### Rheology of Cubic Particles in a Concentrated Colloidal Dispersion Suspending Medium

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Wagner, Norman; University of Delaware, Department of Chemical Engineering |
| Keywords: | Rheology, Colloids, Suspensions, Particulate flows, Complex fluids |
Rheology of Cubic Particles in a Concentrated Colloidal Dispersion Suspending Medium

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Submitted to AIChE Journal

Abstract

The flow behavior of mixtures of micron-sized cubic particles suspended in a concentrated colloidal dispersion is investigated across a broad range of cubic particle concentrations. In the semi-dilute regime, the qualitative shape of the dynamic moduli and flow curves reflect those of the underlying colloidal dispersion medium. These curves are superimposed with the underlying colloidal dispersion using shift factors that are found to be larger than those obtained in a recent study for suspensions of non-colloidal spherical particles in the same concentrated colloidal dispersion medium. At higher concentrations of cubic particles, deviations from this shifting procedure are apparent as depletion attractions and confinement of the underlying colloidal dispersion lead to larger increases in the viscosity at both low and high applied shear stresses. The results of this study provide guidance for formulating suspensions through control of particle shape and mixture concentration.

AREA:  Transport Phenomena and Fluid Mechanics

KEYWORDS:, Rheology, Suspensions, Colloids, Particulate Flows, Complex Fluids
1. Introduction

Particle suspensions are ubiquitous across the industrial and commercial domain. In many cases, the fluids suspending the particles are non-Newtonian. Early work in this area focused on understanding the flow behavior of suspensions of spherical non-colloidal particles in polymer solutions and melts. Despite the complex local flows between particles in a flowing suspension, the flow curves were found to strongly reflect the behavior of the underlying viscoelastic medium. Ohl and Gleissle formalized a procedure to shift the flow curves of these suspensions on to the underlying suspending fluid at constant shear stress, \( \sigma \):

\[
\text{Shift Factor} = \frac{\dot{\gamma}(\phi=0)}{\dot{\gamma}(\phi)}|_\sigma = \frac{\eta(\phi)}{\eta(\phi=0)}|_\sigma
\]

In the above equation, \( \dot{\gamma} \) is the shear rate, \( \phi \) is the particle volume fraction, and \( \eta \) is the steady shear viscosity. This shifting procedure, which treats the suspending medium as a continuous fluid phase, has found remarkable success in capturing the behavior of suspension flow curves across a broad range of spherical particle volume fractions and various types of viscoelastic media.

Recently, Cwalina and Wagner investigated suspensions comprised of non-colloidal spherical particles suspended in a concentrated colloidal dispersion. The concentrated colloidal dispersion was strongly non-Newtonian, exhibiting both shear thinning and shear thickening. It is important to note that such mixed suspensions cannot be treated simply in terms of polydispersity as the spherical non-colloidal particles and colloidal particles are separated by more than an order of magnitude in size and three orders of magnitude in mass. Suspensions comprised of mixtures of non-colloidal and colloidal particles are found in a wide variety of materials such as: concrete, asphalt, coal water slurry fuels, and ice cream, just to name a few. As such, there is a significant engineering interest in understanding the flow behavior of such suspensions and how these properties can be tuned for design purposes. As many of these materials and products contain non-spherical particles, there is significant motivation for fundamental investigations of particle shape effects.

For such mixtures at volume fractions of up to \( \phi = 0.15 \) of spherical non-colloidal particles, Cwalina and Wagner found the dynamic moduli and steady shear flow curves maintained the same qualitative shape of the underlying colloidal dispersion medium. The dynamic moduli curves could be shifted on to that of the neat colloidal dispersion with the shift made at constant frequency. Similar behavior has been reported with spherical particles in other viscoelastic media. Likewise, the steady shear flow curves were successfully shifted onto the flow curve for the neat colloidal dispersion medium when compared at constant shear stress, which is consistent with the hypothesis of Ohl and Gleissle. Deviations from this shifting procedure were observed at higher packing fractions of the spherical non-colloidal particles, as stronger shear thickening was observed. At these high packing fractions, the on-average separation distance between non-colloidal particle surfaces in suspension becomes on the order...
ten colloidal particle diameters, or less. Confinement is known to enhance shear thickening in colloidal dispersions\textsuperscript{20}, and a recent simulation study of hydrodynamically interacting particles revealed that confinement promotes the formation of larger hydrodynamic clusters, ‘hydroclusters’, which leads to the observed increase in the strength of shear thickening\textsuperscript{21}.

In the present work, we investigate the role of particle shape in these suspensions with a concentrated colloidal dispersion medium. The particles in this study are cubic aluminosilicate zeolites. Cwalina et al\textsuperscript{22} recently studied the rheology of these same cubic particles suspended in a Newtonian fluid. Here, we study the effects of particle shape on mixture viscosity by suspending these cubic particles in the concentrated colloidal dispersion medium considered by Cwalina and Wagner\textsuperscript{10} in their study of suspensions of spherical non-colloidal particles. The applicability of the shifting hypothesis of Ohl and Gleissle\textsuperscript{9}, traditionally applied to suspensions of spherical particles, is explored with regard to these suspensions of cubic particles in a non-Newtonian suspending medium. Furthermore, the possibility of enhanced confinement effects due to the shape of the non-colloidal particles is further examined by studying the mixture suspension rheology at high packing fractions of cubic particles. This study complements the existing literature on suspensions with non-Newtonian suspending fluids, and the results are of significant practical interest as they offer insight into how the flow properties of these suspensions can be tuned and engineered through the particle shape.

2. Experimental Section

Materials

The primary suspending medium used in this study was a concentrated colloidal dispersion. The dispersion consists of silica nanoparticles (Seahostar KE-P50, Nippon Shokubai Co., Tokyo, Japan) of radius $a = 260$ nm and particle density $\rho_p = 1.96$ g/cm$^3$\textsuperscript{23} dispersed in a near-index matching polyethylene glycol (PEG) [average molecular weight = 200] suspending fluid (Aldrich Chemical Company, Allentown, PA; $\eta_f = 0.05$ Pa·s at 25$^\circ$C, $\rho_f = 1.12$ g/cm$^3$) at a colloid particle volume fraction of $\phi = 0.40$. This is the identical colloidal dispersion studied by Cwalina and Wagner\textsuperscript{10} in their study of suspensions of spherical non-colloidal particles in a concentrated colloidal dispersion. The colloidal dispersion was gently roll mixed for one week to insure homogeneity throughout the sample.

Suspensions were formulated by the addition of cubic aluminosilicate zeolites (Advera$^\text{®}$ 401) from PQ Corporation (Philadelphia, PA) to the colloidal dispersion medium. The SEM image in Figure 1 reveals the cubic nature of these particles, which includes facets, edges, and corners. The edge length ($l$) distribution as reported by the manufacturer is as follows: $l_{10} = 1.3$ µm, $l_{50} = 3.0$ µm, $l_{90} = 5.8$ µm. The characterization of these cubic particles in a Newtonian fluid was reported recently by Cwalina et al\textsuperscript{22} and the suspension compositions of the present study...
are reported in Table 1. The volume fraction of cubic particles, $\phi_{\text{cubes}}$, is defined as the volume of cubic particles, as calculated from the measured solution density, divided by the total suspension volume. In this manner, the ratio of the volume of KE-P50 colloidal particles to the volume of PEG-200 remains fixed for each suspension at 40% v/v.

![Figure 1. SEM image of cubic aluminosilicate zeolites used in this study. Image used with permission from Cwalina et al.][22]

Table 1. Compositions of suspensions in this study with a colloidal dispersion suspending medium at a colloidal particle volume fraction of $\phi = 0.40$.

<table>
<thead>
<tr>
<th>Suspension</th>
<th>WT% Cubes</th>
<th>$\rho_{\text{suspension}}$ (g/cm$^3$)</th>
<th>$\phi_{\text{cubes}}$</th>
<th>$\phi_{\text{Total Solids}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.4</td>
<td>1.49</td>
<td>0.037</td>
<td>0.422</td>
</tr>
<tr>
<td>2</td>
<td>10.8</td>
<td>1.51</td>
<td>0.076</td>
<td>0.445</td>
</tr>
<tr>
<td>3</td>
<td>16.1</td>
<td>1.54</td>
<td>0.115</td>
<td>0.469</td>
</tr>
<tr>
<td>4</td>
<td>26.6</td>
<td>1.60</td>
<td>0.197</td>
<td>0.518</td>
</tr>
<tr>
<td>5</td>
<td>37.0</td>
<td>1.66</td>
<td>0.284</td>
<td>0.570</td>
</tr>
<tr>
<td>6</td>
<td>42.1</td>
<td>1.69</td>
<td>0.329</td>
<td>0.598</td>
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</table>
A limited study was performed of suspensions of cubic particles in a colloidal dispersion medium where the colloidal particle volume fraction was $\phi = 0.20$. These experiments were performed to assess the effect of possible depletion attractions due to the colloidal dispersion and its effect on suspension rheology. These suspension compositions are reported in Table 2.

Table 2. Compositions of suspensions in this study with a colloidal dispersion suspending medium at a colloidal particle volume fraction of $\phi = 0.20$.

<table>
<thead>
<tr>
<th>Suspension</th>
<th>WT% Cubes</th>
<th>$\rho_{\text{suspension}}$ (g/cm$^3$)</th>
<th>$\phi_{\text{cubes}}$</th>
<th>$\phi_{\text{Total Solids}}$</th>
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<td>7</td>
<td>30.0</td>
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</tr>
<tr>
<td>8</td>
<td>42.0</td>
<td>1.55</td>
<td>0.302</td>
<td>0.442</td>
</tr>
<tr>
<td>9</td>
<td>51.1</td>
<td>1.62</td>
<td>0.384</td>
<td>0.507</td>
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**Rheological Characterization**

Rheological characterization was performed on an AR-2000 Rheometer (TA Instruments, New Castle, DE) with a 40 mm 2° cone and plate tooling. The dynamic moduli were measured during frequency sweeps at a shear stress-amplitude of 0.1 Pa, which were performed in directions of both increasing and decreasing frequency to demonstrate reversibility. The steady shear viscosity was likewise measured with steady flow sweeps in the ascending and descending directions. All measurements in this study were performed at 25° C. The largest particle Reynolds number, $Re_p$, encountered during measurement was on the order of $10^3$, such that the criterion for Stokes flow was satisfied, and particle inertia can be neglected.

The steady flow curve of the primary underlying colloidal dispersion suspending medium (colloidal particle volume fraction $\phi = 0.40$) is shown in Figure 2. The flow curve for a comparable volume fraction of cubic particles in the same Newtonian suspending fluid is shown for reference. The colloidal dispersion exhibits flow behavior characteristic of near hard-sphere dispersions. At low shear stresses, the viscosity shear thins into the high shear plateau, before ultimately increasing toward the shear-thickened state at the highest shear stresses probed. Shear thickening in colloidal dispersions is well-established to be stress-controlled$^{24-26}$, and the onset of shear thickening in this dispersion occurs around $\sigma \sim 100$ Pa. Cwalina et al.$^{22}$ studied the rheology of these cubic particles in a Newtonian fluid and found shear thickening in these suspensions is likewise stress-controlled, with the onset of shear thickening around $\sigma \sim 1$ Pa, which is two orders of magnitude smaller than that of the underlying colloidal dispersion. That
larger particles shear thicken at lower shear stresses is well established\textsuperscript{27}, and efforts have been made to investigate the effects of particle shape\textsuperscript{28}. This large difference in the onset stress for shear thickening will become important later on in the discussion when deciphering the origin of shear thickening in the mixed suspensions of the present study.

![Steady shear viscosity of the $\phi = 0.40$ colloidal dispersion suspending medium (circles) and a $\phi = 0.388$ suspension of cubic particles in a Newtonian suspending medium (squares) [from Cwalina et al.\textsuperscript{22}] plotted as a function of the applied shear stress. The onset of shear thickening in the suspension of cubic particles in a Newtonian fluid occurs around $\sigma \sim 1$ Pa, while that for the colloidal dispersions is around 100 Pa.]

Figure 2. Steady shear viscosity of the $\phi = 0.40$ colloidal dispersion suspending medium (circles) and a $\phi = 0.388$ suspension of cubic particles in a Newtonian suspending medium (squares) [from Cwalina et al.\textsuperscript{22}] plotted as a function of the applied shear stress. The onset of shear thickening in the suspension of cubic particles in a Newtonian fluid occurs around $\sigma \sim 1$ Pa, while that for the colloidal dispersions is around 100 Pa.

3. Results and Discussion

Linear Viscoelastic Regime

The dynamic moduli curves for the suspensions of cubic particles in a concentrated colloidal dispersion suspending medium (colloidal particle volume fraction = 0.40) are shown in Figure 3. Up to a volume fraction of $\phi_{\text{cubes}} = 0.115$, the dynamic moduli curves exhibit the same qualitative shape as that for underlying colloidal dispersion. This behavior is qualitatively similar to that observed for suspensions of non-colloidal spheres in other types of viscoelastic media\textsuperscript{4,16-19}. In this semi-dilute regime, the mixed suspensions’ dynamic moduli curves can be shifted onto that for the underlying colloidal dispersion using a single shift factor that shifts the
curves vertically when plotted against the frequency. This superposition of the dynamic moduli curves in this concentration regime is shown in Figure 4, and it can be seen that the terminal scaling of the moduli is maintained in these suspensions. The shift factors required to achieve superposition of both the storage and loss moduli are shown in Figure 5. Compared to the suspensions of spherical non-colloidal particles in the colloidal dispersion medium, the shift factors required to superimpose the dynamic moduli curves of the suspensions of the present study are substantially larger. Furthermore, in contrast to the suspensions of spherical non-colloidal particles in a colloidal dispersion medium where the shift factors for the storage and loss moduli were essentially identical, the shift factor for the storage modulus is found to be larger than that of the loss modulus for suspensions of cubic particles in a colloidal dispersion medium.

At higher packing fractions of cubic particles, it is not possible to shift the storage moduli curves onto that of the colloidal dispersion, as there is a significant increase in the magnitude of the storage modulus at low frequencies. Interparticle attractive forces are known to lead to large increases in the storage moduli. For the suspensions of the present study, the large increase in the storage moduli at high packing fractions and the larger storage moduli shift factors in the semi-dilute regime may be due to attractive forces between the particles themselves (such as van der Waals forces), or due to a depletion-induced attraction with the colloidal particles acting as the depletant. The possibility of depletion-induced attraction in these mixtures will be revisited later in the discussion.

![Figure 3](image_url)

Figure 3. Storage (left, filled symbols) and loss (right, open symbols) moduli for suspensions of cubic particles in a concentrated colloidal dispersion medium for a range of cubic particle volume fractions.
Figure 4. Suspension storage (left) and loss (right) moduli shifted onto that of the underlying colloidal dispersion medium in the semi-dilute cubic particle concentration regime.

Figure 5. Shift factors required to collapse the storage (filled symbols) and loss (open symbols) moduli onto the underlying colloidal dispersion medium for suspensions of cubic particles (squares) and non-colloidal spherical particles (circles).
In Figure 6, the purely hydrodynamic component of the loss modulus, $\eta'\omega$, is subtracted off to give only the contribution from Brownian and interparticle forces. In this manner, a characteristic relaxation time for the suspensions can be defined from the inverse of the cross-over frequency, $\omega_{\text{cross-over}}$. The cross-over frequency relative to that of the underlying colloidal dispersion medium is plotted in Figure 7 as a function of the volume fraction of cubic particles. At low concentrations, the cross-over frequency is identical to that of the colloidal dispersion. This result is consistent with that of Cwalina and Wagner\textsuperscript{10}, where the addition of small amounts of spherical non-colloidal particles to the colloidal dispersion medium did not change the cross-over frequency. However, at higher concentrations, the cross-over frequency becomes a decreasing function of the cubic particle concentration. At $\phi_{\text{cubes}} = 0.329$, the cross-over frequency of the suspension is almost an order of magnitude smaller than that of the underlying colloidal dispersion.

Figure 6. Storage (filled symbols) and loss moduli with the hydrodynamic component, $\eta' \omega$, subtracted off of the latter (open symbols).
Figure 7. Suspension cross-over frequency relative to that of the underlying colloidal dispersion suspending medium as a function of the concentration of cubic particles.

For mixtures of non-colloidal spheres suspended in the colloidal dispersion medium, it was shown that the relative high frequency viscosity was well-described by the Einstein equation in the dilute limit\(^{30}\), and the expansion in particle volume fraction to order \(\phi^2\) in the semi-dilute regime\(^{31}\). These particular equations were derived for spherical particles in a Newtonian fluid, but found rather surprising applicability in suspensions of spherical particles in a non-Newtonian colloidal dispersion medium. Cwalina et al.\(^{22}\) demonstrated that in the semi-dilute concentration regime (up to \(\sim \phi_{cubes} = 0.137\)), the concentration-dependence of the relative viscosity of suspensions of cubic particles in a Newtonian fluid could be captured by a similar expansion in cubic particle volume fraction up to the order \(\phi^2\) term. In Figure 8, the relative high frequency viscosity of the suspension mixtures in the present study is plotted as a function of the cubic particle volume fraction in the semi-dilute regime. Similar to what was observed for the suspensions of spherical non-colloidal particles, the relative high frequency viscosity for suspensions in a non-Newtonian colloidal dispersion medium is in good agreement with results for cubic particles suspended in a Newtonian fluid in the semi-dilute regime.
Figure 8. Relative high frequency viscosity of mixed suspensions as a function of the cubic particle volume fraction. The dashed line is the dilute limit prediction for cubic particles suspended in a Newtonian fluid and the solid line is the fit to the experimental data in the semi-dilute regime from Cwalina et al.\textsuperscript{22} Error bars are smaller than data points.

Brownian motion in a concentrated colloidal dispersion gives rise to viscoelasticity\textsuperscript{32}. A hallmark of this phenomenon in dispersions of spherical colloids is the emergence of a plateau storage modulus at high frequencies. Although a plateau modulus is not quite reached at the highest frequencies probed in this study, an estimate of the plateau modulus is taken as the value of the storage modulus at the highest frequency (a similar criterion was used by Shikata and Pearson\textsuperscript{32} in their seminal study of viscoelasticity in concentrated colloidal dispersions). As seen in Figure 9, the value of the plateau modulus relative to that of the underlying colloidal dispersion grows by almost an order of magnitude at high concentrations of cubic particles. This increase in suspension elasticity can arise either from interactions between cubic particles, which are not evident when suspended in a Newtonian fluid\textsuperscript{22}, or due to confinement effects of the underlying colloidal dispersion.
Steady Shear Rheology: Semi-Dilute Regime

The steady shear viscosity for these mixed suspensions is plotted in Figure 10 as a function of the applied shear stress and volume fraction of cubic particles. As the concentration of cubic particles is increased, the flow curves maintain the same qualitative shape of the underlying colloidal dispersion, but shift vertically to higher viscosities. Similar behavior was observed by Cwalina and Wagner\textsuperscript{10} for semi-dilute suspensions of spherical non-colloidal particles in the same concentrated colloidal dispersion. In the spirit of Ohl and Gleissle’s hypothesis\textsuperscript{9}, a shift factor was proposed to superimpose the suspension flow curves on to that of the underlying colloidal dispersion medium with a single shift factor. This approach required treating the colloidal dispersion as a single continuous fluid phase. As seen in Figure 11, a successful superposition of the viscosity data is indeed achieved with a single shift factor, demonstrating that the shifting procedure of Ohl and Gleissle\textsuperscript{9} is applicable to this class of suspensions with cubic particles suspended in a non-Newtonian fluid medium that exhibits both shear thinning and shear thickening. This result is quantitatively consistent with recent observations for mixtures with spherical non-colloidal particles suspended in the same colloidal dispersion\textsuperscript{10}. 

Figure 9. Plateau storage modulus relative to that of the underlying colloidal dispersion medium as a function of the concentration of cubic particles.
Figure 10. Steady shear viscosity of mixed suspensions of cubic particles with varying volume fraction in a concentrated colloidal dispersion as a function of the shear stress.

Figure 11. Suspension viscosity curves from Fig. 10 shifted onto that of the underlying colloidal dispersion medium.
The shift factor required to superimpose a suspension’s viscosity curve onto that of the underlying colloidal dispersion medium is essentially a relative viscosity—the suspension viscosity divided by the suspending medium viscosity. The relative viscosity of the suspensions of cubic particles suspended in the concentrated colloidal dispersion medium is shown in Figure 12. Also plotted in this figure are the results obtained by Cwalina et al.\textsuperscript{22} for the cubic particles in a Newtonian suspending fluid in the semi-dilute regime. The measured relative steady shear viscosities of the present suspensions are slightly larger than the expectations for cubic particles in a Newtonian fluid. A similar result was observed by Cwalina and Wagner\textsuperscript{10}, where the relative steady shear viscosity of suspensions of spherical non-colloidal particles in the same colloidal dispersion medium was slightly larger than predictions for spherical particles in a Newtonian fluid. It should be noted that this phenomenon has been observed more broadly for spherical particles in other types of viscoelastic media as well, and this behavior remains unexplained\textsuperscript{19,33,34}.

Due to the possible confining effects afforded by the flat surfaces of the cubic particles on the flow of the colloidal suspension, we consider the possible effects of such confinement on the viscosity of the underlying colloidal dispersion. Swan and Brady\textsuperscript{35} showed that confinement of a colloidal dispersion to length scales of order ten particle radii or less led to an increase in the hydrodynamic viscosity. Physically, this enhanced viscosity comes from interactions between a colloidal particle and the boundary as well as increased hydrodynamic interactions between colloidal particles themselves. While the exact orientation of cubic particles with respect to one another under steady shear is expected to be somewhat random, it is anticipated that there will be configurations where cubic particle faces are oriented parallel to one another. In such an instance, the colloidal particles are confined locally between the much larger faces of the cubic particle, and the calculations of Swan and Brady\textsuperscript{35} can be used to estimate the viscosity increase of the underlying colloidal dispersion medium.

A geometric model can be used to predict the on-average surface separation distance between cubic particles\textsuperscript{24,36}:

\[
\frac{h_{cubes}}{l} = \left( \frac{\phi_{max}}{\phi_{cubes}} \right)^{1/3} - 1
\]

where \(h_{cubes}\) is the on-average surface separation distance between cubic particles, \(l\) is the average cube edge length, and \(\phi_{max}\) is the maximum packing fraction of cubic particles under steady shear, determined by Cwalina et al.\textsuperscript{22} to be 0.69. At \(\phi_{cubes} = 0.076\), the on-average surface separation distance between cubic particles is approximately 12 colloidal particle radii, which is around the characteristic channel spacing where confinement begins to enhance the dispersion viscosity according to the calculations of Swan and Brady\textsuperscript{35}. Thus, as confinement effects become more important and lead to an increase in the viscosity of the underlying colloidal dispersion medium, the suspension’s relative viscosity can be calculated using the higher viscosity of the confined colloidal dispersion. When confinement effects are considered in this
manner for the data in Figure 12, the relative suspension viscosity more closely follows the fit from Cwalina et al.\textsuperscript{22} for cubic particles in a Newtonian fluid. These measurements and calculations suggest that confinement effects may become important in these mixed suspensions when the colloidal dispersion is confined between cubic particle faces at separation distances spanning only a few colloidal particle radii. Future simulations of these suspensions of cubic particles in a colloidal dispersion under steady shear would be useful for validating or refuting the hypothesis that confinement leads to the observed concentration dependence of the suspension relative viscosity in Figure 12.

Figure 12. Measured relative steady shear viscosity of cubic particles suspended in a concentrated colloidal dispersion medium as a function of the cubic particle volume fraction. The solid line is the concentration dependence of the suspension relative viscosity from Cwalina et al.\textsuperscript{22} for the cubic particles in a Newtonian suspending fluid. The X’s indicate the suspensions’ relative viscosities where confinement effects are taken into account in determining the viscosity of the suspending colloidal dispersion. The magnitude of the viscosity increase of the colloidal dispersion is estimated from the calculations of Swan and Brady\textsuperscript{35}. 

\[ \eta_r = 1 + 3.5\phi_{\text{cubes}} + 23.7\phi_{\text{cubes}}^2 \]
Steady Shear Rheology: Concentrated Suspensions

Figure 13 reports the steady shear viscosity as a function of the shear stress and shear rate for concentrated suspensions of cubic particles in a colloidal dispersion suspending medium. Above $\phi_{\text{cubes}} = 0.115$, the qualitative shape of the flow curves deviates significantly from that of the underlying colloidal dispersion and the semi-dilute suspensions at both low and high shear rates (stresses).

Figure 13. Steady shear viscosity of cubic particles suspended in a concentrated colloidal dispersion medium over a broad range of volume fractions plotted as a function of the shear stress (left) and shear rate (right). Open and closed symbols mark steady shear sweeps performed in both ascending and descending directions. The set of arrows in each plot is meant to guide the eye to the same two data points for the $\phi = 0.284$ suspension where two distinct shear thickening transitions are evident.

Above $\phi_{\text{cubes}} = 0.115$, at the lowest measured shear stresses, the steady shear viscosity does not tend toward a zero-shear viscosity and the magnitude of the low shear viscosity rises by several orders of magnitude. Note that this deviation in behavior cannot simply be due to the hydrodynamic confinement effect explored in the previous section, as that would result in a vertical shift in the viscosity. Consequently, a weak, interparticle force acting between cubic particles is suspected to be the source of this enhanced low shear viscosity. A logical candidate is depletion attractions resulting from the excluded volume, with regards to the colloidal particles, due to close approach of the cubic particles, as illustrated in Figure 14. The maximum possible stress from depletion attractions will occur when the cube faces are oriented parallel and aligned with one another. In this configuration, the overlap of excluded volume is maximized.
Figure 14. A to-scale illustration of 3 µm edge length cubic particles and 520 nm colloidal spheres. The dashed line marks the boundary of the excluded region for colloidal particles based on their center location. The shaded region in between the cubes is the overlap of the regions of excluded volume used to estimate possible depletion attractions.

The depletion potential between the two cubic particles, $U^{dep}$, scales with the product of the osmotic pressure, $\pi$, and the overlap of excluded volume, $\Delta V^{38}$:

$$U^{dep} \sim \pi \Delta V$$

(3)

For cubic particles with edge length, $L$, and spherical colloids of diameter, $d$, the overlap of excluded volume can be computed as:

$$\Delta V = 2d (L - 2d)^2$$

(4)

For the suspensions in this study with cubic particles of average edge length, $L = 3 \, \mu m$, and colloidal particles of diameter, $d = 520 \, nm$, the overlap of excluded volume is computed to be $\Delta V \sim 4 \times 10^{-18} \, m^3$. The osmotic pressure of the colloidal dispersion can be computed using the empirical Carnahan-Starling equation of state for hard-sphere fluids $^{39}$:

$$\frac{\pi}{n k T} = \frac{1+\phi+\phi^2-\phi^3}{(1-\phi)^3}$$

(5)

For the $\phi = 0.40$ colloidal dispersion, $\frac{\pi}{n k T} \sim 7$, and the depletion potential between the two cubes is approximately, $\frac{U^{dep}}{kT} \sim 150$. This would be an extremely strong attractive potential between cubic particles, but it should be viewed within the context of being the maximum possible magnitude of the potential given that the calculation is for cube faces that are perfectly aligned.
Any other relative orientation of two cubic particles will result in a smaller overlap of excluded volume. A characteristic stress from these depletion attractions, $\sigma^{\text{dep}}$, can be estimated from the product of the energy per interaction ($U^{\text{dep}}$) and the number of interactions in suspension, the latter quantity being proportional to the number density of cubic particles, $n_{\text{cubes}}$, such that:

$$\sigma^{\text{dep}} \sim U^{\text{dep}} n_{\text{cubes}} \quad (6)$$

Thus, for the largest concentration of cubic particles studied, the estimated stress from depletion attractions is of order $\sigma^{\text{dep}} \sim 10^{-2}$ Pa. The lowest shear stress probed during rheological measurement was comparable ($\sigma = 10^{-2}$ Pa), and although there is no clear rheological signature of a yield stress, the viscosity does begin to rapidly rise on approach to this lower shear stress limit. Further, this effect is more evident for the larger concentrations of cubic particles, in agreement with expectations based on Eqn. (6). These quantitative estimates show it is indeed plausible that the relatively large increase in the low shear viscosity of these mixed suspensions can be attributed to depletion attractions between cubic particles due to exclusion of the colloidal particles. Similar calculations show such depletion effects are much less significant for mixtures of spherical particles\textsuperscript{10}.

In Cwalina and Wagner’s study\textsuperscript{10} of spherical non-colloidal particles in a concentrated colloidal dispersion at high packing fractions, deviations from the shifting procedure of Ohl and Gleissle\textsuperscript{9} were identified at higher shear stresses (much larger than the characteristic depletion stress). Confinement of the colloidal fluid between spherical non-colloidal particle surfaces was shown to increase the shear thickening power law exponent, which is qualitatively consistent with previous experimental\textsuperscript{20} and simulation\textsuperscript{21} studies. The suspensions consisting of cubic particles in a concentrated colloidal dispersion medium exhibit an even more complex behavior. As seen in Figure 13, at $\phi_{\text{cubes}} = 0.284$, the high shear plateau characteristic to the underlying colloidal dispersion and the semi-dilute suspensions begins to disappear. In the plot of viscosity versus shear rate, it is easy to identify two distinct shear thickening transitions marked by the orange arrows. When viewed on a plot of viscosity versus shear stress, it is seen that the onset shear stresses for the two regimes are $\sigma \sim 1$ Pa and $\sigma \sim 100$ Pa. The latter onset stress corresponds to shear thickening of the underlying colloidal dispersion. The former corresponds to the onset stress for shear thickening of the cubic particles in a Newtonian fluid that was identified by Cwalina \textit{et al.}\textsuperscript{22} This is, to the best of the authors’ knowledge, the first documented case of a complex fluid exhibiting multiple, distinct shear thickening transitions under steady shear. At $\phi_{\text{cubes}} = 0.329$, there is only one identifiable shear thickening transition due to the cubic particles that has an onset stress of $\sigma \sim 1$ Pa. Shear thickening of the colloidal dispersion may still be present at high stresses, but its contribution to the stress is likely masked by that of cubic particles, which have a larger contribution to the overall increase in shear viscosity.

Cwalina and Wagner\textsuperscript{10} observed that confinement of the colloidal fluid between surfaces of non-colloidal spheres at high shear stresses led to an increase in the shear thickening power law exponent. Here, the power law exponent from $\sigma = 100$ to 400 Pa (same shear stress range
considered by Cwalina and Wagner\textsuperscript{10}) is examined as a function of the volume fraction of cubic particles in suspension. Only volume fractions up to $\phi_{\text{cubes}} = 0.284$ are considered, as shear thickening in this stress range for the $\phi_{\text{cubes}} = 0.329$ suspension reflects shear thickening from the cubic particles themselves. The shear thickening power law exponent is plotted as a function of particle volume fraction in Figure 15 for the suspensions considered in this study and those from Cwalina and Wagner\textsuperscript{10} containing spherical non-colloidal particles suspended in the same concentrated colloidal dispersion medium.

![Figure 15](image)

Figure 15. Shear thickening power law exponent, $n$, as a function of the particle volume fraction for the cubic particles suspended in a concentrated colloidal dispersion medium (squares) and for the suspensions of Cwalina and Wagner\textsuperscript{10} consisting of spherical non-colloidal particles suspended in the same concentrated colloidal dispersion medium (circles).

A more revealing plot is evident when the shear thickening power law exponent plotted against the on-average surface separation distance between particles in suspension, which can be estimated from Equation 2. This analysis was already conducted previously for the spherical non-colloidal particles in the same colloidal dispersion medium\textsuperscript{10}. The shear thickening power law exponent is replotted in Figure 16 as a function of $h / 2a_{\text{colloids}}$. This parameter physically represents the number of colloidal particles that could span the characteristic gap between either spherical or cubic particle surfaces in suspension.
Figure 16. Shear thickening power law exponent, $n$, as a function of the number of colloidal particles spanning the characteristic gap between particle surfaces for cubic particles suspended in a concentrated colloidal dispersion medium (squares) and for the suspensions of Cwalina and Wagner consisting of spherical colloidal particles suspended in the same concentrated colloidal dispersion medium (circles).

Rather remarkably, the two data sets nearly overlap at small values of $h/2a_{\text{colloids}}$. To understand this result, it is useful to consider a to-scale representation of 520 nm colloidal spheres, 3 µm edge length cubes, and 10 µm spheres as shown in Figure 17. From the perspective of the colloidal particles, the amount of confinement produced by the surface of 3 µm edge length cubes is roughly the same as that produced by 10 µm diameter spheres. This result is further evidence to support the confinement hypothesis introduced by Cwalina and Wagner. Additionally, it demonstrates the need to consider not just the particle shape, but also the particle size when assessing the effects of confinement on the shear thickening power law exponent in suspensions with a concentrated colloidal dispersion suspending medium. Swan and Brady, in their study of hydrodynamic effects for dispersions under confinement, did not consider shear flows leading to shear thickening, but one could expect that the increase in hydrodynamic interactions between the colloidal particles in the presence of the confining surfaces would promote stronger shear thickening.
Figure 17. A to-scale representation of 520 nm colloidal spheres (red), 3 µm edge length cubes (blue), and 10 µm diameter spheres (yellow).

Effect of the Colloid Dispersion Medium Composition

The effect of the colloidal dispersion medium composition was investigated through measurements of suspensions of cubic particles suspended in a colloidal dispersion with a colloidal particle volume fraction of $\phi = 0.20$. As seen in Figure 18, the rheology of this $\phi = 0.20$ colloidal dispersion is only weakly non-Newtonian at this colloidal particle concentration, with a weak shear thickening transition around $\sigma \sim 100$ Pa.

At $\phi_{cubes} = 0.203$, shear thickening is observed at an onset shear stress of $\sigma \sim 1$ Pa, which corresponds to shear thickening of the cubic particles reported by Cwalina et al.\textsuperscript{22} This shear thickening becomes much more pronounced with increasing cubic particle volume fraction. Analysis of the local derivative in Figure 18\textsuperscript{40} reveals that above $\phi_{cubes} = 0.203$ there is no obvious evidence of a second shear thickening transition due to thickening of the spherical colloids at higher stresses. Importantly, the shear viscosity for the mixed suspensions at high stresses is fundamentally different. Unlike the behavior shown in Figure 13, now a second shear thinning regime is encountered that is characteristic of elastohydrodynamic effects observed for the cubic particles suspended in a Newtonian fluid\textsuperscript{22}. This stark difference in behavior at high shear stresses is perhaps the most significant evidence that confinement effects dominate the mixed suspensions in the more concentrated colloidal dispersion in the shear thickening regime.
Figure 18. Steady shear rheology as a function of the applied shear stress for cubic particles suspended in a colloidal dispersion medium with a colloidal particle volume fraction of $\phi = 0.20$.

As noted, any depletion interactions in the mixed suspensions will depend on the concentration of the suspending colloidal dispersion medium. In contrast to the suspensions in the $\phi = 0.40$ colloidal dispersion medium, there is no significant increase in the magnitude of the low shear viscosity in concentrated suspensions of cubic particles in the $\phi = 0.20$ colloidal dispersion medium. From Eqn. (5), the osmotic pressure in the $\phi = 0.20$ colloidal dispersion is calculated to be, $\frac{\pi}{n k T} \approx 2.4$, which leads to a maximum depletion potential between cubic particles of, $\frac{\eta_{dep}}{k T} \approx 26$. The maximum characteristic stress from this depletion potential at the largest concentration of cubic particles considered in this section is calculated from Eqn. (6) to be $\sigma_{dep} \approx 10^3$ Pa. This characteristic stress is an order of magnitude smaller than that calculated for the cubic particle suspensions in the $\phi = 0.40$ colloidal dispersion medium. Thus, the nearly Newtonian rheology at low shear stresses for the suspensions in the $\phi = 0.20$ colloidal dispersion medium is consistent with calculation of depletion attraction strength, further supporting the supposition that the enhancement in low shear viscosity in the mixtures arises from depletion attractions specific to the geometry of the cubic particles.
Constant Total Solids Volume Fraction

We conclude the discussion with an examination of how the rheology of suspensions at nearly constant total solids fraction \( \phi_{\text{Total Solids}} = \phi_{\text{cubes}} + \phi_{\text{KE-P50 Colloids}} \) can be vastly different depending upon the relative ratios of cubes and spherical colloids in suspension. The suspension viscosity is shown in Figure 19 as a function of the shear stress for suspensions of cubic particles and spherical colloids at nearly identical total solids volume fraction. For these suspensions, the magnitude of the viscosity, even at equivalent total solids loadings, is a function of the ratio of cubic particles to spherical colloids and also a function of the applied shear stress. Clearly, the dependence is not simply monotonic with regard to either variable. This comparison suggests a methodology for mixing particles of varying shape and size to tailor the viscosity response to varying levels of applied stresses. A more detailed study would be necessary to map out this highly nonlinear mixing effect, but the results of this study provide guidance based on how the basic physical interactions, hydrodynamic and depletion, are influenced by the particle concentrations.

![Figure 19. Comparison of the steady shear viscosity for suspensions of cubic particles and spherical colloids at nearly identical total solids loadings.](image-url)
4. Conclusions

The rheology of suspension mixtures consisting of cubic particles suspended in a concentrated colloidal dispersion medium was investigated and compared and contrasted with prior work in literature for similar mixtures with spherical non-colloidal particles. For semi-dilute suspensions, the dynamic moduli and the steady shear flow curves could be shifted onto those of the underlying colloidal dispersion medium using simple shift factors following the hypothesis of Ohl and Gleissle. The magnitude of the shift factors required to achieve a superposition of the dynamic moduli and steady shear viscosity curves were larger than those for suspensions of spherical non-colloidal particles in the same concentrated colloidal dispersion medium. Particle shape is known to be an important factor in determining the rheology of suspensions in Newtonian fluids, and clearly particle shape significantly alters the rheology of suspensions in a non-Newtonian colloidal dispersion medium. A possible explanation for this effect is an increase in hydrodynamic interactions due to confinement and a limiting expectation for this behavior can be obtained from recent theoretical work by Swan and Brady.

At higher concentrations of cubic particles in the colloidal dispersion medium, the characteristic relaxation time of these suspensions increases along with the plateau storage modulus. Under steady shear, two distinct shear thickening transitions emerge that reflect shear thickening of both the cubic particles and the spherical colloids. The shear thickening power law exponent corresponding to the thickening of the spherical colloids is shown to increase with the packing fraction of cubic particles, similar to the behavior observed by Cwalina and Wagner for suspensions of non-colloidal spheres in a concentrated colloidal dispersion. These results show that the enhanced shear thickening at high stresses due to confinement of the colloidal fluid at high particle packing fractions appears to be a universal phenomenon, and the increase in the shear thickening power law exponent can be understood in terms of the confining particle shape and size.

At higher concentrations of cubic particles in a concentrated colloidal dispersion medium, a large increase in the magnitude of the low shear viscosity is observed. Scaling calculations identify depletion attractions as a possible source, where exclusion of the colloidal particles upon close approach of the cubic particles can generate large interparticle forces that translate to stresses of the correct order of magnitude. The contribution of these depletion attractions to the suspension stress was found to diminish as the colloidal particle concentration of the suspending medium was reduced. Finally, limited comparison of mixed suspensions of varying colloidal particle and cube concentrations shows a rich, nonlinear behavior that affords an interesting opportunity to tune the response of colloidal dispersions for specific applications.
Acknowledgement

This work was supported by a NASA EPSCoR Grant (NNX11AQ28A) and a Delaware Space Grant Graduate Fellowship (NNX10AN63H). PQ Corporation is acknowledged for providing the cubic aluminosilicate zeolite particles.

References


Figure 1
203x155mm (300 x 300 DPI)
Figure 3
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Figure 4
203x155mm (300 x 300 DPI)
Figure 5
203x155mm (300 x 300 DPI)
Figure 7
203x155mm (300 x 300 DPI)
Figure 8

\[ \eta^{\infty, r}_{\omega, r} = 1 + 3.5 \phi_{\text{cubes}} + 23.7 \phi_{\text{cubes}}^2 \]

\[ \eta^{\infty, r}_{\omega, r} = 1 + 3.5 \phi_{\text{cubes}} \]

203x155mm (300 x 300 DPI)
Figure 9
203x155mm (300 x 300 DPI)
Figure 11

203x155mm (300 x 300 DPI)
Figure 12

\[ \eta_c = 1 + 3.5 \phi_{cubes} + 23.7 \phi_{cubes}^2 \]

203x155mm (300 x 300 DPI)
Figure 13
203x155mm (300 x 300 DPI)
Figure 15
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Figure 16
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Figure 18
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