Mechanics and Microstructures of Concentrated Particle Gels

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It is often assumed that the viscoelastic properties of dense colloids are determined by the colloid volume fraction, the interaction potential, as well as the particle size distribution and shape. The dependence of the viscoelastic behavior of particle suspensions and gels on these parameters has been widely studied, and is well understood in many cases. In contrast, our knowledge on the influence of microstructure on mechanical and rheological properties, in particular for high solid loading suspensions as used in ceramic processing, is much less developed. This aspect has been the focus of recent experiments, which show that small changes in microstructure can have dramatic effects on the mechanics and dynamics of concentrated colloidal gels. In this article, we attempt to give an overview of the influence of microstructure on the mechanical and rheological properties of colloidal systems. Particular attention is given to colloidal particle gels at high volume fractions.

1. Introduction

Colloidal suspensions show a wide range of viscoelastic, dynamic, and structural behavior. Many industrial applications make use of colloidal suspensions and of the possibility to change and control their behavior. In ceramic processing, a variety of different methods are used to exploit the wide-phase behavior of colloids to produce a dense, homogeneous packing of particles via “wet processing” routes. For good reviews of the different processing methods, see Lewis’ and Sigmund et al.’

It is known that the mechanical behavior of a colloidal gel depends on the size and shape of the particles, the interparticle forces, the volume fraction, and the spatial arrangement of the particles or, what is called the microstructure of a particle network. The structural, mechanical, and dynamic properties of a colloidal suspension can change drastically, when one or several of these parameters are varied. However, the main focus in the study of the mechanical behavior of dense colloidal suspensions and gels has been limited to a large extent to the influences of volume fraction and interparticle forces.

The effect of the interparticle pair potential on the rheological behavior of suspensions was studied by several authors. A variety of other contributions focuses mainly on the dependence on the particle volume fraction.

Microstructural characterization is of tremendous importance in ceramic processing and technology. The characterization of microstructure of sintered ceramic bodies is a standard procedure that is essential for the optimization of the mechanical behavior of ceramic parts. It is, therefore, surprising that only a few studies have investigated the microstructures of ceramic materials in the “wet” stage—in a concentrated suspension or gel of particles.

Because of the difficulties involved in characterizing and quantifying a microstructure in a colloidal system, it is easier and more straightforward to study the relation of the macroscopic properties to the other relevant parameters. However, an understanding of the mechanics of flocculated suspensions can only be achieved when the structure of the particle network is taken into account; the interparticle potential alone is not sufficient.

Even one of the simplest colloidal systems, a suspension of hard-sphere particles, shows a complex viscoelastic behavior that is tightly linked to changes in the microstructure. At high volume fractions, such a system shows pronounced shear thinning, reflecting a shear-induced structural rearrangement (see Section II). In order to understand the mechanisms that govern the macroscopic properties of a colloidal system, profound knowledge of the structural properties is thus essential.

Of particular interest is the influence of the microstructure on the mechanical behavior of particle gels. At low solid loadings, theoretical models based on the fractal description of network structures are successful in linking the structural to the mechanical behavior (see Section III). These models are in good agreement with results from experiments and from computer simulations. However, the fractal description of the network structure must break down at some point toward increasing volume fractions, and the measurement of fractal dimensions becomes increasingly difficult at high volume fractions. Nevertheless, the fractal description provides a way to link the microstructure, or at least some characteristic quantities that describe the microstructure, to the viscoelastic behavior directly.

For highly concentrated gels, however, our knowledge on the relations between structural and mechanical properties is rather limited. We identify two main problems that make it difficult to
establish a relation between network structure and mechanical behavior in concentrated colloidal gels.

Firstly, the reproducible formation of a colloidal gel at high volume fractions cannot be performed as easily as in a diluted system. The direct addition of salt or acid/base to stable suspensions will lead to colloidal gels of irreproducible microstructures. Because of the elevated aggregation rates in concentrated suspensions, the system will generally aggregate locally before the salt or acid/base is homogeneously distributed. In rheological studies of concentrated gels, a high shear rate is usually applied prior to the measurements in order to set reproducible starting conditions. However, in this case the microstructures of the resulting gel networks are determined mainly by the shearing process, and not by the initial aggregation process itself. As a consequence, the formation of different concentrated gels of significantly different microstructure will be difficult to achieve if a high shear rate has to be applied. It is also important to note that strong shearing of a particle gel will not always make its structure more homogeneous. By contrast, strong shearing will lead to a highly inhomogeneous structure, as it favors the formation of strong, densely packed aggregates in the system.

Secondly, the characterization of microstructures in concentrated colloids proves difficult, as the standard methods used for the characterization of diluted colloidal suspensions cannot be easily applied to highly concentrated systems. For example, static light scattering, the standard method for the characterization of structure in colloidal gels, fails for systems that exhibit strong multiple scattering.

II. Role of Microstructure in Stable Suspensions

As mentioned before, the microstructure has an important influence on the rheological properties even in a stable colloidal suspension. At high concentrations, colloidal suspensions can show pronounced non-Newtonian effects in their flow, in particular, shear thinning and shear thickening. The viscosity of the suspension is no longer independent of the shear rate, but changes with the shear rate. Both phenomena can be explained by a change in microstructure in the suspension, induced by the shear. The occurrence of structural rearrangements upon shear has been experimentally confirmed by both static light scattering and neutron scattering. In the following, we will focus on the shear thinning effect to illustrate the importance of microstructure on the viscoelastic behavior of stable particle suspensions. For a review of shear thickening (dilatancy) in concentrated suspensions, we refer to Barnes.

By comparing the typical timescale for Brownian motion and for the shearing process, one can estimate the typical shear rate at which the structure of the suspension should begin to be perturbed by the flow. A characteristic time $t_B$ for diffusion is given by the time it takes a sphere to move a distance equal to its own size. A characteristic time $t_{sheat}$ for the flow is given by the inverse of the shear rate. The ratio between these two characteristic times is known as the Peclet number $Pe$ and is thus given by:

$$Pe = \frac{6\pi \eta a^3}{k_B T}$$

where $\eta$ is the viscosity of the liquid phase, and $a$ is the particle size.

For Brownian motion, the structure of the suspension changes in a state essentially indistinguishable from the unsheared state. At shear rates corresponding to a Peclet number greater than unity, Brownian motion can no longer restore the structure of the suspension to its equilibrium state. Experiments on model systems have shown that flow curves for suspensions of different particle sizes fall onto a single master curve, when plotted as a function of the dimensionless Peclet number. The high- and low-shear limits of the viscosity $\eta$ are in good agreement with:

$$\frac{\eta}{\eta_0} = \left(1 - \frac{\Phi}{\Phi_c}\right)^{-2}$$

where $\Phi_c \approx 0.63$ and $\Phi_c \approx 0.71$ for the low- and high-shear limits, respectively. Whereas for the low-shear limit, the critical volume fraction corresponds to the volume fraction of random close packing, for the high-shear limit it is closer to a crystalline volume fraction. The value of the critical volume fraction $\Phi_c \approx 0.71$ reflects the fact that in the high-shear limit, ordering occurs only in layers and not in a three-dimensional (3D) crystalline structure. Thus, although Eq. (2) is purely empirical, the values for the characteristic volume fractions themselves reflect the importance of microstructural arrangement. In Fig. 1, we illustrate the shear thinning effect with a plot of viscosity as a function of shear stress in a model hard sphere system.

As a model system, we use poly(methyl methacrylate) particles of radius $a = 136$ nm dispersed in a mixture of cyclohexyl bromide and decane; the volume fraction is $\Phi = 0.41$. For details regarding this model system, see Prasad, Manley, Segre, Pham, Poon and Van Blaaderen. The viscosity $\eta$ in the transition region between the low- and high-shear region is well described by:

$$\eta = \eta_{\infty} + \eta_0 \frac{1}{1 + (\sigma/\sigma_c)^n}$$

A fit to the data in Fig. 1, shown as a dotted line, yields $n = 2$ and $\sigma_c = 0.83$ Pa.

The shear-thinning and shear-thickening effects in a concentrated suspension illustrate the importance of the microstructure; the viscoelastic properties of colloidal systems. It is obvious that in a colloidal gel, microstructure could play an even more important role, while a thorough understanding of these effects will be harder to achieve than for a stable suspension.

III. Fractal Description of Microstructures for Low Volume Fraction Colloidal Gels

If the interaction between colloidal particles is strongly attractive, a colloidal system will form aggregates. At low volume fractions, the structure of such aggregates is accurately described as fractal. This means that the number of particles contained in an aggregate scales with its size as a power law:

$$N \propto R^d$$

where the exponent $d_c$, called the fractal dimension, is smaller than the Euclidean dimension $d$. This implies, because the den-

![Fig. 1](image-url)  
Fig. 1. Shear thinning effect for a model hard sphere system at volume fraction $\Phi = 0.41$. Normalized viscosity as a function of the shear stress $\sigma$. The dotted line shows a fit to the data using Eq. (3).
sity of the fractal clusters thus decreases as their size increases, that upon formation of fractal aggregates in a suspension, the system will ultimately form a volume-filling gel. The values of the fractal dimension $d_f$ for different aggregation mechanisms are well established from computer simulations as well as from experiments at low volume fractions.11-14

Aggregation mechanisms can be divided into two different categories: diffusion-limited cluster aggregation (DLCA) and reaction-limited cluster aggregation (RLCA). In DLCA, each collision between particles during aggregation leads to an irreversible bond, whereas in RLCA, particles can escape from a bond site and penetrate deeper into the aggregated structures. Therefore, aggregates formed by RLCA are denser and have a higher fractal dimension than DLCA aggregates.

The size of flocks in a fractal gel network follows directly from the condition that the density $\phi_c$ of the fractal clusters will decrease during aggregation until, when the volume of the flocks fills all space, it reaches the volume fraction $\phi$ of particles in the overall suspension. Thus, the characteristic size $R_c$ of fractal clusters scales as

$$R_c \propto \phi^{1/(d_c - d)}$$  \hspace{1cm} (5)

As a result of the fractal nature of the microstructure, the mechanical properties of fractal gels can be directly linked to the parameters that describe their microstructure. The fractal dimension $d_f$ describes the overall structure of the fractal clusters. As the elastic constant $k_c$ of a cluster depends on the mechanism for bearing stress, two additional parameters, the parameters $\varepsilon$ and $d_b$, are needed to describe the geometry of the main stress-bearing chain of particles within a cluster. The elastic constant $k_c$ of a cluster then scales as

$$k_c \propto \frac{1}{R^{\varepsilon} R_c^{d_b}}$$  \hspace{1cm} (6)

where the exponent $\varepsilon$, with $0 \leq \varepsilon \leq 1$, describes the stress-bearing mechanism of the chain. The case $\varepsilon = 0$ applies to a straight chain, where the stress is transmitted by bond stretching.

For straight chains (bond stretching), the parameters $\varepsilon$ and $d_b$ are not independent. For straight chains (bond stretching), the parameters $\varepsilon = 0$ and $d_b = 1$. For a more detailed description, see De Rooij et al.31 and Potamkin.39

The scaling behavior of the shear modulus $G'$ follows directly from Eq. (6):

$$G' \propto \frac{k_c}{R_c^{d_b}} \propto R_c^{(1+2\varepsilon+d_b)/d_c}$$  \hspace{1cm} (7)

For a fractal structure, with Eq. (5), one finally obtains

$$G' \propto \phi^{(1+2\varepsilon+d_b)/(d_c - d)} = \phi^{m_1}$$  \hspace{1cm} (8)

Through similar scaling arguments, de Rooij et al. derive an expression for the scaling behavior of the yield stress $\sigma_y$ of a particle network as follows 37:

$$\sigma_y \approx \frac{\sigma_{\text{ext}}}{R_c^{d_b}} \propto R_c^{(2+\varepsilon)/(d_c - d_b)} = \phi^{m_2}$$  \hspace{1cm} (9)

Thus, the fractal description of the network structure and the above scaling concepts provide a clear-cut relation between the structural and mechanical properties of fractal particle networks at low volume fractions. However, at very high volume fractions, the fractal description of network structure is no longer appropriate. Nevertheless, the scaling concepts summarized in this section might be useful to some extent in describing the behavior of highly concentrated systems as well.

IV. Microstructural Characterization of Gels

Information on microstructures is one of the most useful and essential measures when it comes to understanding the macroscopic properties of materials. In Table I, we list some of the methods that can be used to access microstructures in particle suspensions and gels. For a comprehensive review of aggregate characterization techniques, we refer to a recent article by Bushell et al.41

In the following, we will briefly discuss the various methods, as well as their advantages and disadvantages with respect to the characterization of the microstructure in dense, highly turbid colloidal suspensions.

The characterization of the structure in dense colloidal suspensions and gels is often an experimental challenge. In particular for ceramic systems it is hard to access the microstructure experimentally. One reason for this is that the refractive index difference between the solid and the liquid phases is usually too high to enable measurement of their microstructure using standard light scattering techniques (Table I (1)).42 A meaningful evaluation of standard light scattering experiments relies on samples that show only negligible multiple scattering. By using more advanced light scattering setups such as a multicolor or a 3D setup (Table I (2)),3,44 contributions of multiple scattering to the detected signal can be suppressed. However, these methods are still limited to samples of rather low turbidity, as some measurable amount of single scattering intensity always has to be present.

Using diffusing-wave spectroscopy (DWS) (Table I (3)),45,46 the dynamics of highly turbid systems can be analyzed. DWS extends traditional dynamic light scattering to media with strong multiple scattering by treating the transport of light as a diffusion process. No direct structural information is obtained from
Table I. Different Techniques Applied in Characterizing the Microstructures of Particle Gels

<table>
<thead>
<tr>
<th>Method and references</th>
<th>Capabilities</th>
<th>Limitations</th>
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<tbody>
<tr>
<td>(1) Standard static and dynamic light scattering(^{42})</td>
<td>Allows the characterization of structure and dynamics in colloidal systems of low volume fraction</td>
<td>Limited to samples of very low turbidity, where multiple scattering can be neglected</td>
</tr>
<tr>
<td>(2) Multicolor or 3D setup for static and dynamic light scattering(^{43,44})</td>
<td>Allows suppression of contributions of multiple scattering in the signal</td>
<td>Still limited to rather low turbidity, as some measurable amount of single scattering always has to be present</td>
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<tr>
<td>(3) Diffusing wave spectroscopy(^{45,46})</td>
<td>Allows to extend dynamic light scattering to highly turbid suspensions and gels. Gives information on the average dynamics of particles in the system</td>
<td>Only limited structural information(^{47})</td>
</tr>
<tr>
<td>(4) Small-angle X-ray scattering(^{48-50})</td>
<td>Gives structural information in terms of the static structure factor (S(q))</td>
<td>Upper limit to length scales that can be accessed because of small wavelength</td>
</tr>
<tr>
<td>(5) Small-angle neutron scattering</td>
<td>Gives structural information in terms of the static structure factor (S(q))</td>
<td>Present detectors set an upper bound to the accessible length scales at around 200 nm</td>
</tr>
<tr>
<td>(6) Spin-echo small-angle neutron scattering(^{52,56})</td>
<td>Gives structural information in terms of the static structure factor (S(q)) on length scales between 10 nm and 7 (\mu)m</td>
<td>Facilities not readily available</td>
</tr>
<tr>
<td>(7) Freeze-fracture techniques(^{57,58})</td>
<td>Gives real space structural information</td>
<td>Crystal formation in the liquid phase during freezing is likely to distort microstructure</td>
</tr>
<tr>
<td>(8) High-pressure freezing and fracture(^{59,61})</td>
<td>Gives real space structural information</td>
<td>Limited to aqueous systems</td>
</tr>
<tr>
<td>(9) Confocal microscopy(^{62,64})</td>
<td>Crystal formation in aqueous systems can be adequately suppressed</td>
<td>Limited to low-turbidity samples or to measurements near the cover slip (wall effects). Fluorescent labeling necessary</td>
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3D, three-dimensional.

such a measurement, although measuring the turbidity itself gives some information on the homogeneity of the microstructure.\(^{47}\) The single-scattering regime can also be accessed by using X rays instead of visible light. However, accessing large enough length scales requires detection at very low angles. Small-angle X-ray scattering (Table I (4))\(^{48-50}\) is suitable for the characterization of microstructures only if the particle size is sufficiently small.

Also, in small-angle neutron scattering (SANS) (Table I (5)),\(^{58,59}\) present detectors set an upper bound to the accessible length scales at around 200 nm.

However, a recently developed technique called spin-echo SANS (SESANS) (Table I (6))\(^{52-56}\) allows to extend the accessible length scales dramatically. Structural information can be obtained at length scales spanning three orders of magnitude: from 10 nm up to 7 \(\mu\)m.\(^{56}\) The technique is based on the Larmor precession of polarized neutrons in magnetic fields with inclined faces. The precession of the polarization vector of neutrons in a magnetic field is proportional to the wavelength, magnetic field, and path length through this field. It is therefore possible to determine the \(z\) component of the wave vector momentum transfer \(Q\) as a function of the precession angle \(\phi\). The SESANS signal can be interpreted in real space; it is possible to determine the particle density autocorrelation function directly from the measurement. In the first applications of the SESANS technique to the characterization of colloidal systems, Krouglov et al.\(^{57}\) show this directly by measuring the structure of hard-sphere suspensions at different concentrations; Bouwman et al.\(^{56}\) show that the technique is able to directly identify the phase transition of a colloidal system from a gas via a liquid to a solid. The large range of accessible length scales combined with the possibility of measuring samples of very high volume fraction, confers this method with considerable potential for future studies of the structure of concentrated colloidal systems.

For aqueous systems, freeze-fracture techniques can be used to access the microstructure (Table I (7))\(^{7,58}\). This can be performed by applying a coating to the surface of the frozen fracture surface and then examining this templated layer using transmission electron microscopy. Alternatively, one can examine the fracture surface directly by using a scanning electron microscope (SEM) equipped with a Cryo stage. However, the standard freezing techniques are likely to produce large ice crystals in the liquid phase of the samples and thereby distort the microstructure. The best method to preserve the structure of aqueous samples during freezing is high-pressure freezing (Table I (8)).\(^{59}\) As the crystallization of water requires more energy at high pressures than at ambient pressure, the formation and growth of ice crystals in the liquid phase can be adequately suppressed. This technique has recently been applied to ceramic systems.\(^{60,61}\)

The most direct way of accessing 3D microstructure is confocal microscopy (Table I (9)).\(^{62-64}\) However, this technique also requires a low refractive index mismatch between the colloids and the solvent. It is therefore not suitable for ceramic systems or for attractive systems that rely on van der Waals forces. This technique has recently been used to study weakly attractive gels and colloidal glasses in model systems.\(^{62-64}\)

V. Structure and Mechanical Properties of Concentrated Gels

Linking microstructure to macroscopic behavior is of central interest in materials science and technology. Nevertheless, relatively little is known about the relation between microstructures and mechanical properties of concentrated colloidal suspensions and gels. The main difficulties in this endeavor lie in the experimental limitations when it comes to studying and quantifying the microstructure of these systems.

Channell et al.\(^{10}\) report one of the few studies that elucidate this relation in a systematic way. The study focuses on the characterization of the mechanical behavior of gels. The compressive yield stress \(\sigma_y\) as a function of volume fraction \(\phi\) is obtained by analyzing the density profiles of samples after subjecting them to a compressive stress in a centrifuge. A detailed discussion of this technique is given elsewhere.\(^{65,66}\) The advantage of the technique is that a whole curve of yield stress versus volume fraction is obtained from a single measurement. The stress at a given point in the sample is given by the load of all the material on top of this point. Thus, the equilibrium volume fraction for a whole spectrum of stresses can be obtained by
analyzing a single sample. In order to achieve different microstructures, the authors use a very simple, yet efficient, technique. Different levels of homogeneity are achieved by preparing the samples in different ways, but with identical chemical composition. Homogeneous samples are obtained by preparing suspensions at a given volume fraction \( \phi_0 \) and subsequent homogenization by high-shear mixing. Lower levels of homogeneity are achieved by carefully diluting samples gelled at a higher volume fraction \( \phi > \phi_0 \) and subsequent shearing by either hand mixing or by ultrasonication. During the measurement of the compressive yield stress, this low volume fraction structure is then consolidated in the centrifuge, which leads to a volume fraction gradient in the sample. The lowest volume fraction is found at the upper surface of the gel, where the volume fraction after centrifugation should still be the same as the overall volume fraction \( \phi_0 \) before centrifugation. Figure 3 shows a schematic illustration of a microstructure obtained from diluting a more concentrated gel under gentle stirring. The new gel network is built up from individual clusters that are connected only through a few weak bonds to form the new volume-spanning network.

The experimental data indicate that lower mixing intensities lead to lower compressive yield stresses. Figure 4 shows the compressive yield stress as a function of volume fraction for gels that were obtained from the different homogenization methods. If high-shear mixing is used for homogenization of these samples, the compressive yield stress is independent of the volume fraction where the gels were initially prepared. Thus, the applied high-shear mixing seems to be sufficient to achieve a reproducible microstructure, dependent only on the sample composition, but not the sample's preparation history. The lowest compressive yield stresses are observed for samples subjected to the lowest mixing intensity (hand mixing). Note also that above the volume fraction where the samples were originally prepared, the yield stresses are independent of the homogenization used in the dilution process.

By using different mixing intensities and starting volume fractions \( \phi > \phi_0 \), samples of different microstructures are obtained. Even though the authors do not characterize microstructures experimentally, it is reasonable to assume that the different levels of homogenization lead to different aggregate sizes. The lower the mixing intensity, the larger the aggregates and the lower the compressive yield stresses.

A recent study by Franks et al.\(^9\) focuses on the relationship between aggregate size and the rheological properties of a packed sediment of aggregates. The authors induced the formation aggregates by flocculation of alumina particles in a dilute suspension, varying for instance the salt concentration to achieve different aggregate sizes. The aggregates formed subsequently settle to form a dense sediment at the bottom of the container. By adjusting the salt concentration of the sediment, the interparticle forces for different samples can be equilibrated between samples of originally differing salt concentration. Thus, the presented method enables the separation of the effects of aggregate size (i.e., microstructure) from those of interparticle forces. Aggregate sizes can be measured in the dilute suspension, before the aggregates settle to form a dense sediment.

They find that when other aggregate properties are held constant, the shear and compressive yield stresses of sediments formed from larger aggregates are generally higher at all volume fractions. Also, the larger aggregates produce a sediment of lower maximum packing fractions than smaller aggregates.

Using a different approach to control microstructure, another recent study by Franks et al.\(^9\) has focused on both the characterization of the microstructure as well as the mechanical properties of concentrated gels. Control over the microstructure is achieved by using different chemical pathways of coagulating electrostatically stabilized gels, using a destabilization method originally developed for the processing of high-performance ceramics, direct coagulation casting (DCC).\(^7\) The method is based on enzyme-catalyzed chemical reactions, which can be controlled by both enzyme concentration and temperature. It allows the formation of gels of highly concentrated particles without perturbing the microstructures that develop during the gelation process. The gels can be produced by two different destabilization mechanisms that lead to significantly different microstructures: either the \( \text{pH} \) of the suspensions is shifted toward their isoelectric point (\( \Delta \text{pH} \) method), or the ionic strength of the suspensions is increased at a constant \( \text{pH} \) (\( \Delta I \) method) (DCC technique (see Box 1)).
The authors use these reactions and apply them to concentrated particle gels to investigate the relations between the kinetics of the destabilization process, the dynamics of particles, the evolving microstructure, and the resulting mechanical properties. The dynamics of particles during the aggregation process is followed by using DWS. This light scattering technique allows deriving quantitative information about the dynamics of particles in very turbid suspensions. While in conventional light scattering experiments the samples have to be highly diluted, DWS extends traditional dynamic light scattering to media with strong multiple scattering by treating the transport of light as a diffusion process. We derive quantitative information about the sol-gel transition and the viscoelastic properties of the gels, as well as a characterization of changes in the microstructure. Δt gels show stronger elastic moduli and exhibit a less homogeneous microstructure than Δp gels.63

To further characterize the dynamics of the destabilization process as well as the evolving microstructures, the authors performed static light scattering measurements on suspensions of concentrated silica particles. Here, problems because of multiple scattering can be avoided by using a very thin sample thickness. In addition, the refractive index difference between the aqueous phase and the particles can be reduced by adding sucrose to the liquid phase of the suspensions. While during the ΔpH destabilization, the scattering curve shows significant changes only after some characteristic delay time, it changes continuously during the Δt destabilization. This behavior is attributed to the formation of a weak pre-gel structure in the suspensions, as a shallow secondary minimum appears in the interparticle potential.

The real-space structure of concentrated gels is directly accessed by combining high-pressure freezing with Cryo-SEM. By using the high-pressure freezing technique, the formation and growth of the ice crystals are adequately reduced.59

Microstructures can thus be examined on fracture surfaces of high-pressure frozen particle gels. In Fig. 5(a), we show the obtained SEM images of systems at a volume fraction of ϕ = 0.4, for a ΔpH destabilized suspension and a Δt destabilized suspension. Structural differences are evident and in good agreement with a recent Brownian dynamics simulation study.75,76 A visualization of the structures obtained in this simulation is shown in Fig. 5(b). Results show a less homogeneous structure for Δt gels, with inhomogeneities on the length scale of a few particle diameters.

The viscoelastic behavior of concentrated ΔpH and Δt gels is characterized by using standard macroscopic rheological measurements and, for samples that can support their own weight, compressive tests. In Fig. 6, we show these results for the two different destabilization methods as a function of volume fraction. Notable differences in the mechanical behavior of the two systems are observed. For the inhomogeneous Δt gels, significantly higher yield stresses are observed. In oscillatory rheological measurements, the same behavior is observed; both the yield stresses and the storage moduli G’ are significantly higher for the less homogeneous Δt systems.61,69,77

An analysis of the scaling behavior of yield strains suggests a fundamental difference in the stress-bearing mechanism of the two systems, with stresses supported by a bond-bending mechanism for ΔpH gels and a bond-stretching mechanism for Δt gels.69

All results combined strongly indicate that microstructure has a tremendous influence on the mechanical behavior of these systems. The two different variants of the in situ destabilization process naturally lead to gels of significantly different microstructures.

A logical step in these experiments is to determine what happens if the structure formed in situ is perturbed by applying a large shear rate (as done in many rheological experiments to set reproducible starting conditions). The result is surprising and shows again the strong dependence of mechanical behavior on the structural arrangement of particles in a gel network. Results again suggest an increase in mechanical properties of concentrated particle gels with decreasing homogeneity of their microstructures. Shearing a homogeneous ΔpH gel leads to a shear-induced increase of the modulus and yield stress, while shearing the more inhomogeneous Δt gel instead leads to a strong decrease of the elastic and yield properties. The influence of the microstructure is very evident here, as all the other parameters (including the interparticle potential) remain unchanged during the shearing process.

Another very direct and simple way to manipulate the microstructures of gelling colloids is to introduce voids into the structure intentionally. This can be achieved by adding alkaline swellable thickeners (ASTs) to the liquid phase of a colloidal alumina suspension. Hesselbarth et al.79 use polyacrylic acids, such as Acosul 820 or Acosul 830, that are slightly internally cross-linked. These are introduced at low pH (pH 4.5) into high volume fraction ceramic suspensions. At this pH, these AST polymers are small (diameter ≈ 80 nm) insoluble polymer particles that have only a minor influence on the viscosity of the suspensions.

In Fig. 7, we plot the diameter of these polymers, as measured by dynamic light scattering in dilute aqueous suspension, as a function of pH. The diameter of the AST polymers increases by approximately a factor of 10 between pH 4 and pH 9, the isoelectric point of Al₂O₃. Thus, increasing the pH in such an alumina suspension from pH 4 to pH 9 by using the DCC technique (see Box 1) then leads not only to destabilization of the colloids but also to a drastic increase in the size of these AST polymers. The AST polymers thus produce inhomogeneities in the evolving microstructure, which can be controlled by the size and the concentration of the added AST polymer.

The presence of small amounts of AST polymers (0.4 wt% with respect to alumina) results in a more than 10-fold increase in the yield strength and elastic modulus of the wet coagulated gels. Figure 8 shows the compressive yield stress σc, as a function of the AST polymer content. This drastic change in the mechanical behavior is a result of the formation of a less homogeneous microstructure, caused by the presence of the swollen AST polymers. In case higher urea concentrations are used the reaction first produce a coagulated gel with swollen polymers and high yield strength but further ions created at the buffer pH (= 9) of the urea hydrolysis reaction lead to shielding of the deprotonated sidegroups of the polymers. This causes the polymer particles to shrink again and the gel relaxes to a more homogeneous microstructure with a lower yield strength (arrows in Fig. 8).

Thus, in contrast to the study of Channell et al.,10 the results of Wyss et al.47,60,61,68,69 and Hesselbarth et al.79 show a significant increase of the elastic and yield properties of concentrated particle gels with decreasing homogeneity of their microstructures.

In the following, we discuss this apparent contradiction and attempt to provide a qualitative explanation. Figure 9 shows a schematic representation of the different kinds of microstructure. Figure 9(a) shows a microstructure obtained by diluting a more concentrated, homogeneous gel under slow stirring. The resulting structure consists of dense aggregates that are loosely packed with only a few bonds between aggregates.

Although the mechanical behavior of the aggregates themselves will be much stronger than that of a homogenous network (Fig. 9(b)), the overall gel structure will be weaker because of the sparse and weak bonds between the aggregates. Channell et al.10 present a model that takes into account both the inter-aggregate and intra-aggregate bonds and agrees well with their experimental data. It is also evident from this model that the overall mechanical behavior for a packing of large aggregates will be dominated by the weakness of the inter-aggregate bonds. Alternatively, one could view the aggregates as stiff particles and consider the scaling of the expected mechanical behavior with the size of these “aggregate-particles.” For packed particles with fixed coordination number and fixed interaction strength, one expects the mechanical properties to scale with the number of bonds per volume. This implies that the mechanical strength, for
Box 1. DCC

DCC\textsuperscript{70-72} is one of the few methods\textsuperscript{73} that allow a true \textit{in situ} destabilization of colloidal suspensions by a direct change of the interparticle potential. Electrostatically stabilized suspensions are destabilized by shifting the pH of the suspensions toward their IEP or by increasing the ionic strength in the system. The DCC technique allows for \textit{in situ} destabilization of the suspensions, without perturbing the gel formation. The onset and speed of the reaction are controlled by both temperature and enzyme concentration. This is achieved by the use of time-delayed internal chemical reactions, such as enzyme-catalyzed hydrolysis reactions, or hydrolysis reactions induced by elevated temperatures. For the destabilization of alumina suspensions, the hydrolysis of urea,

\[
\text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_3 \rightarrow \text{HCO}_3^- + 2\text{NH}_4^+ \quad (B1)
\]
catalyzed by the enzyme urease can be used. The pH of the suspension is shifted because of the products of this reaction to a buffer pH of 9 in the presence of the enzyme urease. For other oxides with IEPs different from that of alumina, many other enzymatic destabilization systems are available.\textsuperscript{74}

Furthermore, the ionic strength in a suspension is increased homogeneously and continuously at the buffer pH of 9 by the products of Eq. (B1).

\textbf{ΔpH and ΔI methods} At low ionic strength and at pH values far from the IEP, an oxide particle suspension is electrostatically stabilized. This is shown in the schematic stability diagram in Fig. B1. Thus, the suspension is destabilized by either shifting the pH toward the IEP or by increasing the ionic strength to high values. The two different destabilization pathways are referred to as ΔpH destabilization and ΔI destabilization, respectively.

Although in the final stage of destabilization, the interparticle potentials for the two routes might be comparable, the pathway of destabilization—the way the interparticle potentials change during the continuous destabilization process—is completely different.

For the two different methods, the evolution of DLVO potentials shows characteristic differences. Interaction potentials, as predicted by the DLVO theory using parameters typical for alumina suspensions, are plotted in Fig. B2. A secondary minimum in the DLVO potential appears during the ΔΔI destabilization, whereas for the case of ΔpH destabilization, no secondary minimum is observed.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{schema.png}
\caption{Schematic stability diagram for a colloidal suspension. At low ionic strength and at pH values far from the isoelectric point (IEP) the suspension is electrostatically stabilized. Moving the pH toward the IEP (pathway (a), ΔpH destabilization) or increasing the ionic strength to high values (pathway (b), ΔI destabilization) leads to aggregation of the suspension as the surface charge or the Debye screening length, respectively, is reduced.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{dlvo.png}
\caption{Evolution of Derjaguin–Landau–Verwey–Overbeek-potentials for the two destabilization mechanisms. A Hamaker constant of A_\text{HI} = 5 \times 10^{-20} \text{J} and a particle radius of 200 nm is used. (a) Decrease of surface charge at a constant ionic strength of I = 0.001 \text{mol/L} (ΔpH destabilization). ζ potential values in the curves are ζ = 60 \text{mV} (i), 30 \text{mV} (ii), 20 \text{mV} (iii), 10 \text{mV} (iv), and 0 \text{mV} (v). (b) ΔI destabilization: Increase of ionic strength at constant surface charge (The ζ potential is kept constant at ζ = 60 mV). Ionic strength values in the curves are I = 0.001 \text{mol/L} (i), 0.02 \text{mol/L} (ii), 0.1 \text{mol/L} (iii), 0.2 \text{mol/L} (iv), 1.0 \text{mol/L} (v).}
\end{figure}

DCC, direct coagulation casting; IEP, isoelectric point; DLVO, Derjaguin–Landau–Verwey–Overbeek.
DWS extends DLS to the highly multiple scattering regime. Traditional DLS relies on samples that show only negligible multiple scattering. In this case, the length scale $l/q$ that one observes in an experiment is related to the scattering angle $\theta$ via

$$q = \frac{4\pi n}{\lambda} \sin(\theta/2)$$  \hspace{1cm} (B2)

where $\lambda$ is the wavelength of the laser, and $n$ is the refractive index of the sample. Observations of the fluctuations in the detected intensity then yields information on the dynamics of the system on the length scale $l/q$. The fluctuations in intensity are characterized by the temporal intensity autocorrelation function $g_2(q, t)$:

$$g_2(t) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t)^2 \rangle}$$ \hspace{1cm} (B3)

The intensities at time $t$ and at time $(t+\tau)$ are correlated as long as the lag time $\tau$ the particles have moved only over a distance much shorter than the length scale $1/q$. When the particle displacements become much larger than this length scale, the two intensities will no longer be correlated. For a stable suspension of monodisperse particles, the electric field autocorrelation function

$$g_1(t) = \sqrt{g_2(t) - 1}$$ \hspace{1cm} (B4)

will decay as

$$g_1(t) = e^{-D_{\text{eff}}\tau}$$ \hspace{1cm} (B5)

where $D$ is the diffusion constant of the particles. The size of the particles can thus be derived from such a measurement.

In the case of a highly multiple scattering sample, the scenario is different. The detection angle $\theta$ no longer yields any useful information about length scales, as each photon passing through the sample would have been scattered by many particles before it reaches the detector. The movement of each of these particles will contribute to the total loss of temporal correlation in the detected signal. In DWS, the transport of photons through a highly multiple scattering sample is treated as a diffusion process.\(^{45,46}\) This allows the theoretical prediction of the distribution of the path length of photons through the sample for different sample geometries. An important parameter is the transport mean free path $\ell$. It is the distance traveled in the sample after which the direction of the photon is completely randomized. The electric field autocorrelation function is then given by

$$g_1(t) = \int_0^{\infty} P(s)e^{-[(s/\ell)^2][\langle \Delta \rho^2 \rangle]} ds$$ \hspace{1cm} (B6)

where $P(s)$ is the distribution of photon path lengths, $L$ is the cell thickness, and $\langle \Delta \rho^2 \rangle$ is the mean square displacement of the particles. Thus, DWS allows measurement of particle sizes in stable suspensions. The analysis of the particle dynamics can also be used to characterize the viscoelastic behavior of colloidal gels.\(^{84}\)

The main drawback of the technique is its inability to access different length scales. As many particles contribute to the loss of temporal correlation for each photon path, all measurements represent average properties of the system. On the other hand, this fact also implies that the technique allows measurement of the dynamics of the system at extremely short length scales. Each particle only has to move a very short distance (typically sub-nanometers) in order for a photon path length to change by a wavelength of light.

However, the best advantage of DWS is the possibility to characterize highly turbid colloidal systems that cannot be studied by means of conventional light scattering. DWS is thus ideally suited for the characterization of ceramic suspensions, whose strong turbidity excludes them from access by other techniques.

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**VI. Summary and Conclusions**

The microstructure of concentrated particle gels strongly influences their rheological properties. A significant number of studies have focused on this issue in recent years, aiming at describing relations between the structural and rheological and mechanical properties of colloidal gel networks. Nevertheless, our understanding of the role of microstructure in concentrated colloids is still rather limited. More work remains to be carried out to gain a more thorough understanding.

The reasons for this lack of understanding are twofold:

A first important issue is the way microstructure is quantified. Even if detailed knowledge on the microstructure of a particle gel is experimentally accessible, for instance as a full set of particle positions in the network, this information has to be translated into a useful measure that describes the macroscopic structure and allows a link to, for instance, the rheological

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example, the compressive yield stress $\sigma_y$ decreases with the size $R_{\text{agg}}$ of the aggregate as:

$$\sigma_y \propto R_{\text{agg}}^{-3}$$ \hspace{1cm} (12)

The structures shown schematically in Figs. 9(c) and 9(d) are completely different. They were formed by an in situ process, yielding structural properties that cannot be achieved by mixing or shearing. In a Gedanken Experiment, we view this kind of structure as a two-component system, with one phase consisting of voids (filled with water) and the other phase consisting of a more concentrated, homogeneous gel phase. The gel phase is percolating the whole macroscopic volume, while the other phase consists of isolated pores. This is in contrast to the case of Fig. 9(a), where the liquid phase between aggregates spans the overall volume.
behavior of the system. It is unclear whether quantities like the radial pair correlation function $g(r)$, or the structure factor $S(q)$, are able to capture the essential properties of microstructures that can be related to the properties of a macroscopic gel network in a meaningful way. Alternative ways of quantifying microstructures should be considered in the future. They might provide us with a much better measure of the essential structural properties of particle networks.

A second problem is the lack of control on the possible microstructures that can be experimentally realized in a reproducible way. In concentrated and strongly attractive colloidal suspensions, the aggregation times are too fast to allow the formation of a homogeneous and reproducible microstructure by direct addition of salt or acid/base. In order to reach reproducible conditions, the aggregated gels have to be strongly sheared prior to measurement. However, this implies that the microstructure will be governed mainly by the pre-shearing process and not by the particle aggregation kinetics themselves. In situ destabilization methods offer the possibility of inducing formation gels in a reproducible way without shearing or mixing. Even different kinds of aggregation kinetics, leading to significantly different microstructures, can be realized. This allows to directly study the effect of different kinds of microstructures on the bulk properties of the formed colloidal gels. Another way to realize different microstructures is to concentrate dilute suspensions of aggregated clusters into dense gels by centrifugation or pressure filtration. The morphology and size of particle aggregates in dilute suspension can be controlled by applying different shear rates to the suspension. A gel of the compacted clusters will then have properties that will depend on the structure and

Fig. 6. Compressive yield stress $\sigma_y$ as a function of volume fraction $\phi$ for $\Delta pH$- vs $\Delta I$-destabilized gels.

Fig. 7. Diameter of the alkaline swellable thickener (AST) particles in H$_2$O, as measured via dynamic light scattering, as a function of pH. The concentration of the AST was 0.05 wt% of dry polymer, relative to H$_2$O.

Fig. 8. Compressive yield strength of wet green bodies with 57 vol% alumina, as a function of polymer content and urea concentration (UC). The yield strength is around 10 kPa for coagulated suspensions without polymers. High yield strength results for coagulated gels with swollen polymers inducing inhomogeneities in the gel microstructures upon changing pH from 4 to 9. In case of much higher urea concentrations (1.96 mol/L), after shifting pH from 4 to 9, the salt concentration is increased and the swollen polymers shrink as a result of shielding the negative charges of the deprotonated polymer side groups. Thereby, the gel microstructures relax, leading again to more homogenous microstructures and to lower yield strengths (indicated by the arrows in the figure).
Fig. 9. Schematic illustration of microstructures obtained from different gel-forming methods: structure obtained by diluting a more concentrated, homogenous gel under slow stirring (a). Homogeneous particle network (b) as for instance formed by DCC using the ΔpH method (see Box 1). Inhomogeneous, but strongly interconnected network (c) as for instance formed by DCC using the ΔM method (see Box 1). Particle gel with intentionally introduced voids (d), as achieved by introducing alkaline swellable thickeners into the suspension. Note that the homogeneity of the gel structures is not sufficient to explain differences in mechanical properties.

References

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the ETH-Zurich in Switzerland. Her research interests include colloidal aspects of ceramic processing and ceramic foams.

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Ludwig Gauckler and his co-workers received several national and international awards for their work on colloid chemistry for ceramic processing and high-temperature solid oxide fuel cells, rapid prototyping of ceramics (Cercon), among them, the Award for Real Advances in Materials from NASTS (National Association for Science, Technology, and Society) and the Federation of Materials Societies in 1994. He is a Fellow of the American Ceramic Society and served as President of the scientific advisory board of the Swiss Academy of Technical Sciences, and is a member of the Academy of Ceramics. His research interests include structural ceramics, high Tc-superconductors, computer-assisted modeling of thermodynamics, mixed ionic-electronic conducting oxides and colloidal chemistry for ceramic processing. Prof. Gauckler has published more than 180 scientific papers, and holds 15 patents.