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Microstructure of sheared monosized colloidal suspensions resulting from hydrodynamic and electrostatic interactions

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Hydrodynamic and near-particle interactions in sheared suspensions are communicated through suspension microstructure to produce a wide variety of rheological behaviors. To characterize this microstructure, the individual positions of monosized silica particles flowing through a microchannel are obtained with near simulation-level detail. The pair distribution functions of the microstructure at moderate to high Péclet number shear rates are very similar to previous numerical studies. Viscometric functions calculated based on the detailed microstructure obtained through this technique show qualitative agreement with computational results. These results elucidate the origins of shear-thickening of suspensions at high shear rates. While efforts are taken to screen electrostatic interactions to study hydrodynamic and Brownian interactions, the role of electrostatic interaction between particles is also investigated by reducing suspension ionic strength. These non-hydrodynamic electrostatic interactions result in a loss of anisotropy that generally agrees with previous findings of “soft” particle systems. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4875589]

I. INTRODUCTION

Understanding and controlling the rheology of concentrated particle suspensions is of great interest throughout areas including foods and beverages, pharmaceuticals, ceramics, paints, paper making, cements, and drilling fluids. Multi-body hydrodynamic interactions between particles greatly affect the suspension microstructure and rheology. In systems where it is believed that particles interact solely through hydrodynamic and Brownian interactions, rheology depends not only on particle volume fraction but also on the applied shear rate. This is often characterized by the Péclet number, Pe = 6πρ0σa3/κT, describing the relative rate of advection to diffusion. Rheological experiments on suspensions in a steady shear flow reveal Newtonian behavior at relatively low shear rates due to the isotropic nature of suspensions, shear-thinning behavior at intermediate shear rates as a result of the relative reduction of Brownian dissipation, and thickening at high shear rates, largely as a result of changes in suspension microstructure. Normal and yield stresses have been measured in concentrated suspensions and attributed to structural changes as well. Oscillatory shear experiments also discovered thixotropy and strain-dependent behavior through studies of complex viscosity and normal stresses. Gadala-Maria and Acrivos discovered that stress in a suspension undergoes transient development if the direction of shear is reversed, providing strong evidence that shear-induced anisotropic microstructure exists in suspensions and determines rheology. Microstructural changes in inertial-free systems where pure hydrodynamic interactions are reversible and other modes of dissipation resulting in structure are not well understood.

Microstructure, in this context, refers to how particles arrange in location under convection, thermal fluctuation, and interparticle forces. Measurements of microstructure have illuminated the complexity in suspension rheology. Experimental studies on the shear flow of suspensions are mostly based on scattering techniques, e.g., light scattering, laser sheet imaging, and small-angle neutron scattering, which yield a pair distribution function and demonstrate that shear-induced anisotropy exists on the flow-gradient plane. Specifically, there are high correlations about the compressive axis and low correlations about the extensional axis. Changes in suspension microstructure are used to explain shear-thickening mechanisms found in dense suspensions. These state that thickening is a result of the formation of dynamic hydroclusters under shear supported by small-angle neutron scattering experiments. Observations of hydrodynamic interaction-driven microstructure from confocal microscopy show anisotropy and hydroclusters in highly confined systems.

To date, the most fruitful and informative results on suspension microstructure have been realized from numerical simulations. For instance, Stokesian Dynamics and Accelerated Stokesian Dynamics have been applied to obtain microstructural data in order to investigate rheology of Brownian suspension for varying Péclet number, velocity fluctuation in sheared suspensions, phase/order transition, shear-thickening, and cluster formation. Pan et al. adopted Dissipative Particle Dynamics to simulate suspension flow and found similar results. These computational results reveal details of the shape of the near contact boundary layer of the pair distribution function. While computational methods and new theoretical frameworks are quickly evolving, high-resolution optical methods to obtain microstructural data are increasingly necessary to validate discrepancies.
In experimental work, the paucity and coarseness of data are due to practical difficulties and availability. Gao et al. devised an approach in which a flowing suspension is stopped quickly and scanned using high-speed confocal microscopy. This shows an arrested structure of the suspension under flow in experiments where Brownian motion is negligible during short timescales after the arrest of flow. This method produces high-throughput nanoscale microstructural detail. It also explores, in a single experiment, the structure resulting from a range of shear rates, or Pe, given the nonlinear nature of channel flow. The pair distribution function obtained by Gao et al. agree reasonably well with computational work; nevertheless, notable discrepancies exist. In this paper, we present a revised methodology for the experimental study of suspension microstructures under shear using fluorescent core particles for higher resolution imaging and the further investigation of microstructures resulting from hydrodynamic interactions. In addition, being aware of experimental imperfections in screening near-particle non-hydrodynamic interactions, the ionic strength is intentionally reduced to add “soft” electrostatic interactions. Soft particle interactions are common in suspensions and have been studied previously to understand interactions of repulsive particles, grafted particles, and deformable particle suspensions that approximate the unscreened electrostatic interactions studied here. This work helps elucidate the roles that electrostatic interactions may have on microstructure.

II. METHODS
A. Fluorescent particle synthesis and suspension preparation

Two-step Stöber synthesis is used to fabricate core-shell silica microspheres. In the first step, APTES (3-aminopropyltriethoxysilane, Acros, 99%) covalently bonded with RITC (Rhodamine B isothiocyanate, Sigma-Aldrich), was added in a well-mixed reactor of TEOS (tetraethyl orthosilicate) and H₂O in ethanol. The hydrolysis of TEOS and APTES was catalyzed through an ammonia solvent, present as ammonium hydroxide. Additional TEOS and H₂O were periodically added. Here, fluorescent silica spheres nucleated and grew, through progressive added shells, to approximately 600 nm in diameter and the solution was cleaned. Next, particles were re-dispersed in a reactor without APTES and RITC. Additional hydrolysis of TEOS synthesized a non-fluorescent silica shell atop the seed particles. The final, core-shell product was washed in ethanol and water, and centrifuged many times to remove impurities, reagents, and secondarily nucleated particles. The resulting particles were fairly monodisperse with an average diameter of 880 nm.

Dried particles were added to a liquid mixture of glycerol and water (volume ratio 3:1) approximating the microsphere refractive index. Sodium hydroxide (NaOH) and sodium chloride (NaCl) were added to the suspension with upper limits of pH = 8 and [NaCl] = 10⁻³ M in the highest screening conditions. This configuration maintains charge stabilization in suspension, but with a small screening length relative to the particles size (the Debye length $\kappa^{-1} = 8$ nm).

These conditions approximate a hard-sphere suspension where interparticle forces are present only where particles are in near contact. Suspensions were dispersed using a sonic dismembrator prior to use in experiments.

B. Microchannel fabrication

Straight rectangular microchannels were templated from a silicon wafer mask fabricated at the Cornell Nanoscale Science and Technology Facility. Two plastic connectors (Harvard Apparatus) filled with water were placed at each end of the ridge structure to serve as inlet and outlet. Next, polydimethylsiloxane polymer base (PDMS, Dow Corning) mixed with proper amount of curing agent, was poured atop the wafer and cured at 80°C for at least 60 min using a hot plate. The cured structure and glass coverslip (cleaned by Piranha solution beforehand) were oxidized in a plasma cleaner (Harrick Plasma) for 45 s and subsequently bonded to form a closed channel structure with dimensions of 100 μm × 40 μm × 50 mm (width × height × length). The channels were stored for a minimum of 48 h before usage in order to neutralize charges generated during plasma-bonding.

SiO₂ suspension is injected into the channel inlet with compressed nitrogen driving the flow. An electropneumatic converter (Omega Engineering) transforming analytic signal to pneumatic response enables precise and fine control of nitrogen flow. These experimental parameters allow fast flow cessation within a few strain units with minimal flow reversal. Similar experiments have been performed with these particles in lower viscosity suspending fluids and the results presented here are consistent with those which are more sensitive to the driving pressure and have faster Brownian motion during scanning.

C. Confocal microscopy

A VT-Eye confocal microscope (VisiTech International) was used to probe suspension microstructure under flow. This high-speed laser scanning microscope images a 0.5 μm thick focal plane while blocking out of plane signal. A 100× magnification oil-immersion objective is controlled through a piezoelectric motor enabling a total vertical range of 100 μm with 0.1 μm step size. Scan rates range as high as 100 fps for 512 × 512 pixel² images. In these experiments, the channel (with the glass coverslip downward) was oriented such that the microscope scans in the velocity gradient (Vₓ or y-direction) direction orthogonal to the flow direction (v or x-direction) and vorticity (Vₓv or z-direction).

The experimental framework is described in Fig. 1. Suspension with a bulk volume fraction of 0.4 is injected into the channel inlet. The channel is then viewed via confocal microscopy from below, with the coverslip (channel bottom) a few millimeters downstream from the inlet. Compressed nitrogen is connected to the inlet to drive suspension flow, controlled by the electropneumatic converter.

Steady flow is maintained for a few minutes, much longer than the average residence time of particles in the channel. During this period, velocimetry measurements are conducted where the channel is scanned from bottom-to-top, along the
vertical, velocity-gradient, direction. Within these scans, 10 images are taken every 0.1 μm in the velocity gradient direction at 100 fps. The velocity at each point is then calculated by comparing particle displacements between frames and averaging over at least ten particles in each frame, confirmed using PIV. Next, the flow is quickly arrested by reducing the nitrogen pressure. Immediately upon flow cessation, a confocal scan through the system is started, in the same fashion as the velocimetry measurement. In these series, 1 image was taken per 0.1 μm. After scanning, the flow is restarted and the stopped-flow operation is repeated at least ten times in each experiment and scanning direction is reversed in each scan to ensure minimal distortion that may result from fast scanning. The stopped-flow scans were processed in IDL. Particle-tracking routines developed by Dr. Eric Weeks at Emory University, based on a subpixel averaging scheme for spherical particles, were used to reconstruct three-dimensional particle distributions. The approximate resolution of particle locations is 20–40 nm in the flow and vorticity direction, and 40–80 nm in the velocity gradient direction. Local volume fraction reported is calculated using the number of particles imaged in the local volume. The index for microstructure in this study is the pair distribution function, g( r), obtained by integrating the N-particle configuration probability, P_N(x_1, x_2, ..., x_N) by N−1 times defined as

$$g(\mathbf{r}) = \frac{P_{11}(\mathbf{r})}{n}, \quad (1)$$

where P_{11}(\mathbf{r}) is the conditional probability of finding a particle at position r with respect to a reference particle, and n is the particle number density. In pressure-driven channel flow, the shear rate varies along velocity-gradient direction, thus g( r) is obtained locally. In the determination of shear rate, and Péclet number, along a specific shear plane, particles outside one particle diameter from the plane were cropped. Scans across the channel allow the acquisition of microstructures for a variety of Péclet values in a single experiment.

### III. RESULTS AND DISCUSSION

The maximum particle Reynolds number within this system is Re_p = 3.2 × 10^{-5} suggesting inertia plays an insignificant role. The remaining key parameter affecting g( r) is the Péclet number, Pe = \frac{6\pi \eta a^3}{kT}. The Péclet number reflects the competition between hydrodynamic and Brownian forces that dictates the microstructure. Foss and Brady conducted systematic studies on g( r) for varying Pe in a hard-sphere suspension. Increasing amounts of anisotropy are observed on the velocity-velocity gradient plane with increasing Pe; conversely isotropic structures are observed near equilibrium at Pe ≪ 1. This anisotropy shows accumulation around the compressional axes and depletion around the extensional axes and is significant at the onset of shear-thickening and normal stresses as strong evidence of the coupling between rheological properties and the underlying microstructure.

### A. Hard-sphere microstructure

A suspension with κ^{-1} = 8 nm and pH = 8.0 was examined. Given the small Debye length relative to particle size, this highly screened system can be regarded as a suspension of hard spheres with negligible interparticle forces similar to those studied through previous simulations and experiment. The velocity and shear rate profiles across the lower half of the channel are presented in Fig. 2. Since ϕ changes with shear rate as a result of shear-induced migration, the redistribution of concentration in a nonlinear shear profile to balance normal stress, Pe and ϕ both change with distance from the wall. Results shown are far from the inlet of the microchannel where shear-induced migration has fully developed. Microstructures at different Pe from one single experiment are shown in Fig. 3. For each Péclet number, the local g( r) is calculated and plotted on three orthogonal planes along the direction of flow (x), velocity gradient (y), and vorticity (z). The near-wall particles (distance < 8a) are ignored in order to exclude hydrodynamic effects that result from the channel floor. It should be noted that the boundary is smooth and particles experience slip near the boundary. The
FIG. 3. (a)-(o) Pair distribution function, $g(r)$, as a function of $Pe$ and $\phi$ from the channel wall to the channel center. Strong anisotropy in the $\nabla v$ vs. $v$ plane at high $Pe$ is less pronounced in the center of the channel.

spatial coordinates are normalized by particle diameter with color indicating the magnitude of $g(r)$. For increasing contrast and better presentation, an upper cut-off value at $g(r) = 2$, denoted in red, is imposed.

In Fig. 3, each column is dedicated to a specific local condition, with $Pe$ and $\phi$ specified and $Pe$ decreasing from left to right. Figs. 3(a), 3(f), and 3(k) in the first column demonstrate a high degree of agreement with simulations by Foss and Brady\textsuperscript{23} and Kulkarni and Morris.\textsuperscript{22} Not only is the signature anisotropy clearly evident in experiments, but fine details in the parallel techniques, including vague tails near the opening of the innermost ring, also match. The experiment suggests strong correlations along the flow direction with two red dots about the $0^\circ$ and $180^\circ$ directions, while simulations show a more uniform boundary layer thickness. Both techniques show stronger correlations along the $z$- than $x$-direction in the first ring on $x$-$z$ plane, and a uniform first ring on $z$-$y$ plane. Note that experiments exhibit more layering along the $y$-direction. These disagreements could be a result of a mismatch between $Pe$ and $\phi$ in the separate studies, near wall effects in experiment, or simplifications in simulation regarding particle interactions.

From left to right, with decreasing $Pe$ and increasing $\phi$, structural ordering and symmetry are enhanced as a consequence of reduced hydrodynamic forces and increased volume fraction. On all three planes, the inner and outer high-density rings are enhanced from left to right due to increasing $\phi$. For $\phi > 0.36$, the third outer ring is clearly identifiable, implying a longer range of correlation. Although all $x$-$y$ plots demonstrate characteristic anisotropy, it is gradually reduced with decreasing $Pe$. This is particularly clear on the $x$-$y$ plane—the accumulation of probability near the compression axes in Figs. 3(a) and 3(b) relaxes toward the extensional axes in 3(c) and 3(d), eventually joining to form a continuous inner ring in 3(e). These plots confirm that, with decreasing $Pe$, the three projections converge toward an equilibrated, isotropic structure.

B. Stress calculation

Extensive experiments are used to determine the shear viscosity of suspensions. Normal stress measurements are challenging. Experimental techniques\textsuperscript{6} have only recently developed to the point where they are comparable with computational work.\textsuperscript{39} The first and second normal stress differences, $N_1$ and $N_2$, defined as $N_1 = \Sigma_{11} - \Sigma_{22}$ and $N_2 = \Sigma_{22} - \Sigma_{33}$, where $\Sigma_{ii}$ is the normal stress in the $i$ direction, are both negative with $|N_2| > |N_1|$. Constitutive relations of the normal stress have been applied to model shear-induced migration\textsuperscript{37,38,40} and viscous resuspension.\textsuperscript{42}

In this study, shear viscosity and the normal stress differences are calculated based on $g(r)$ data. It is assumed that the leading contribution to rheology is from near-contact pairwise interactions, i.e., lubrication and Brownian forces. Stress tensors are approximated using the method developed by Foss and Brady:\textsuperscript{23}

$$S^H \approx S^H_{b.l.} = -n^2 \int_{b.l.} \mathbf{r} F^{\text{s\text{shear}}} g(r) d\mathbf{r}, \quad (2)$$

$$S^B \approx S^B_{b.l.} = -n^2 k T a \int_{r=2a} \mathbf{r} \mathbf{\hat{r}} g(r) dS. \quad (3)$$

$S^H$ and $S^B$ are the hydrodynamic and Brownian contributions to the total stress tensor, b.l. stands for a boundary layer with thickness of $O(Pe^{-1})$ near particle-particle contact,\textsuperscript{43} $a$ is the particle radius, $n$ the number density, $\mathbf{\hat{r}}$ the unit vector in $r$ direction, and

$$F^{\text{s\text{shear}}} \approx -3\pi \eta^\prime \phi a^2 \gamma \mathbf{\hat{r}} (\mathbf{\hat{r}} \cdot \mathbf{E} \cdot \mathbf{\hat{r}}), \quad (4)$$
where $\eta'_\infty(\phi)$ is the high-frequency dynamic viscosity. Since $\phi$ is not constant across the channel, the data must be scaled for a fair comparison. We followed the scaling method of Foss and Brady,\textsuperscript{23} where Pe is normalized by $\eta'_\infty(\phi)/\eta$ and the newly scaled relative viscosity is

$$\eta_{r,n} = \left(\frac{\eta_r}{\eta'_\infty(\phi)} - 1\right)/\phi^2 g^0(2; \phi).$$ \hfill (5)

$g^0(2; \phi)$ is the equilibrium pair distribution function for hard spheres, given by the Carnahan-Starling equation of state for $\phi < 0.50$;\textsuperscript{44}

$$g^0(2; \phi) = \frac{1 - \frac{1}{2} \phi}{(1 - \phi)^3}. \hfill (6)$$

Tanner et al.\textsuperscript{41} show that a cubic dependence on $\phi$ fit their experimental data; across the narrow range of volume fractions in this study both are adequate for comparison. Using experimental data in these calculations gives uncertainty because of the remaining positional error in our image analysis. At higher Pe, experimental results would not capture the thickness of the boundary layer scaling as $\text{Pe}^{-1}$ and the intensity of the boundary layer would not increase. However, since the boundary layer is averaged over a finite depth, its anisotropy has the leading order effect on these calculations.

The rescaled data are plotted in Figs. 4 and 5. While both show a thinning-thickening transition, the scaling law of Foss and Brady\textsuperscript{23} does precisely match the data onto their master curve. The Brownian contribution to viscosity as calculated from experimentally obtained microstructure is roughly two orders of magnitude lower than simulations, while the total, or hydrodynamic, viscosity is greater than that predicted by simulation by a factor of 2. Foss and Brady\textsuperscript{23} compare relative viscosity in simulation with measured rheology,\textsuperscript{3, 5} and they underestimate the thickening that occurs for high-shear-rate and high-concentration conditions. Factors including interparticle forces, uncertain volume fraction in experiments, and how data are averaged in the experiments may lead to this quantitative deviation.\textsuperscript{23}

Normal stress differences are obtained in a similar manner as to the shear stresses (Figs. 6 and 7). The negative signs of $N_1$ and $N_2$ agree with previous results\textsuperscript{6, 34} confirming the compressive nature of sheared suspensions. The normal stress differences are again scaled by the factor $\eta'_\infty(\phi)^2 g^0(2; \phi).$\textsuperscript{23} It is obvious that, even after rescaling, the data of Foss and Brady\textsuperscript{23} still show a fair amount of scatter. Besides the qualitative agreement between these results and their data, these results demonstrate a smooth ascending trend of normalized $|N_1|$ and descending normalized $|N_2|$ as the scaled Pe increases from $10^3$ to $10^4$ where $|N_1|$ and $|N_2|$ crossover. This feature is not clear in the results of Foss and Brady.\textsuperscript{23} Zarraga et al.\textsuperscript{6} report a maximum positive $N_1 - N_2$ as shear rate is increased but was likely an artifact of their edge conditions. It is also interesting that the normal stress in the vorticity direction, $\Sigma_{33},$ is almost as large as $\Sigma_{22}$ at high shear rates. Significant $\Sigma_{22},$
the “dilatancy” effect, is a predominant feature of sheared suspensions, as well as shear-induced particle diffusion. Evolution of $\Sigma_{33}$ and the corresponding diffusion are worthy of further investigation.

C. Microstructural analysis

The widely accepted mechanism for shear thickening is hydrocluster formation, though details of these structures are elusive. When particles pass each other in shear flow, hydrodynamic forces bring them close together to form dynamic clusters. Due to lubrication and interactions between near-contact particles, clusters greatly increase system resistance to shear, thus causing thickening. Brady and Bossis $^{18}$ first observed this clustering in their numerical simulations of a monolayer of spheres. Bossis and Brady $^{18}$ discussed the role of Brownian motion in destroying large clusters and proposed hydrocluster formation as the mechanism for shear-thickening at high shear rates. Results from Rheo-SANS measurements of suspensions of spherical $^{4,16,45}$ and prolate ellipsoidal particles $^{46}$ agreed well with the hydrocluster model. Kalman and Wagner $^{47}$ performed Rheo-USANS experiments on hard-sphere suspensions to probe the structure and confirmed that hydroclusters are transient and precede the measured shear-thickening. Gopalakrishnan and Zukoski $^{48}$ extended the hydrocluster model to suspension of attractive particles. Nevertheless, direct experimental investigation of hydroclusters did not appear until Cheng et al. $^{21}$ Again, their experimental design was in sufficient in that it did not eliminate wall effects and particle tracking errors due to shear-induced diffusion.

Clustering is readily quantified from our particle tracking data. With all particle locations available, any two particles where the center-to-center distance is less than or equal to one particle diameter are considered part of a hydrocluster. This arbitrary and aphysical cutoff intentionally highlights that the definition of hydroclusters is arbitrary in itself, but the trend in changes in numbers and size can give insight into the longer-range structure. Reasonable variation of the criterion for center-to-center distances affect the resulting number and size of clusters. However, qualitative behavior is preserved, as observed by Bossis and Brady $^{18}$.

Here, we define the total number of all particles identified as part of a cluster, having a nearest neighbor whose center-to-center distance is less than $r = 2a$, $N_c$, and total number of clusters, $N_c$. Then the average cluster length for specific $Pe$ and $\phi$ are obtained as $\lambda = N_p/N_c$. Taking into account concentration variation, it is reasonable to rescale $\lambda$ as $\lambda_n = \lambda/\phi^2$. The normalized cluster size, $\lambda_n$, vs $Pe$ is plotted in Fig. 8. At low $Pe$, the average size of the hydroclusters is roughly constant $\lambda_{n,0} \approx 30$. In the shear thickening regime identified in Fig. 4 ($Pe > Pe_C \approx 800$), the hydrocluster size dramatically increases. Shifting the data to this onset of significant growth by plotting $(\lambda_n - \lambda_{n,0})$ vs. $(Pe - Pe_C)$ results in a power law trend of exponent $\sim 0.5$. The underlying physics of this growth rate are unclear and in this nonlinear shear profile it may be difficult to compare this result to other methods of analysis. $Pe_C$ may depend on particle properties such as surface roughness and chemistry. The assumption is that as $Pe$ increases, hydroclusters will increase in size until they span the boundaries of the system as a continuous, localized stress network and jam.

D. Effect of electrostatic interactions

One additional factor in these systems is the presence of electrostatic interactions. The most common and effective way to tune electrostatic interactions in a colloidal system is to control the ionic strength. A reduction of [NaCl] in suspension will increase particle Debye length where electrostatic interactions should force particles apart and reduce shear thickening.
As shown in Figs. 9(a) and 9(b), when $\kappa^{-1}$ increases from 8 to 30 nm, the first and second rings of nearest-neighbor in the x-y plane is attenuated and dissipated. The same trend, a decrease in the intensity of nearest neighbor rings, is observed on the other two planes. This suggests that enhanced non-hydrodynamic interactions are induced by electrostatic interactions between particles and reduce the degree of order observed, similar to Brownian motion. However, as $\kappa^{-1}$ was increased to 80 nm, order is restored. Particularly in Fig. 9(c), anisotropy along the compressional axes is replaced with a more symmetric structure. One may argue that electrical repulsion alters the original structure after flow is stopped, but $\kappa^{-1}$ is still an order of magnitude less than one particle diameter, the length scale for the $g(r)$ calculations. Additionally, the pair distribution is symmetric. Thus, when particles push against one another, the net force on one particle is statistically zero. Therefore, these isotropic structures are likely due to the long range ordering induced by strong electrostatic forces during deformation. Plots on all three planes, when viewed from left to right, indicate that electrostatic forces can reduce order by reinforcing fluctuations and promote order when they are strong enough to induce long-range interactions.

Microstructural variations across the channel are shown for systems with the farthest reaching electrostatic interactions. Fig. 10 shows $g(r)$ on all three planes at different Pe and $\phi$ (Pe decreasing from left to right). Long range correlation in the form of secondary and tertiary rings of higher probability is clearly enhanced in the x-y and z-y planes as Pe decreases. In the x-y plane, the anisotropic boundary layer gradually closes to form roughly a uniform distribution in the extensional/compressional plane, even while Pe $\gg$ 1. The crossover from hydrodynamic-dominated to electrostatic-dominated interactions results in the relative isotropy seen at high Pe. However, on the x-z plane, as compared with Figs. 3(f)–3(j), this system exhibits secondary and tertiary rings of higher probability at much lower Pe than the electrostatically screened system and for decreasing Pe these rings are moderated. The volume fractions of these systems are slightly higher and the effective volume fractions, including an excluded annulus where particles are electrostatically repelled, is even higher than in the suspensions having higher ionic strength. Qualitatively, these results agree with the excluded annulus model.

Large Debye length raises particle interactions, but also increases the effective particle volume fraction. The trend...
observed in Figs. 9 and 10 shows increasing anisotropy at high Pe and smaller \( \kappa^{-1} \), and radial symmetry at lower Pe along with less screening of electrostatic interactions. More systematic studies are needed to elucidate hidden factors that could affect structure and/or account for the discrepancies noted. In addition, further work could explain how interparticle forces alter suspension stability.

IV. SUMMARY

This work improves upon previous experimental methods developed in our laboratory for the direct measurement of microstructure in suspension flows. These experiments typically operate under high Pe conditions, where anisotropy in the x-y plane, predicted by theory, is clearly identified. Results from a spectrum of Péclet numbers in a near-hard-sphere system demonstrate the interplay between hydrodynamics and concentration, with the former favoring anisotropy and the latter favoring order and symmetry. Calculated viscosity and normal stress differences agree qualitatively with the SD simulation by Foss and Brady,\(^2\) e.g., shear-thickening at high Pe, and the trends with \( |N_1| \) and \( |N_2| \). However, a quantitative mismatch highlights the gap between computation and reality. Preliminary analyses on growth of hydroclusters under shear suggest show the growth of normalized hydroclusters scale with \( \sim \text{Pe}^{0.5} \) in the shear thickening regime. The orientation and dependence of these hydroclusters on Pe and \( \phi \) needs to be investigated in systems where constant shear spans a greater distance than the flows in these microchannels. The effect of electrostatics on microstructure is also investigated. Electrostatic forces play a complex role in particle ordering resulting in long range ordering. Shear-induced crystallization is also affected by these forces in that they are noticeable under lower Pe than in hard-sphere systems.\(^4\)

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