanation is complicated by three factors: first, for $\xi q > 1$, deviations from the mean-field scaling are anticipated; second, the ε dependence of ξ in the fluid close to the gel point is not known (ξ might diverge or smoothly cross over to the gel ξ); third, β itself is a function of ε (cf. Fig. 8) above the gel point.

This approach cannot explain the ε dependence of the divergence of τ_β, since in the region below the gel point the cluster radius does not vary significantly with temperature. In the absence of a significant effect of ε on the cluster radius, ξ, in the gel regime, we conclude that the rapid decrease in τ_β below the gel point as the temperature is decreased indicates the local stiffening of the gel network. The decrease in the maximum mean-squared displacement ($\delta^2 \sim \varepsilon^{-1.05}$) below the gel point is a further manifestation of the stiffening.

Thus the dramatic changes in dynamics below the gel point, which occur without accompanying changes in static structure, point to an unexpected sensitivity of the single bond relaxation time τ_0 (and thus also the bond spring constant κ_0) to the temperature and interparticle potential in the vicinity of the gel point. To demonstrate the sensitivity, we recall $\tau \sim \tau_0(\xi/a)^{\beta+1}$ for fractal clusters [5]. Since below the gelation temperature neither β nor ξ exhibits a significant ε dependence, we conclude that dynamical effects must originate with changes in the local parameter τ_0. Direct observation of local gel structure and dynamics is being pursued to address this unresolved issue.

The long-time decay of $f(q,t)$, characterized by the time τ_γ, observed for all samples below the gel temperature, possesses some similarities to recently reported observations in dilute aqueous polystyrene gels [17]. In the latter case, the decay was attributed to long time aging and gel structural evolution. To summarize the results of Cipelletti *et al.*, the decay in $f(q,t)$ was faster than exponential (argument of the exponential ~1.5), and scaled as $q^{-1.02\pm0.02}$. These observations were found to be consistent with gel syneresis. For the thermoreversible gels studied here, we find different behaviors: the long-time relaxation of $f(q,t)$ is exponential, and the decay time, τ_γ, scales as $q^{-0.53\pm0.06}$. The observed differences between the thermoreversible and dilute aqueous polystyrene gels might be explained by the very different potential interactions present in the two systems. For aqueous polystyrene gels that aggregate due to van der Waals interactions, the interaction potential at contact is very strong: $\Delta E_{\min}/kT > 1000$. For the thermoreversible gels, the potential interaction at contact is much weaker: $\Delta E_{\min}/kT \sim 10$. In the former case aggregation is irreversible, syneresis may occur, and the particle surfaces may even deform due to the strong attraction [17]. In the latter case, where interaction is weaker, disaggregation processes may occur with a probability governed by the Boltzmann factor $\exp(-\Delta E_{\min}/kT)$, that is small but not zero. Thus rare disaggregation events would provide an additional mechanism for the long-time decay of $f(q,t)$. Consequently, according to our description, whether the long-time decay of $f(q,t)$ in a particular system would occur due to a syneresis or disaggregation mechanism would depend upon the strength of the interparticle potential at contact. It is interesting to note that the disaggregation-aggregation hypothesis is not necessarily an aging mechanism, since such rare events would occur even at equilibrium. In fact, no observable evolution of the static intensity of the gels was observed over times up to three times as long as the photon correlation spectroscopy measurement times of this study. Nevertheless, aging studies to times on the order of 10^6 s, as performed, for example, by Cipelletti *et al.*, have not been performed for adhesive sphere gels at this time.

The detailed study of the role of disaggregation in the long-time decay of $f(q,t)$, necessary to predict both the magnitude and scattering vector dependence of τ_γ quantitatively, is beyond the scope of the present paper. Here we note that the observed values of τ_γ are not inconsistent with the disaggregation hypothesis. Specifically, for $q \sim a^{-1}$, we expect $\tau_\gamma \sim \tau_0 \exp(\Delta E_{\min}/kT) \sim \tau_0 \exp(\tau_B^{-1})$, where τ_B is the Baxter interaction parameter, and τ_0 is the single particle relaxation time. Given the observed values of τ_α, τ_β, and ξ/a, $\tau_0 \sim 10^{-1}-10^{-2}$ s, close to the gel point. Previous measurements lead us to expect $\tau_B \sim 0.1$ at gelation for the volume fraction range studied [3]. Thus disaggregation processes are predicted to contribute to the decay of $f(q,t)$ at $\tau_\gamma \sim 10^2-10^3$ s, which is the observed range. Consequently, this simple analysis does not rule out the possibility that more than one mechanism [i.e., disaggregation (this work) and syneresis (Cipelletti *et al.*)] may contribute to the long-time dynamics of colloidal gels, especially when the strength of interparticle interactions is weak. However, this conclusion requires further investigation, since neither the q nor ε dependence of τ_γ can currently be explained by such qualitative arguments.

In conclusion, this study has shown the usefulness of the fractal cluster model of Krall and Weitz for extracting characteristic times in the decay of density correlations of thermoreversible gels of adhesive spheres. Interesting differences between the dynamic structure of previously studied dilute aqueous polystyrene gels and thermoreversible gels have been quantified. As evidenced by differences in their elasticity exponents β, which characterizes the spatial scaling of the gel compliance, the structure of thermoreversible colloidal gels appears to possess greater angular rigidity than the dilute aqueous polystyrene gels. Differences in the behavior of the long-time decay of $f(q,t)$ were attributed to differences in the strength of interaction between the two materials. Finally, the remarkable sensitivity of the characteristic times τ_α and τ_β to $\varepsilon=(T-T_{\mathrm{gel}})/T_{\mathrm{gel}}$ could not be fully understood in terms of the dynamics of fractal clusters. Thus we suggest that alternative approaches that directly consider coordinate local dynamics might prove more fruitful in understanding the ε dependence of the divergence of characteristic times in the vicinity of the gelation transition.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation (CTS-9813824), DuPont, and the Donors of the Petroleum Research Fund, administered by the American Chemical Society. We acknowledge discussions with Dr. R. Butera, Professor R. G. Larson, and Professor R. A. Lionberger.

[1] C. J. Brinker and G. W. Scherer, *Sol-Gel Science: the Physics and Chemistry of Sol-Gel Processing* (Academic, Boston, 1990).

[2] J. Bergenholtz and M. Fuchs, Phys. Rev. E **59**, 5706 (1999).

[3] M. C. Grant and W. B. Russel, Phys. Rev. E **47**, 2606 (1993).

[4] S. M. Ilett, A. Orrock, W. C. K. Poon, and P. N. Pusey, Phys. Rev. E **51**, 1344 (1995); W. C. K. Poon, A. D. Pirie, and P. N. Pusey, Faraday Discuss. **101**, 65 (1995); N. A. M. Verhaegh, D. Asnaghi, H. N. W. Lekkerker, M. Giglio, and L. Cipelletti, Physica A **242**, 104 (1997).

[5] A. H. Krall and D. A. Weitz, Phys. Rev. Lett. **80**, 778 (1998).

[6] W. van Megen and S. M. Underwood, Phys. Rev. E **49**, 4206 (1994); W. van Megen, S. M. Underwood, and P. N. Pusey, Phys. Rev. Lett. **67**, 1586 (1991); W. van Megen and P. N. Pusey, Phys. Rev. A **43**, 5429 (1991).

[7] M. Carpineti and M. Giglio, Phys. Rev. Lett. **70**, 3828 (1993).

[8] M. Carpineti and M. Giglio, Phys. Rev. Lett. **68**, 3327 (1992).

[9] A. T. J. M. Woutersen, J. Mellema, C. Blom, and C. G. de Kruif, J. Chem. Phys. **101**, 542 (1994).

[10] H. Verduin and J. K. G. Dhont, J. Colloid Interface Sci. **172**, 425 (1995).

[11] M. Chen and W. B. Russel, J. Colloid Interface Sci. **141**, 564 (1991).

[12] C. J. Rueb and C. F. Zukoski, J. Rheol. **41**, 197 (1997).

[13] F. Pignon, A. Magnin, J. M. Piau, B. Cabane, P. Lindner, and O. Diat, Phys. Rev. E **56**, 3281 (1997).

[14] A. Mourchid, E. Lecolier, H. van Damme, and P. Levitz, Langmuir **14**, 4718 (1998).

[15] W. K. Kegel and A. van Blaaderen, Science **287**, 290 (2000).

[16] E. R. Weeks, J. C. Crocker, A. C. Levitt, A. Schofield, and D. A. Weitz, Science **287**, 627 (2000).

[17] L. Cipelletti, S. Manley, R. C. Ball, and D. A. Weitz, Phys. Rev. Lett. **84**, 2275 (2000).

[18] P. D. Patel and W. B. Russel, J. Colloid Interface Sci. **131**, 192 (1989).

[19] R. J. Baxter, J. Chem. Phys. **49**, 2770 (1968).

[20] P. W. Rouw, A. Vrij, and C. G. de Kruif, Prog. Colloid Polym. Sci. **76**, 1 (1988).

[21] C. G. de Kruif and J. C. van Miltenburg, J. Chem. Phys. **93**, 6865 (1990).

[22] W. Stober and A. Fink, J. Colloid Interface Sci. **26**, 62 (1968).

[23] G. H. Bogush, M. A. Tracy, and C. F. Zukoski, J. Non-Cryst. Solids **104**, 95 (1988).

[24] A. K. van Helden, J. W. Jansen, and A. Vrij, J. Colloid Interface Sci. **81**, 354 (1981).

[25] A. Cumming, P. Wiltzius, F. S. Bates, and J. H. Rosedale, Phys. Rev. A **45**, 885 (1992).

[26] P. Varadan and M. J. Solomon (unpublished).

[27] P. N. Pusey and W. van Megen, Physica A **157**, 705 (1989).

[28] S. K. Sinha, T. Freltoft, and J. Kjems, in *Kinetics of Aggregation and Gelation*, edited by F. Family and D. P. Landau (North-Holland, Amsterdam, 1984); F. Ferri, B. J. Frisken, and D. S. Cannell, Phys. Rev. Lett. **67**, 3636 (1991).

[29] R. G. Larson, *The Structure and Rheology of Complex Fluids* (Oxford University Press, New York, 1999).

[30] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, 1989).

[31] P. Meakin, J. Phys. A **17**, L975 (1984).

[32] A. H. L. West, J. R. Melrose, and R. C. Ball, Phys. Rev. E **49**, 4237 (1994).

[33] W. Gotze and L. Sjogren, Phys. Rev. A **43**, 5442 (1991).

[34] L. Fabbian, W. Götze, F. Sciortino, P. Tartaglia, and F. Thiery, Phys. Rev. E **59**, R1347 (1999).