

Scaling behavior of the elastic properties of colloidal gels

Wei-Heng Shih, Wan Y. Shih, Seong-Il Kim, Jun Liu, and Ilhan A. Aksay

Department of Materials Science and Engineering, University of Washington, Seattle, Washington 98195

and Advanced Materials Technology Center, Washington Technology Centers, University of Washington, Seattle, Washington 98195

(Received 4 May 1989)

The scaling behavior of the elastic properties of colloidal gels that are well above the gelation threshold is studied both theoretically and experimentally. A scaling theory was developed by considering the structure of the gel network as a collection of flocs, which are fractal objects closely packed throughout the sample. Two regimes are found based on the relative value of the elastic constant of the interfloc links to that of the flocs. In the strong-link (interfloc) regime, the elastic constant of the gels increases but the limit of linearity decreases with increasing particle concentration, whereas in the weak-link regime both the elastic constant and the limit of linearity increase with increasing particle concentration. Rheological studies on the elastic behavior of two types of boehmite alumina gels, Catapal and Dispal powders, were performed. Both types of gels in the concentration range studied showed the strong-link behavior and the results are in good agreement with the theoretical predictions. The value of the fractal dimension of the flocs $D \cong 1.95$, deduced from the rheological measurements, is in agreement with the value $D \cong 2.04$ deduced from the static light-scattering measurements on dilute suspensions. Therefore the scaling theory we developed also enables us to extract structural information from the rheological measurements.

I. INTRODUCTION

Colloidal suspensions can be either dispersed or flocculated, depending on (i) the magnitude of particle-particle interaction energy and (ii) particle concentration.¹ Various conditions such as pH, surfactant additives, and particle size can affect the interparticle interaction energy and thus cause the transition from the dispersed to the flocculated state.² A colloidal gel is a special state of flocculated systems in which a continuous network of particles is formed before settling occurs, with the resulting suspension having a very high viscosity and a finite shear modulus. The gel state occurs most often with small particles ($< 0.1 \mu\text{m}$) and the particle volume fraction in the gel state can be as low as a few percent. Although there have been many studies²⁻¹² on the scaling behavior of the structural properties of colloidal aggregates (flocs) and colloidal gels, the scaling behavior of the physical properties has been explored less. In this paper, we present both experimental and theoretical studies of the elastic properties of colloidal gels well above the gelation threshold. Since the system is now far from the gelation threshold, the scaling is no longer of the percolation type but rather is affected mainly by the structure of the individual flocs.

In polymeric systems, it is known that gels are formed by crosslinking polymers in semidilute solutions. Colloidal gels are very similar to polymer gels in that both are viscoelastic. Furthermore, colloidal gels are formed by particle aggregation and polymer gels are formed by polymerization and/or crosslinking, both of which are also aggregation processes. In view of this similarity, we developed a scaling theory for the elastic properties of colloidal gels by applying the scaling concepts which have been proved to be successful with polymer gels.¹³ When

colloidal gels are well above the gelation threshold, the scaling for both the elastic constant K and the limit of linearity γ_0 with respect to the particle concentration φ is dictated by the fractal nature of the colloidal flocs. The gel network is considered to be a collection of fractal flocs which are closely packed throughout the sample. Depending on the strength of the links between the flocs in comparison to that of the flocs, there can be two types of behavior, namely, strong-link behavior and weak-link behavior. In the strong-link regime, $K \sim \varphi^{(d+x)/(d-D)}$ and $\gamma_0 \sim \varphi^{-(1+x)/(d-D)}$; whereas in the weak-link regime, $K \sim \varphi^{(d-2)/(d-D)}$ and $\gamma_0 \sim \varphi^{1/(d-D)}$ where d is the Euclidean dimension, D is the fractal dimension of the flocs, and x is the backbone fractal dimension of the flocs. The main differences in the two regimes are (1) K increases more slowly in the weak-link regime than in the strong-link regime and (2) γ_0 increases with increasing particle concentration in the weak-link regime but decreases with increasing particle concentration in the strong-link regime. A colloidal gel may cross over from the strong-link regime to the weak-link regime with increasing particle concentration. Brown¹⁴ has also derived an expression for the shear modulus of colloidal gels which is similar to our expression of K for the strong-link regime.

The experimental studies were performed on the colloidal boehmite alumina gels of two different powders (Catapal and Dispal) using both rheological measurements and static light-scattering measurements. The rheological studies showed that both the storage modulus G' and the limit of linearity γ_0 exhibit a power-law behavior with respect to particle concentration φ , i.e., $G' \sim \varphi^{4.1}$ and $\gamma_0 \sim \varphi^{-2.1}$ for the Catapal powder and $G' \sim \varphi^{4.2}$ and $\gamma_0 \sim \varphi^{-2.3}$ for the Dispal powder. A similar scaling behavior for the shear modulus has also been observed by Buscall¹⁵ and by Sonntag and Russel¹⁶ for other

colloidal gels.

Comparison of our rheological measurements with the scaling theory indicates that the boehmite alumina gels we studied here are in the strong-link regime. Applying the scaling theory to analyze the rheological data, we obtained a fractal dimension $D \cong 2.0$ for the Catapal powder and $D \cong 1.95$ for the Dispal powder. The static light-scattering experiments on the dilute Dispal suspensions give a fractal dimension $D \cong 2.04$, which is in good agreement with the value deduced from the rheological measurements. Thus, the scaling theory not only explains the power-law behavior of the elastic constant and the limit of linearity but also allows the extraction of the structural information of the flocs such as the fractal dimensions from rheological experiments. It should be noted that, in the present study, there is no swelling of the fractal flocs in dilute suspensions since the screening of the interparticle interactions was kept the same at all particle concentrations.

The remainder of the paper is organized as follows. Sections II and III deal with the theory and the experiments, respectively. Conclusions and discussions are given in Sec. IV.

II. SCALING THEORY

Scaling theory has proven to be very successful in describing the elastic properties of polymer gels well above the gelation threshold. The basic concept of the scaling theory for polymer gels is to relate the elastic properties of a gel to its network structure. In a semidilute polymeric solution, the chains (polymers) overlap. One can define a correlation length ξ as follows: on a length scale that is smaller than ξ , a chain does not interact with other chains, and its swollen-coil structure can still be identified; while on a scale that is larger than ξ , the system is uniform. Thus, the structure of a semidilute polymeric solution can be approximated as closely packed blobs (meshes) (Ref. 13) of size ξ . When one crosslinks polymers in a semidilute solution, the system becomes a gel. Thus the static structure of a gel is identical to that of a semidilute polymeric solution, except that the polymeric network in a semidilute solution is transient. Many properties of a gel are determined from the bloblike network structure.

We assume that the structure of a colloidal gel is analogous to that of a polymer gel. The blobs in polymer gels are replaced by the flocs formed during aggregation. The blob size in polymer gels now represents the average floc size in the colloidal network. A schematic representation of colloidal gels is shown in Fig. 1 where the details of individual flocs are not shown. In reality, colloidal flocs (aggregates) can look more complicated than what we draw in Fig. 1. As an example, a transmission electron microscopy (TEM) micrograph of part of a colloidal floc formed by ZrO_2 particles is shown in Fig. 2. The flocs are considered to be fractal objects since there is much experimental evidence that colloidal aggregates behave like fractals, although the fractal dimension may vary with experimental conditions. For instance, the fractal dimension $D = 1.75$ for fast aggregation,²⁻⁵ which is coincident with the result of the cluster-cluster aggrega-

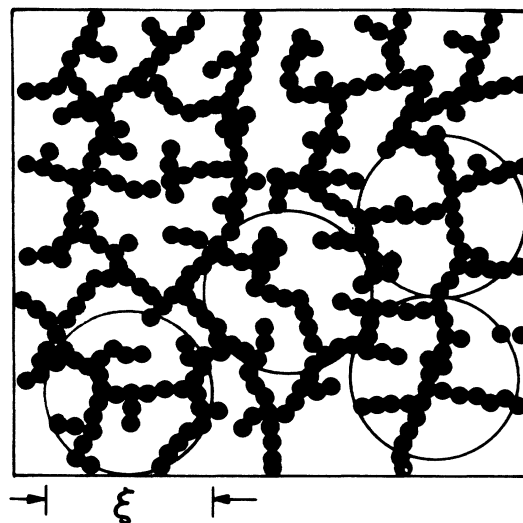


FIG. 1. Schematic structure of a colloidal gel. The circles indicate fractal flocs of size ξ . The regions between flocs are regarded as links.

tion model^{6,7} (CLCLA) and $D = 2.0$ for slow aggregation,⁸⁻¹⁰ which is coincident with the result of the reaction-limited aggregation model¹¹ (RLA). These fractal flocs pack closely and fill the sample volume as repeating units of the colloidal gel network. If the fractal di-

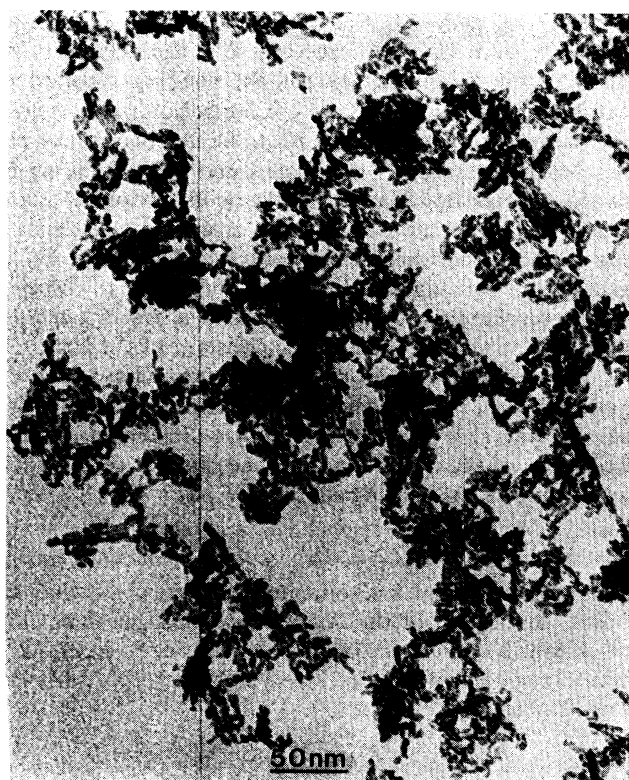


FIG. 2. Transmission electron micrograph of part of a colloidal ZrO_2 floc.

mension of the flocs is D , the scaling relation between the average floc size ξ and the particle concentration φ can be found by approximating the concentration inside the flocs as the overall particle concentration φ :

$$\xi \sim \varphi^{1/(D-d)}, \quad (1)$$

where d is the Euclidean dimension of the system. This relation is well known in semidilute polymer solutions¹³ where D is the inverse of the Flory's number ν ($D = \frac{5}{3}$ for polymers in a good solvent and 2 for polymers in a poor solvent) and has been shown recently to be correct for colloidal silica gels.¹²

The next step is to find the scaling relation of the elastic constant K_ξ of a floc of size ξ . The elastic properties of a floc are dominated by its effective backbone whose size is also ξ . One may approximate the elastic backbone to be a linear chain of springs. This assumption is justified in view of the fact that aggregates formed by the CLCLA model, the RLA model, or the diffusion-limited aggregation model (DLA) have very few loops. Kantor and Webman¹⁷ illustrated that in two dimensions, the elastic constant K_s of a linear chain of N_{bb} springs that belong to the backbone, when both stretching of springs and bending between neighboring springs are considered, is

$$K_s = \frac{K_0}{N_{bb} S^2}, \quad (2)$$

where K_0 is the bending constant between two neighboring springs and S is the radius of gyration of the projection of the nodes of the chain in the $\mathbf{F} \times \mathbf{Z}$ direction where $\mathbf{F}$ is the applied force and $\mathbf{Z}$ is the normal of the plane of the chain. In general, the bending constant K_0 can be a function of particle concentration. However, in the present study we assume K_0 to be independent of particle concentration. It was also found¹⁷ that bending between springs dominates the elastic behavior of a long chain, therefore the contribution from the stretching of the springs is not included in Eq. (2). Meanwhile, Eq. (2) also holds for higher Euclidean dimensions. When a spring represents a bond between two adjacent particles, we may approximate the elastic constant of the backbone K_ξ to be that of a linear chain of springs whose radius of gyration is ξ . Furthermore, the backbones of the flocs can be fractal objects with a fractal dimension different from that of the flocs. Namely, the number of springs in a floc that belong to the backbone N_{bb} is

$$N_{bb} \sim \xi^x, \quad (3)$$

where the exponent x is some number that is less than the fractal dimension of the flocs D and is larger than unity to provide a connected path. The quantity S^2 in Eq. (2) is now the square of the floc size ξ^2 . Therefore, combining Eqs. (2) and (3), we have

$$K_\xi \sim \frac{K_0}{\xi^{2+x}}. \quad (4)$$

Here, we see that the elastic constant of the individual flocs decreases rapidly with increasing floc size with a

power $2+x$ which is greater than 3. Thus, if flocs are allowed to grow bigger, they would behave as weaker springs. The macroscopic elastic constant K of a system of size L can be written in terms of that of the individual flocs:

$$K \sim \left[\frac{L}{\xi} \right]^{d-2} K_\xi. \quad (5)$$

Since the elastic constant of the individual flocs can vary widely depending on the floc size ξ and the backbone fractal dimension x as shown in Eq. (4), the elastic constant of the links between flocs may be different from that of the flocs. Therefore, as discussed in the following sections it is necessary to divide our discussion into two regimes: strong-link and weak-link.

A. Strong-link regime

The strong-link regime may be achieved by first allowing the individual flocs to grow very big so that each floc is a very weak spring as discussed above. One way to grow large flocs is to use a system of low particle concentration as indicated in Eq. (1). When the links between flocs (interfloc links) have a higher elastic constant than those of the flocs, the macroscopic elastic constant K as a function of φ is dominated by the behavior of the elastic constant of the flocs K_ξ . Combining Eqs. (1), (4), and (5), we have

$$K \sim \varphi^{(d+x)/(d-D)}. \quad (6)$$

Therefore the elastic constant of a gel increases with particle concentration in a power-law fashion with the exponent $(d+x)/(d-D)$. It is worth noting that Ref. 14 did not distinguish between the strong-link and the weak-link regimes and did not study the limit of the linear behavior shown below. It should be emphasized that Eq. (6) is a result of the change of floc size as the particle concentration is varied. The interactions between particles and, hence, the spring constants are assumed to be independent of particle concentration.

In the strong-link (interfloc) regime, the breaking of bonds occurs within a floc. Suppose that we impose a macroscopic deformation on the system ΔL , the deformation of a floc is then

$$(\Delta L)_\xi \sim \frac{\Delta L}{L/\xi}. \quad (7)$$

The force on a floc is thus

$$F_\xi = K_\xi (\Delta L)_\xi = \frac{K_0}{\xi^{2+x}} \frac{\Delta L}{L/\xi}. \quad (8)$$

The weakest bonds in a floc would be the singly connected bonds on which the force is exactly F_ξ . When the force on a bond is beyond a certain criterion, e.g., 1, the bond breaks. Therefore we set $F_\xi = 1$ and obtain the limit of linearity γ_0 at which the weakest bonds break and the linear elastic behavior vanishes

$$\gamma_0 = \frac{\Delta L}{L} \sim \xi^{1+x} \sim \varphi^{-(1+x)/(d-D)}. \quad (9)$$

Thus Eq. (9) predicts that the observable linear region (where Hooke's law applies) shrinks with increasing particle concentration in the strong-link regime.

B. Weak-link regime

The weak-link regime may be achieved with very small flocs. As one can see from Eq. (4), small flocs are stronger springs compared to large flocs. One way of forming small flocs is to start with a higher particle concentration as we have shown in Eq. (1). In the case of weak interfloc links, the elastic behavior of the gels is dominated by the elastic constant of the interfloc links K_l since the flocs are now more rigid when compared to the interfloc links. Again, one can write the elastic constant of a system of L in terms of that of the interfloc links

$$K \sim \left[\frac{L}{\xi} \right]^{d-2} K_l \sim \xi^{-(d-2)} \sim \varphi^{(d-2)/(d-D)}. \quad (10)$$

Similarly the behavior of the limit of linearity γ_0 can be obtained by

$$\gamma_0 \sim \xi^{-1} \sim \varphi^{1/(d-D)}. \quad (11)$$

Comparing Eqs. (6) and (10), one can see that in the weak-link regime the elastic constant of the system increases more slowly than in the strong-link regime. Moreover, Eq. (11) predicts that the limit of linearity increases with increasing concentration in the weak-link regime, in contrast to the strong-link case.

Before ending this section, it should be emphasized that in this paper, we are dealing with the scaling behavior of the elastic properties of colloidal gels that are well above the gelation threshold. The scaling behavior of the elastic properties well above the gelation threshold is dominated by the fractal nature of the flocs that form the building blocks of the system. This is in contrast to the scaling behavior near the gelation threshold where a threshold and critical phenomena are involved. Furthermore, the fractal dimension of the flocs should be those of the colloidal aggregates rather than that of the percolation clusters since the flocs were formed by aggregation processes and the gels were well above the gelation threshold. For example, this point has been clearly demonstrated in polymeric systems.¹³ Near the gel point, the shear modulus of a gel behaves like $G \sim (\varphi - \varphi_g)^t$ which is characteristic of a percolation transition and the exponent t is not related to the exponent ν ($R_G \sim N^\nu$) of the individual polymers. Whereas far from the gel point, while the system is still in the semidilute regime, the shear modulus behaves as $G \sim \varphi^{2.25}$ for a good solvent and $G \sim \varphi^3$ for a poor solvent. The exponent 2.25 (or 3) is related to the exponent ν of the individual polymers.

III. EXPERIMENTS

Experiments were carried out with aqueous suspensions of two boehmite alumina powders, i.e., Catapal and Dispal, supplied by Vista Chemical Co. in Houston, Texas. Two systems were shown in order to demonstrate the

generality of our results. The Catapal system was studied at constant pH while the Dispal system was studied at a constant electrolyte concentration. The Catapal powders are agglomerated platelike boehmite alumina crystallites. The dried agglomerates are irregular in shape with an average size of 65 μm . The agglomerates can be dispersed in acidic solution and broken up into single crystallites (50–100 Å in diameter and 10–20 Å in thickness) or smaller agglomerates.¹⁸ The Dispal powder can be readily dispersed in water. The dried Dispal agglomerates appear more spherical and much smaller in size than the Catapal agglomerates.

The Catapal powder suspensions of 3 to 10 vol % were prepared by electrostatic stabilization. The Catapal powder was mixed with distilled water and 0.03 mol of nitric acid was added to 1 mol of boehmite and was shaken in a wrist-action shaker for 48 h to break up the agglomerates. To eliminate the hard agglomerates the suspensions were left for 48 h resulting in a sediment in the bottom of the suspension. The top portions of the suspensions were decanted and used for the experiments. The pH was adjusted to 5.5 by adding 1N NaOH solution to obtain a gel. The gels were then placed in the rheometer for measurements. The Dispal powder suspensions of 3 to 11 vol % were also prepared by electrostatic stabilization. The Dispal powder was mixed with distilled water. The pH of the suspensions was 3.5 ± 0.5 .

In order to compare with the scaling theory described earlier, we kept the interparticle interaction independent of particle concentration by adding a large amount of electrolyte. In the case of the Dispal powders, we have added 0.244M KCl to all samples to induce gelation, including the sample on which the light-scattering experiment was performed. The ξ potential of the boehmite particles was about 40 mV. Therefore, each particle carries about 10 electron charges and releases the same number of counter ions in the suspension. In our most concentrated sample with about 10 vol % of boehmite particles, the particle number density was about 10^{17} cm^{-3} and the number concentration of the counter ions released by the particles was about 10^{18} cm^{-3} , both of which are much smaller than the number concentration of the added electrolytes, which is about $2 \times 10^{20} \text{ cm}^{-3}$. Under the electrostatic condition, within the Derjaguin, Landau, Verwey, and Overbeek¹⁹ (DLVO) theory, the screening of the interparticle repulsion is dominated by the added electrolytes but not the particles nor the counter ions released by the particles. Therefore, the interaction between particles should be independent of particle concentration. In the Catapal system, the screening of the interparticle interaction is dominated by the added nitrate. In a 10 vol % Catapal suspension, the number concentration of nitrate was about 10^{20} cm^{-3} which was again much larger than both the number density of the particles and that of the counter ions.

Unlike the Catapal gels, the Dispal gels were grown *in situ* within the rheometer. However, we found that for the experimental conditions we have chosen, the measurements of the boehmite alumina gels were not affected much whether the gels were grown in the rheometer *in situ* or not. This is very different from silica gels,

where the behavior of the gels after shear is different from that of the freshly grown gels.²⁰

For both the Catapal and the Dispal suspensions, the gelation threshold is between 1 and 2 vol %. A 1 vol % suspension never gels and a 2 vol % suspension gels after several days. Thus the concentration range (≥ 3 vol %) we studied for the Catapal and Dispal gels is well above the gelation threshold, i.e., $\phi/\phi_c > 1$, where ϕ_c denotes the gelation threshold. Therefore, the elastic behavior of the gels is not determined by the scaling of the percolation transition as it might be near the gelation threshold but is instead dominated by the fractal nature of the colloidal flocs as we have argued above.

We performed dynamic rheological measurements on the boehmite alumina gels using the Rheometrics Fluids Spectrometer (RFS-8400). The storage (G') and loss (G'') moduli were measured at various oscillating strain amplitudes γ with angular frequency $\omega = 0.7$ rad/s for Catapal gels and $\omega = 1.0$ rad/s for Dispal gels. The test fixture used was parallel plates (50 and 25 mm in diameter) and the gap between the plates was between 1 and 1.5 mm. The storage modulus G' measures the elastic response and the loss modulus G'' measures the viscous dissipation per cycle of sinusoidal deformation of a gel. Typical behavior of G' and G'' as a function of strain is shown in Fig. 3. G' is constant at small strain and decreases at higher strain. We interpret the onset of the nonlinearity (decrease in G') to be the breaking of the weak bonds in the gel network. The limit of linearity γ_0 , defined as the end point of the linear region—which we chose experimentally as the point beyond which G' deviates more than 5% from its maximum value—is shown in Fig. 4 as a function of particle concentration for Catapal gels and in Fig. 5 for Dispal gels. Figures 6 and 7 show the value of the storage modulus in the linear region G'_0 as a function of the particle concentration for Catapal gels and Dispal gels, respectively. Both G'_0 and γ_0 show a power-law behavior and can be fitted to the forms

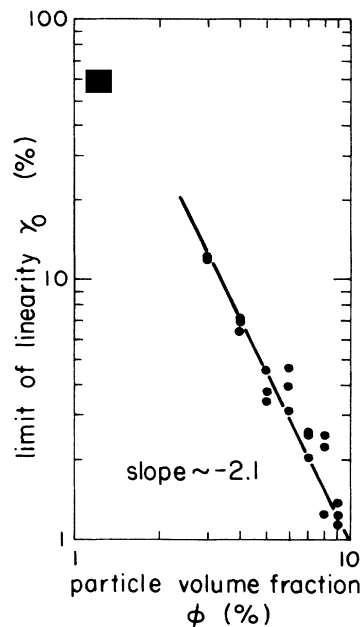


FIG. 4. Limit of linearity as a function of Catapal particle concentration at pH=5.5. The limit of linearity is defined as in the text.

$$G'_0 \sim \begin{cases} \phi^{4.1} & \text{for Catapal gels} \\ \phi^{4.2} & \text{for Dispal gels} \end{cases} \quad (12)$$

and

$$\gamma_0 \sim \begin{cases} \phi^{-2.1} & \text{for Catapal gels} \\ \phi^{-2.3} & \text{for Dispal gels} \end{cases} \quad (13)$$

The exponents 4.1 and 4.2 for G'_0 are comparable to that for colloidal silica gels,¹⁵ which is 4.0 ± 0.5 , while the scaling behavior for the limit of linearity is observed here for the first time. The trend of decreasing limit of lineari-

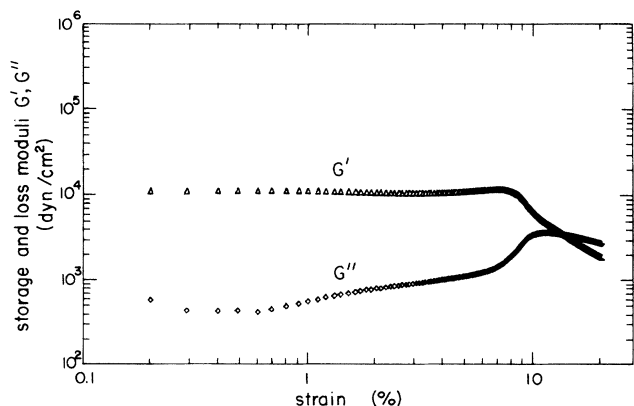


FIG. 3. The storage modulus G' and loss modulus G'' of Dispal boehmite alumina gels at 4.5 vol %, as a function of strain amplitude. The electrolyte concentration is 0.244M.

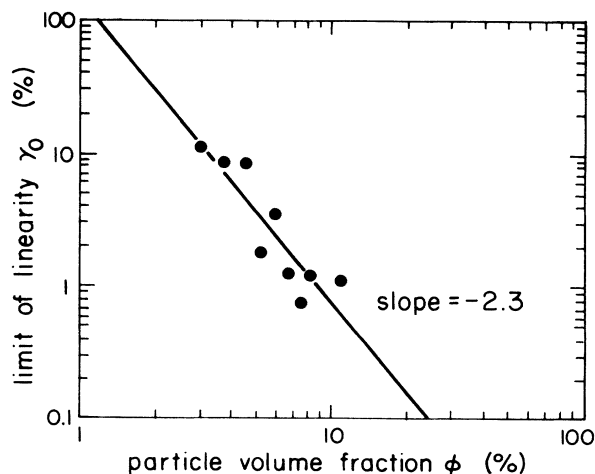


FIG. 5. Limit of linearity as a function of Dispal particle concentration at electrolyte concentration 0.244M.

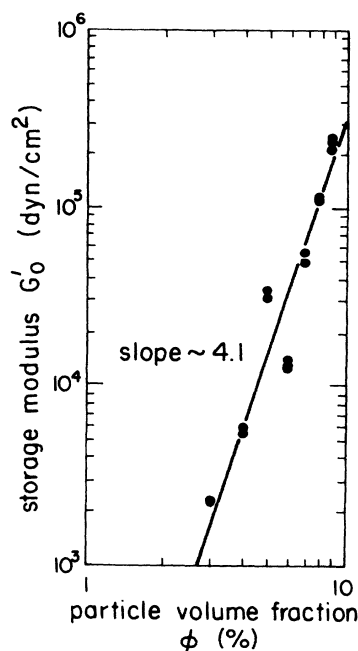


FIG. 6. Storage modulus in the linear region as a function of Catapal particle concentration at pH=5.5.

ty with increasing concentration indicates that the system is in the strong-link regime. Comparing Eq. (12) with Eq. (6) and Eq. (13) with Eq. (9), one obtains $x \approx 1.1$ and $D \approx 2.0$ for the Catapal gels and $x \approx 1.4$ and $D \approx 1.95$ for the Dispal gels studied here.

To check our prediction more closely, we also performed static light-scattering experiments on the dilute Dispal suspensions to determine the fractal dimension D of the flocs. The light-scattering unit has a 50-mW helium-neon laser with a wavelength $\lambda = 632.8$ nm and

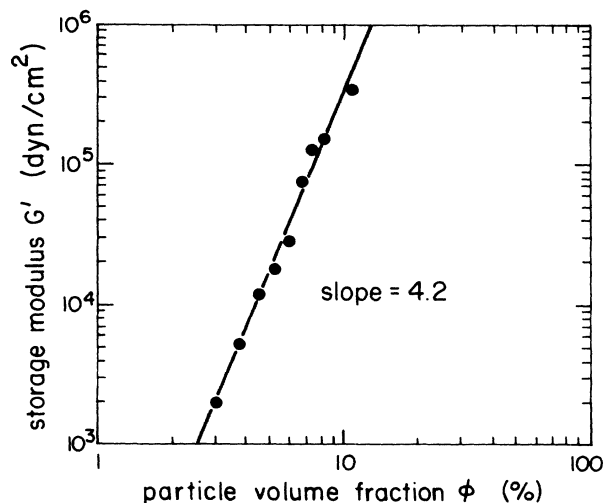


FIG. 7. Storage modulus in the linear region as a function of the Dispal particle concentration. The electrolyte concentration is the same as in Fig. 5.

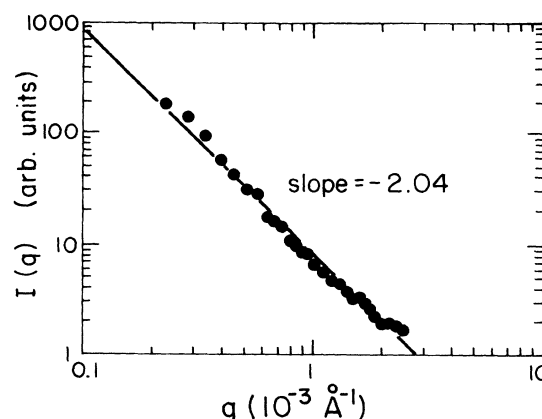


FIG. 8. $I(q)$ vs q for the dilute Dispal suspensions at 0.0075 vol % where $I(q)$ is the light-scattering intensity and the definition of q is given in the text. The electrolyte concentration is the same as in Figs. 5 and 7.

was manufactured by Brookhaven Instrument Corporation. The scattering intensity $I(q)$ versus q of a Dispal suspension at 0.0075 vol % and electrolyte concentration of 0.244M is shown in Fig. 8 where q is related to the scattering angle θ by $q = (4\pi n / \lambda) \sin(\theta/2)$ with n as the refractive index of the fluid. The negative of the slope of the least-squares fit to the double-logarithmic plot of $I(q)$ versus q in Fig. 8 gives the fractal dimension of the flocs,²¹ $D \approx 2.04$, which is in agreement with the value $D = 1.95$ deduced from the rheological measurements.

Under electrostatic conditions, the interaction between two colloidal particles is described by the DLVO theory. The interparticle interaction has two minima; the primary minimum is essentially infinitely deep and occurs at contact, whereas the second minimum is very shallow, often shallower than $k_B T$, and occurs at a farther separation distance where k_B is the Boltzmann constant and T is the room temperature. Between the two minima there is a repulsive barrier whose height changes with the particle surface charge, electrolyte concentration, etc. At low electrolyte concentrations, the repulsive barrier prevents particles from aggregating. When a high concentration of electrolyte is added to the suspension, the repulsive barrier is much reduced. The thermal energy is enough to activate particles to overcome the repulsive barrier, resulting in slow aggregation. The aggregates formed by slow aggregation under electrostatic conditions exhibit a fractal dimension around 2.0 which is consistent with the result of the computer simulations of the RLA model. Furthermore, the fractal dimension 2.0 for aggregates formed by slow aggregation has been shown to be quite universal for various colloidal particles ranging from colloidal gold, to colloidal silica, to colloidal polystyrene particles.²² Since our gels were formed by slow aggregation under electrostatic conditions it is reasonable to expect that the aggregates are of the RLA type with a fractal dimension $D \sim 2.0$.

In general, clusters may swell in dilute suspensions if

the interparticle interaction has a particle-concentration dependence.^{13,23} The concentration dependence of the interaction results from the screening of the interparticle interaction by the presence of other particles at concentrated suspensions. This has been observed in many polymeric systems.¹³ The dimension D , which is the inverse of the Flory number ν , is 1.67 in a dilute solution with a good solvent, and D becomes 2.0 in a polymer melt.¹³ The experiment by Martin, Wilcoxon, and Adolf²⁴ also indicated that clusters swelled in dilute solutions in their polymeric silica gels. However, in the present study, the fractal dimension obtained by the light-scattering experiment in the dilute suspension agrees with that obtained from the rheological measurements at the gel state, indicating that there is no swelling of clusters in the dilute suspensions. This is expected since in the Dispal samples, we added the same concentration of KCl to all samples to ensure that the screening of the interparticle interaction is dominated by the added electrolytes but not by the particles and the counter ions they released. A similar result was also obtained in colloidal silica gels¹² where a high concentration of NaCl (about 0.45M) was added. Light-scattering measurements on gels of 1.2–10 wt % gave a fractal dimension of 2.16 ± 0.10 consistent with the value 2.08 obtained by light-scattering measurements in dilute suspensions.¹²

We also performed dynamic light-scattering experiments on the dilute suspensions. Clusters begin to grow when 1N KNO₃ is added such that the electrolyte concentration is 0.244M. After a day or two, an average cluster size of 0.1 μm is observed. This indicates that the average floc size ξ is on the order of 0.1 μm , similar to the size observed in the silica gels.¹²

IV. SUMMARY AND DISCUSSIONS

By assuming a certain structure for colloidal gels, a simple but systematic scaling theory for both the elastic constant and the limit of linearity of colloidal gels that are well above the gelation threshold can be derived. The scaling of the elastic properties of colloidal gels under such conditions is dominated by the fractal nature of the flocs and is different from the scaling near the gelation threshold where a percolation-type scaling may apply. The exponents for both the elastic constant and the limit of linearity can be expressed in terms of the fractal dimension D and the backbone fractal dimension x of the flocs. The fractal dimension D of the flocs should be that of the colloidal aggregates. In general, there can be two types of scaling behavior, i.e., the strong-link behavior and the weak-link behavior. The scaling of both the storage modulus and the limit of linearity depends on whether the interfloc links are stronger than the flocs. The linear region shrinks with increasing concentration in the strong-link regime but increases with increasing concentration in the weak-link regime. The theory also enables us to extract from the rheological measurements structural information about the individual flocs, such as the fractal dimension of the flocs and the fractal dimen-

sion of the elastic backbones of the flocs. The rheological measurements are in good agreement with the scaling predictions. The value of the fractal dimension of the flocs of the Dispal gels $D \cong 1.95$ deduced from the rheological measurements is in agreement with the value $D \cong 2.04$ deduced from light scattering measurements on dilute suspensions. Moreover, both the rheological and the light-scattering measurements support that the fractal dimension of the flocs is indeed that of the colloidal aggregates but not that of the percolation clusters. Previously, structural information could only be obtained by other techniques, such as light-scattering experiments or box counting on TEM micrographs. In the present study, there is no swelling of the clusters in the dilute suspensions since the screening of the interparticle interaction was kept the same by adding the same concentration of KCl to all samples.

The backbone fractal dimension x for elasticity has not been measured directly. However, it is known that the backbone for elasticity is the same as that for electrical conduction if both bending and stretching of springs are considered for the elasticity case.¹⁷ Thus, we may determine x by working on an easier problem, namely the fractal dimension of the backbones for electrical conduction. Recently we calculated x for two-dimensional CLCLA systems.²⁵ We found that x is a function of concentration; it increases from 1 to 1.3 as concentration is lowered. Therefore, the experimentally-deduced values of $x \cong 1.1$ and 1.4 are quite reasonable for three-dimensional systems.

Finally, we comment on the crossover behavior between the strong-link and weak-link regimes. Since K_ξ increases with increasing concentration, a higher concentration should correspond to the weak-link regime. The crossover concentration from the strong-link to the weak-link regime can be estimated. The crossover point corresponds to $K_0/\xi^{2+x} \sim K_l$, and we get

$$\xi_c \sim \left[\frac{K_0}{K_l} \right]^{1/(2+x)}, \quad \varphi_c \sim \left[\frac{K_0}{K_l} \right]^{(D-d)/(2+x)}. \quad (14)$$

In order for the crossover behavior to occur, K_0 has to be larger than K_l . In polymeric gels with crosslinkers, the links correspond to the crosslinkers and thus K_l is usually larger than or equal to K_0 . Therefore, polymeric gels seldom show the crossover behavior. However, there are no crosslinkers in colloidal gels and K_0 can be larger than K_l . Recently, Liu *et al.*²⁶ have observed the crossover from the strong-link behavior to the weak-link behavior in silica gels when particle concentration is increased.

ACKNOWLEDGMENTS

This work was supported by the U.S. Air Force Office of Scientific Research and the U.S. Defense Advanced Research Project Agency under Grant No. AFOSR-87-0114 and the U.S. Army Research Office under Grant No. DAAG 29-85-K0136.

- ¹I. A. Aksay and R. Kikuchi, in *Science of Ceramic Chemical Processing*, edited by L. L. Hench and D. R. Ulrich (Wiley, New York, 1986), p. 513.
- ²For example, see C. Aubert and D. S. Cannell, *Phys. Rev. Lett.* **56**, 738 (1986).
- ³D. A. Weitz and M. Olivera, *Phys. Rev. Lett.* **52**, 1433 (1984).
- ⁴P. Dimon, S. K. Sinha, D. A. Weitz, C. R. Safinya, G. S. Smith, W. A. Varady, and H. M. Lindsay, *Phys. Rev. Lett.* **57**, 595 (1986).
- ⁵C. Bolle, C. Cametti, P. Codastefano, and P. Tartaglia, *Phys. Rev. A* **35**, 837 (1987).
- ⁶P. Meakin, *Phys. Rev. Lett.* **51**, 1119 (1983).
- ⁷M. Kolb, R. Botet, and R. Jullien, *Phys. Rev. Lett.* **51**, 1123 (1983); R. Jullien, M. Kolb, and R. Botet, in *Kinetics of Aggregation and Gelation*, edited by F. Family and D. P. Landau (Elsevier, Amsterdam, 1984), p. 101.
- ⁸D. A. Weitz, J. S. Huang, M. Y. Lin, and J. Sung, *Phys. Rev. Lett.* **54**, 1416 (1985).
- ⁹D. A. Schaefer, J. E. Martin, P. Wiltzius, and D. S. Cannell, *Phys. Rev. Lett.* **52**, 2371 (1984).
- ¹⁰J. C. Rarity and P. M. Pusey, in *On Growth and Form*, edited by H. E. Stanley and N. Ostrowsky (Nijhoff, Dordrecht, 1986), p. 219.
- ¹¹M. Kolb and R. Jullien, *J. Phys. (Paris) Lett.* **45**, 977 (1984).
- ¹²G. Dietler, C. Aubert, D. S. Cannell, and P. Wiltzius, *Phys. Rev. Lett.* **57**, 3117 (1986).
- ¹³P. G. De Gennes, *Scaling Concepts of Polymer Physics* (Cornell University Press, Ithaca, New York, 1979).
- ¹⁴W. D. Brown, Ph.D. thesis, University of Cambridge, 1987.
- ¹⁵R. Buscall, P. D. Mills, J. W. Goodwin, and D. W. Lawson, *J. Chem. Soc. Faraday Trans.* **84**, 4249 (1988), and references therein.
- ¹⁶R. C. Sonntag and W. B. Russel, *J. Colloid Interface Sci.* **116**, 485 (1987).
- ¹⁷Y. Kantor and I. Webman, *Phys. Rev. Lett.* **52**, 1891 (1984).
- ¹⁸J. D. F. Ramsay, S. R. Daish, and C. J. Wright, *Faraday Discuss. Chem. Soc.* **65**, 65 (1987).
- ¹⁹For example, see J. Th. G. Overbeek, *J. Colloidal Interface Sci.* **58**, 408 (1977).
- ²⁰W.-H. Shih, J. Liu, W. Y. Shih, S. I. Kim, M. Sarikaya, and I. A. Aksay, in *Processing Science of Advanced Ceramics, MRS Symposium Proceedings*, edited by I. A. Aksay, G. L. McVay, and D. R. Ulrich (Materials Research Society, Pittsburgh, 1989), Vol. 155, p. 83.
- ²¹J. Teixeira, in *On Growth and Form*, edited by H. E. Stanley and N. Ostrowsky (Nijhoff, Dordrecht, 1986), p. 145.
- ²²M. Y. Lin, H. M. Lindsay, D. A. Weitz, R. C. Ball, R. Klein, and P. Meakin, *Nature* **339**, 360 (1989).
- ²³J. Isaacson and T. C. Lubensky, *J. Phys. (Paris)* **41**, L469 (1980).
- ²⁴J. E. Martin, J. Wilcoxon, and D. Adolf, *Phys. Rev. A* **36**, 1803 (1987).
- ²⁵W.-H. Shih, W. Y. Shih, I. A. Aksay, in *Fractal Aspect of Materials: Disordered Systems*, edited by D. A. Weitz, L. M. Sander, and B. B. Mandelbrot (Materials Research Society, Pittsburgh, 1988), p. 239.
- ²⁶J. Liu, W.-H. Shih, W. Y. Shih, M. Sarikaya, and I. A. Aksay (unpublished).

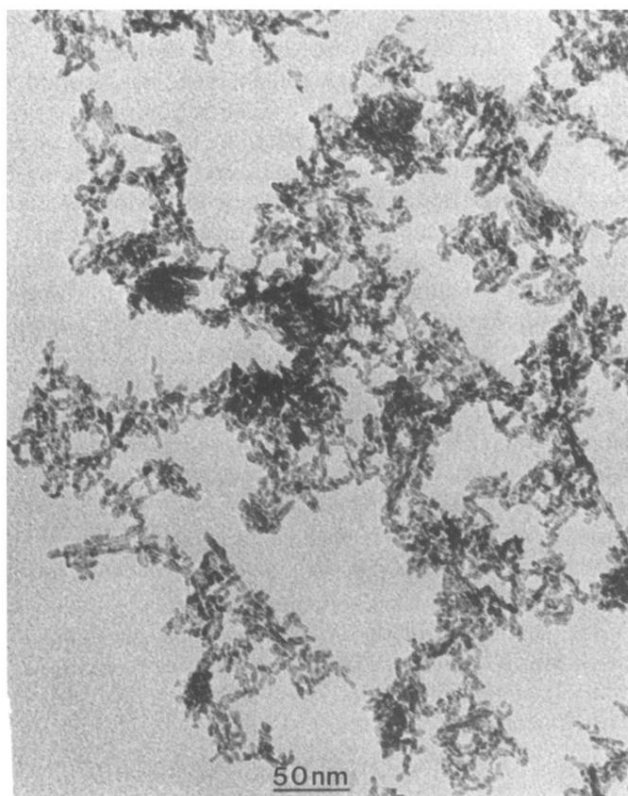


FIG. 2. Transmission electron micrograph of part of a colloidal ZrO_2 floc.