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Role of Particle Orientational Order During Shear-thickening in Suspensions of Colloidal Rods

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Rheology of dense anisotropic colloidal suspensions often exhibits unsteady flow at a constant imposed shear stress/shear-rate. Using simultaneous high resolution confocal microscopy and rheology, we find that the temporal behavior arises due to a strong coupling between shear flow and particle orientation. At smaller applied stresses, the orientation of rods fluctuates around the flow direction. A transition to an intermittent disordered state is observed at higher stresses when the angle between the flow and the rod orientation reaches a critical value. This disordered state is associated with transient drop in shear rate and an increase in viscosity. Simultaneous visualization of boundary stresses and orientation shows that the disordered regions lead to heterogeneous stresses and positive normal forces at the boundary indicating the formation of systems spanning disordered particle contact networks.

When subjected to shear stresses beyond a material-dependent threshold value, most dense suspensions shear-thicken - their viscosity η increases with the stress σ [1–3]. Recent studies suggest that while the hydro-cluster mechanism [4, 5] can account for a modest increase in η , a larger increase stems from particles forming a stress-induced frictional contact network [6–13]. These studies are limited to mainly spherical or compact particles, despite the fact that altering the particle shape greatly affects rheological response [14–16]. It has been shown that an increase in the particle aspect ratio, α , reduces the volume fraction ($\phi = \text{total particle volume/total system volume}$) at which shear-thickening sets in [16, 17]. Previous small angle neutron scattering measurements of suspensions of elongated particles in the shear thickening regime indicated that particle flow-alignment was retained in the shear-thickened state [15]. Since scattering approaches are inherently ensemble-averaged measurements, these do not capture changes in local orientational order. These concerns notwithstanding, the strong coupling between flow and particle shape anisotropy is known to result in rich time-dependent flows [14, 18, 19]. A complex temporal behavior has in fact been observed during shear thickening in both Brownian and non-Brownian suspensions of spherical [6, 13] or compact particles [20, 21] highlighting the importance of investigating temporal dynamics of orientable particles during shear-thickening.

In this Letter, we investigate the mechanism of shear thickening in colloidal rod suspensions by direct imaging of particle orientational order under shear and spatially-resolved boundary stress measurements [22]. Our key results are that shear-thickening in these systems is primarily an outcome of the rich interplay between fluctuations in particle orientational order and the formation of gap spanning contact networks.

We synthesized colloidal silica rods following the pro-

cedure first developed by Kuijk et al. [23]. We obtained the rods having a typical diameter $d = 400\text{nm}$ and length of $l = 4\mu\text{m}$ ($\alpha \equiv l/d \sim 10$) (SI, section S1). The particles were dispersed in a glycerol-water mixture (85% glycerol by vol.) at different ϕ s and η was measured as a function of σ in a cone-plate geometry on a stress controlled rheometer (AntonPaar, Austria). We varied ϕ from 0.19 to 0.45 where the suspensions form a nematic phase in equilibrium and the flow response is typical of shear-thickening particulate suspensions (Fig. 1A) [12]. On increasing σ , the suspensions shear-thin and reach a viscosity plateau, $\eta_N(\phi)$. This plateau persists up to an onset stress σ_c beyond which the suspensions shear-thicken. Like in suspensions of spherical particles [11, 12], and in a recent study on shear jamming in colloidal rods [25], we also found σ_c to be approximately independent of volume fraction ϕ (Fig. 1A). At even larger stresses, η almost plateaus to a constant value that corresponds to the viscosity of the shear-thickened state, $\eta_{ST}(\phi)$. In the shear-thickening regime, $\eta \propto \sigma^\beta$, where the shear-thickening exponent β is positive and steadily grows with ϕ but remains below unity (continuous shear-thickening) for $0.19 \leq \phi < 0.38$. However, for $\phi \geq 0.38$, $\beta = 1$ i.e. the suspension viscosity increases at a fixed shear-rate, $\dot{\gamma}$, which is a characteristic of discontinuous shear-thickening (DST). Remarkably, our suspensions show shear-thickening at particle loadings that are substantially smaller than those required for isotropic particles ($\beta > 0$ even for $\phi = 0.19$). This dependence on β with ϕ is consistent with earlier reports on similar system [25], which find that the larger effective excluded volume of anisotropic particles [26–28] in comparison to isotropic ones aid in achieving shear-thickening even at low volume fractions. The behavior of $N_1(\sigma)$ at various ϕ s is similar to that seen in [12] (Fig. 1B). For $\phi < 0.34$, N_1 hovers around zero for small applied stresses and turns negative beyond σ_c indicating dominating hydrodynamic

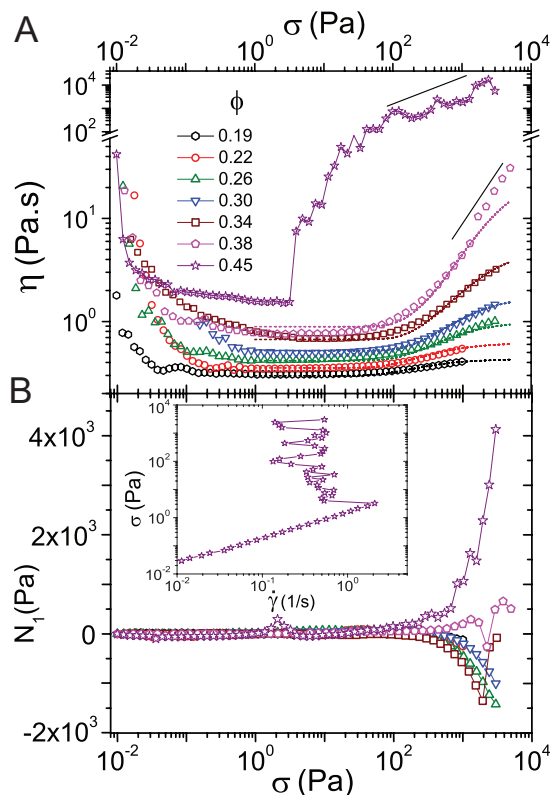


FIG. 1: (A) Flow curves and (B) first Normal stress difference N_1 at various ϕ s, for colloidal rods of aspect ratio (α) $\equiv l/d \sim 10$. The dotted lines in A are fit to $\eta(\sigma, \phi) = (1 - \phi/\phi_c(\sigma))^{-2}$, where $\phi_c(\sigma) = f\phi_m + (1 - f)\phi_o$, f is the fraction of frictional contacts, ϕ_o and ϕ_m corresponds to viscosity divergences for purely frictionless and frictional contacts, respectively. Inset (B) shows σ vs $\dot{\gamma}$ at $\phi = 0.45$.

forces. However, at $\phi = 0.34$, N_1 first becomes increasingly negative above σ_c , but abruptly changes sign and becomes more positive for $\sigma \geq 2000$ Pa, due to dominating contact forces (Fig. 1B, open squares). On increasing ϕ , N_1 becomes positive beyond σ_c (Fig. 1B, open pentagons and open stars). While the observed behaviour of N_1 with increasing ϕ is similar to suspensions of spheres, we note that the algebraic sign of N_1 is not always directly indicative of the presence of frictional contact networks. Experiments on non-Brownian particles, where frictional interactions are known to be dominant [29], have observed a negative N_1 during shear-thickening [30, 31].

Fluids that show DST often have an S-shaped flow curve [32] with an intermediate region where $d\sigma/d\dot{\gamma} < 0$ (Figure 1B inset). Since homogeneous flow is impossible in these regions, the system behaves heterogeneously, through the formation of shear bands. In many complex fluids, the canonical example being shear-thinning wormlike micellar gels [33–35], the bands themselves can become unstable and can exhibit *rheochaos* - time-dependent flows at fixed σ or $\dot{\gamma}$ at Reynold's number $Re \ll 1$ [36]. In dense Brownian as well as non-

Brownian suspensions the flow is unsteady [6, 13, 37] and exhibits rheochaos in the DST regime [20, 21, 38, 39]. Such complex flow response is not captured by the mean field WC model. Motivated by these findings, we set out to ascertain if bulk flow in the DST regime (stars in Fig. 1A) was unstable.

Accordingly, we carried out shear rate relaxation measurements at various imposed stresses. Figure 2A shows forward (hollow symbols) and reverse (solid symbols) flow curves for $\phi = 0.36 < \phi_m$ (circles), $\phi = 0.4 \approx \phi_m$ (squares) and $\phi = 0.42 > \phi_m$ (triangles), respectively. Figure 2B summarizes the complex dynamics observed for few representative stresses. When $\sigma \approx 400$ Pa, where the flow curve is single-valued, $\dot{\gamma}$ is approximately constant 2B (Panel 1). For regions of the flow curve where the stress is multi-valued (Panels 2-5), $\dot{\gamma}$ shows rich temporal dynamics. At $\sigma = 2100$ Pa, $\dot{\gamma}$ first increases and then saturates before rapidly dropping close to its original value. This behaviour is cyclic. On increasing σ (Panels 3 - 5), not only does the cycle duration increase substantially, we also see small amplitude oscillations preceding the drop in $\dot{\gamma}$. As the drop in $\dot{\gamma}$ is approached, the amplitude of the oscillations grows, and their frequency increases. Most remarkably, oscillations in $\dot{\gamma}$ are also well-correlated with those in N_1 (Fig. 2C). The time period of the oscillations (≈ 25 s) is much larger than the rotational time period of the cone (≈ 0.5 s) and inertial time period (≈ 0.2 s), indicating these are not an outcome of instrument imperfections [20]. At even larger σ s (Panel 6 in Fig. 2B), where the flow curve is once again single-valued, the time-dependence entirely vanishes.

To gain microscopic insights into these observations, we tracked the dynamics of rods using a confocal-rheometer [40, 41]. The sample was doped with a small amount of fluorescently labeled rods [42] for determining the local orientation. Under shear, we estimated the angle $\bar{\theta}$ between the average orientation of rods, \hat{n} , in the field of view with respect to the flow direction \mathbf{v} , by calculating the distribution of local orientation in each image (see SI for details).

Owing to the very high particle velocities in the ST regime for the $\phi = 0.36$ sample, particles could not be tracked. Thus we increased ϕ to 0.4, where $\sigma_c \approx 10$ Pa and the $\dot{\gamma}$ values during DST are substantially smaller (Fig. 2A). We also observed hysteresis during the forward and reverse stress sweeps (Fig. 2A, squares). For $\sigma = 30$ Pa ($> \sigma_c$), we observed stable oscillations in $\bar{\theta}$ with a clear correlation between $\bar{\theta}$ and $\dot{\gamma}$, where both quantities fluctuate between two limiting values, as shown in Fig. 3A (SI, Movie S1). Surprisingly, when $\bar{\theta}$ is positive, i.e. when average orientation of the rods is towards the free surface, $\dot{\gamma}$ is higher. A gradual decrease in $\bar{\theta}$ towards negative values (rod orientation towards $-\nabla \times \mathbf{v}$) is accompanied by a decreases in $\dot{\gamma}$. The correlation between the orientation, which is determined from a small region of the sample, and the average rheological response suggests that the orientation oscillations occur coherently throughout the sample. At $\sigma = 100$ Pa, along with oscil-

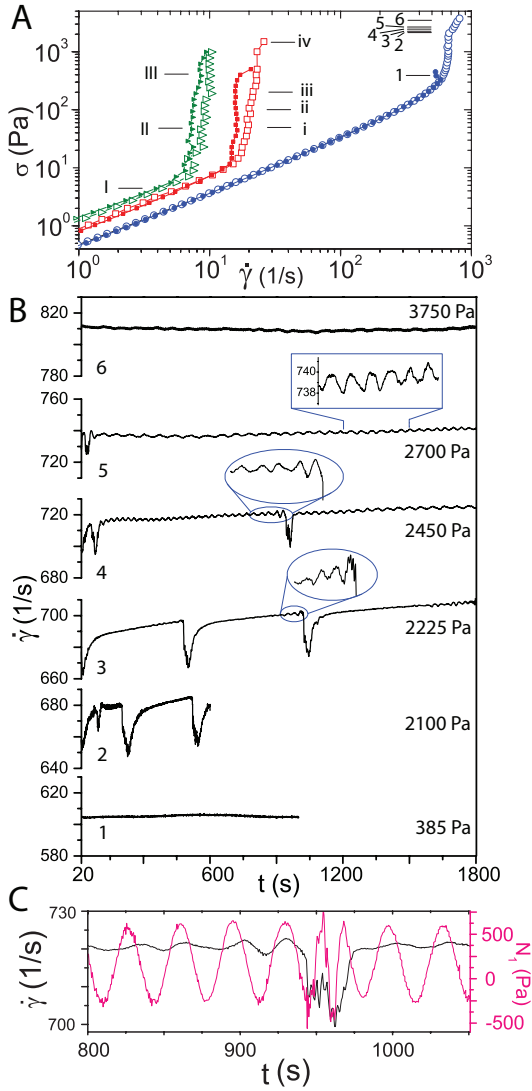


FIG. 2: (A) Flow curves for $\phi = 0.36$ (blue circles), $\phi = 0.4$ (red squares) and $\phi = 0.42$ (green triangles) samples. Forward and reverse stress sweeps are shown by hollow and solid symbols, respectively. The stress values at which shear-rate relaxation measurements were carried out are indicated on the flow curves. (B) Shear rate relaxation i.e. time-dependence of shear-rate, $\dot{\gamma}$, at various σ s for $\phi = 0.36$. The panel numbers in (B) correspond to those indicated in flow curve ((blue circles) in (A)). (C) $\dot{\gamma}$ (black line) and N_1 (dark pink line) for $\sigma = 2450$ Pa. The data corresponds to the highlighted region in Panel 3 in Fig. 2B.

lations, we observed intermittent disordered regions represented by an instantaneous jump in $\bar{\theta}$ (Fig. 3B). A representative snapshot corresponding to this state (Fig. 3F) shows a substantial number of rods oriented along the ∇v direction (seen as circles since the rod orientation is perpendicular to imaging plane) and many rods also tilted towards the vorticity direction. The orientation changes occur when an order-disorder transition either takes place in the field-of-view or a disordered re-

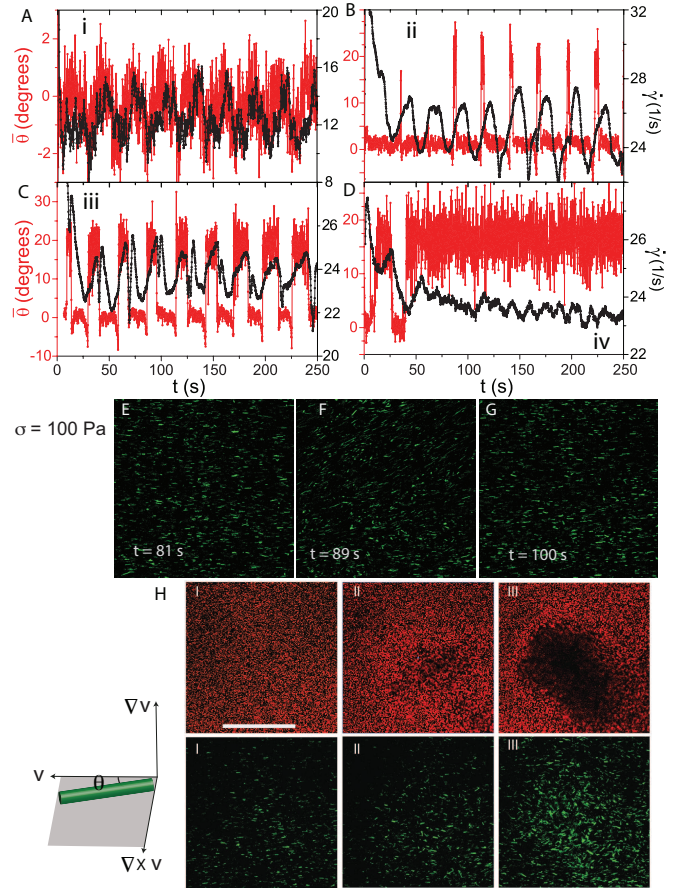


FIG. 3: (A-D) Time-dependence of $\dot{\gamma}$ (black symbols) and the angle $\bar{\theta}$ between S and \mathbf{v} (red symbols) at various σ s for $\phi = 0.4$. (A) $\sigma = 30$ Pa. (B) $\sigma = 100$ Pa. (C) $\sigma = 200$ Pa. (D) $\sigma = 1100$ Pa. (A), (B) (C) and (D) correspond to points labeled (i), (ii), (iii) and (iv) on the flow curve, respectively (Fig. 2A) (red circles). Snapshots of tracer rods at $\sigma = 100$ Pa (Fig. 3B) at times when $\bar{\theta}$ is (E) small (and negative), (F) large positive at the beginning of disordered region, (G) small (and positive) when the order is restored again. (H) Simultaneous boundary stress microscopy and confocal imaging of rod orientations during flow curve measurements at $\phi = 0.42$. The top panels are images of fluorescent colloids attached to a elastic substrate (bottom plate) and correspond to different stress values along the flow curve for $\phi = 0.42$ (Fig. 2A, green triangles). Bottom panels are the corresponding images of tracer rods. (I) $\sigma = 5$ Pa, (II) $\sigma = 50$ Pa, and (III) $\sigma = 400$ Pa. Black regions in (H) appears when the elastic substrate is pushed down due to large normal stresses which results in these regions going out-of-focus. Scale bar: $70 \mu\text{m}$. The inset shows a sketch of coordinate system in 3D.

gion is advected into the field of view. At $\sigma = 200$ Pa, the oscillations in $\bar{\theta}$ are more pronounced and occur for longer duration. Remarkably, this abrupt transition occurs when $\bar{\theta}$ reaches a critical negative angle (Fig. 3C, SI, Movie S2). Also apparent in Movie S2, there is a coupling between the rod orientation and non-affine flow, with the rod orientation indicating the local flow direction. For $\sigma = 1100$ Pa, where the flow curve is almost

single-valued, the amplitude of oscillations in $\dot{\gamma}$ are considerably smaller, with the dynamics in $\dot{\gamma}$ and $\bar{\theta}$ appearing noisy (Fig. 3D, SI, Movie S3). However, before reaching this steady state, $\bar{\theta}$ first dropped to a negative value and then jumped to a large positive value similar to $\sigma = 200$ Pa. Note that in the disordered state, the determination of $\bar{\theta}$ is not straight forward, but the algorithm produces a robust positive value (Fig. 3B-D, and SI).

There are a number of surprising aspects to the behavior described above. The existence of a positive angle at low ϕ (SI, Fig. S5 and Movie S4) represents an asymmetry that is not present in simple shear, where there would be no preference for positive vs negative deflection. However, the shear geometry here has a free surface and curved flow lines even for affine flow. It has been observed that anisotropic particles under shear are often tilted in the positive $\dot{\gamma}$ direction as a result of shear induced interparticle interactions [43–45] and some similar mechanism may be at play here. At higher concentrations the tilt is suppressed and replaced by collective oscillations about $\theta = 0$, that are accompanied by oscillations in $\dot{\gamma}$ and \hat{n} (Fig. 3A). As the angle varies from zero in either direction, the degree of alignment reduces and when orientations exceed a critical negative $\bar{\theta}$ it results in unstable flow and the formation of disordered particle clusters above σ_c (Fig. 3). In our case we do not observe unstable state if the angle is positive possibly due to presence of free surface. Similar behavior is observed in a parallel plate geometry for $\phi = 0.39$ (DST regime) and also for different background solvent viscosity, suggesting that these findings are intrinsic to the suspension rheology and do not depend on rheometer inertial time as observed by Hermes et al. (SI and Figs. S6-S10) [20].

To determine if particle orientational disorder in the DST regime results in a positive N_1 and locally higher shear stresses, we employed a technique known as Boundary Stress Microscopy (BSM), which provides spatio-temporal information of normal and shear forces [13, 46, 47]. Here, we covalently attached fluorescent microspheres to a polydimethylsiloxane (PDMS) layer of known elasticity bonded to a glass coverslip that serves as bottom boundary of the sample in the confocal rheometer (see SI). The out-of-plane motion of the beads, i.e. along ∇v , provides information about local normal stresses. Regions of high N_1 generate out-of-plane motion of the microspheres, resulting in dark patches in the images as particles move out of the confocal imaging plane. During ST in suspensions of colloidal spheres, stress heterogeneities at the boundary indicate the existence of transient gap spanning particle contact networks [13]. The top and bottom panels in Fig. 3H show images of the spheres on bottom surface and tracer rods just above this surface, respectively, for various applied σ s labeled (I)-

(III) on the flow curve for $\phi = 0.42$ (triangles in Fig. 2A). When $\sigma < \sigma_c$, the rods are flow aligned and stress heterogeneities are absent (all beads appear in focus in panel labeled (I)). For $\sigma = 50$ Pa $> \sigma_c$, the beads intermittently appear slightly out-of-focus and the rod orientation above this region appears slightly disordered (panel (II) in Fig. 3H). At even larger stresses, the beads move completely out of the imaging plane, as the orientationally disordered region pushes down on the elastic substrate (panel (III) of Fig. 3H, $\sigma = 400$ Pa, SI, Movie S5). As can be seen in the movie, these disordered regions are associated with a local increase in the flow velocity. With increasing σ , we observed a concomitant increase in the frequency of these regions of large local displacement. The out of focus movement of beads is an indication of positive normal forces (F_N) and in cone-plate geometry $N_1 = F_N/(\text{plate area})$. An increased frequency and amplitude of heterogeneous stresses indicate that N_1 increases with applied stress and is in good agreement with the increase in N_1 observed in flow curve measurements in Fig. 1B. Further, the combination of confocal-rheology and BS measurements clearly show that the coupling of particle orientation to shear and normal stresses plays a prominent role in the ST of anisotropic particles and stands in contrast to findings from previous Rheo-SANS measurements [15].

The collective picture which emerges from our study is that shear-thickening even in suspensions of anisotropic particles has its origins in particles forming a disordered contact network as evident in particle imaging and boundary stress measurements. It seems surprising at first that rods of large aspect ratio shear thicken at relatively low volume fractions than spheres despite the fact that these can pack more densely in a shear aligned state. However it is known that anisotropic particles can form more contacts in a disordered state, resulting in jamming at a volume fraction that decreases with increasing aspect ratio [27]. The coupled oscillations in average orientation, suspension viscosity and normal stress that we observe are similar to those observed in other rod suspensions [14, 18, 19]. In general, the degree of orientational order is coupled with the flow alignment, and we speculate that as the magnitude of $\bar{\theta}$ becomes large, the degree of order decreases, resulting in an increase in high-stress particle collisions, producing frictional interactions and an instability to the fully disordered, shear jammed state.

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[1] H. A. Barnes, *J. Rheol.* 33:329 (1989).

[2] N. J. Wagner and J. F. Brady, *Phys. Today* 62(10), 27

- (2009).
- [3] E. Brown and H. M. Jaeger, *Rep. Prog. Phys.* 77(4), 046602 (2014).
- [4] D. R. Foss and J. F. Brady, *J. Fluid Mech.* 407,167 (2000).
- [5] X. Cheng, J. H. McCoy, J. N. Israelachvili and I. Cohen, *Science* 333, 1276 (2011).
- [6] D. Lootens, H. van Damme, Y. Hemar and P. Hebraud, *Phys. Rev. Lett.* 95, 268302 (2005).
- [7] N. Fernandez et al., *Phys. Rev. Lett.* 111(10), 108301 (2013).
- [8] R. Seto, R. Mari, J. F. Morris and M. M. Denn, *Phys. Rev. Lett.* 111(21), 218301 (2013).
- [9] M. Wyart and M. E. Cates, *Phys. Rev. Lett.* 112(9), 098302 (2014).
- [10] N. Y. Lin et al., *Phys. Rev. Lett.* 115(22), 228304 (2015).
- [11] B. M. Guy, M. Hermes and W. C. K. Poon, *Phys. Rev. Lett.* 115, 088304 (2015) .
- [12] J. Royer, D. L. Blair and S. Hudson, *Phys. Rev. Lett.* 116, 188301 (2016).
- [13] V. Rathee, D. L. Blair and J. S. Urbach, *Proc. Natl. Acad. Sci. USA* 114, 8740 (2017).
- [14] P. M. Lettinga, Z. Dogic, H. Wang, and J. Vermant. *Langmuir* 21, 8048 (2005).
- [15] R. G. Egres and N. J. Wagner, *J. of Rheol.* 49, 719 (2005).
- [16] E. Brown et al., *Phys. Rev. E* 84, 031408 (2011) .
- [17] Y. Ye et al., *ACS Appl. Nano Mater.* 1(6), 2774 (2018).
- [18] V. Faraoni, M. Grosso, S. Crescitelli, and P. L. Maffettone *J. of Rheology* 43, 829 (1999).
- [19] M. Grosso et al., *Phys Rev Lett* 90, 98304 (2003).
- [20] M. Hermes et al., *J. Rheol.* 60:905-916 (2016).
- [21] B. Saint-Michel, T. Gibaud and S. Manneville, *Phys. Rev. X* 8, 031006 (2018).
- [22] Some of the key findings from this study were first presented at the KITP Conference on “Non-linear mechanics and rheology of dense suspensions: Nanoscale structure to macroscopic behavior” held in January 2018 and is available online at http://online.kitp.ucsb.edu/online/suspensions_c18/sood/
- [23] A. Kuijk, A. van Blaaderen and A. Imhof, *J. Am. Chem. Soc.* 133, 2346 (2011).
- [24] See Supplemental Material
- [25] N. M. James, H. Xue, M. Goyal and H. M. Jaeger, *Soft Matter* 15, 3649 (2019).
- [26] L. Onsager, *Ann. of the N. Y. Acad. of Sci* 51(4), 627 (1949).
- [27] A. P. Philipse, *Langmuir* 12, 1127 (1996).
- [28] C. Ferreiro-Cordova and D. S. van Duijneveldt, *J. Chem. Eng. Data* 59, 3055 (2014) and references therein.
- [29] S. Gallier, E. Lemaire, F. Peters and L. Lobry, *J. Fluid Mech.* 757, 514 (2014).
- [30] A. Singh and P. R. Nott, *J. Fluid Mech.* 490, 293 (2003).
- [31] Z. Pan, H. de Cagny, M. Habibi and D. Bonn, *Soft Matter* 13, 3734 (2017).
- [32] Z. Pan, H. de Cagny, B. Weber and D. Bonn *Phys. Rev. E* 92, 032202 (2015).
- [33] R. Bandyopadhyay, G. Basappa and A. K. Sood (2000) *Phys. Rev. Lett.* 84, 2022-2026 (2000).
- [34] R. Ganapathy and A. K. Sood, *Phys. Rev. Lett.* 96, 108301 (2006).
- [35] R. Ganapathy, A. K. Sood, *J. Non-Newton. Fluid* 149, 78-86 (2008).
- [36] P. D. Olmsted, *Rheol. Acta* 47,283 (2008).
- [37] V. Rathee, D. L. Blair, J. S. Urbach, *J. of Rheology* 64, 299 (2020).
- [38] M. Grob, A. Zippelius and C. Heussinger, *Phys. Rev. E* 93, 030901 (2016).
- [39] R. N. Chacko, R. Mari, M .E. Cates and S. M. Fielding, *Phys. Rev. Lett.* 121, 108003 (2018).
- [40] S. Gokhale et al. *Proc. Natl. Acad. Sci. USA* 109, 20314 (2012).
- [41] S. K. Dutta, A. Mbi, R. C. Arevalo, and D. L. Blair, *Rev. of Sci. Inst.* 84, 063702 (2013).
- [42] A. Kuijk et al., *Particle and Particle Systems Characterization* 31, 706 (2014).
- [43] A. Borzsonyi et al., *Phys. Rev. Lett.* 108, 228302 (2012).
- [44] T. Nath and C. Heussinger, *arXiv:1812.00757v1* (2019).
- [45] R. Mari, *J. of Rheology* 64, 239 (2020).
- [46] R. C. Arevalo, P. Kumar, J. S. Urbach, D. L. Blair, *PLoS One* 10:e011802 (2015).
- [47] N. Park, V. Rathee, D. L. Blair, J. C. Conrad, *Phys. Rev. Lett.* 122, 228003 (2019).