

Microstructure and Rheology Relationships for Shear Thickening Colloidal Dispersions

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The non-Newtonian shear rheology of colloidal dispersions is the result of the competition and balance between hydrodynamic (dissipative) and thermodynamic (conservative) forces that lead to a nonequilibrium microstructure under flow. We present the first experimental measurements of the shear induced microstructure of a concentrated, near hard-sphere colloidal dispersion through the shear thickening transition using small angle neutron scattering (SANS) measurements made in three orthogonal planes during steady shear. New instrumentation coupled with theoretical derivations of the stress-SANS rule enable rigorously testing the relationship between this nonequilibrium microstructure and the observed macroscopic shear rheology. The thermodynamic and hydrodynamic components of the stress that drive shear thinning, shear thickening and first normal stress differences are separately defined via stress-SANS rules and compared to the rheological behavior of the dispersion during steady shear. Observations of shear-induced hydrocluster formation is in good agreement with Stokesian Dynamics simulation results by Foss & Brady (2000). This unique set of measurements of shear rheology and nonequilibrium microstructure of a model system provides new insights into suspension mechanics as well as a method to rigorously test constitutive equations for colloidal suspension rheology.

Key words: Colloidal Dispersions, Shear Thickening, Rheology, Hydrodynamics, Suspensions, Microstructure

1. Introduction

Concentrated hard sphere colloidal dispersions subjected to increasing shear stress display a reversible, rise in viscosity with increasing shear rate known as shear thickening (Hoffman 1974; Barnes 1989; Bender & Wagner 1996). Shear thickening colloidal suspensions have the potential to be implemented in a wide variety of applications. In recent research these shear thickening fluids (STF) have been investigated for applications such as personal protective armor (Lee *et al.* 2003; Kalman *et al.* 2009; David *et al.* 2009), medical devices, and sports equipment (Helber *et al.* 1990; Fischer *et al.* 2007). STFs also find application in vibrating systems to reduce resonance amplitudes (Helber *et al.* 1990), interlayers of sandwich beam structures (Fischer *et al.* 2007) and as a “speed activated” damper under dynamic loadings (Zhang *et al.* 2008; Helber *et al.* 1990). Mitigating shear thickening has proven equally critical for a broad range of industries from coatings to cement production (Toussaint *et al.* 2009) and chemical mechanical planarization of semiconductors (Crawford *et al.* 2013). All of these applications require a fundamental

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understanding of the colloidal dispersion’s reversible thinning and thickening behavior and underlying microstructure during shear flow.

Suspension stresses are calculated as ensemble averages of the forces acting between particles where the spatial arrangement of the particles, or microstructure, is represented by the pair distribution function (Batchelor & Green 1972; Batchelor 1977). Thus, the non-Newtonian shear behavior of concentrated colloidal suspensions is intimately linked to the microstructure changes that occur when the suspension is forced out of equilibrium during shear. The total measured stress is comprised of components derived from conservative or thermodynamic forces, such as Brownian motion and interparticle forces, and those arising from dissipative sources, such as hydrodynamic interactions. These two classes of forces couple to the structure differently to yield the stress tensor, such that measurements of the structure provide a unique method to determine structure-property relationships in colloidal dispersions (Wagner *et al.* 1988; Mewis & Wagner 2011). Consequently, it is essential to understand quantitatively this microstructure under flow in order to predict the behavior of STFs and facilitate rational design and formulation of concentrated colloidal suspensions for commercial and industrial applications. Two directions of scientific discovery drive the research dedicated to understanding the microstructure-rheology property relationship of concentrated colloidal suspensions. The first is theoretical and simulation driven research using the Smoluchowski equation and Stokesian Dynamics simulations of Brownian hard sphere suspensions (Bergenholtz *et al.* 2002; Melrose & Ball 2004; Nazockdast & Morris 2013; Wagner & Ackerson 1992; Bossis & Brady 1989; Foss & Brady 2000). The second is experimental measures of a colloidal dispersion’s microstructure during shear deformation (Wagner *et al.* 1988; D’Haene *et al.* 1993; Bender & Wagner 1996; Maranzano & Wagner 2002; Kalman 2010; Cheng *et al.* 2011*a*; Xu & Gilchrist 2014). The two methods are by no means mutually exclusive and oftentimes, as is the case here, they complement each other.

Of significant interest to many investigating shear thickening colloidal dispersions is identifying the microstructure responsible for the shear thinning and thickening behavior. Initially, simultaneous flow and small angle light scattering (SALS) experiments were performed by Hoffman (1974) in the 1-2 plane of shear where an order-to-disorder transition was observed at the onset of shear thickening. The formation of ordered layers of particles parallel to the velocity direction and normal to the velocity gradient direction formed under low shear rates and as the shear rate increased the layers were observed to break up into a randomized structure. Although Hoffman (1974) was first in offering a significant microstructure-rheology relationship for shear thickening, the order-disorder transition has since been shown not to be a prerequisite for shear thickening as confirmed by Stokesian Dynamics simulations (Bossis & Brady 1989) and experimental results (Laun *et al.* 1992; D’Haene *et al.* 1993; Bender & Wagner 1995, 1996).

The reversible shear thickening observed in colloidal suspensions is driven by short-range lubrication interactions that lead to density fluctuations of particles during shear and ultimately, particle clustering (termed “hydroclusters” by Brady & Bossis (1985, 1988); Maranzano & Wagner (2002)). The development of the technique of Stokesian Dynamics simulations for Brownian suspensions properly accounted for both the short-range lubrication interactions and long-range hydrodynamics including many-body interactions (Brady & Bossis 1985; Brady & Vicic 1995). Results of these simulations showed particle cluster formation due to lubrication interactions between particles through the suspending fluid (Bossis & Brady 1989; Phung *et al.* 1996; Foss & Brady 2000; Banchio & Brady 2003; Melrose & Ball 2004). The most accurate set of calculations for the viscosity as a function of increasing shear rate was performed by Banchio & Brady (2003) using accelerated Stokesian Dynamics simulations. Equally important, shear thickening due to

shear-induced density fluctuations of particles is also predicted from theory that properly includes the short-range, lubrication hydrodynamic interactions (Bergenholtz *et al.* 2002; Nazockdast & Morris 2013).

Recently, shear thickening in noncolloidal suspensions has been studied by combining classical methods of macroscopic contact friction adapted from granular mechanics with suspension hydrodynamics (Seto *et al.* (2013); Mari *et al.* (2014)). Simulations can capture many features of continuous and discontinuous shear thickening and it has been suggested that such surface friction may be relevant for shear thickening in colloidal dispersions (Mari *et al.* (2014)). Modeling the transition from a hydrodynamically dominated regime to a frictional regime can yield multiple, coexisting stress states that provide a possible mechanism for discontinuous shear thickening observed in dilatant suspensions (Cates & Wyart (2014)). However, one can rule out any significant role of contact friction in the continuous shear thickening of colloidal dispersions as contact friction leads to the incorrect sign of the first normal stress difference, which is measured to be negative in the shear thickened state (Cwalina & Wagner (2014); Lee *et al.* (2006); Mewis & Wagner (2011)) but predicted to be positive for systems with frictional contacts (Mari *et al.* (2014)). Indeed, this negative first normal stress difference is a hallmark of suspensions dominated by hydrodynamics (see Chapter 2 of Mewis & Wagner (2011) for a review and Morris & Boulay (1999) for theory), and is predicted for shear thickening colloidal suspensions using Stokesian Dynamics simulations by Foss & Brady (2000) and theory by Bergenholtz *et al.* (2002), in agreement with experiments. This positive normal stress difference is a direct consequence of fore-aft symmetry breaking in the plane of shear and is well understood for systems with interparticle forces and frictional contacts alike. Finally, it is important to note that most colloidal dispersions are typically stabilized by adsorbed or grafted surfactant or polymer (such as for the dispersions under consideration here (Kalman & Wagner (2009)) and direct measurements of the friction for such surfaces show extremely low coefficients of friction (in the range from 0.0006 to 0.001 as reported by Klein and co-workers (Raviv *et al.* (2003))), whereas values close to one are assumed in the simulations showing shear thickening (Mari *et al.* (2014)). Indeed, direct measurements of colloidal friction coefficients by Henderson *et al.* (2001) using optical tweezers quantitatively agreed with predictions of colloidal hydrodynamics. Only under the most extreme pressures such that stabilizing brushes are highly compressed are order one coefficients of friction achieved (Raviv *et al.* (2003)). Importantly, very high impact stress measurements of shear thickening colloidal suspensions in confinement (Lim *et al.* (2010*b*, 2011, 2010*a*)) show a response that is consistent with elasto-hydrodynamics, i.e. due to lubrication hydrodynamics coupled to the elastic deformation of the core hard colloidal particles (Kalman *et al.* (2009); Mewis & Wagner (2011)). Indeed, increasing the adsorbed or grafted polymer layer thickness, which would increase contact friction according to surface forces measurements but mitigate lubrication hydrodynamics, all but eliminates shear thickening in colloidal dispersions (Krishnamurthy *et al.* (2005)). This brief review of the evidence concerning friction in colloidal dispersions provides context for the differences in shear-induced microstructures measured by experiment and simulated for frictional, noncolloidal suspensions, which will be shown here as well through experimental determination of the structure in the relevant plane of shear along with the rheological functions.

Wagner & Ackerson (1992) derived the relationship between the microstructure measurable in a scattering experiment and the suspension stress for colloidal dispersions through a spherical harmonic expansion of the microstructure during shear flow that provides a rigorous micromechanical basis for stress-optical (Wagner *et al.* 1988; Bender & Wagner 1995) and stress-SANS rules (Maranzano & Wagner 2002). Specifically, they

derived a quantitative relationship between the flow-distorted microstructure and the stresses arising from the Brownian and hydrodynamic interactions. Importantly, it was found that the contribution of Brownian forces to the stress can be distinguished from the contributions from hydrodynamic interactions as arising from distinct terms in the spherical harmonic expansion of the microstructure. A similar approach was employed by Bergenholtz *et al.* (2002) to calculate the microstructure and stresses for a dilute colloidal dispersion. This theoretical work provides the basis for an important avenue of experimental investigations into the fundamentals of colloidal dispersion rheology as deconvolution of the shearing microstructure enable calculations of the contributions of conservative forces (e.g. Brownian and interparticle) and dissipative forces (e.g. hydrodynamic and frictional) to the total macroscopic suspensions stress.

Small angle neutron scattering (SANS) experiments have also been used to examine colloidal suspensions (Ackerson *et al.* 1986; Bender & Wagner 1996; Johnson *et al.* 1988; Laun *et al.* 1992; Lee & Wagner 2006; Maranzano & Wagner 2002; Newstein *et al.* 1999; deKruif *et al.* 1990; Watanabe *et al.* 1998). In particular, Maranzano & Wagner (2002) and Lee & Wagner (2006) use rheo-SANS to investigate the microstructure in the tangential and radial planes of shear resulting in quantitative resolution of the hydrodynamic contribution from the microstructure to the total stress. Ultra-SANS (USANS) experiments conducted by Kalman & Wagner (2009) probe the microstructure of a hard-sphere suspension in the velocity-velocity gradient plane of shear for which increased structure formation is observed during shear flow. Although these flow-USANS measurements provided important information about the scale and spatial organization of hydroclusters in a shear thickening suspension, the data is obtained as 1-D such that inversion to determine the real-space structural anisotropy is not possible. Finally, Kalman and co-workers were the first to investigate the formation of hydroclusters in the velocity-velocity gradient plane of shear using SANS experiments (Kalman (2010)). The results for the microstructure agree qualitatively with predictions from Stokesian Dynamics simulation for the real-space pair-distribution function during shear flow (Foss & Brady (2000)). In addition, these experiments provide key results toward establishing a stress-SANS rule for colloidal suspensions measured using flow-SANS experiments. Thus, an understanding of the relationship between the rheology and microstructure of colloidal suspensions is established based on the independent contributions to the total stress arising from hydrodynamic and thermodynamic forces. For completeness we note that flow-Small Angle Light Scattering (SALS) (Wagner *et al.* 1988) and flow-Small-Angle X-ray Scattering (SAXS) have also been used to probe colloidal dispersions, specifically the work by Hoekstra *et al.* (2005) as well as Versmold *et al.* (2001, 2002). However for colloidal suspensions SAXS proves to be difficult as multiple scattering and background scattering are problematic for concentrated suspensions.

Most recently, efforts using fast confocal microscopy provide direct visualization of colloidal suspensions during shear. Besseling *et al.* (2009) successfully demonstrate 3-D imaging of a colloidal glass under steady shear while Cohen *et al.* (2004) and Cheng *et al.* (2011a,b) use confocal microscopy to look at the effects of confinement on suspensions of colloidal particles and the microstructure responsible for the shear thinning and shear thickening rheology. Gao *et al.* (2010) study the microstructure of colloidal suspensions in pressure driven flows. Cheng *et al.* (2011a) use confocal microscopy to elucidate the microscopic single-particle dynamics concluding, in agreement with previous work, that shear thinning is a result of a decreasing relative contribution of entropic forces and shear thickening arises from particle clustering induced by hydrodynamic interactions. Cheng *et al.* (2011a,b) observe “log-rolling” strings of particles normal to the plane of shear for experiments which have a maximum gap between the shear plates of 10.6 times the

diameter of a particle. Based on previous work by Cohen *et al.* (2004); significant confinement effects are present at this particular gap height that influence the microstructure. Cheng *et al.* (2011b) perform a systematic study using Stokesian Dynamics simulations to address the mechanism for the “log-rolling”-like structure that are observed for high Pe . Three key observations are made: The first is that if there are no hydrodynamic interactions there is no vorticity aligned structure and strings form along the velocity direction of shear; The second being that if slip is introduced at the particle-fluid interface, a qualitatively similar, vorticity-aligned microstructure is observed; Finally, the vorticity aligned strings do not form when there is only one particle layer. These observations suggest that in order to form strings in the vorticity direction both thermodynamic and hydrodynamic interactions are important and it is critical for particles to be able to migrate across different layers in the velocity gradient direction during shear. In addition, the small gap widths used in the experiments (on the order of 10 particle diameters) proves to have significant effects on the measured microstructure of the flowing suspension (see also Bian *et al.* (2014)). Although, useful for defining single-particle dynamics, the confocal microscopy is limited in resolution to particle sizes on the order of a micron. Because of limits on positional resolution, such methods are critically unable to resolve the lubrication layer essential for shear thickening.

In the present manuscript, the microstructure of a concentrated colloidal suspension is measured using rheo-SANS and flow-SANS methods to interrogate all three orthogonal planes of a 3-dimensional microstructure formed during steady shear for length scales spanning the interesting region of particle nearest neighbors. Resultant 2-D scattering patterns are presented for shear rates at moderate and high Pe , corresponding to shear thinning and shear thickening behavior. The scattering patterns are also analyzed and discussed to provide insight into the 3-D microstructure of a flowing suspension under shear. The first quantitative analysis of all three planes of scattering for a concentrated colloidal suspension undergoing steady shear deformation is presented and the microstructure contributions to the hydrodynamic and thermodynamic stresses are resolved. We employ the spherical harmonic expansion of the structure factor by Wagner & Ackerson (1992) to systematically deconvolute the 2-D patterns by weighted interpretations and averaging over the most relevant length scales to identify the microstructural components that most significantly contribute to the stresses. Stress-SANS coefficients for the hydrodynamic and thermodynamic components are defined by comparing stresses determined by the microstructure to the measured stresses. These results agree well with the suspension’s rheology during steady shear and to Accelerated Stokesian Dynamics simulation results by Foss & Brady (2000).

2. Experimental Methods and Materials

2.1. Materials

A concentrated near, hard-sphere colloidal suspension comprised of silica particles ($r = 61.1$ nm) with polydispersity of 8 % ($\rho = 1.89$ g/mL) are purchased in powder form from Seahoster Company, L.L.C., Japan. The particles are suspended at a particle loading volume fraction of 0.40 (for which the effective volume fraction is $\phi_{\text{eff}} = 0.465$, Figure 1) in a mixture of deuterated-ethylene glycol (d-EG) (68 % by volume) and polyethylene glycol, Mw. = 600 (PEG-600) (32 % by volume). The suspension is placed on a roll mixer for 72 hours prior to experiments (Table 1).

	Symbol	Value	Units
volume fraction	ϕ	0.40	-
d-EG density	ρ_{d-EG}	1.234	g/mL
PEG-600 density	$\rho_{PEG-600}$	1.125	g/mL
particle density	ρ_p	1.89	g/mL
particle core radius	a	61.1	nm
shell thickness	t	1.65	nm
suspending fluid viscosity	η_f	0.04	Pa s
polydispersity		8	%
scattering length density difference	$\Delta\rho_{sld}$	0.482×10^{-6}	\AA^{-2}
relative zero shear viscosity	$\eta_{r,0}$	25.4	-
relative high shear viscosity	$\eta_{r,\infty}$	7.97	-
relative high frequency viscosity	$\eta'_{r,\infty}$	5.90	-
effective hard sphere volume fraction	ϕ_{eff}	0.465	-
average relaxation time	λ_{ave}	0.045	s

TABLE 1. Summary of suspension properties

2.2. Rheometry

The suspension shear rheology is measured using an ARES-G2 strain-controlled rheometer measured with a 1° cone and plate geometry equipped with Peltier plate temperature control. The suspension is placed on the Peltier plate, the upper tool is lowered to the gap height and the sample is trimmed. The measurement protocol starts with a pre-shear consisting of 60 s of 10 s^{-1} steady shear rate and then steady shear rate sweeps increasing and decreasing from 0.1 s^{-1} to 500 s^{-1} this protocol is repeated eight times. The purpose of such an extensive pre-shear method is two fold: the first is to erase any shear history induced by loading the sample and the second is to break up any remaining aggregates of particles in suspension that were not fully dispersed during the 72 h of roll-mixing. After this pre-shear protocol, the steady shear rheology is measured from 0.1 s^{-1} to 500 s^{-1} (again increasing and decreasing in shear rate) where at each shear rate the suspension equilibrates to a constant shear response for 30 s. The steady shear and linear viscoelastic rheology is measured at three temperatures ($T = 5, 15$ and $25 \text{ }^\circ\text{C}$). Time-temperature superposition (TTS) according to the analysis methods by Shikata & Pearson (1994) defines the steady shear and linear viscoelastic rheology reported in Figure 1A , B and C for which the $T_{ref} = 25 \text{ }^\circ\text{C}$.

The dimensionless Péclet number (Pe) is the dimensionless shear rate defined as the ratio of the shear rate to the rate of diffusion by Brownian motion in the dilute limit and is used to compare with simulations and theory:

$$Pe = \frac{6\pi\eta_f a^3 \dot{\gamma}}{k_B T}. \quad (2.1)$$

2.3. Small Angle Neutron Scattering (SANS)

Rheo- and flow- Small Angle Neutron Scattering (SANS) experiments are performed at the Institute Laue-Langevin, Grenoble, France on the D-22 SANS beamline. For the three different shear sample environments (radial-, tangential- and flow- SANS) the sample to detector distance is 17.6 m, the wavelength is 10 \AA and the slit dimension is 0.5 mm. Rheo-SANS experiments are performed to measure the SANS scattering in the radial direction interrogating the velocity-vorticity (1-3) plane and the tangential direction to interrogate the velocity gradient- vorticity (2-3) plane during shear flow. These experiments are conducted using an Anton Paar 501 rheometer with quartz Couette geometry to apply a

steady shear flow (Porcar *et al.* 2011). Measurements in the velocity-velocity gradient (1-2) plane of shear were performed using a flow-SANS sample environment (Gurnon *et al.* 2014)). Scattering data is presented in terms of the scattering vector \mathbf{q} or its amplitude $|\mathbf{q}| = q = \frac{4\pi \sin(\theta/2)}{\lambda}$ where θ is the scattering angle. Data was reduced to an absolute scale using GRASP (Dewhurst 2011) and the subsequent application of the weighting functions to each reduced 2-D data set is performed using SASET (Muthig *et al.* 2013).

3. Results and Discussion

Steady shear measurements in Figure 1A show the typical shear thinning and shear thickening response of a concentrated colloidal suspension undergoing increasing steady shear flow. From the steady shear rheology we define the zero shear viscosity ($\eta_{r,0} = 25.4$) and the high shear viscosity ($\eta_{r,\infty} = 7.97$), which is taken as the viscosity minimum. Comparison to hard-sphere theory (Russel *et al.* 2013) defines the effective hard sphere volume fraction to be $\phi_{\text{eff}} = 0.465$ (Table 1). Figure 1B presents the first normal stress difference of the suspension during steady shear flow. In agreement with other measures of $N_1(\dot{\gamma})$ by Cwalina & Wagner (2014) during shear thinning the first normal stress is slightly positive and then becomes increasingly negative as the shear rate increases during shear thickening.

Figure 1C shows the linear viscoelastic moduli of the suspension for three different temperatures shifted using time-temperature superposition and subtracting the purely viscous contribution to the loss modulus to define the linear viscoelastic moduli G' and $G'' - \omega\eta'_{\infty}$ as a function of frequency. The suspension's relaxation time is identified as the inverse of the cross-over frequency ($\lambda = 1/\omega$) reported in Table 1 as $\lambda = 0.045$ s.

Figure 1D shows a core-shell hard-sphere model fit to 1-D quiescent scattering data in the rheo- and flow- SANS sample environments using the parameters in Table 1. The corresponding structure factor is reported in Figure 2A. The effective volume fraction calculated from the core-shell model is 0.468, which agrees well with the effective volume fraction from the rheology reported in Table 1. The maximum in the structure factor occurs at slightly larger q than the peak in the intensity $I(q)$. The maximum in the structure factor corresponds with the length scale for nearest neighbor interactions shaded in Figure 2 where $q_{\text{peak}} = 0.042 - 0.064 \text{ nm}^{-1}$ corresponding to length scales of 100-150 nm.

3.1. SANS scattering results in three planes during steady shear flow

Rheo- and flow-SANS microstructure measurements of a concentrated colloidal dispersion are reported for experiments made in all three planes during steady shear flow. The top two rows of figure 3 shows those results from measurements made in the velocity-velocity gradient (1-2) plane of shear. The 2-D scattering results are reported for increasing shear rates from left to right. The second row reports subtracted 2-D scattering patterns, where the equilibrium scattering (Figure 3, left) has been subtracted from the scattering measured during shear, thus highlighting changes upon applying shear flow. We begin by observing that the anisotropic features of the scattering grows in intensity with increasing shear rate, indicating that shear distorts the dispersion's microstructure. The experimental coordinate system is given in the figure and it is important to recognize the inherent inverse relationship between reciprocal space scattering patterns and the real-space microstructure, such that the scattering patterns correspond to a 90° rotation of the real-space structure. The increased intensity observed with increasing shear rate in the 2-D scattering patterns is oriented along the extension axis, such that particle neighbors are enhanced along the compression axis of the shear flow. This experimental result

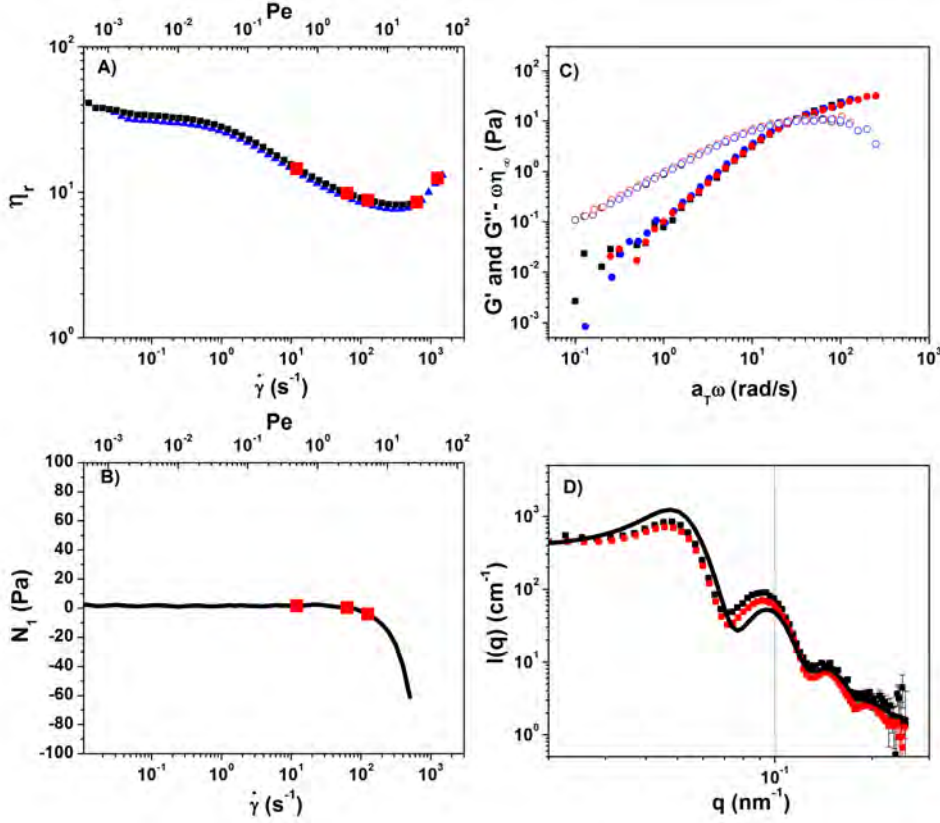


FIGURE 1. Steady shear viscosity (A) and first normal stress (B) as a function of shear rate and Pe , (symbols: line at 5 °C (black), and 25 °C (blue), red points taken as peak holds at rheo-SANS conditions) (C) linear viscoelastic moduli ((closed symbols) G' and (open symbols) $G'' - \omega\eta'_\infty$, colors correspond to 5 °C (black), 15 °C (red) and 25 °C (blue)) as a function of frequency for constant $\gamma_0 = 0.05$ and (D) 1-D SANS $I(q)$ as a function of q (nm $^{-1}$) for 5 mm pathlength flow-SANS shear cell (■) and 2 mm pathlength rheo-SANS Couette geometry (■) at equilibrium. Black line is a core-shell hard sphere model for $\phi = 0.40$, $a = 611$ nm and shell thickness, $t = 1.65$ nm (Table 1).

is consistent with that previously reported in work by Kalman (2010) and predicted using Stokesian Dynamics simulations by Foss & Brady (2000) and theory by Bergenholtz *et al.* (2002). In the velocity-velocity gradient plane of shear, our scattering experiments show a real-space microstructure under shear for which an increased number of nearest neighbors exist along the compression axis of shear and a depletion of neighboring particles along the extension axis.

Scattering results from experiments in the velocity-vorticity (1-3) plane during shear flow are shown in the middle block of Figure 3. Just as in the 1-2 plane, the increasing SANS scattered intensity is an indication of microstructure changes increasing with increasing shear rate. The experiment is such that the neutron beam passes through the sample twice. Therefore, in the velocity-vorticity plane, under laminar flow the microstructure should have mirror symmetry across the vorticity and velocity axes. Important observations about shear induced structure is evident as in increasing intensity for low q along the direction of shear. An interpretation of this increased intensity under shear relative to equilibrium preferential organization of particles along the vorticity axis.

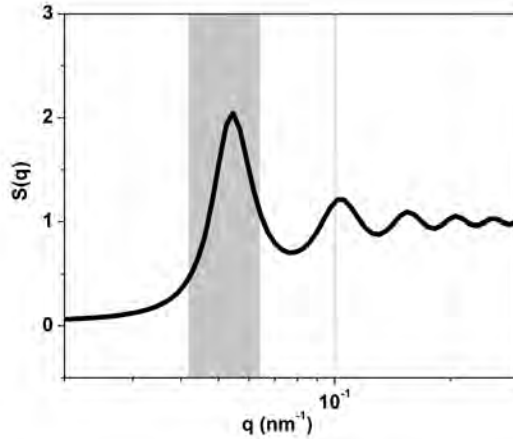


FIGURE 2. Hard sphere structure factor, $S(q)$, where $q_{peak} = 0.0546 \text{ nm}^{-1}$ for $\phi = 0.40$ and $a = 61.1 \text{ nm}$. Shaded portions of each figure correspond to the nearest neighbor peak ($q_{peak} = 0.042 - 0.064 \text{ nm}^{-1}$).

Previous experiments by Cheng *et al.* (2011a) using confocal microscopy have observed similar structures that they define as “chaining” along the vorticity direction.

The measurements in the velocity gradient - vorticity (2-3) plane are reported as the lower block in Figure 3. These rheo-SANS experiments are also performed in the Couette sample environment by alignment of the beam tangential to the Couette cell. As a consequence there is a loss of resolution due to both the increase in pathlength, leading to multiple scattering, as well as sampling over curved streamlines. Nevertheless, a qualitative comparison of these results also show increasing scattering with increasing shear rate. As observed for the 1-3 plane, here again we observe structure and apparent alignment along the vorticity direction of shear flow.

The three planes interrogated with the rheo- and flow-SANS experiments reported here are orthogonal to one another and provide the first scattering measurements in all three planes of flow spanning the shear thinning and shear thickening transition. From these we can build an understanding of the three-dimensional real-space microstructure that exists for a concentrated colloidal suspension during steady shear.

Figure 4 presents a direct comparisons between predictions for the pair distribution function ($g(\mathbf{r})$) from accelerated Stokesian Dynamics simulations by Foss & Brady (2000) for a concentrated suspension of hard-sphere particles at a comparable concentration ($\phi = 0.45$) and those experimental results for ($I(\mathbf{q})$) from the SANS experiments presented in the previous section for the velocity-velocity gradient (1-2), velocity-vorticity (1-3) and velocity gradient-vorticity (2-3) planes during shear. The top rows in each block of Figure 4 show the Stokesian Dynamic simulations, where the lighter regions indicates a higher probability for finding a particle at that location in the shear flow. The best resolution using Stokesian Dynamics simulations reported in the figures is around the nearest neighbor (i.e., innermost) ring. Longer length-scale structures are resolved by SANS experiments presented in the 2-D scattering patterns in the bottom rows of each block in Figures 4. For reference, black circles are superimposed on the scattering patterns to delineate the q -range corresponding to the nearest neighbor position, as identified in Figure 2.

Good qualitative agreement is observed for the microstructures simulated and measured, especially for the the velocity-velocity gradient plane shown in the top rows in

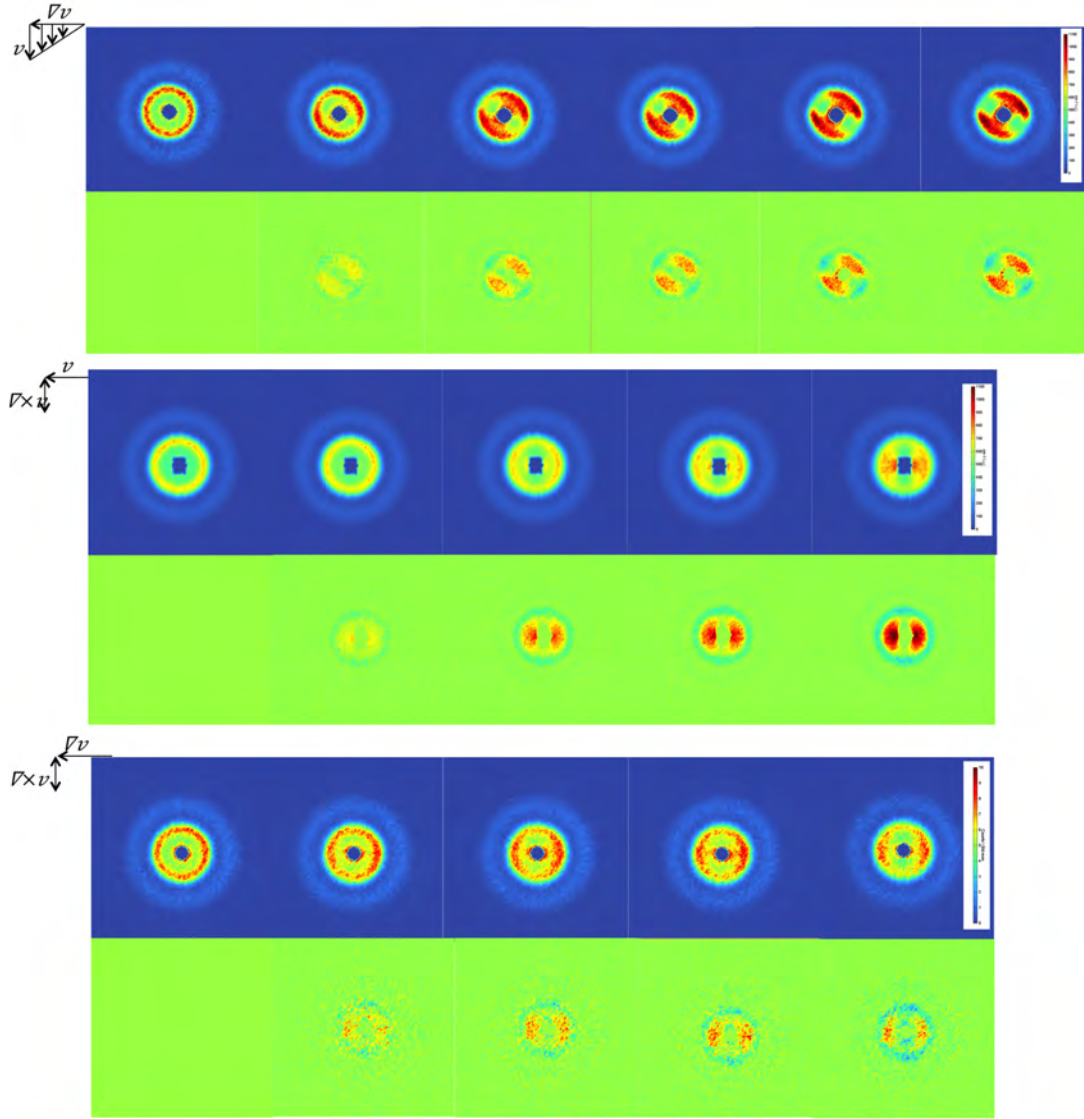


FIGURE 3. Flow-SANS 2-D scattering patterns (top row) and subtracted patterns (bottom row) for which the equilibrium scattering (at $\dot{\gamma} = 0$) is subtracted from the scattering measured during shear. Top block is the velocity-velocity gradient plane, middle block is the velocity-vorticity plane, and the bottom block is the vorticity-velocity gradient plane. From left to right $\dot{\gamma} = 0, 12, 63, 125, 627, 1258 \text{ s}^{-1}$, with the highest shear rate only measured for the velocity-velocity gradient plane.

Figure 4. In particular, there are clear increases in the intensity with increasing shear rate along the compression axis of shear on length scales associated with nearest neighbors. Furthermore, at the highest shear rates we observe particularly good agreement at the $\sim 0^\circ$ and $\sim 180^\circ$ positions where brighter spots of intensity are evident in both simulation and experiment. The scattering observed from the 1-2 plane of shear identifies the signature hydrocluster microstructure of colloidal dispersions Kalman (2010). These hydroclusters have been shown to be the result of density fluctuations caused by applying a

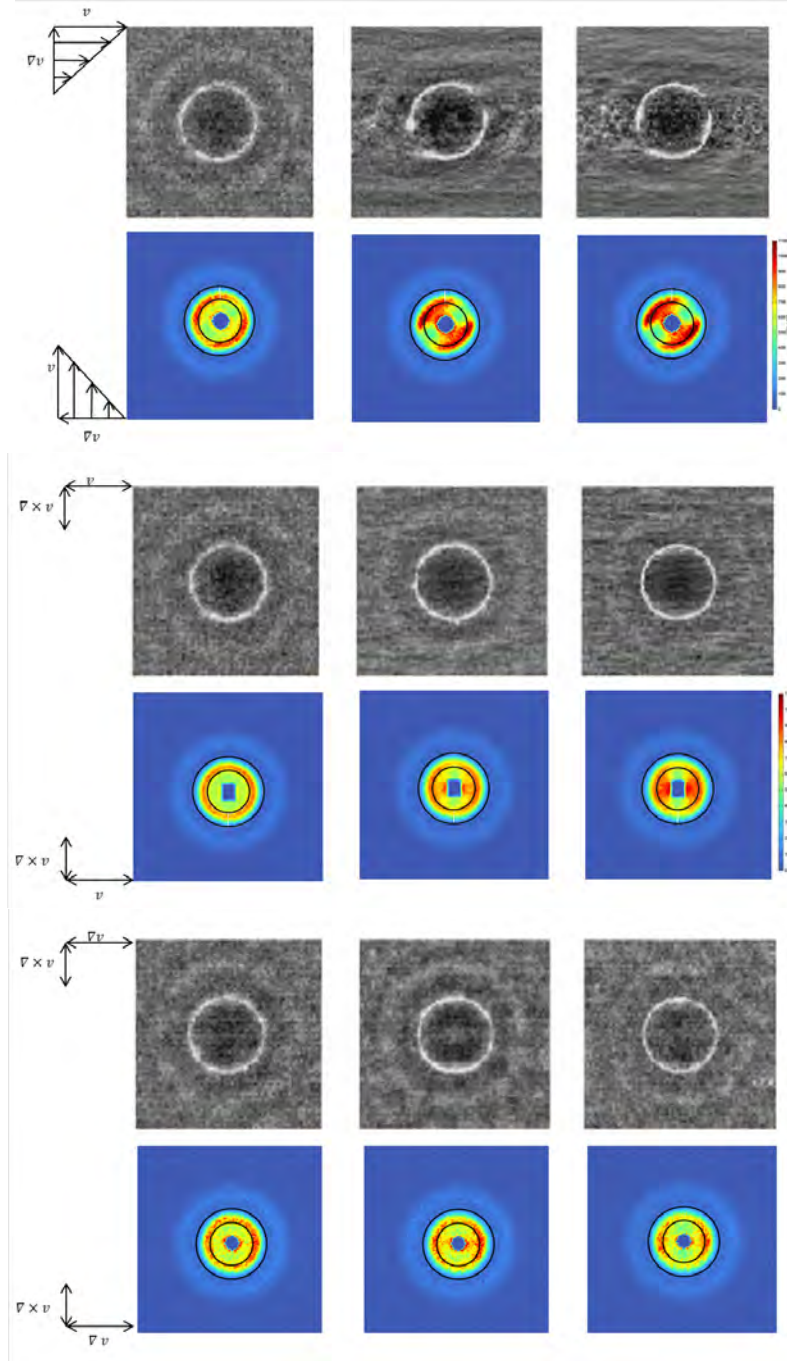


FIGURE 4. Comparison of Stokesian Dynamics simulations with SANS results for: velocity-velocity gradient (Top), velocity-vorticity (Middle), and velocity gradient-vorticity (Bottom) planes of shear. In each block the top row shows the corresponding projection of $g(r)$ from Stokesian Dynamics simulations from Foss & Brady (2000) for $Pe = 0.43, 10, 100$ where lighter colors are indicative of higher concentration of particles, darker colors are lower concentration. The bottom row of each block shows SANS pattern from flow-SANS experiments for $Pe = 0.52, 5.23, 52.6$ where warmer colors are indicative of more scattering events and cooler colors are fewer scattering events according to the scale bar to the right. The black circles indicate the nearest neighbor peak in the structure factor from Figure 2 for $q_{\text{peak}} = 0.042 - 0.064 \text{ nm}^{-1}$.

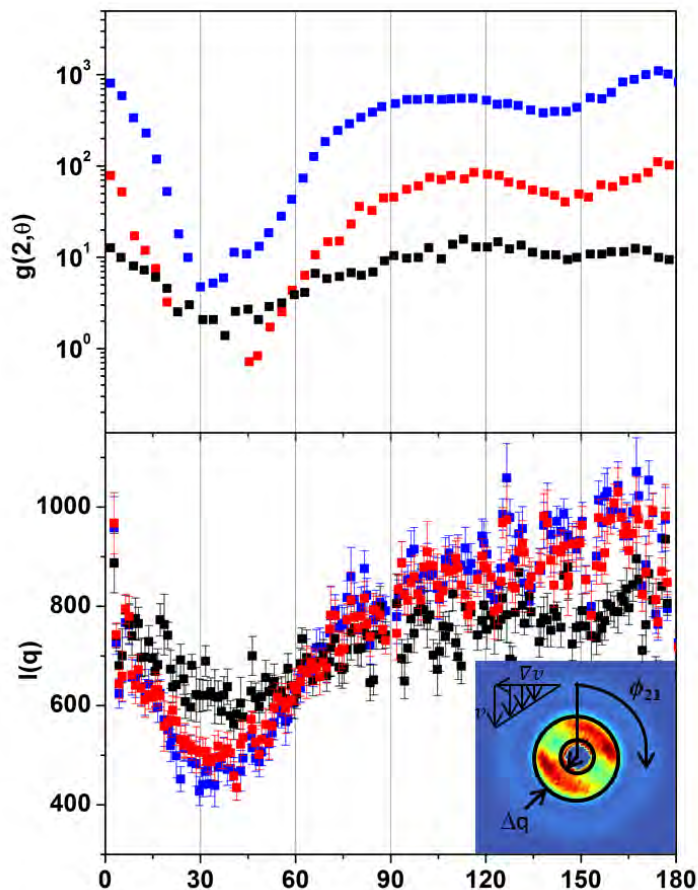


FIGURE 5. Top: $g(r, \theta)$ from accelerated Stokesian Dynamics simulations from Foss & Brady (2000) for $Pe = 1$ (\blacksquare), 25 (\blacksquare) and 1000 (\blacksquare). Bottom: $I(q, \phi_{21} + 90^\circ)$ for $Pe = 2.62$ (\blacksquare), 26.2 (\blacksquare) and 52.6 (\blacksquare) ($\dot{\gamma} = 12, 627, 1258 \text{ s}^{-1}$). The abscissa in both cases is the angle ϕ as defined in the inset figure.

shear of significant rate to a colloidal suspension such that the particles become strongly coupled by lubrication hydrodynamic interactions acting in the thin fluid layer between particles driven close together. This results in an increase in energy dissipated reflected in the bulk stress response of the shear thickening suspension. The hydroclusters have been shown to form with structure along the compression axis of shear in previous flow-SANS experiments by Kalman (2010) as well as predicted by Stokesian Dynamics simulations by Foss & Brady (2000). In these experiments, we observe the hydroclusters are evident on longer length scales, which are associated with q -values inside the smallest circle superimposed over the 2-D scattering pattern. The experiments here further corroborate these findings, where in the 1-2 plane particles associate with one another primarily along the compression axis that contribute to the increase in the stress observed during bulk rheometry experiments as a shear thickening response.

A comparison between Stokesian Dynamics simulation results and flow-SANS experiments in the velocity-vorticity plane is presented in Figures 4. Interestingly, for length scales associated with the nearest neighbor ring (as those predicted by Stokesian Dynamics by Foss & Brady (2000)) the SANS and simulation results both show only slight

changes in scattering intensity associated with nearest neighbor interactions (highlighted in the SANS patterns by the black circles). The largest changes in scattering upon shear observed in the 1-3 plane occur at longer length scales (at low- q values). Note that these structures are not readily detected in the real space pair distribution functions calculated by Stokesian Dynamics as these second and third nearest neighbor correlations are washed out and of low amplitude relative to the nearest neighbor correlations. Such larger length scale structures are readily apparent in scattering measurements however, corresponding to smaller q values (inside of the smallest circle in Figure 4). This observation suggests that the anisotropy detected in the SANS scattering patterns are from larger microstructures associated with correlations spanning multiple particles. The increased intensity indicates there is a preference for particles to align along the vorticity direction. The scattering patterns reveal structures for length scales corresponding to 3-4 particle diameters, as reported previously for hydrocluster formation by Kalman & Wagner (2009). Associations across multiple particles in the vorticity direction, which grow with increasing shear gives rise to the SANS scattering patterns in the 1-3 plane. This vorticity alignment is also evident in the velocity gradient-vorticity (2-3) plane scattering, although the patterns suffer from a longer scattering path length and lower resolution. These scattering patterns indicate particles are preferentially align along the vorticity plane during shear with increasing shear rate. The particle alignment along the vorticity direction of shear has been observed using confocal microscopy experiments and Stokesian Dynamics simulations by Cheng *et al.* (2011*a,b*), which suggest the particle chaining observed along the vorticity direction is caused by hydrodynamic interactions where particles migrate across the velocity gradient direction of shear flow.

The qualitative comparison shows that many key features of the colloidal microstructure elucidated by our measurements in all three planes of symmetry by scattering are captured in the Stokesian Dynamics simulations. These measured structures can be quantitatively used to understand the rheological response through micromechanical relationships that account for hydrodynamic interactions. Differences in our measured microstructures and those recently reported for noncolloidal suspensions with friction further serve to highlight the importance of colloidal hydrodynamics in shear thickening colloidal dispersions. Mari *et al.* (2014) show that the structure in the discontinuous shear thickened state in the plane of shear becomes more isotropic, whereas the measured microstructure of the colloidal suspension develops a very distinct and prominent anisotropy under shear flow that is most evident in the plane of flow (velocity-gradient plane). As discussed in the introduction, this difference may be in part due to the very low coefficient of friction under high loads for organically coated particles such as those used here (reported to be 0.08) in comparison to the high friction reported for bare SiO₂ particles (0.39, Kappl *et al.* (2006)). The quantitative link between the measured microstructures for shear thickening colloidal dispersions and the measured mechanical stresses are presented and discussed in the next section in the context of colloidal hydrodynamics.

3.2. *Microstructure-stress relationship*

The stress-SANS rule establishes a quantitative connection between the flowing microstructure measured using SANS and the stress response of a complex fluid during shear (Maranzano & Wagner 2002). This is accomplished via a spherical harmonic expansion of the 3-D microstructure given in 3.1 (Wagner & Ackerson 1992). Importantly for colloidal dispersions, the stress and microstructure both have contributions from two fundamentally separate, but equally important, forces: thermodynamic (superscript T) and hydrodynamic (superscript H). This section will discuss the systematic methods

used to describe the total shear stress (superscript σ) and normal stress (superscript N_1) response of the suspension and define the stress-SANS rule for this colloidal dispersion.

$$S(\mathbf{q}; Pe) = 1 + \sum_{l,m} B_{l,m}^+(q; Pe)(Y_{l,m}(\Omega_k) + (-1)^m Y_{l,-m}(\Omega_k)), \quad (3.1)$$

where the scalar coefficients $B_{l,m}^+(q; Pe)$ are determined from the scattering measurements as described below.

For reference, we present the expressions derived in Wagner & Ackerson (1992) here for the thermodynamic (Equations 3.2 to 3.4) and hydrodynamic (Equations 3.5 to 3.7) contributions to the total shear and normal stress responses. Both types of stress contributions are functions of the $B_{l,m}^+$ microstructure terms defined for a spherical harmonic expansion of the microstructure in reciprocal space and Pe (Equation 2.1), the dimensionless shear rate of deformation and ρ the particle number density.

$$\sigma^T(Pe) = -\frac{\rho}{\pi\sqrt{30}\pi} \int \theta^*(q) B_{2,1}^+(q; Pe) q^2 dq, \quad (3.2)$$

$$\Psi_1^T(Pe) = \frac{\rho}{\pi\sqrt{30}\pi} \int \theta^*(q) (B_{2,2}^+(q; Pe) - \sqrt{6} B_{2,0}^+(q; Pe)) q^2 dq, \quad (3.3)$$

$$\Psi_2^T(Pe) = \frac{\rho}{\pi\sqrt{30}\pi} \int \theta^*(q) (B_{2,2}^+(q; Pe) + \sqrt{6} B_{2,0}^+(q; Pe)) q^2 dq, \quad (3.4)$$

$$\frac{\sigma^H(Pe)}{2\dot{\gamma}\eta_f} = 1 + \frac{5}{2}\phi(1+\phi) + 2.7\phi^2 + \frac{5}{2}\phi\sqrt{\pi} \int \left[\begin{array}{l} B_{0,0}^+(q; Pe)(2\alpha(q) + \frac{4}{15}\zeta_0(q)) \\ + B_{2,0}^+(q; Pe) \left(\frac{2}{3\sqrt{5}}\beta(q) + \frac{4\sqrt{2}}{15\sqrt{7}}\zeta_2(q) \right) \\ + B_{2,2}^+(q; Pe) \left(\frac{2\sqrt{2}}{105}\zeta_2(q) + \sqrt{\frac{2}{15}}\beta(q) \right) \\ + B_{4,0}^+(q; Pe) \left(\frac{-16}{105}\zeta_4(q) \right) \\ + B_{4,2}^+(q; Pe) \left(\frac{4\sqrt{2}}{21\sqrt{5}}\zeta_4(q) \right) \end{array} \right] q^2 dq \quad (3.5)$$

$$\frac{N_1^H(Pe)}{2\dot{\gamma}\eta_f} = -5\phi\sqrt{\pi} \int \left[\begin{array}{l} B_{4,1}^+(q; Pe) \left(\frac{5\sqrt{2}+24\sqrt{5}}{105\sqrt{30}}\zeta_4(q) \right) \\ + B_{4,3}^+(q; Pe) \left(\frac{1}{3\sqrt{35}}\zeta_4(q) \right) \end{array} \right] q^2 dq \quad (3.6)$$

$$\frac{N_2^H(Pe)}{2\dot{\gamma}\eta_f} = -5\phi\sqrt{\pi} \int \left[\begin{array}{l} B_{2,1}^+(q; Pe) \left(\frac{2\sqrt{2}}{\sqrt{15}}\beta(q) + \frac{2\sqrt{2}}{7\sqrt{15}}\zeta_2(q) \right) \\ + B_{4,1}^+(q; Pe) \left(\frac{5\sqrt{6}+24\sqrt{5}}{105\sqrt{30}}\zeta_4(q) \right) \\ + B_{4,3}^+(q; Pe) \left(\frac{1}{3\sqrt{35}}\zeta_4(q) \right) \end{array} \right] q^2 dq \quad (3.7)$$

The stresses can also be expressed in terms of an expansion in real space and the derivation for the hydrodynamic stresses is presented in the appendix to this manuscript. Comparison of the expressions in reciprocal space shown above with the results for real space in the appendix shows the same symmetries contributing to each stress component. This facilitates the direct comparison of structural anisotropy evident in scattering experiments with those evident in direct observation or simulations of the pair distribution function. (Note that Eqs. 3.6 & 3.7 corrects a typographical error in Eq. 62 of Wagner & Ackerson (1992).)

The spherical harmonic expansion of the 3-D microstructure in reciprocal space, Eq. 3.1, is projected onto the three planes of flow measured during the flow- and rheo-SANS

experiments to define the weighted functions ($W_n(q, \dot{\gamma})$) (the full derivation of this expansion is presented in the supplemental materials (Gurnon 2014)). These measurable functions are defined for the velocity-velocity gradient (1-2) plane where the neutron beam travels parallel to the ‘vorticity’ direction (hence the ‘vorticity’ superscript in Equation 3.10), the velocity-vorticity (1-3) plane where the (‘gradient’ superscript is used in Equation 3.11) and the velocity gradient-vorticity (2-3) plane for which the neutron beam travels parallel to the velocity direction (here the ‘velocity’ superscript is used in Equation 3.12). Note these are also functions of Pe through $B_{l,m}^+(q; Pe)$.

We define the weighted average functions $W_n(q, \dot{\gamma})$ s for each plane. Operationally, to determine the $W_n(q, \dot{\gamma})$ s experimentally for each plane, the measured scattering during shear is divided by the equilibrium scattering (measured under quiescent conditions). In this way, we focus on the changes in the microstructure caused by shear. The analysis of the flow- or rheo-SANS experimental 2-D scattering data proceeds by integrating over the azimuthal angle weighted by the functions $\cos(n\theta)$ where n is an integer (0, 2 or 4) or $\cos(\theta)\sin(\theta)$.

$$W_n(q, \dot{\gamma}) = \frac{1}{2\pi} \int_0^{2\pi} \cos(n\phi) \frac{I(q, \phi, \dot{\gamma})}{I(q, \dot{\gamma} = 0)} d(\phi), \quad n = 0, 2, 4, \dots \quad (3.8)$$

$$W_{21}(q, \dot{\gamma}) = \frac{1}{2\pi} \int_0^{2\pi} \cos(\phi) \sin(\phi) \frac{I(q, \phi, \dot{\gamma})}{I(q, \dot{\gamma} = 0)} d(\phi), \quad (3.9)$$

Inserting the spherical harmonic expansion for the structure factor identifies the contributions of specific symmetries of the structure to each weighted integral over the scattering patterns, as:

$$\begin{aligned} W_0^{vorticity}(q)S^{eq}(q) &= 1 + B_{0,0}^+(q) \left(\frac{1}{\sqrt{\pi}} \right) + B_{2,0}^+(q) \left(\frac{1}{4} \sqrt{\frac{5}{\pi}} \right) + B_{2,2}^+(q) \left(\frac{1}{4} \sqrt{\frac{15}{2\pi}} \right) \\ &\quad + B_{4,0}^+(q) \left(\frac{27}{64\sqrt{\pi}} \right) + B_{4,2}^+(q) \left(\frac{9\sqrt{5}}{32\sqrt{2\pi}} \right) + B_{4,4}^+(q) \left(\frac{9\sqrt{35}}{64\sqrt{2\pi}} \right) + \dots (l > 4) \\ W_2^{vorticity}(q)S^{eq}(q) &= B_{2,0}^+(q) \left(\frac{1}{4} \sqrt{\frac{5}{\pi}} \right) - B_{2,2}^+(q) \left(\frac{1}{8} \sqrt{\frac{15}{2\pi}} \right) + B_{4,0}^+(q) \left(\frac{60}{128\sqrt{\pi}} \right) \\ &\quad + B_{4,2}^+(q) \left(\frac{3\sqrt{5}}{16\sqrt{2\pi}} \right) - B_{4,4}^+(q) \left(\frac{3\sqrt{35}}{32\sqrt{2\pi}} \right) + \dots (l > 4) \\ W_4^{vorticity}(q)S^{eq}(q) &= 2 \left(B_{4,0}^+(q) \left(\frac{105}{64\sqrt{\pi}} \right) - B_{4,2}^+(q) \left(\frac{21\sqrt{5}}{16\sqrt{2\pi}} \right) + B_{4,4}^+(q) \left(\frac{3\sqrt{35}}{64\sqrt{2\pi}} \right) \right) \\ W_6^{vorticity}(q)S^{eq}(q) &= 0 \\ W_{21}^{vorticity}(q)S^{eq}(q) &= \frac{1}{8} \left(B_{2,1}^+(q) \left(\sqrt{\frac{15}{2\pi}} \right) + B_{4,1}^+(q) \left(\frac{3\sqrt{5}}{8\sqrt{\pi}} \right) \right) + \dots (l > 4) \end{aligned} \quad (3.10)$$

$$\begin{aligned} W_0^{gradient}(q)S^{eq}(q) &= 1 + B_{0,0}^+(q) \left(\frac{1}{\sqrt{\pi}} \right) - B_{2,0}^+(q) \left(\sqrt{\frac{5}{4\pi}} \right) + B_{4,0}^+(q) \left(\frac{9}{8\sqrt{\pi}} \right) + \dots (l > 4) \\ W_2^{gradient}(q)S^{eq}(q) &= B_{2,2}^+(q) \left(\sqrt{\frac{15}{8\pi}} \right) + B_{4,2}^+(q) \left(\frac{-3\sqrt{5}}{4\sqrt{2\pi}} \right) + \dots (l > 4) \\ W_4^{gradient}(q)S^{eq}(q) &= 4B_{4,4}^+(q) \left(\frac{3\sqrt{35}}{32\sqrt{2\pi}} \right) + \dots (l > 4) \\ W_6^{gradient}(q)S^{eq}(q) &= W_{12}^{gradient}(q)S^{eq}(q) = 0 \end{aligned} \quad (3.11)$$

$$\begin{aligned}
W_0^{velocity}(q)S^{eq}(q) &= 1 + B_{0,0}^+(q) \left(\frac{1}{\sqrt{\pi}} \right) + B_{2,0}^+(q) \left(\frac{1}{4} \sqrt{\frac{5}{\pi}} \right) + B_{2,2}^+(q) \left(\frac{1}{4} \sqrt{\frac{15}{2\pi}} \right) \\
&\quad + B_{4,0}^+(q) \left(\frac{27}{64\sqrt{\pi}} \right) - B_{4,2}^+(q) \left(\frac{15\sqrt{5}}{32\sqrt{2\pi}} \right) - B_{4,4}^+(q) \left(\frac{9\sqrt{35}}{64\sqrt{2\pi}} \right) + \dots (l > 4) \\
W_2^{velocity}(q)S^{eq}(q) &= \frac{1}{2} \left(B_{2,0}^+(q) \left(\frac{3}{4} \sqrt{\frac{5}{\pi}} \right) - B_{2,2}^+(q) \left(\frac{1}{4} \sqrt{\frac{15}{2\pi}} \right) - B_{4,0}^+(q) \left(\frac{60}{64\sqrt{\pi}} \right) \right. \\
&\quad \left. - B_{4,2}^+(q) \left(\frac{6\sqrt{5}}{32\sqrt{2\pi}} \right) + B_{4,4}^+(q) \left(\frac{12\sqrt{35}}{64\sqrt{2\pi}} \right) \right) + \dots (l > 4) \\
W_4^{velocity}(q)S^{eq}(q) &= 2 \left(-B_{4,0}^+(q) \left(\frac{105}{64\sqrt{\pi}} \right) + B_{4,2}^+(q) \left(\frac{21\sqrt{5}}{64\sqrt{2\pi}} \right) \right. \\
&\quad \left. - B_{4,4}^+(q) \left(\frac{3\sqrt{35}}{64\sqrt{2\pi}} \right) \right) + \dots (l > 4) \\
W_6^{velocity}(q)S^{eq}(q) &= W_{12}^{velocity}(q)S^{eq}(q) = 0
\end{aligned} \tag{3.12}$$

These three sets of equations relate quantifiable functions obtainable from the rheo- and flow- SANS measurements to the $B_{l,m}^+$ microstructure terms. In this work we use the experimental results from rheo- and flow- SANS experiments to define the $(W_n(q, \dot{\gamma}))$ functions in order to gain a quantitative measure for the microstructure which is, within a constant, equal to the stress. As is discussed here the proportionality constants $(C^{\sigma,T}, C_0^{\sigma,H}, C_4^{\sigma,H}, C^{N1,H}$ and $C^{N1,T})$ are scalars defined once for a particular colloidal dispersion under steady shear and then can be employed to predict those corresponding stresses under other steady and dynamic shear conditions.

Figure 6 shows the $W_n(q, \dot{\gamma})$ as defined from Equations 3.8 and 3.9 for each shear rate and plane measured during flow- and rheo-SANS experiments. It is best to discuss and understand the rich shear-induced microstructure presented in this way because significant differences in the microstructure are detectable at different scattering lengths and shear rates. To begin with, the W_0 in all three planes is the intensity normalized by the zero shear intensity with no weighting applied to the annular integrated scattering. This function provides a quantitative measure of the number of nearest neighbors regardless of angular position (see Figures 7A and 7E). In Figure 6 W_0 shows clear increases in the scattered intensity. As the functions are normalized by the equilibrium values, this increase for low- q values and decrease for q values above the primary peak position corresponds to a shift to lower- q of the primary peak. The increase in magnitude is indicative of a greater number of neighboring particles is probed whereas a shift in the peak to lower q suggests that larger length scale structures are observed, such as those reported by Kalman & Wagner (2009). In the 1-2 plane of shear the intensity saturates for $\dot{\gamma} > 62$ s^{-1} , suggesting that increasing shear rates does not lead to more nearest neighbors in this regime. This is important for understanding why the first-order microstructure contribution to the stress is not adequate for predicting the shear thickening response as noted previously (Maranzano & Wagner 2002; Kalman 2010). In the other two planes, a decrease in the *total* intensity is observed for $\dot{\gamma} > 627$ s^{-1} . At these higher shear rates the sample integrity is compromised, air bubbles are introduced in the cup and bob Couette geometry during radial and tangential rheo-SANS experiments such that the intensity in the scattering decreases. Transmission measurements confirm this instability and no further analysis will be performed on these conditions. Note that no such problems are observed for the 1-2 shear cell at these shear rates as it is sealed and air bubbles are not observed, again confirmed by transmission measurements.

The W_2 weighting functions reported in Figure 6 give a quantitative measure for any changes in the 2-fold symmetry structure that might exist during flow in each of the three planes, where the specific microstructural symmetries involved depend on the plane of measurement (see Equations 3.10, 3.11 and 3.12). Figure 7C shows the $\cos(2\phi)$ weighting function is positive in the lobes along the 0° and 180° detector angles whereas it is

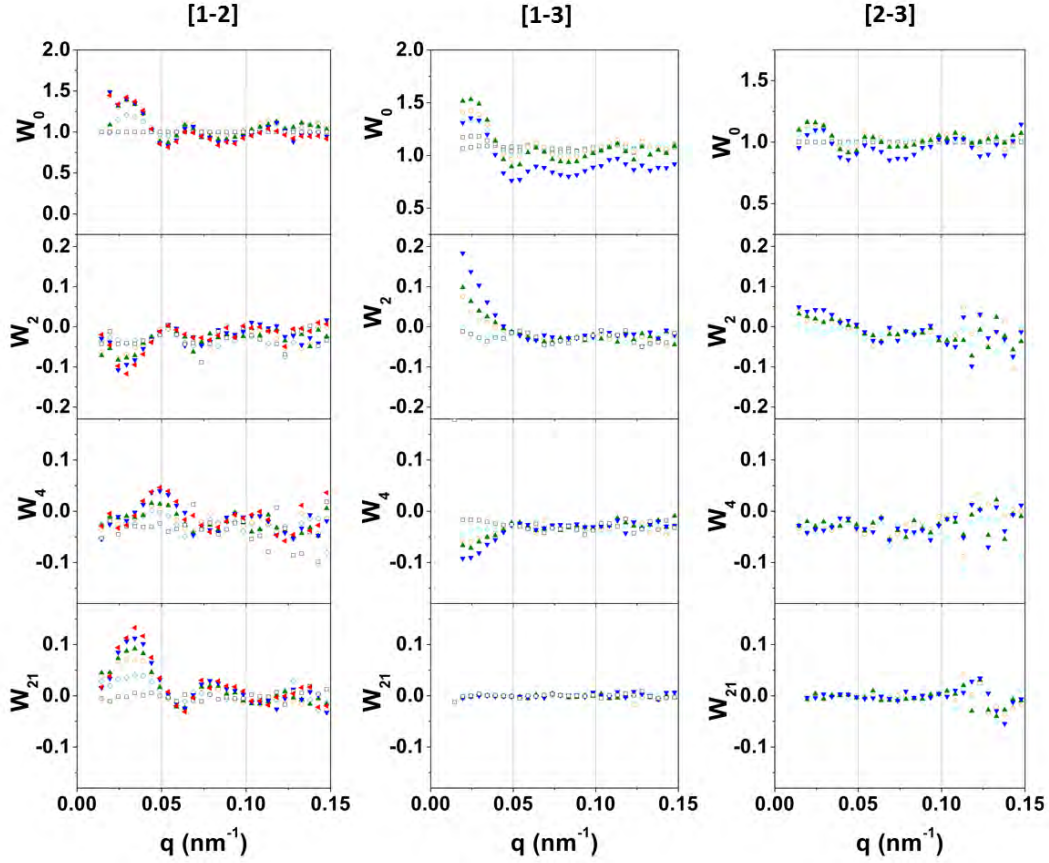


FIGURE 6. W_n as a function of q (nm^{-1}) as defined in Equation 3.8 and 3.9 where $\dot{\gamma} = 0 \text{ s}^{-1}$: \square , 12 s^{-1} : \diamond , 62 s^{-1} : \circ , 127 s^{-1} : \blacktriangle , 627 s^{-1} : \blacktriangledown and 1255 s^{-1} : \blacktriangleleft . Columns left to right correspond with scattering experiments performed in the 1-2, 1-3 and 2-3 planes.

negative at detector angles of 90° and 270° . Since more structure is observed along the $\phi_{21} = 90^\circ$ and 270° detector angles in the 1-2 plane of shear the function becomes more negative with increasing shear rate. Precisely the opposite is the case for the 1-3 plane (Figure 7G) where the W_2 function increases to more positive values with increasing shear rate, indicative of more structure along the $\phi_{13} = 0^\circ$ and 180° detector angles for the velocity-vorticity plane. In the 1-3 plane, the q -range accessible is not small enough to capture the peak in the intensity, indicating that larger structures (consisting of more than a particle and its nearest neighbor) form in the velocity-vorticity plane. This observation is consistent with observations made based on the 2-D scattering patterns discussed in the previous sections, which indicate particles have a propensity to associate along the vorticity direction. The trend in the velocity gradient-vorticity (2-3) plane is similar to that in the 1-3 plane; however, the magnitude of the changes are less.

The four-fold symmetry microstructure changes are defined using the W_4 weighting function (Figure 7D). In the velocity-velocity gradient plane of shear the four-fold symmetry increases with increasing shear rate at a q larger than observed for the changes in the 2-fold symmetry (Figure 6). The shift to larger q is indicative of the 4-fold symmetric microstructure occurring at length scales on the order of nearest neighbor peak in the

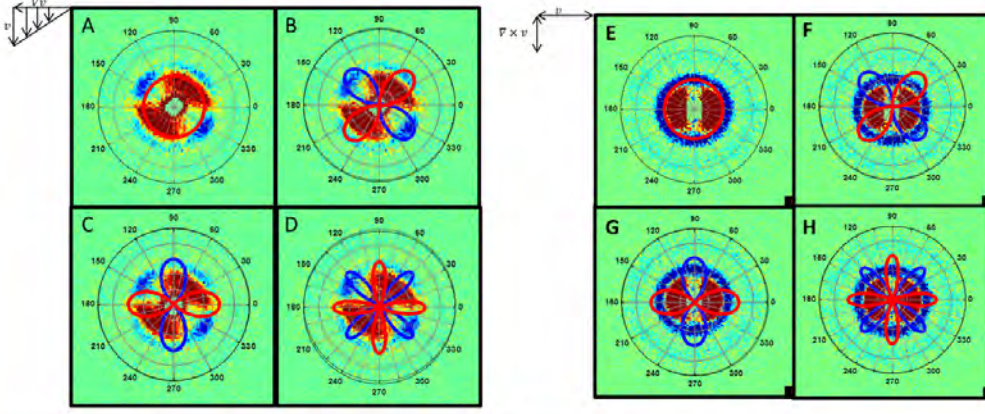


FIGURE 7. Scattering results overlaid with the weighting functions in two planes 1-2 flow-SANS (left) and 1-3 rheo-SANS (right). Weighting functions are used in Equation 3.8, $\cos(n\phi_{21})$ where $n = 0, 2, 4$ (for A/E, C/G and D/H) and Equation 3.9, $\cos(\phi_{21})\sin(\phi_{21})$ in for B/F. The function is either red or blue indicating a positive or negative value of the function, respectively. Similarly, the SANS scattering patterns are subtracted patterns from a quiescent scattering pattern therefore, the warmer colors indicate more scattering events while the cooler colors indicate fewer scattering events during shear than those that occur at equilibrium.

Plane interrogated	Weighting function	$q_{min} - q_{max}$ [nm^{-1}]	Real space ($\sim 2\pi/q$) [nm]
1-2	$\cos(0\theta)$	0.0194 - 0.0539	$\sim 116 - 323$
	$\cos(2\theta)$	0.0194 - 0.049	$\sim 116 - 323$
	$\cos(4\theta)$	0.0342 - 0.0638	$\sim 99 - 183$
	$\cos(\theta)\sin(\theta)$	0.0194 - 0.0539	$\sim 116 - 323$
1-3	$\cos(0\theta)$	0.0194 - 0.0342	$\sim 183 - 324$
	$\cos(2\theta)$	0.0194 - 0.049	$\sim 128 - 324$
	$\cos(4\theta)$	0.0194 - 0.049	$\sim 128 - 324$
	$\cos(\theta)\sin(\theta)$	0.0194 - 0.049	$\sim 128 - 324$
2-3	$\cos(0\theta)$	0.0194 - 0.0391	$\sim 160 - 324$
	$\cos(2\theta)$	0.0194 - 0.049	$\sim 128 - 324$
	$\cos(4\theta)$	0.0194 - 0.049	$\sim 128 - 324$
	$\cos(\theta)\sin(\theta)$	0.0194 - 0.049	$\sim 128 - 324$

TABLE 2. q_{min} and q_{max} used to define $\overline{W}_n(\dot{\gamma})$

structure factor ($q_{peak} = 0.042 - 0.064 \text{ nm}^{-1}$) in Figure 2A. Interestingly, this shift in q is not observed in either of the other planes of shear. The four-fold symmetry in the 1-2 plane is caused by increased intensity along the velocity and velocity gradient directions (Figure 7D). At such a high concentration of suspended particles ($\phi_{eff} = 0.465$) it is possible that this four-fold symmetry is the result of packing effects made more apparent by the high shear rates that induce hydrocluster formation in the shear thickening regime. The onset of four-fold symmetry in the microstructure of concentrated suspensions has been observed in simulation by Nazockdast & Morris (2013). Their calculations show a propensity to find four-fold coordination of nearest neighbors at higher ($> 30\%$) packing fractions. However, for this symmetry to become apparent in our scattering measurements it will need to be oriented by the flow. Clearly, this four-fold symmetry becomes apparent at high shear rates where shear thickening is evident. There are only small

changes in W_4 in the 1-3 plane of shear. If anything the function trends to more negative values with increasing rates. Figure 7H shows that this is the result of the $\cos(4\phi_{13})$ function's constructive weighting of the increasing intensity in the vorticity direction of shear, thereby resulting in increases in four-fold symmetry opposite in sign to those 2-fold microstructure changes defined by W_2 . There are no four-fold symmetry microstructures measured in the 2-3 plane.

The higher order two-fold and four-fold symmetric scattering functions show measurable changes during shear flow. However, care needs to be taken in defining priority to the contributions bearing in mind the initial weighting functions used to assess the microstructure's symmetry. In fact, based on the definitions for the two- and four-fold symmetry these functions could be different measures of the same structural features. The increases in two-fold and four-fold weighted scattering functions are not independent given the weighting functions used to assess the microstructure in the 1-2 plane (Figure 7C and D). As changes in fourth-order harmonics can also appear in the definition of $W_2(\dot{\gamma})$ we focus our attention on the readily apparent increases in $W_4(\dot{\gamma})$.

Specifically, the four-fold symmetric functions increase in intensity in the velocity and velocity gradient directions observed in the 2-D scattering patterns, which is a symmetry that also contributes to two-fold symmetry increases, given the definitions of $W_2(\dot{\gamma})$ and $W_4(\dot{\gamma})$. Therefore it is most important to include the four-fold symmetry microstructure in the velocity-velocity gradient plane of shear. An analogous argument can be made for the velocity-vorticity (1-3) plane, assessing Figure 7G and H show these microstructures in the velocity-vorticity plane and velocity-velocity gradient planes. It is clear that the microstructure with true two-fold symmetry could also contribute to W_4 , given the definition for the weighting function applied. However, by inspecting the 2-D scattering pattern we find it is most important to include the shear induced 2-fold symmetry in the 1-3 plane.

A rigorous evaluation of the stresses from the SANS data requires evaluating $W_n(q, \dot{\gamma})$ for all q , but it is not experimentally possible to measure to infinite q . Thus, following previous work we choose to define a q -range for which the maximum microstructure changes due to shear are observed during the experiment (Maranzano & Wagner 2002). Figure 6 indicates the location of the largest changes in weighted intensity as a function of scattering vector, q . Table 2 give the q_{\min} and q_{\max} for which the integral defined in Equation 3.13 is taken for each of the different weighting functions in each of the planes according to:

$$\overline{W_n(\dot{\gamma})} = \frac{1}{\Delta(aq)} \int_{aq_{\min}}^{aq_{\max}} W_n(q, \dot{\gamma}) (aq)^2 d(aq). \quad (3.13)$$

The $\overline{W_n(\dot{\gamma})}$ are now only a function of shear rate and define the weighting functions integrated over the scattering vector ($q \text{ nm}^{-1}$) in Table 2, which is always normalized by the particle radius ($a = 61.1 \text{ nm}$). Figure 8 reports those $\overline{W_n(\dot{\gamma})}$ for the 1-2, 1-3 and 2-3 planes.

Inspection of Figure 8 shows that both the $\overline{W_2^{\text{vorticity}}(\dot{\gamma})}$ and the $\overline{W_4^{\text{vorticity}}(\dot{\gamma})}$ vary substantially with shear rate and are of the same order (but opposite in sign) and therefore, could both potentially be the next order contribution to the hydrodynamic stress. The relationship between these two contributions are entrenched in the expressions given in Equation 3.4, such that it is not immediately obvious which contribution should be used to define the additional hydrodynamic stress responses in the shear thickening regime. Furthermore, the $\overline{W_2^{\text{vorticity}}(\dot{\gamma})}$ decreases with increasing shear rate while the $\overline{W_4^{\text{vorticity}}(\dot{\gamma})}$ shows a significant increase in values between the $\dot{\gamma} = 125$ and 627 s^{-1} (a

trend line is provided to illustrate this) corresponding to a transition from the shear thinning to the shear thickening regime. Since there is a significant change in the stress contribution for the shear thickening regime ($\dot{\gamma} > 295 \text{ s}^{-1}$, $Pe > 12.3$) we choose to associate the $\overline{W_4^{\text{vorticity}}}(\dot{\gamma})$ with the additional hydrodynamic microstructure contributions to the stress.

The W_{21} weighting function is clearly only measured in the velocity-velocity gradient plane as is expected given Equations 3.10, 3.11 and 3.12. These measurements show increases in intensity at a constant q-range clearly indicative of more structure forming with increasing shear rate (Figure 8). This type of symmetry is caused by particles being forced together along the compression axis of flow as the sample is sheared. Neither the radial or tangential planes measure the microstructure in the shear plane where one can interrogate the compression axis therefore this weighted scattering function is expected to be and is exactly zero in the other two planes for all shear conditions.

In the following section, the $\overline{W_n^{\text{vorticity}}}(\dot{\gamma})$ given in Figure 8 are used to define the stress-SANS rule such that the microstructure stress contribution is comparable to the shear stress response measured during a rheometry experiment. Figure 8 clearly shows that there are contributions from higher-order microstructures ($W_2(\dot{\gamma})$ and $W_4(\dot{\gamma})$) in all of the planes of equal magnitude to those microstructures that contribute to the thermodynamic stress during steady shear. Most notably are those measurements in the 1-2 plane of shear for the $\overline{W_2^{\text{vorticity}}}(\dot{\gamma})$ and $\overline{W_4^{\text{vorticity}}}(\dot{\gamma})$ terms. As was discussed previously, there is difficulty in deconvoluting these two types of symmetries into separate contributions to the hydrodynamic stress. As will be shown in the next section, it is sufficient to include those fourth order harmonic microstructure terms to reconcile the hydrodynamic stresses in the shear thickening regime.

All three planes of shear flow are necessary for fully determining the 3-D microstructure and all contributions to the stress tensor, but with some simplifying assumptions a reduced set of measurements can be used to obtain the stresses from the harmonic expansion of the microstructure. Importantly in this work, the new scattering measurements in the velocity-velocity gradient (1-2) plane of shear (first column of Figure 6) will be used to define the majority of the structure harmonics necessary for defining the stress-SANS rule. Previous research (Kalman (2010); Maranzano (2001); Foss & Brady (2000)) have shown that the only plane of observation capable of defining the thermodynamic contribution to the shear stress is the 1-2 plane. Note that the dominant hydrodynamic contribution can be defined in the plane of shear as well. However, defining the thermodynamic contribution to the normal stress differences requires measurements in the 1-3 plane, as will be shown. The corresponding stress-SANS rules are defined in the following.

3.2.1. Stress-SANS rule: Thermodynamic shear stress

The thermodynamic stress contribution is formally exact and the shear stress is shown to be proportional to only those contributions arising from the $B_{2,1}^+$ symmetry term of the microstructure (Equation 3.2). Equation 3.10 is the only equation that includes the $B_{2,1}^+$ microstructure term in the expansion for the microstructure in any plane measured during a rheo- or flow-SANS experiment. Therefore the $\overline{W_{21}^{\text{vorticity}}}$ measured by flow-SANS experiments made in the 1-2 plane of shear defines the thermodynamic stress contribution to the total stress response measured during a rheometry experiment.

The $\overline{W_{21}^{\text{vorticity}}}$ microstructure contribution is proportional to the thermodynamic stress contribution. At the lowest shear rates the thermodynamic contribution to the total stress is largest; therefore, the lowest shear rate for which the microstructure has been measured

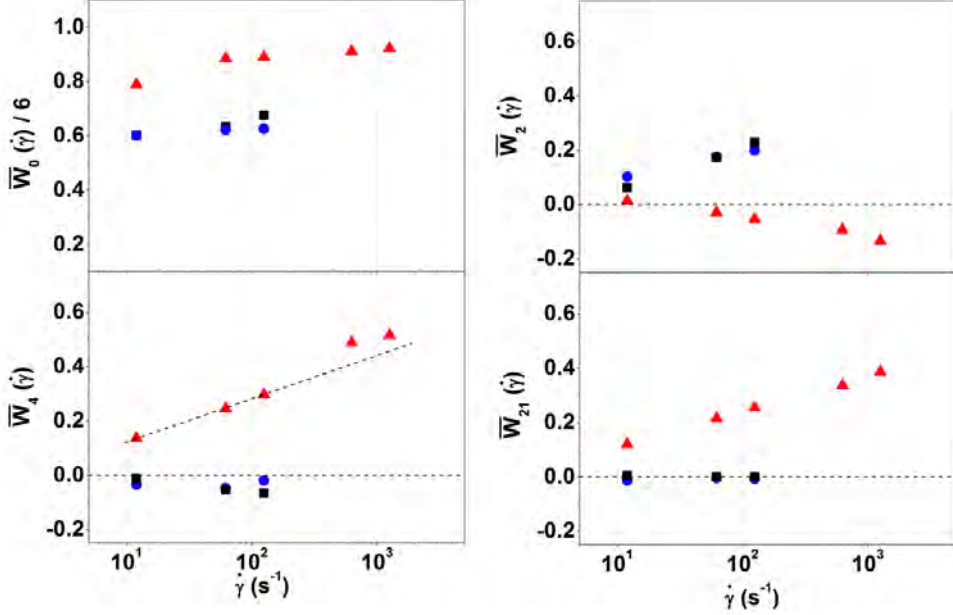


FIGURE 8. For 1-2 (\blacktriangle), 1-3 (\blacksquare), and 2-3 (\bullet) planes the $\overline{W}_n(\dot{\gamma})$ as defined in Equation 3.13 where q_{\min} and q_{\max} are defined in Table 3.2. The $\overline{W}_n(\dot{\gamma})$ have been shifted such that the $\overline{W}_n(\dot{\gamma} = 0) = 0$. and a trend line has been added for $\overline{W}_4(\dot{\gamma})$ for clarity.

is chosen to determine the thermodynamic constant. The proportionality constant will be defined for $\dot{\gamma} = 12 \text{ s}^{-1}$ condition and hereafter will be applied to each microstructure measured to determine the thermodynamic stress contribution from the microstructure at any other shear rate. The thermodynamic stress constant ($C^{\sigma,T}$) is equal to:

$$C^{\sigma,T} = \frac{\sigma_r(\dot{\gamma}) - \sigma_{fit}(\dot{\gamma})}{W_{21}^{vorticity}(\dot{\gamma})}, \quad (3.14)$$

where σ_r is the stress measured during a rheometry measurement and σ_{fit} is the hydrodynamic stress extrapolated from a linear fit of the stress at shear rates close to the critical shear rate for shear thickening ($\dot{\gamma}_c = 295 \text{ s}^{-1}$, $Pe = 12.3$) given in Figure 9A. This is justified because the stress response at shear rates greater than or equal to the critical shear rate for a shear thickening fluid are largely hydrodynamic in nature (Banchio & Brady (2003); Bender & Wagner (1996)). Figure 9B confirms this, where the high shear viscosity ($\eta_{r,\infty}$) prior to shear thickening is quantitatively consistent with that for hard spheres. In addition, the hydrodynamic microstructure's contribution to the stress is proportional to the shear rate (see Equation 3.5). Therefore, a good approximation for the hydrodynamic stress at the lowest shear rates is the extrapolation of the fit to high shear rates. A similar procedure was used in previous work analyzing the other planes of flow (Maranzano & Wagner 2002). The coefficient is defined using the microstructure measured at the $\dot{\gamma} = 12 \text{ s}^{-1}$ condition and the fit shown in Figure 9. For this suspension, $C^{\sigma,T} = 22 \text{ Pa}$ and is also reported in Table 3.

Now that the thermodynamic coefficient is defined, the thermodynamic stress contribution at any shear rate $\sigma^T(\dot{\gamma})$ is defined given $\overline{W}_{21}^{vorticity}$ from a flow-SANS microstructure

Coefficient	Value	Units
$C^{\sigma,T}$	22	Pa
$C_0^{\sigma,H}$	0.063	-
$C_4^{\sigma,H}$	4.6	-
$C^{N1,H}$	-5.2	-
$C^{N1,T}$	18	Pa

TABLE 3. Summary of coefficients for stress-SANS rule

measurement made in the velocity– velocity gradient plane of shear and the following expression:

$$\sigma^T(\dot{\gamma}) = C^{\sigma,T} \left(\overline{W_{21}^{vorticity}}(\dot{\gamma}) \right). \quad (3.15)$$

Figure 9 shows the thermodynamic stress contribution calculated from the stress-SANS rule as a function of shear rate and Pe . Clearly, the thermodynamic stress is always increasing with Pe . However, as expected this stress contribution grows more slowly at higher $\dot{\gamma}$ due to saturation of the microstructure deformation (Wagner *et al.* 1988; Bender & Wagner 1995). As the thermodynamic stress is directly proportional to the microstructure deformation and this deformation cannot continue to increase linearly with the shear rate for even modest Pe , it ultimately increases as a function of shear rate with power law exponent of $\sim \frac{1}{2}$. The thermodynamic stress contribution is strongly shear thinning and this change is largely responsible for the shear thinning rheology observed in Figure 9, right.

3.2.2. Stress-SANS rule: Hydrodynamic shear stress

In contrast to the thermodynamic stress, the hydrodynamic stress in Equation 3.5 includes many terms from the structure factor expansion including up to fourth-order terms ($B_{0,0}^+$, $B_{2,0}^+$, $B_{2,2}^+$, $B_{4,0}^+$ and $B_{4,2}^+$). The definition of the $W_0^{vorticity}$ weighting function defined in Equation 3.10 includes all of these microstructure contributions. As expected from previous experimental measures by Maranzano & Wagner (2002), the $\overline{W_0^{vorticity}}(\dot{\gamma})$ term measured from the microstructure is an order of magnitude larger than any of the other microstructure contributions shown in Figure 8. The first order contribution to the hydrodynamic stress is proportional to those microstructure changes captured in $\overline{W_0^{vorticity}}(\dot{\gamma})$. Therefore, the coefficient for the first-order hydrodynamic stress contribution ($C_0^{\sigma,H}$) is defined by:

$$C_0^{\sigma,H} = \frac{\left(2\eta_f\dot{\gamma}\right)^{-1} \left(\sigma_r(\dot{\gamma}) - \sigma^T(\dot{\gamma})\right) - \left(1 + \frac{5}{2}\phi(1 + \phi) + 2.7\phi^2\right)}{\overline{W_0^{vorticity}}(\dot{\gamma})}. \quad (3.16)$$

We anticipate that the shear thickening regime will have additional higher-order microstructure contributions to the total stress. However, this first-order contribution is expected to accurately predict the hydrodynamic stress contributions in the shear thinning regime. The hydrodynamic stress contribution is defined for the SANS condition measured at the largest shear rate in the shear thinning regime (and closest to the critical shear rate for shear thickening). For the measurements made here, the shear condition $\dot{\gamma} = 125 \text{ s}^{-1}$ gives a constant coefficient for the hydrodynamic stress contribution reported in Table 3 and is $C_0^{\sigma,H} = 0.063$.

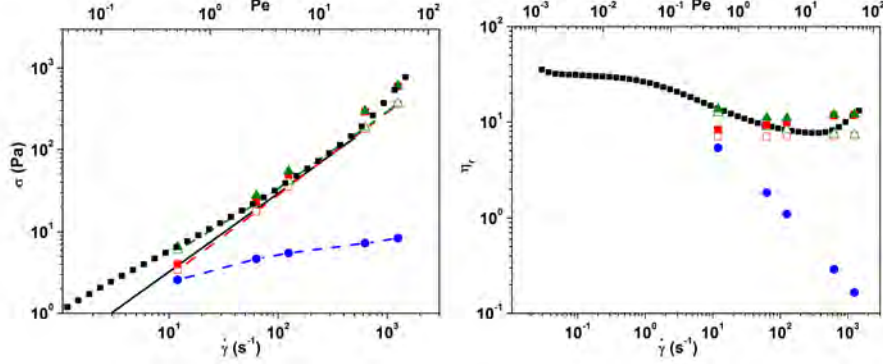


FIGURE 9. Stress (left) and relative viscosity, $(\eta_r = \frac{\eta(T)}{\eta_f(T)})$ (right) as a function of $\dot{\gamma}$ and Pe . Rheometry results: \blacksquare , stress-SANS rule thermodynamic stress: \bullet , first-order hydrodynamic stress: \square and total stress: \triangle . Also included are stress-SANS rule higher-order hydrodynamic contributions for hydrodynamic stress: \blacksquare and total stress \blacktriangle . The line (black) is fit to the stress responses for $\dot{\gamma} = 199.6 - 500.1 \text{ s}^{-1}$ around the critical shear rate $\dot{\gamma} = 295 \text{ s}^{-1}$.

Now that the first order hydrodynamic stress-SANS coefficient ($C_0^{\sigma,H}$) is defined it is possible to predict the first order hydrodynamic stress contribution $\sigma_0^H(\dot{\gamma})$ given a measure of the $\overline{W_0^{vorticity}}(\dot{\gamma})$ from the microstructure at any shear condition with the expression:

$$\frac{\sigma_0^H(\dot{\gamma})}{2\eta_f\dot{\gamma}} = C_0^{\sigma,H} \left(\overline{W_0^{vorticity}}(\dot{\gamma}) \right). \quad (3.17)$$

Figure 9 shows the first order hydrodynamic stress contribution as a function of shear rate and Pe . For all Pe probed, the hydrodynamic stress is always larger than the thermodynamic stress response, which is anticipated for $Pe \sim O(1)$ or larger. In addition, the sum of the hydrodynamic and thermodynamic stress responses in the shear thinning regime $Pe < 12.3$ agree well with those stresses measured in a bulk rheology experiment. However for those measurements made in the shear thickening regime, the microstructure's total stress defined using only the first order contribution from the hydrodynamic stress and the thermodynamic stress is significantly lower than those measured responses from a rheometry experiment.

It is with this discrepancy in mind that we look at higher order microstructure contributions to the hydrodynamic stress such that the shear thickening response will also be well predicted from the microstructural changes experimentally measured during shear thickening. Therefore, the constant for the higher order hydrodynamic stress contribution is defined here:

$$C_4^{\sigma,H} = \frac{(2\eta_f\dot{\gamma})^{-1} \left(\sigma_r(\dot{\gamma}) - \sigma^T(\dot{\gamma}) - \sigma_0^H(\dot{\gamma}) \right) - \left(1 + \frac{5}{2}\phi(1+\phi) + 2.7\phi^2 \right)}{\overline{W_4^{vorticity}}(\dot{\gamma})}. \quad (3.18)$$

where the higher order coefficient for four-fold symmetry is defined by the microstructure measured for the shear thickening condition at $\dot{\gamma} = 1258 \text{ s}^{-1}$. The coefficient is therefore $C_4^{\sigma,H} = 4.6$ (also reported in Table 3). Analogous to the expression given in Equation 3.17, for all conditions the higher order hydrodynamic stress contribution is calculated

by:

$$\frac{\sigma_4^H(\dot{\gamma})}{2\eta_f\dot{\gamma}} = C_4^{\sigma,H} \left(\overline{W_4^{\text{vorticity}}}(\dot{\gamma}) \right). \quad (3.19)$$

The total stress is then defined as the sum of the stress contributions from the thermodynamic, first order hydrodynamic and higher-order hydrodynamic stresses from four-fold microstructure symmetry defined in Equations 3.15, 3.17 and 3.19 and given here:

$$\sigma^{\text{total}}(\dot{\gamma}) = \sigma^T(\dot{\gamma}) + 2\eta_f\dot{\gamma} \left(1 + \frac{5}{2}\phi(1+\phi) + 2.7\phi^2 \right) + \sigma_0^H(\dot{\gamma}) + \sigma_4^H(\dot{\gamma}). \quad (3.20)$$

Figure 9 shows the final results, which include the four-fold symmetry hydrodynamic microstructure contribution to the stress in comparison to the rheometry measured stress. By including the higher order hydrodynamic stress contribution contained in this structure component we can largely reconcile the stress response in the shear thickening regime. However, the stresses in the shear thinning regime are slightly over-predicted having included an additional hydrodynamic microstructure contribution. Including the four-fold symmetric structure contributions in the stress-optic law for the hydrodynamics semi-quantitatively accounts for the increased dissipation in the shear thickening state.

Finally, Figure 9, right presents the relative viscosity $\left(\eta_r = \frac{\eta(T)}{\eta_f(T)} \right)$ as a function of Pe as defined from rheometry measurements and the stress-SANS rule. For which the zero shear viscosity $(\eta_{0,r} = 25.4)$ and the high frequency viscosity $(\eta'_{\infty,r} = 5.90)$ are defined according to theory for a hard-sphere suspension having an effective volume fraction of $\phi_{\text{eff}} = 0.465$. The significant decrease in thermodynamic contribution to the viscosity is expected given the relatively small thermodynamic stress response measured at high Pe , shown in Figure 9. The hydrodynamic stress response including the first- and fourth-order contributions tend toward the known limit of $\eta'_{\infty,r} = 5.90$ at low shear rates as expected given that for $Pe > 0$ the hydrodynamic viscosity should be greater than the high frequency viscosity (Russel *et al.* (2013)). In addition, as the thermodynamic viscosity contribution decreases with increasing Pe while the hydrodynamic contributions increase. These experimental results are qualitatively consistent with those Stokesian Dynamics simulation results reported by Banchio & Brady (2003). Importantly, including contributions from fourth-order terms in the hydrodynamic contribution to the shear stress reconciles in part the quantitative discrepancies observed in the shear thickening regime.

3.2.3. Stress-SANS rule: Hydrodynamic normal stresses

In addition to the shear stresses, the expressions in Equations 3.3, 3.4, 3.6 and 3.7 also predict the first and second normal stress differences (N_1 and N_2). According to Equation 3.6 only fourth order microstructure symmetries $B_{4,1}^+$ and $B_{4,3}^+$ contribute to the hydrodynamic first normal stress. The thermodynamic normal stress is positive for suspensions and so, the measurement of a large negative first normal stress difference in the shear thickened state as shown in Figure 1 necessitates that there are significant fourth order symmetries in the microstructure. The microstructural symmetry is not independently isolated but appears in the term $\overline{W_{21}^{\text{vorticity}}}(\dot{\gamma})$, which also includes the second order term $B_{4,1}^+$. Although we cannot isolate these fourth order symmetries independently, we know they exist as the first normal stress difference becomes large and negative, indicating a significant hydrodynamic contribution. Therefore, the first normal stress due to hydrodynamic interactions is given in Eq. 3.6 and is proportional to those changes measured by $\overline{W_{21}^{\text{vorticity}}}(\dot{\gamma})$. Therefore the coefficient for the first normal stress

difference is:

$$C^{N1,H} = \frac{N_{1,r}(\dot{\gamma})}{2\eta_f \dot{\gamma} \overline{W_{21}^{vorticity}(\dot{\gamma})}}, \quad (3.21)$$

and defined for the microstructure condition measured at the $\dot{\gamma} = 627 \text{ s}^{-1}$ shear rate condition. The coefficient for the first normal stress is given in Table 3 ($C^{N1,H} = -5.2$). The coefficient is used to predict the first normal stress for all other conditions using the $\overline{W_{21}^{vorticity}(\dot{\gamma})}$ microstructure measured during a flow-SANS experiment and the expression given here:

$$\frac{N_1^H(\dot{\gamma})}{2\eta_f \dot{\gamma}} = C^{N1,H} \left(\overline{W_{21}^{vorticity}(\dot{\gamma})} \right). \quad (3.22)$$

Figure 10 shows a comparison between the normal stress measured during a rheometry experiment and the stress predicted using the stress-SANS rule defined in Equation 3.22. As the normal stress difference is normalized upon loading a sample, the first normal stress should be exactly 0 Pa for quiescent conditions. Stokesian Dynamics simulations predict the hydrodynamic contribution to the first normal stress to be increasingly negative and in the limit of large Pe increase as Pe^{-1} as the suspension shear thickens (Foss & Brady (2000)). Indeed, the largest normal stress effect measured for these particular rheometry measurements is the large negative values for the normal stress at high shear rates in the shear thickening regime. The hydrodynamic contribution to the normal stress should always be negative, as observed for these shear rates using the stress-SANS rule.

According to Stokesian dynamic simulations by Banchio & Brady (2003) and Foss & Brady (2000) the thermodynamic contribution to N_1 decreases with increasing Pe for $Pe > 1$, therefore it is not surprising the excellent agreement observed between the hydrodynamic contribution to the first normal stress difference and the normal stress measured during a rheometry experiment at high shear rates. In a rheometry measurement the shear and normal stresses are measurements made simultaneously during steady shear but are independent from one another. As has been discussed in previous work by Kalman (2010), the remarkable agreement observed in Figure 10 also provides confidence in the SANS 1-2 shear flow measurements that the $\overline{B_{2,1}^+}$ microstructure term is properly measured, isolated and analyzed using $\overline{W_{21}^{vorticity}(\dot{\gamma})}$. This term accurately predicts the thermodynamic contribution to the shear stress and the hydrodynamic contribution to the first normal stress difference (defined in Equations 3.2 and 3.6).

3.2.4. Stress-SANS rule: Thermodynamic normal stresses

The thermodynamic contribution to the first normal stress is defined by Equations 3.3 where only the $B_{2,0}^+$ and $B_{2,2}^+$ microstructure terms are required to define N_1 . Given the spherical harmonic expansion in reciprocal space the $B_{2,2}^+$ and $B_{4,2}^+$ microstructure terms define the $\overline{W_2^{gradient}(\dot{\gamma})}$ (Equation 3.11) measured in the 1-3 plane during a rheo-SANS experiment. The coefficient for the first normal stress difference is defined for the lowest shear rate for which we expect the largest contribution to the first normal stress difference from thermodynamic stresses where:

$$C^{N1,T} = \frac{N_{1,r}(\dot{\gamma}) - N_1^H(\dot{\gamma})}{\overline{W_2^{gradient}(\dot{\gamma})}}. \quad (3.23)$$

The thermodynamic coefficient for the first normal stress is defined for the microstructure condition measured at the $\dot{\gamma} = 12 \text{ s}^{-1}$ condition from which we take the difference between the measured N_1 from a rheometry experiment and the hydrodynamic stress contribu-

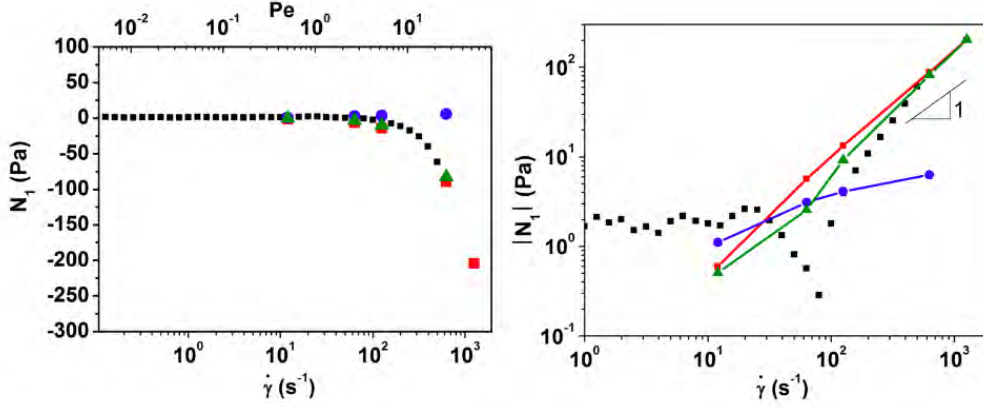


FIGURE 10. N_1 stress as a function of $\dot{\gamma}$ and Pe for steady shear rheometry measurements (\blacksquare) and defined by the stress-SANS rule for the hydrodynamic contribution (\bullet), thermodynamic contribution (\blacklozenge) and the total (\blacktriangle). Also reported in Table 4. The inset shows the absolute value of the first normal stress and corresponding hydrodynamic, thermodynamic and total stress contributions defined by stress-SANS rules.

Pe	N_1^H (Pa)	N_1^T (Pa)	N_1 (Pa) <i>et al.</i>
0.50	-0.60	1.1	0.50
2.63	-5.70	3.12	-2.58
5.23	-13.4	4.13	-9.27
26.22	-88.4	6.33	-82.0
52.6	-204		

TABLE 4. Summary of first normal stress contributions using the stress-SANS rule

tion predicted by Equation 3.22. The coefficient for the first normal stress is given in Table 3 ($C^{N1,T} = 18$ Pa). Not surprisingly, this coefficient is close in value to $C^{\sigma,T} = 22$ used to predict the thermodynamic contribution to the shear stresses. The coefficient is used to predict the first normal stress for all other conditions using the $\overline{W_2^{gradient}(\dot{\gamma})}$ microstructure measured during a flow-SANS experiment and the expression given here:

$$N_1^T(\dot{\gamma}) = C^{N1,T} \left(\overline{W_2^{gradient}(\dot{\gamma})} \right). \quad (3.24)$$

Figure 10 and Table 4 report those predictions for the thermodynamic contribution to the first normal stress according to Equation 3.24 and the sum of the thermodynamic and hydrodynamic normal stresses. Notice, the thermodynamic and hydrodynamic normal stress contributions are opposite in sign. This is in good qualitative agreement with theory using the Smoluchowski equation for a pair of Brownian hard-sphere particles having hydrodynamic interactions as reported by Bergenholtz *et al.* (2002). Figure 10 demonstrates that including the thermodynamic contribution to the first normal stress difference improves the quantitative agreement with measurements of N_1 from rheometry experiments. In addition, Table 4 shows the total first normal stress difference switches in sign from a slightly positive value at $Pe = 0.50$ to an increasingly negative response for $Pe > 1$ also in agreement with Bergenholtz *et al.* (2002).

The coefficients used for the stress-SANS rules for the shear and normal stresses are of the same order of magnitude as those reported by previous works using similar stress-

SANS rules for colloidal suspensions (Kalman (2010); Maranzano & Wagner (2002)). The coefficients for the thermodynamic shear ($C^{N1,T} = 22$ Pa) and normal stress ($C^{N1,H} = 18$ Pa) contributions are of similar magnitude, see also Table 3. The coefficient used to define the first-order hydrodynamic contribution to the stress ($C_0^{\sigma,H} = 0.063$) is significantly smaller due to the definition of $\overline{W}_0(\dot{\gamma})$ since these values are an order of magnitude larger than those values for $\overline{W}_2(\dot{\gamma})$, $\overline{W}_4(\dot{\gamma})$ and $\overline{W}_{21}(\dot{\gamma})$. However, the coefficients for the hydrodynamic contribution to the first normal stress ($C^{N1,H} = -5.2$) and the higher-order shear stress ($C_4^{\sigma,H} = 4.6$) are both of the same order of magnitude as each other and opposite in sign, as they should be given the definitions for the shear and first normal stresses in Equations 3.3 - 3.7. At present there are no theoretical or simulation predictions of these coefficients.

The microscopic viewpoint presented in this paper provides both new insights into suspension rheology as well as a means to test theory and simulation at a more fundamental level than simply the macroscopic properties. Terms of fourth order symmetry in the microstructure couple to the hydrodynamic interactions to contribute to the stresses and lead to negative first normal stresses and an increasing shear stress in the shear thickened state. This further illustrates that only a few of the components of the structure needs to be resolved when considering their effect on the macroscopic stress. *Thus, only a small set of microstructure measurements are necessary to critically test simulations and theory.* Significantly, the three projections of the microstructure measured by scattering in this work are shown to be able to predict the steady shear thinning and shear thickening states, which has not been demonstrated by any other experimental methods to date.

4. Conclusions

The microstructure of a concentrated near hard-sphere colloidal dispersion ($\phi_{\text{eff}} = 0.465$) is measured for the first time in all three planes of shear using flow- and rheo-SANS experiments. In all three planes the SANS scattering patterns change with increasing shear, indicative of an evolving, shear-induced microstructure. Most notably are those measurements made in the velocity-velocity gradient plane of shear in which the signature hydrocluster microstructure of colloidal suspensions is captured in agreement with previous experiments by Kalman (2010) and Stokesian Dynamics simulations by Foss & Brady (2000). In addition, SANS scattering results in the velocity-vorticity plane and less so in the velocity gradient-vorticity plane indicate particles preferentially align along the vorticity direction during strong shearing.

The implementation of the stress-SANS rule successfully predicts the shear and first normal stresses of a concentrated colloidal suspension during steady shear flow from SANS measurements. In addition, using the stress-SANS rule the thermodynamic and hydrodynamic contributions to the stress are individually defined during steady shear, where the thermodynamic contribution dictates the shear thinning response of the suspension and the hydrodynamic contribution becomes important as the shear rate increases and is ultimately responsible for shear thickening. These results are in agreement with predictions from Stokesian Dynamics simulations (Banchio & Brady (2003); Foss & Brady (2000)). Here, we find that the leading order contribution to the shear-induced microstructure is sufficient to define the hydrodynamic contribution to the shear stress for shear rates in the shear thinning regime. However, higher-order microstructure contributions (particularly those with four-fold symmetry in the 1-2 plane of shear) are necessary to define the shear thickening response of the colloidal suspension. Earlier derivations showed the possibility that shear-induced structure with these fourth order

symmetries could couple to the hydrodynamic interactions and thereby contribute to the shear stress. Future advances in rheo-SANS and flow-SANS sample environments as well as SANS diffractometers should enable better resolution of the 3-D microstructure across a broader range of shear rates and scattering vectors to better quantify this relationship in the colloidal shear thickened state. Such advances may enable studies of discontinuous shear thickening colloidal dispersions where and dilatancy become evident and the role of other effects, such as interparticle friction may become important (Brown & Jaeger 2009; Seto *et al.* 2013; Mari *et al.* 2014; Cates & Wyart 2014).

The first normal stress difference is also shown to have contributions from the hydrodynamic and thermodynamic interactions. The contribution to the first normal stress difference from hydrodynamic interactions is predominantly negative and arises only from microstructure with four-fold symmetry, whereas the thermodynamic first normal stress contribution is positive, such that with increasing Pe the total stress contribution switches from a slightly positive value to an increasingly negative response in agreement with theory (Bergenholtz *et al.* 2002) and experiment (Cwalina & Wagner 2014; Lee *et al.* 2006). This observation further confirms that the shear thickened state is dominated by hydrodynamic interactions.

The results presented here show that scattering measurements of the steady shear microstructure can be used to predict the stress of a shearing concentrated colloidal suspension using stress-SANS rules and including terms of fourth-order symmetry. Importantly, the spherical harmonic expansion of the flowing microstructure and subsequent projection into planes of observation provide a robust framework for comparing this and related experimental data directly to future simulation results. Insights gained from examination of the contribution of these structure harmonics to the stresses enables focusing on the relatively few symmetries that contribute to the shear rheology. Future work will show how colloidal suspensions respond and shear thicken under dynamic oscillatory shear flow by applying the stress-SANS relationships developed herein to microstructure measurements from SANS experiments performed under large amplitude oscillatory shear.

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6. Appendix: Hydrodynamic Stresses in Real Space:

The complementary expressions for the hydrodynamic stresses expressed as a spherical harmonic expansion in real space is presented here to facilitate the analysis of simulation and direct microscopy measurements of the microstructure. The starting point is the exact expression for the hydrodynamic stresses in the limit of pairwise interactions as given by (Batchelor & Green 1972):

$$\sigma_{ij}^H = \mu(2 + 5\phi(1 + \phi) + 5.4\phi^2) E_{ij} + 5\phi\rho\mu \int_{r \geq 2}^{\infty} \left[\frac{\sigma_{ij}^{Hydro}}{\frac{20}{3}\pi a^3 \mu} - E_{ij} \right] h(\mathbf{r}) d\mathbf{r} \quad (6.1)$$

where the hydrodynamic interactions are given as:

$$\frac{\sigma_{ij}^{Hydro}}{\frac{20}{3}\pi a^3 \mu} - E_{ij} = K(r)E_{ij} + L(r)E_{kl} \left[\frac{r_i r_j I_{jl} + r_j r_k I_{il}}{r^2} - \frac{2}{3} \frac{r_k r_l}{r^2} I_{ij} \right] + M(r)E_{kl} \left[\frac{r_k r_l}{r^2} \left(\frac{r_i r_j}{r^2} - \frac{1}{3} \frac{r_k r_l}{r^2} I_{ij} \right) \right] \quad (6.2)$$

The structure can be expanded in a spherical harmonic expansion in spherical harmonics in a manner complementary to Eq. 3.1:

$$h(\mathbf{r}) = 2B_{0,0}^+(r)Y_{0,0} + 2B_{2,0}^+(r)Y_{2,0} + B_{2,1}^+(r)(Y_{2,-1} - Y_{2,1}) + B_{2,2}^+(r)(Y_{2,2} + Y_{2,-2}) + 2B_{4,0}^+(r)Y_{4,0} + B_{4,1}^+(r)(Y_{4,-1} - Y_{4,1}) + B_{4,2}^+(r)(Y_{4,2} + Y_{4,-2}) + B_{4,3}^+(r)(Y_{4,-3} - Y_{4,3}) + B_{4,4}^+(r)(Y_{4,4} + Y_{4,-4}) \dots l \geq 6 \quad (6.3)$$

Note that terms odd in the l index do not appear by symmetry and that terms of $l \geq 6$ are not important for the calculation of the stress as the hydrodynamic stress has only terms up to fourth order symmetry.

Inserting this expansion into the stress expression and integrating over the angles yields the following terms for the stress components:

$$\frac{\sigma^H}{\mu \dot{\gamma}} = (2 + 5\phi(1 + \phi) + 5.4\phi^2) + \phi^2 \frac{15}{4\pi} \int_{r \geq 2}^{\infty} \left[K(r)4\sqrt{\pi}B_{0,0}^+(r) + L(r) \left(\frac{8\sqrt{\pi}}{3}B_{0,0}^+(r) - \frac{4}{3}\sqrt{\frac{\pi}{5}}B_{2,0}^+(r) \right) + M(r) \left(\frac{4\sqrt{\pi}}{15}B_{0,0}^+(r) + \frac{4}{21}\sqrt{\frac{\pi}{5}}B_{2,0}^+(r) - \frac{16\sqrt{\pi}}{105}B_{4,0}^+(r) + \frac{4}{21}\sqrt{\frac{2\pi}{5}}B_{4,2}^+(r) \right) \right] r^2 dr \quad (6.4)$$

$$\frac{N_1^H}{\mu \dot{\gamma}} = \phi^2 \frac{15}{4\pi} \int_{r \geq 2}^{\infty} \left[M(r) \left(-\frac{4}{3}\sqrt{\frac{\pi}{5}}B_{4,1}^+(r) + \frac{4}{3}\sqrt{\frac{\pi}{35}}B_{4,3}^+(r) \right) \right] r^2 dr \quad (6.5)$$

$$\frac{N_2^H}{\mu \dot{\gamma}} = \phi^2 \frac{15}{4\pi} \int_{r \geq 2}^{\infty} \left[L(r)4\sqrt{\frac{2\pi}{15}}B_{2,1}^+(r) + M(r) \left(\frac{8}{7}\sqrt{\frac{2\pi}{15}}B_{2,1}^+(r) + \frac{4\sqrt{5\pi}}{21}B_{4,1}^+(r) + \frac{4}{3}\sqrt{\frac{\pi}{35}}B_{4,3}^+(r) \right) \right] r^2 dr \quad (6.6)$$

These equations can be directly compared to those given in reciprocal space (Eqs. 3.5, 3.6, & 3.7) and inspection shows that the same structural symmetries appear in each rheological function. This must be true by the orthogonality properties of spherical harmonics and the symmetry between real and reciprocal space, which is evident from the definitions:

$$h(\mathbf{k}) = S(\mathbf{k}) - 1 = \rho \int h(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \quad (6.7)$$

$$h(\mathbf{r}) = g(\mathbf{r}) - 1 = \frac{1}{\rho(2\pi)^3} \int h(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{k} \quad (6.8)$$

and the Rayleigh expansion:

$$\exp(-i\mathbf{k} \cdot \mathbf{r}) = \sum_{l,m} (-i)^l j_l(kr) Y_{l,m}(\Omega_k) * Y_{l,m}(\Omega_r) \quad (6.9)$$

where j_l is the spherical Bessel's function of l^{th} order. Therefore, the coefficients are related as:

$$B_{l,m}^+(r) = \frac{(-i)^{l2}}{3\pi\phi} \int j_l(kr) B_{l,m}^+(k) k^2 dk \quad (6.10)$$

and:

$$B_{l,m}^+(k) = \frac{(i)^{l\phi}}{3} \int j_l(kr) B_{l,m}^+(r) r^2 dr \quad (6.11)$$

This result provides a method to compare the structural coefficients of the spherical harmonic expansion in reciprocal space to those in real space.

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