MECHANICAL PROPERTIES OF COLLOIDAL GELS
SUBJECT TO PARTICLE REARRANGEMENT

WAN Y. SHIH, WEI-HENG SHIH, and ILHAN A. AKSAY
Department of Materials Science and Engineering; and
Advanced Materials Technology Center, Washington Technology Centers,
University of Washington, Seattle, WA 98195

INTRODUCTION

In a colloidal suspension with attractive interaction, particles form aggregates that settle to the bottom of the container. As the concentration of particles is increased, the overlapping of the aggregates (flocs) produces a continuous network throughout the suspension before settling occurs and a colloidal gel is formed. Colloidal gels may be divided into hard gels and soft gels.1 Hard gels are those formed by fine particles such as silica or boehmite of about 0.01 μm in size with high interparticle attraction energies. Under small shear rates, there is little restructuring in the gel network. The flocs that pack to form the gel network still retain their fractal structure, which gives rise to the scaling behavior of various mechanical properties of a gel with respect to particle concentration. For example, the storage modulus $G'$ of a hard gel remains constant at small strain and increases in a power-law fashion with particle concentration, $\varphi$, as $G' \sim \varphi^n$. There can be two regimes, a strong-link regime and a weak-link regime. In both regimes, the exponent $n$ can be expressed in terms of the fractal dimension of the flocs, $D$, and the fractal dimension of the backbone of the flocs, $x$, while the form of $n$ depends on what regime the system is in. Furthermore, a gel may crossover from the strong-link regime to the weak-link regime as the particle volume fraction is increased.2

The soft gels are formed by particles with much smaller interparticle bonding energies. Gels formed by silica particles coated with surfactant are examples. Because of the small interparticle attraction energies, the storage modulus $G'$ of a soft gel is about three orders of magnitude smaller than that of a hard gel at the same concentration. Furthermore, restructuring of the gel network occurs at even smaller shear strain. Therefore, the gel is no longer linear viscoelastic. The storage modulus $G'$ does not increase with particle concentration with a power law as in hard gels. Instead, $G'$ increases exponentially with particle concentration. A similar exponential behavior of $G'$ with $\varphi$ was also observed with ordered polystyrene suspensions.3

The exponential behavior exhibited by a soft gel under small shear stress has also been observed with hard gels under high pressures. In the pressure filtration experiments of boehmite particulate gels, the applied pressure $P$ increases exponentially with the final packing density $\varphi$ of the gel as $P \sim e^{\beta \varphi}$ in the pressure range from 0.1 to 10 MPa. The slope $\beta$ decreases with increasing interparticle attraction energy.

The exponential relationship between the shear modulus and the particle volume fraction of soft gels under small shear stresses and the exponential relationship between the applied pressure and the final packing density of the pressure-filtrated hard gels result from the restructuring of the particulate network. The rearrangement of particles in the gel network involves overcoming barriers. Here, we present an argument to show how the exponential behavior may come about. Suppose that $\Delta \varphi$ is the change in the density due to a pressure change $\Delta P$. One can argue that $\Delta \varphi / \Delta P$ is proportional to the probability of overcoming a barrier whose height is proportional to the density. Thus, $\Delta \varphi / \Delta P \sim e^{(-\beta \varphi)}$. Integrating over, one obtains $P \sim e^{\beta \varphi}$. In the following we will illustrate this point with Monte Carlo simulations using an aggregation model which allows for restructuring.
MODEL

The model is a modification of the diffusion-limited-cluster-aggregation (DLCA) model. The computer simulations were done in a two-dimensional square lattice. The diffusion and the aggregation part of the present model is the same as in the DLCA model. Namely, the simulation starts with a given number of particles uniformly distributed on the lattice. Particles are performing Brownian motion (random walk). When two particles collide, they form a cluster. A cluster, just like a particle, then random-walks as a unit and may collide with particles or clusters to form a larger cluster later. The diffusion time constant $T(N)$ for a cluster of $N$ particles is taken as $T(N) = \tau_0 N^\alpha$ where $\tau_0$ is the diffusion time constant of a single particle and $\alpha$ is a parameter ranging from 0 to $-1$.

The major difference between the present model and the DLCA model is that the present model considers a finite nearest-neighbor interparticle interaction $-E$ so that at finite temperatures, a particle within a cluster may break its bonds with its neighboring particles. At temperature $T$, the rate for a particle to unbind from its neighbors is $(1/\tau_R) e^{-nET}$ where $\tau_R$ is the time constant for unbinding, and $n$ is the number of neighbors of the particle. Here, the units are chosen such that the Boltzmann constant is unity. The unbinding time constant of a particle $\tau_R$ may be different from the diffusion time constant $\tau_0$. $\tau_R$ would depend more on the surface properties of the particles and $\tau_0$ would depend more on the particle size.

The bond-breaking process is simulated with the Monte Carlo method. That is, in every $\tau_R$, each particle is checked with a random number ranging from zero to unity. If the random number is larger than the Boltzmann factor $e^{-nET}$, the particle breaks all the bonds with its neighbors or otherwise stays unchanged. After the particle breaks the bonds with its neighbors, it then goes to one of the unoccupied neighboring sites at random. This way, a cluster may break into as many as three segments. Each individual segment then becomes an independent cluster and may collide with another at a later time.

The bond-breaking process allows clusters to restructure and densify. One may regard the restructuring and densification in the present model as thermal annealing of the aggregates since the bond-breaking process is controlled by the Boltzmann factor. The DLCA model corresponds to the case when $E$ is infinite and may be regarded as the quenched state.

In the simulations, only the translational motion of particles and clusters is considered explicitly. However, when there is sufficient sampling from the simulations to allow many configurations of two colliding clusters, the rotational motion should not affect the result. The simulations use either periodic boundary conditions or hard-wall boundary conditions. In the hard-wall conditions, the hard walls only prohibit particles from penetrating. Other than that, the walls do not interact with particles. Generally, the two boundary conditions give similar results. The hard-wall conditions are used to obtain the first-layer particle concentration near a hard wall, which may be used as a measure of the system's pressure, $P$. This model has been used to study the energy dependence of the fractal dimension of aggregates in dilute suspensions, which was later observed with gold particles coated with surfactant. The present paper will focus on higher concentrations and use quantities such as the largest-cluster size and the first-layer concentration near a hard wall to illustrate the exponential dependence on the particle volume fraction.

RESULTS

When particles can both aggregate and break bonds, the system may reach a dynamic equilibrium state in which the size of the clusters become saturated. As an example, Figure 1 shows $N_m$, the number of particles in the largest cluster in the system, as a function of time for two cases, $E/T = 1.67$ (filled circle) and $E/T = 1.33$ (open circle). For both cases, $\tau_R/\tau_0 = 2$ and $\varphi = .011$. In undisturbed hard gels, the fractal nature of the flocs dominates the power-law-concentration dependence of many physical quantities. If the exponential concentration dependence of the modulus (or the pressure) results from restructuring of the particulate networks, then other physical quantities may have the same exponential
concentration dependence. As an example, we show the saturated \( N_m \) as a function of density for high-concentration suspensions for two cases, \( E/T = 2 \) and \( E/T = 1 \) in Figure 2. The simulations were done with hard-wall conditions on a 20 x 20 lattice with the high restructuring rate \( \tau_R/\tau_D = 0.2 \). One can see that \( N_m \) increases exponentially with the particle concentration \( \varphi \) and the slope increases with decreasing interparticle attraction energy. Notice that the trend of an increasing slope with a decreasing interparticle attraction is similar to that found in the pressure filtration experiments.

![Figure 1. \( N_m \) vs. \( t \) where \( N_m \) is the number of particles in the largest cluster in the system and \( t \) is time. Filled circles denote \( E/T = 1.67 \) and open circles \( E/T = 1.33 \). For both cases, \( \tau_R/\tau_D = 2 \) and \( \varphi = 0.11 \) on a 40 x 40 lattice.](image-url)
The increase in the slope with decreasing interparticle attraction energies in Figure 2 may be understood qualitatively as follows. When the concentration is very high, aggregation is no longer limited by the diffusional process. Large clusters that span the entire system form instantaneously from crowding. As the concentration is decreased, the cluster size will decrease. Here, the decrease of the cluster size is limited by the breaking process. A smaller $E$ gives more frequent breaking and hence a larger slope in the $\log N_m$ vs. $\phi$ plot. It should be noted that the network is under constant restructuring so that the connectivity and the shape of the clusters are changing with time even though the time average cluster size has saturated. This is illustrated in Figure 3, where the structure of a gel network at $\phi = 0.45$ is shown at different times. At an earlier time, the network is more ramified and later becomes more compact. Also notice that the shape of the network is constantly changing.

To relate the exponential concentration dependence of $N_m$ to that of the shear modulus $G$ or that of pressure $P$, one may argue as follows. At such high concentrations, the largest cluster in the system has spanned the system in a dynamic sense even though it may not span the entire system at all times. The modulus of the system is determined by this largest cluster. The dynamic rheological measurements taken at nonzero frequencies can still probe the modulus of this ever-changing cluster. Since the largest cluster has spanned the system, $N_m \sim W L$ where $L$ is the sample size and $W$ is the average width of the largest cluster. The sample size $L$ is fixed. $N_m \sim e^{W \phi}$ implies that $W \sim e^{W \phi}$. Furthermore, one may think of the largest cluster as a collection of $W$ parallel springs. Thus, the bulk modulus $K$ of the largest cluster is proportional to the number of parallel springs, resulting in $K \sim e^{W \phi}$. The shear modulus $G$ is expected to behave similarly. Furthermore, since $K = \phi dP / d\phi$, it also follows that $P \sim e^{W \phi}$. As an example, Figures 4(a) and 4(b) show the network structure at $\phi = 0.35$ and at $\phi = 0.5$ to illustrate that the width of the backbone of the largest cluster increases with particle concentration. Notice that the width of the backbone of the largest cluster increases about four times when the concentration is increased from 0.35 to 0.5 and $e^{(0.50 - 0.35)}$ is about 4.

To relate the exponential concentration dependence of $N_{\text{max}}$ to that of the modulus or that of the pressure, one may argue as follows. At such high concentrations, the largest cluster in the system has spanned the system in a dynamic sense even though it may not span the entire system at all times. The modulus of the system is determined by this largest cluster. The dynamic rheological measurements taken at non-zero frequencies can still probe the modulus of this ever-changing cluster. Since the largest cluster has spanned the system, $N_{\text{max}} \sim W L$ where $L$ is the sample size and $W$ is the average width of the largest cluster. The sample size $L$ is fixed. That $N_{\text{max}} \sim e^{W \phi}$ implies that $W \sim e^{W \phi}$. Furthermore, one may think of the largest cluster as a collection of $W$ parallel springs. Thus, the bulk modulus $K$ of the largest cluster is proportional to the number of parallel springs, resulting in $K \sim e^{W \phi}$. The storage modulus $G'$ is expected to behave similarly. Furthermore, since $K = \phi dP / d\phi$, it also goes like $P \sim e^{W \phi}$. As an example, Figs. 4(a) and (b) show the network structures at $\phi = 0.35$ and at $\phi = 0.5$ to illustrate that the width of the backbone of the largest cluster increases with particle concentration. Notice that the width of the backbone of the largest cluster increases by about four times when the concentration is increased from 0.35 to 0.5 and $e^{(0.50 - 0.35)}$ is about 4.

In a lattice model, one may use the first-layer concentration as a measure of the pressure of the system. We calculated the first-layer concentration near a hard wall, $\phi_1$, using hard-wall boundary conditions. In Figure 5, we show $\phi_1$ as a function of $\phi$. One can see that at high enough concentrations, $\phi_1$ increases exponentially with $\phi$, in agreement with the experiments.
Figure 2. $N_m$ vs. $\phi$, where $N_m$ is the saturated number of particles in the largest cluster in the system and $\phi$ is number concentration. For both $E/T = 2$ and $E/T = 1$ cases, hard-wall boundary conditions were used on a 20 x 20 lattice. $\tau_R/\tau_D = 0.2$.

Figure 3. The structure of a particle network with $\phi = 0.45$ at different times. $t =$ (a) 100, (b) 400, (c) 800, (d) 1900. The darkened circles are the particles in the largest clusters. The network not only undergoes compaction but also changes its shape constantly. The lattice is 20 x 20 with hard-wall boundary conditions. $E/T = 2$ and $\tau_R/\tau_D = 0.5$. 


Figure 4  Structures of the networks at (a) $\phi = 0.35$ and (b) $\phi = 0.5$, taken at $t = 2000$ $\tau_D$. The dardened circles are the particles in the largest clusters. The lattice is $30 \times 30$ with hard-wall boundary conditions. $E/T = 2. \tau_R/\tau_D = 0.5$. 
SUMMARY

We have simulated colloidal gels under restructuring using an aggregation model which also allows particles to unbind. The unbinding probability is proportional to a Boltzmann factor which takes into account the effect of the interparticle attraction energies. We have shown that at high concentrations, the largest-cluster size increases exponentially with particle concentration and the slope of the $\log N_m$ vs. $\varphi$ increases with a decreasing interparticle attraction energy. The exponential concentration dependence is due to restructuring of the particulate networks. By approximating the largest cluster at high concentration as spanning parallel springs, we argued that the modulus and hence the pressure are linear with the size of the largest cluster. The exponential concentration dependence of $N_m$ in the simulations reflects the exponential concentration dependence of the shear modulus and the pressure found in the experiments. The trend of an increasing slope in the $N_m$ vs. $\varphi$ plot with a decreasing interparticle attraction energy is in agreement with that found in the experimental $\log P$ vs. $\varphi$ plot. Furthermore, we have shown that at high concentrations, the first-layer concentration near a hard wall, which is used as a measure of the pressure, also increases exponentially with concentration. When the concentration is increased to about $\varphi = 0.45$, on average, a particle is constantly surrounded by other particles, and aggregation is less limited by the diffusion of particles and clusters.

Figure 5  The first-layer concentration $\varphi_1$ near a hard wall versus the overall concentration $\varphi$. The lattice is 40 x 40 with hard walls. $E/T = 2$ and $\tau_R/\tau_D = 0.2$. The data are the average over 200 samples in an 1000 $\tau_D$ interval.
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