MECHANICAL PROPERTIES OF COLLOIDAL GELS


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INTRODUCTION

A colloidal suspension can be either dispersed or flocculated depending on the interaction between the colloidal particles. If the interaction is repulsive, particles can relax to the minimum of the potential due to their neighboring particles, and the system can reach an equilibrium dispersed state. In the case of attractive interaction, particles form aggregates that settle to the bottom of the container. As the concentration of particles is increased, the overcrowding of the aggregates produces a continuous network throughout the suspension before they settle and a colloidal gel is formed. A major difference between a colloidal gel and a colloidal suspension is that the gel can sustain finite stress and is therefore viscoelastic. Previously we studied the storage modulus and the yield strain of boehmite gels and found that they are related to the particle concentration in a power-law fashion [1]. Similar scaling behavior of the shear modulus was found for other colloidal particulate networks by Buscall et al. [2]. We developed a scaling theory [1] which successfully explains the experimental results on boehmite gels. The theory further predicts that there can be two types of power-law behavior depending on the relative elastic strength of the clusters to that of the links between clusters within the gel network. Furthermore, there can be a crossover from one type of behavior to the other as the particle concentration is varied.

In this paper, with a dynamical rheology study on colloidal silica gels we clearly demonstrate the crossover. In addition, we find that depending on whether surfactant is added or not, we may have two types of mechanical behavior of colloidal gels: hard gels and soft gels. (1) In hard gels, the storage modulus $G'$ increases with particle volume fraction in a power-law fashion as described by the scaling theory. (2) In soft gels, $G'$ increases with concentration in an exponential fashion. Monte Carlo simulations on restructuring of clusters show an exponential relationship between the largest cluster size and the concentration, indicating that the exponential behavior in $G'$ may be a result of the restructuring of clusters. Moreover, the exponential behavior of $G'$ with respect to particle concentration is similar to the behavior of the applied pressure as a function of resultant cake density in pressure filtration, suggesting that the pressure filtration behavior may also be understood in terms of the restructuring of the particle network.

In the following, we briefly summarize our theory on the elastic constant and yield strain of colloidal gels, followed by the experimental results on silica gels. Finally, we end with discussions and conclusions.
Figure 1. The schematic structure of a gel network is shown in la in which some clusters with average size $\xi$ are circled. lb shows TEM micrograph of a typical colloidal silical gel.
\[ K \sim \varphi^{(d+x)/(d-D)}. \]  

In the weak-link regime, \( K_\xi > K_f \), we replace \( K_\xi \) in Eq. (3) with \( K_f \) and obtain

\[ K \sim \varphi^{(d-2)/(d-D)}. \]  

The yield strain \( \gamma_y \) of a colloidal gel can also be obtained by studying the breaking of the weakest springs in the network. In the strong-link regime,

\[ \gamma_y \sim \varphi^{-1/(d-D)} \]  

while in the weak-link regime,

\[ \gamma_y \sim \varphi^{1/(d-D)}. \]  

As is clear from Eqs. (4)-(7), the scaling behavior of the elastic constant and that of the yield strain are different in the two regimes. Although the elastic constant increases with concentration in a power-law fashion in both regimes, the exponent in the strong-link regime is larger than that in the weak-link regime. Moreover, the yield strain decreases with increasing concentration in the strong-link regime whereas the yield strain increases with concentration in the weak-link regime. The scaling theory further predicts that there can be a crossover from the strong-link behavior to the weak-link behavior as concentration is increased since increasing concentration reduces the average cluster size and thus increases \( K_\xi \) as is clear from Eq. (2).

**EXPERIMENTS**

Silica gels were prepared from Ludox Colloidal Silica H30. The particle size was 12 nm and the as-received suspensions were electrostatically stabilized. Two types of samples were prepared. In the first type which we call hard gels, the pH of the suspensions was adjusted to 9.5 and the suspensions were mixed with KCl. The particle concentration was adjusted to a predetermined value (0.65 to 11.25%) and the KCl concentration was set at 0.25M. In the second type of samples which we call soft gels, the suspensions were adjusted to pH = 2 first, followed by the addition of the nonionic surfactant, octyphenol, such that the surfactant-to-particle weight ratio was 15.64%. The gels were grown in situ within the test fixtures to prevent disturbance, and the growth of gels took about 10 minutes to 1 hour, depending on the particle concentration.

Two types of test fixtures were applied in the dynamic-rheological study using Rheometrics Fluids Spectrometer (RFS-8400). In the couette fixture, the gels were grown between two cylinders with a gap of 1 mm. We exert torsional stress on the outside cylinder and measure the response of a torsion wire attached to the inner cylinder. In the parallel plate fixture, the gels were grown between two parallel disks 25 mm in diameter and the gap between the disks was between 1 to 2 mm. When the bottom disk was stressed, the dynamic response of the sample was obtained by looking at the torsion wire attached to the upper disk. An oscillatory strain is imposed on the system by either rotating the bottom disk or outer cylinder with a
SCALING THEORY

A scaling theory has been developed to correlate the elastic constant and the yield strain of colloidal gels to their structures [1]. Here we briefly summarize the main results of the theory and refer readers to Ref. 1 for a more detailed description of the theory. The theory is based on the fact that in the dilute regime of flocculated systems there are isolated clusters which are fractal objects with a fractal dimension $D$. As the concentration of particles increases, individual clusters begin to overlap and eventually form a continuous network before they settle to the bottom of the container. In a simple approximation, we may view the continuous gel network as a system of uniformly-sized clusters closely packed together. A schematic representation of a gel structure is shown in Figure 1a and a transmission electron micrograph (TEM) of a silica gel is shown in Figure 1b for comparison. The model structure is similar to the TEM picture and contains the essential features of a gel network. The average cluster size $\xi$ can be related to the particle volume fraction $\phi$ as

$$\xi \sim \phi^{1/(D-d)} \tag{1}$$

by assuming the average mass density within a cluster to be the same as the total particle density. $d$ is the Euclidean dimension of the system. Equation (1) has been confirmed for silica gels by Dietler et al. [3].

The next step in constructing the theory is to calculate the elastic constant of a cluster $K_\xi$, and then relate $K_\xi$ to the macroscopic elastic constant $K$ of the system. To calculate the elastic properties, we replace the particulate network with a network of springs which represent the elastic bonds between two particles. Furthermore, we replace the fractal spring network with a backbone network, which is also a fractal, since many dangling springs do not contribute to the elastic properties of the system. There are two elastic constants involved. One is the spring constant of each spring. The other is the bending constant between two springs connected to the same particle. It has been shown by Kantor and Webman [4] that for a very long, tortuous spring network, the elastic constant is dominated by the bending constant and can be related to its radius of gyration, in this case $\xi$, as

$$K_\xi \sim K_0 / \xi^{2+x} \tag{2}$$

where $K_0$ is the local bending constant between two adjacent springs and the exponent $x$ is the fractal dimension of the elastic backbone, which may be different from that of the clusters, $D$. The macroscopic elastic constant $K$ is related to $K_\xi$ as

$$K \sim (L / \xi)^{(d-2)} K_\xi \tag{3}$$

where $L$ is the sample size.

We now need to divide our discussion into two situations since the elastic constant of the link between the clusters $K_I$ can be quite different from $K_\xi$. In the strong-link regime in which $K_I >> K_\xi$, by combining Eqs. (1), (2), and (3), we get
certain frequency and amplitude. The frequency of the oscillation was fixed at 1 rad/sec and the amplitude was varied over a range from 0.1 to 50%. The viscoelastic properties of the gels are characterized by the storage and the loss moduli, $G'$ and $G''$, respectively. In the present study, we focus our attention on the storage modulus $G'$.

The storage and the loss moduli, $G'$ and $G''$, as a function of particle volume fraction for silica gels without surfactant are shown in Figure 2. Note that there is a clear change in the slope of $G'$ at around 9% volume fraction. We interpret the change in the slope of $G'$ as the crossover from the strong-link behavior to the weak-link behavior as predicted by the theory. The slope in the weak-link regime at higher concentrations is indeed much smaller than in the strong-link regime at smaller concentrations. Furthermore, the crossover from the strong-link regime at low concentrations to the weak-link regime at higher concentrations is also evidenced in the behavior of the yield strain as shown in Figure 3. In Figure 3, the storage modulus as a function of the strain amplitude for several volume fractions of silica gels is presented. As can be seen from Figure 3, the constant $G'$ region decreases in the strong-link regime when the particle volume fraction is small and it begins to increase in the weak-link regime at higher concentrations. The crossover of the yield strain also takes place at around 9% volume fraction and is consistent with the crossover of $G'$ as shown in Figure 2.

![Figure 2. $G'$ and $G''$ of silica gels at pH = 9.5 as a function of particle volume fraction $\phi$. A clear crossover occurs at around $\phi = 9\%$.](image-url)
Figure 3. The storage modulus $G'$ of silica gels as a function of the strain amplitude $\gamma$ for various concentrations. Figure 3a shows results in the strong-link regime in which $\gamma_y$ is shrinking with increasing concentration. Figure 3b shows results in the weak-link regime in which $\gamma_y$ increases with concentration. The crossover occurs at around 9% volume fraction, which is consistent with the crossover of $G'$ in Figure 2.

In the strong-link regime, the behavior of the $G'$ can be fitted to

$$G' \sim \phi^5$$

(8)
while in the weak-link regime,

\[ G' \sim \varphi^{1.2} \]  

(9)

with an error bar of 0.2 in the exponent since we have only four data points. Using the result of the scaling theory, we estimated \( D = 2.17 \) and \( x = 1.17 \). The value of \( D \) obtained from the rheological study is consistent with that obtained from our preliminary light scattering studies on diluted samples where we found \( D \) to be between 2.0 and 2.2.

Adding surfactant to the silica suspensions greatly changes the behavior of \( G' \). The \( G' \) of silica gels with surfactant as a function of particle volume fraction is shown in Figure 4. The data can not be fitted to a straight line in a log-log plot, indicating that it is not a power-law behavior. Rather the behavior of \( G' \) can be described better by

\[ G' \sim \exp(a\varphi) \]  

(10)

with \( a = 13.48 \) with unit \( \ln(\text{dyne/cm}^2) \).

**DISCUSSIONS AND CONCLUSIONS**

While the scaling behavior of the hard gels results from the fractal nature of the clusters, which is a result of the aggregation process, the exponential behavior of \( G' \) as a function of
particle volume fraction is probably due to the restructuring of the clusters before they form the network. The attraction between surfactant-coated particles is weakened by the adsorbed surfactant layers which prevent particles from strong attraction at contact, resulting in more frequent and, hence, observable restructuring of the gel network. With restructuring, there will be a distribution of cluster sizes within the gel network. The mechanical behavior of the network will be dominated by the weakest cluster which is also the largest cluster in the network (see Eq. (2)). A possible explanation of Eq. (10) is that Eq. (1) no longer holds for the largest cluster $\xi_{\text{max}}$ and is replaced by an exponential relation

$$\xi_{\text{max}} \sim \exp(-a\varphi). \quad (11)$$

To see whether this is true, we did Monte Carlo simulations on the aggregation of particles and clusters with restructuring [5]. Both particles and clusters are allowed to move according to the relation between the diffusivity and the cluster size. In the present calculation, the diffusivity is assumed to be independent of the cluster size. Figure 5 shows the number of particles in the largest cluster $N_{\text{max}}$ as a function of concentration in the dilute regime. $N_{\text{max}}$ is found to be related to the concentration exponentially,

$$N_{\text{max}} \sim \exp(b\varphi). \quad (12)$$

Since $N_{\text{max}} \sim \xi_{\text{max}}^D$, we expect $\xi_{\text{max}}$ to be an exponential function of concentration as well. This suggests that at higher concentrations when overlapping among clusters occurs, Eq. (11) may be expected, leading to Eq. (10).

The exponential behavior of $G'$ as a function of concentration provides a basis for understanding pressure filtration. In pressure filtration of colloidal suspensions, a typical particle volume-vs.-pressure curve is shown in Figure 6 for alumina. For dispersed suspensions, the final density is high and is insensitive to the applied pressure, while for flocculated suspensions, the final density is usually a logarithmic function of the applied pressure

$$P = A \ln(P) + \varphi_0, \quad (13)$$

where $A$ is the slope and $\varphi_0$ is some constant. This equation can be inverted to be

$$P = \exp((\varphi - \varphi_0) / A), \quad (14)$$

which is essentially an exponential relation between the applied pressure and the resultant concentration, similar to the behavior of $G'$. This suggests that the pressure filtration behavior is also governed by the restructuring of the network under pressure.

In conclusion, two types of elastic behavior of colloidal gels are found: hard gels and soft gels. In the case of hard gels, there are two regimes that need to be specified depending on the relative elastic strength of the clusters to that of the link between clusters [1]. The storage modulus $G'$ increases with concentration in a power-law fashion in both regimes, but the exponent is larger in the strong-link regime than in the weak-link regime [2]. The yield strain decreases with concentration in the strong-link regime, whereas it increases in the weak-link
Figure 6. The cake density as a function of the applied pressure in pressure filtration for alumina at pH = 3.0, 7.0, 7.5, and 8.5.

regime [3]. There is a crossover from the strong-link behavior to the weak-link behavior as the concentration is increased. The predictions of the scaling theory are shown to be in good agreement with the results from the rheological study of silica gels.

In the case of soft gels, which were achieved by surfactant addition in the present studies, the power-law behavior of $G'$ with concentration changes to exponential. Monte Carlo simulations on the restructuring of clusters showed that the largest cluster size increases exponentially with concentration, indicating that the exponential behavior of $G'$ may be a result of the restructuring of clusters. Finally, we have shown that in the pressure filtration of flocculated colloidal suspensions, the applied pressure also increases exponentially with the resultant density. The exponential behavior of the applied pressure can also be understood in terms of the restructuring of the particulate networks.

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