Supplementary Information

Local Elasticity in Nonlinear Rheology of Interacting Colloidal Glasses Revealed by Neutron Scattering and Rheometry

Zhe Wang,^{1,2,3,*} Takuya Iwashita,⁴ Lionel Porcar,⁵ Yangyang Wang,⁶ Yun Liu,⁷ Luis E. Sánchez-Díaz,³ Bin Wu,³ Guan-Rong Huang,⁸ Takeshi Egami,⁹ and Wei-Ren Chen^{3,+}

¹Department of Engineering Physics, Tsinghua University, Beijing 100084, China

²Key Laboratory of Particle & Radiation Imaging (Tsinghua University), Ministry of Education, Beijing 100084, China

³Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

⁴Department of Electrical and Electronic Engineering, Oita University, Oita 870-1192, Japan

⁵Institut Laue-Langevin, B.P. 156, F-38042 Grenoble CEDEX 9, France

⁶Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

⁷Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-6100, USA

⁸Physics Division, National Center for Theoretical Sciences, Hsinchu 30013, Taiwan

⁹Department of Materials Science and Engineering and Department of Physics and Astronomy, The University of Tennessee, Knoxville, TN 37996-1508, USA

*zwang2017@mail.tsinghua.edu.cn

+chenw@ornl.gov

S1. Samples Preparation and Zeta Potential Measurements

Commercially obtained silica particles (Seahostar KE-W10, Nippon Shokubai Co. Ltd.) were suspended in a mixture of ethylene glycol and glycerol. Because of the deprotonation reaction of hydroxyl groups on its surface, the silica nanoparticle used in our study is negative charged. To bypass the crystallization induced by shear, we used the mixture of silica particles with diameter of 120 nm and 80 nm respectively. The number density ratio of 120 nm particle to 80 nm particle was 4 to 1. The total volume fraction of the silica particles was 0.4 and the mass ratio of the ethylene glycol to glycerol mixture was 2.27 to 1 according to reference (*S1*). By adjusting the proton to deuterium ratio, the scattering length density of the solvent was set to be $5 \times 10^{-6} \text{ cm}^{-2}$ to avoid the possible multiple scattering. This is crucial to the experiment, as demonstrated in Figure S1.



Figure S1. Effect of multiple scattering. Panel (a) gives the two I(Q) of the colloidal suspension in this experiment. Red points denote the data obtained from the 1 - 2 plane (the path length of neutron is 5 mm), black points denote the data obtained from the 1 - 3 plane (the path length of neutron is 1 mm). In this case, the two curves are very close to each other. As seen in panel (a), by carefully choosing the proton to deuterium ratio of the solvent, we can avoid the multiple scattering effect. Panel (b) gives the two I(Q) of a colloidal suspension with fully protonated solvent as used in reference (*S1*). It is seen that the multiple scattering from the 1 - 2 plane is very significant. In this case, multiple scattering signal dominates the measured spectrum at high Q, which makes the quantitative analysis impossible.

The zeta potential measurement was carried out to quantify the long-range electrostatic repulsion among the silica particles. The zeta potential is found to be -30.49 mV and the surface charge density is found to be 3.3×10^{-3} C/m².

S2. Small-Angle Neutron Scattering Experiment and Data Analysis

Small-angle neutron scattering (SANS) measurements were respectively performed at the D22 SANS spectrometer at the ILL and at the NG7 SANS instrument at the NCNR NIST. The

wavelength of the incident neutron beam was chosen to be 8.0 Å, with a wavelength spread $\frac{\Delta\lambda}{\lambda}$ of 10%, to cover values of the scattering wave vector Q ranging from 10^{-3} to 10^{-1} Å⁻¹. The measured intensity I(Q) was corrected for detector background and sensitivity and for the scattering contribution from the empty cell and placed on an absolute scale using a direct beam measurement. All of the SANS measurements at ILL and NCNR were carried out at 20.0 ± 0.1 °C. Both 1 - 2 (*S3*) and 1 - 3 (*S4*) configurations of shear cells were used to investigate the flow structure. The range of shear rate is from 1 to 10^3 s⁻¹.

The coherent scattering intensity $I(\mathbf{Q})$ from SANS measurements on colloidal suspensions can be expressed as:

$$I(\boldsymbol{Q}) = nV^2 \Delta \rho^2 P(\boldsymbol{Q}) S(\boldsymbol{Q}) \tag{S1}$$

where *n* is the particle number density; *V*, the volume of an individual colloidal particle; $\Delta \rho$, the contrast term; *P*(*Q*), the normalized form factor; and *S*(*Q*), the inter-particle structure factor. In this study, the system is composed of two kinds of particles with diameters of 120 nm and 80 nm. The number density ratio between the large particles and small particles is 4:1. With these knowledges, it is able to estimate the SANS intensities contributed from these two kinds of particles by: $I_{\text{large}}/I_{\text{small}} = n_{\text{large}}V_{\text{large}}^2/n_{\text{small}}V_{\text{small}}^2 \approx 45$. It is seen that the SANS intensity is dominated by the contribution from the large particles. Therefore, we can reasonably ignore the contribution from small particles, and obtain the landscape of the structure factor of the large particles by dividing the measured intensity *I*(*Q*) by the form factor of the large particle *P*_{large}(*Q*): $S_{\text{large}}(Q) \propto I(Q)/P_{\text{large}}(Q)$.

In quiescent state, it is also able to find S(Q) by model fitting. For the form factor of the silica particles we used the analytical equations of a spherical particle. The corresponding S(Q) is obtained numerically by solving the Ornstein-Zernike equation with the MPB-RMSA (*S5*) closure for a repulsive Yukawa potential. The values of *K* and *z* were used as inputs in our BD simulation.

For the sample in its quiescent state, the neutron scattering profile is isotropic. The system in this study, however, is apparently anisotropic due to external shear. Consequently, the scattering profile does not only depend on the magnitude of momentum transfer but also its direction. It is understandable that the anisotropy arises from shear-induced angular dependent particle packing reflected by S(Q) rather than the deformation of silica particles.

The framework of describing the flow-induced structural anisotropy on the basis of spherical harmonic expansion has been first proposed Hess (*S6*) and has been commonly used to analyze the microstructural distortion of sheared materials observed by computer simulations and scattering experiments. However it is instructive to indicate a subtle but critical difference between its implementation in trajectory analysis of computational results and that for extracting the structural distortion from scattering experiments: For computational studies the determination of the expansion coefficients, namely the anisotropic pair distribution function (APDF) $g_l^m(r)$ or anisotropic structure factor $S_l^m(Q)$, from the computationally generated 3D trajectory is conveniently facilitated by the orthogonality of the real spherical harmonic basis functions. However, for scattering experiments, the information of 3D distorted structure is projected onto the 2D detector arrays. The orthogonality cannot be directly applied to extract $g_l^m(r)$ since the spherical harmonics no longer form an orthonormal basis set on 1 - 2 and 1 - 3 planes. Therefore additional normalization is required to unbiasedly extract the expansion coefficients.

We have developed the framework for properly analyzing the anisotropy of structure factor from the measured 2D spectra. $S(\mathbf{Q})$ can be expanded in the following expression:

$$S(\boldsymbol{Q}) = \sum_{l,m} S_l^m(Q) Y_l^m(\boldsymbol{\Omega})$$
(S2)

where Ω is solid angle $(d\Omega = sin\theta d\theta d\phi)$, $Q = \sqrt{Q_x^2 + Q_y^2 + Q_z^2}$, and Y_l^m is the spherical harmonic function of degree *l* and order *m*. Each of them characterizes a well-defined symmetry and is referred to as a specific mode hereafter. It is defined as:

$$Y_{l}^{m}(\mathbf{\Omega}) = Y_{l}^{m}(\theta, \phi) = \begin{cases} \sqrt{2}\sqrt{(2l+1)\frac{(l-|m|)!}{(l+|m|)!}}P_{l}^{|m|}(\cos\theta)\sin(|m|\phi) & (m<0) \\ \sqrt{2l+1}P_{l}^{0}(\cos\theta) & (m=0) \\ \sqrt{2}\sqrt{(2l+1)\frac{(l-m)!}{(l+m)!}}P_{l}^{m}(\cos\theta)\cos(m\phi) & (m>0) \end{cases}$$

Where P_l^m are associated Legendre polynomials. Here we list the first few spherical harmonic functions in real form:

$$Y_0^0(\theta, \phi) = 1 \tag{S3}$$

$$Y_1^{-1}(\theta,\phi) = \sqrt{3}sin\theta sin\phi \tag{S4}$$

$$Y_1^0(\theta,\phi) = \sqrt{3}cos\theta \tag{S5}$$

$$Y_1^1(\theta,\phi) = \sqrt{3}sin\theta cos\phi \tag{S6}$$

$$Y_2^{-2}(\theta,\phi) = \frac{\sqrt{15}}{2} \sin^2\theta \sin 2\phi \tag{S7}$$

$$Y_2^{-1}(\theta,\phi) = \sqrt{15} \sin\theta \cos\theta \sin\phi \tag{S8}$$

$$Y_2^0(\theta,\phi) = \frac{\sqrt{5}}{2}(3\cos^2\theta - 1)$$
(S9)

$$Y_2^1(\theta,\phi) = \sqrt{15} \sin\theta \cos\theta \cos\phi \tag{S10}$$

$$Y_2^2(\theta,\phi) = \frac{\sqrt{15}}{2} \sin^2\theta \cos 2\phi \tag{S11}$$

In three-dimensional space the spherical harmonic functions are mutually orthogonal, meaning

$$\int d\Omega Y_l^m(\Omega) Y_{l'}^{m'}(\Omega) = 4\pi \delta_{ll'} \delta_{mm'}$$
(S12)

The spherical harmonic functions have well defined parity, which is expressed as follows:

$$Y_l^m(\theta,\phi) \to Y_l^m(\pi-\theta,\pi+\phi) = (-1)^l Y_l^m(\theta,\phi)$$
(S13)

It is seen that the parity of the harmonic function is determined by *l*.

Within the accessed range of shear rate we found that the contribution from terms with $l = 3, ..., \infty$ to 2D scattering pattern is negligible. Therefore, eq. S2 can be effectively simplified to:

$$S(\boldsymbol{Q}) = \sum_{l=0}^{2} \sum_{m} S_{l}^{m}(Q) Y_{l}^{m}(\boldsymbol{\Omega})$$
(S14)

In the 1 - 2 plane, it is conceivable that $Q_z = 0$, or $\theta = \pi/2$. Therefore, Y_2^{-1} and Y_2^1 , and their coefficients S_2^{-1} and S_2^1 , are 0. In addition, as shown in Figure 2 in the main text, all 2D patterns in the 1 - 2 plane exhibit even parity. It requires that the coefficients of the spherical harmonics

with odd parity should be 0. In this case, it leads to $S_{l=1}^m = 0$. In fact, it is convenient to demonstrate that the modes with l = 1 are 0 when angular average is made.

With above considerations, the general expression for the 1-2 plane is obtained as follows:

$$S(Q_x, Q_y, Q_z = 0) = S_0^0(Q)Y_0^0(\Omega) + S_2^{-2}(Q)Y_2^{-2}(\Omega) + S_2^0(Q)Y_2^0(\Omega) + S_2^2(Q)Y_2^2(\Omega)$$
(S15)

It is important to note that in one specific two-dimensional plane, such as the 2D detector-array plane, the orthogonality among spherical harmonic functions may not hold any more. In this case,

 Y_0^0 and Y_2^0 are both isotropic in 1 - 2 plane and are related by $\frac{Y_2^0}{Y_0^0} = -\sqrt{\frac{5}{4}}$. Therefore the above expression can be rewritten as:

$$S(Q_x, Q_y, Q_z = 0) = \left[S_0^0(Q) - \sqrt{\frac{5}{4}}S_2^0(Q)\right]Y_0^0(\Omega) + S_2^{-2}(Q)Y_2^{-2}(\Omega) + S_2^2(Q)Y_2^2(\Omega)$$
(S16)

It is important to understand which modes are included in the 2D scattering pattern when the angular average weighted with the spherical harmonic function is made

$$S_{lm}^{xy}(Q) = \frac{1}{4\pi} \int d\Omega S(Q_x, Q_y, Q_z = 0) Y_l^m(\Omega)$$
where $Q = \sqrt{Q_x^2 + Q_y^2}$. (S17)

With above considerations, it is easy to obtain the results for spherical harmonics expansion in 1 - 2 plane:

$$S_{00}^{xy}(Q) = \frac{1}{2\pi} \int_0^{2\pi} S\left(Q, \theta = \frac{\pi}{2}, \phi\right) Y_0^0 \left(\theta = \frac{\pi}{2}, \phi\right) d\phi = \frac{1}{2\pi} \int_0^{2\pi} S\left(Q, \theta = \frac{\pi}{2}, \phi\right) d\phi$$

= $S_0^0(Q) - \sqrt{\frac{5}{4}} S_2^0(Q),$ (S18)

$$S_{2,-2}^{xy}(Q) = \frac{1}{2\pi} \int_0^{2\pi} S\left(Q, \theta = \frac{\pi}{2}, \phi\right) Y_2^{-2} \left(\theta = \frac{\pi}{2}, \phi\right) d\phi = \frac{1}{2\pi} \int_0^{2\pi} S\left(Q, \theta = \frac{\pi}{2}, \phi\right) \frac{\sqrt{15}}{2} \sin(2\phi) d\phi$$

= $\frac{15}{8} S_2^{-2}(Q),$ (S19)

$$S_{22}^{xy}(Q) = \frac{1}{2\pi} \int_0^{2\pi} S\left(Q, \theta = \frac{\pi}{2}, \phi\right) Y_2^2\left(\theta = \frac{\pi}{2}, \phi\right) d\phi = \frac{1}{2\pi} \int_0^{2\pi} S\left(Q, \theta = \frac{\pi}{2}, \phi\right) \frac{\sqrt{15}}{2} \cos(2\phi) d\phi$$

= $\frac{15}{8} S_2^2(Q),$ (S20)

where $\mathbf{Q} = (Q\cos\phi, Q\sin\phi, Q_z = 0)$. This demonstrates that the isotropic component in 2D scattering pattern S_0^{xy} includes both $S_0^0(Q)$ and $S_2^0(Q)$, while other components are identical to those for 3D.

Similar considerations can also be applied to the analysis of the 2D patterns in 1 - 3 plane. After eliminating the terms breaking the even parity and the terms containing $sin\phi$ or $sin2\phi$, one can obtain the following expansion for 1 - 3 plane:

$$S(Q_x, Q_y = 0, Q_z) = S_0^0(Q)Y_0^0(\Omega) + S_2^0(Q)Y_2^0(\Omega) + S_2^2(Q)Y_2^2(\Omega)$$
(S21)

From Eqs. (S3) - (S11), and Eqn. (S21), it is straightforward to obtain the following results for spherical harmonics expansion in 2D pattern:

$$S_{00}^{xz}(Q) = \frac{1}{2} \int_0^{\pi} d\theta \sin\theta S(Q_x, Q_z) = S_0^0(Q) + \sqrt{\frac{15}{9}} S_2^2(Q),$$
(S22)

$$S_{2,0}^{xz}(Q) = \frac{1}{2} \int_0^{\pi} d\theta \sin\theta S(Q_x, Q_z) \left[\sqrt{\frac{5}{4}} \frac{-Q_x^2 + 2Q_z^2}{Q^2} \right] = S_2^0(Q) - \sqrt{\frac{1}{3}} S_2^2(Q).$$
(S23)

Clearly we can see that in x-z plane the $S_2^2(Q)$ contributes to both $S_{00}^{xz}(Q)$ and $S_{20}^{xz}(Q)$. In summary, Eqns. (S20) and (S22) allow us to determine isotropic $S_0^0(Q)$ as

$$S_0^0(Q) = S_{00}^{xz}(Q) - \frac{8}{3\sqrt{15}} S_{22}^{xy}(Q)$$
(S24)

Also anisotropic structure functions relevant to the shear flow problem are given by

$$S_2^{-2}(Q) = \frac{8}{15} S_{2,-2}^{xy}(Q),$$
(S25)
and

$$S_2^2(Q) = \frac{8}{15} S_{2,2}^{xy}(Q) \tag{S26}$$

Based on this approach, $S_0^0(Q)$ and $S_2^{-2}(Q)$ required for generating $g_0^0(r)$ and $g_2^{-2}(r)$ are obtained from 1 - 2 and 1 - 3 planes. The results are given in Figures S2 and S3. Then, $g_0^0(r)$ and $g_2^{-2}(r)$ can be obtained with the Bessel transform:

$$g_l^m(r) = \frac{i^l}{2\pi^2\rho} \int S_l^m(Q) J_l(Qr) Q^2 dQ,$$

where $J_l(Qr)$ is the spherical Bessel function.



Figure S2. Experimental $S_0^0(Q)$ as a function of shear rate. The height of the first peak is seen to decrease progressive with the increase in shear rate. This observation is consistent with the increase of the effective temperature caused by increasing applied steady shear. $g_0^0(r)$ is obtained by Fourier transforming $S_0^0(Q)$.



Figure S3. Experimental $S_2^{-2}(Q)$ as a function of shear rate. $g_2^{-2}(r)$ is obtained from $S_2^{-2}(Q)$ via inverse spherical Bessel transform.

S3. Brownian Dynamics (BD) Simulation

Brownian dynamics simulations of binary mixture of 3000 particles was carried out to complement the SANS experiment. The algorithm used in this simulation was proposed by Ermak and McCammon (S7), without hydrodynamic interactions and with an additional shear flow in the x direction. The resulting equation can be written as the following prescription to generate the new position $r_i(t + \Delta t)$ from the current position $r_i(t)$,

$$r_i(t + \Delta t) - r_i(t) = \left(\dot{\gamma}y_i\hat{e}_x + \beta D_0F_i(t)\right)\Delta t + X_i(t),\tag{S27}$$

where $\dot{\gamma}$ is the shear rate, y_i is the coordinate of particle *i* along the *y* direction, \hat{e}_x is the unit vector along the *x* direction, $\beta \equiv 1/k_BT$ is the thermal energy, and with $D_0 \equiv (k_BT/\zeta)$ being the shorttime self-diffusion coefficients of the particle. The random displacement $X(t) \equiv +\beta D_0 f_0(t)$ is extracted from Gaussian distributions with zero mean and variance given by $6D_0\Delta t$.

The interaction between the simulated binary colloidal particles with the electrostatic interaction is described by the pairwise repulsive hard-core Yukawa potential. Mathematically, this may be written as

$$u_{ij}(r) = \begin{cases} K_{ij} \left(\frac{\sigma_{ij}}{r}\right)^{36}, \ r \le \sigma_{ij} \equiv (\sigma_i + \sigma_j)/2\\ K_{ij} \frac{e^{-z(r-\sigma_{ij})}}{r/\sigma_{ij}}, \ r \ge \sigma_{ij} \end{cases}$$
(S28-a)

For hard-sphere colloids, the interparticle potential is written as:

$$u_{ij}(r) = \begin{cases} K_{ij} \left(\frac{\sigma_{ij}}{r}\right)^{36}, \ r \le \sigma_{ij} \equiv (\sigma_i + \sigma_j)/2\\ 0, \ r \ge \sigma_{ij} \end{cases}$$
(S28-b)

where σ_i and σ_j are the diameter of the particles, *z* the screening length, and K_{ij} the interaction strength. We define the shear velocity to lie in the *x* direction, the shear gradient to lie in the *y*

direction, and the vorticity in the z direction. The simulations were performed in a cubic simulation box. In order to avoid crystallization we chose a binary mixture of small A particles and large B particles with number density ratio $n_A/n_B = 4$, radius ratio $\sigma_A/\sigma_B = 1.5$, $K_A = K$, $K_B = 0.5K$ and $K_{AB} = 0.75K$. The total volume fraction, z and K used in our simulation are 0.4, 9.89 k_BT and $\frac{4.86}{\sigma_A}$ determined from the SANS data analysis, where k_B is the Boltzmann constant. Applied shear was incorporated into the boundary conditions using the "sliding brick" boundary conditions of Lees and Edwards (S8). The initial configurations were generated using the following procedure: First particles were placed randomly in the simulation box with specified density. The overlap between the particles were later reduced or eliminated. Once the initial configuration was constructed, several thousand cycles were performed to lead the systems to equilibrium, followed by at least two million cycles where the data was collected. Throughout this paper we use the following reduced units for length ($r^* = r/\sigma_A$). The time unit is related to $\tau_0 = \sigma_A^2/6D_0$, the time required for the particle to diffuse a distance of σ_A .

The Eqn. (S27) in reduced units reads,

$$r_i^*(t + \Delta t) - r_i^*(t) = \left(\dot{\gamma}^* y_i^* \hat{e}_x + F_i^*(t)\right) \Delta t + X_i^*(t) , \qquad (S29)$$

where $\gamma := \dot{\gamma}\tau_0$, $F^* = F\sigma_A/6k_BT$, the time $\Delta t^* = \Delta t/\tau_0$, and variance $\langle X(t)X(0) \rangle = \Delta t^*$. The dimensionless Péclet number *Pe* used in this paper is defined as

$$Pe = \frac{\dot{\gamma}\sigma_A^2}{6D_0} = \dot{\gamma}^* \tag{S30}$$

During the simulation we calculate the inter-particle stress tensor for a differentiable pairwiseadditive interaction (*S9*),

$$\sigma_{xy} = \frac{1}{2V} \sum_{i \neq j}^{N} \sum_{j=i}^{N} \frac{r_{ij}^{x} r_{ij}^{y}}{r_{ij}} \frac{du_{ij}(r)}{dr_{ij}}$$
(S31)

where the subscripts *x* and *y* denote the Cartesian component of vector quantities. At finite shear rate, the effect of inter-particle stress on the viscosity η^{I} is given by

$$\eta^I = <\sigma_{xy} > /\dot{\gamma} \tag{S32}$$

The anisotropic components of the PDF can be calculated thorough the trajectories of particles. For example,

$$g_2^{-2}(\mathbf{r}) = \frac{1}{4\pi r^2 \rho N} \sqrt{15} \sum_{ij} \frac{x_{ij} y_{ij}}{r_{ij}^2} \delta(\mathbf{r} - \mathbf{r}_j + \mathbf{r}_i)$$
(S33)

$$g_{2}^{0}(r) = \frac{1}{8\pi r^{2} \rho N} \sqrt{5} \sum_{ij} \left[3 \left(\frac{z_{ij}}{r_{ij}} \right)^{2} - 1 \right] \delta(r - r_{j} + r_{i})$$
(S34)

$$g_2^2(r) = \frac{1}{8\pi r^2 \rho N} \sqrt{5} \sum_{ij} \left(\frac{x_{ij}^2 - y_{ij}^2}{r_{ij}^2} \right) \delta(\mathbf{r} - \mathbf{r}_j + \mathbf{r}_i)$$
(S35)

The structure factor S(Q) can either be performed as a time average of the one-particle average

$$S(\boldsymbol{Q}) = \frac{1}{N} \left[(\sum_{i} \cos(\boldsymbol{Q} \cdot \boldsymbol{r}_{i}))^{2} + (\sum_{i} \sin(\boldsymbol{Q} \cdot \boldsymbol{r}_{i}))^{2} \right]$$
(S36)

where r_i is the position vector of particle *I*, *N* is the total particle number. The allowed wave-vector *Q* has to be chosen appropriately for the cubic scattering volume (with length *L*), which is smaller than or equal to the periodicity box. To mimic a small angle detector normal to the *z*-plane the *Q* values $Q_x = n_x Q_0$, $Q_y = n_y Q_0$, $Q_z = 0$ with $Q_0 = \frac{2\pi}{L}$ and $n_x, n_y = 0$, ± 1 , ± 2 , ... are chosen. Detectors normal to the other directions are obtained in a similar way.

The $g_2^{-2}(r)$ and $-\frac{\gamma_0}{\sqrt{15}}r\frac{dg(r)}{dr}$ obtained from trajectories analysis for both the charged colloids and hard-sphere colloids are given in Figure S4. For charged colloids, γ_0 is determined by $\frac{\sigma_{xy}}{G_{\infty}}$, where σ_{xy} is given by Eqn. (S31) and G_{∞} is given by the following expression (S10)

$$G_{\infty} = \frac{1}{15V} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} r_{ij}^{-2} \frac{d}{dr_{ij}} \left(r_{ij}^{4} \frac{d}{dr_{ij}} u_{ij} \right)$$
(S37)

 $g_2^{-2}(r)$ and $-\frac{\gamma_0}{\sqrt{15}}r\frac{dg(r)}{dr}$ are seen to be in quantitative agreement for charged colloids. This agreement suggests the existence of the elastic coherency in the flow. For hard-sphere colloids, however, the oscillations of these two functions do not match each other: $g_2^{-2}(r)$ is significantly lags behind $-\frac{\gamma_0}{\sqrt{15}}r\frac{dg(r)}{dr}$. The mismatch between the two quantities indicate the breakdown of the TEZ in the HS case at the volume fraction of 0.4. This comparison highlights the key role of the interparticle electrostatic repulsion in establishing the TEZ.



Figure S4. The comparison between the anisotropic pair distribution function $g_2^{-2}(r)$ and $-\frac{\gamma_0}{\sqrt{15}}r\frac{dg(r)}{dr}$ at different shear rate calculated from BD simulation as a function of shear rate and Péclet number.

One can also calculate the SANS spectra from the trajectory of BD simulations. We present the results for the charged colloids in Figure S5. To compare with the experimental data presented in Figure 1, the influence of finite particle size, the so-called form factor P(Q), is also incorporated. In both configurations 1 - 2 and 1 - 3 planes, the spectral evolution presented in Figure S5 is seen to be qualitatively identical to that of Figure 1. Moreover, in Figure S5(c), it is noticed that the two additional spots are developed along the y-axis when $\dot{\gamma} = 165 \text{ s}^{-1} (P_e = 3.3)$. As demonstrated by the movie generated by BD simulation, no discernible formation of layers along the flow direction is observed. We therefore conclude that the origin of two spots is the difference in the density fluctuation along and perpendicular to the flow direction.

It is instructive to comment the role of BD simulation in this study: The importance of hydrodynamic interactions has been demonstrated by a series of computational (S11-S12) and experimental (S13) studies. As far as the simulation of colloidal suspension under shear is concerned, the limitations of BD and the superiority of Stokesian dynamics (SD) have been thoroughly demonstrated (S14). However the goal of BD was not placed on generating the structural and rheological data for rigorously quantitative comparison with scattering and rheometry. Instead the focus of BD simulation aims at demonstrating the existence of TEZ and providing the initial clue for developing the framework of rheo- and flow-SANS data analysis.



Figure S5. The SANS intensity of a charged colloidal suspension subjected to steady shear generated by BD. The volume fraction ϕ is 0.4. σ_A is the particle diameter of the big particle. The effect of particle forma factor is also incorporated. Panels (a) to (c) give the spectra obtained from the flow-velocity (ν - $\nabla \nu$ or 1 - 2) gradient plane with shear rate $\dot{\gamma} = 0$, 41.5 and 165 s⁻¹ ($P_e = 0$, 0.83 and 3.3) respectively. The ones obtained from flow-vorticity plane (ν - ω or 1 - 3) are given in panels (d) to (f) for the same shear rates. The spectra and the dependence of their features as a function of shear rate are qualitatively similar to those presented in Figure 1 in the main text.

Moreover, we would like to indicate that the identification of TEZ does not depend on the details of simulation. We are currently using a direct numerical simulation method (*S15-S17*), which takes into account hydrodynamic interactions and thermal fluctuations accurately, to repeat the simulation with under the same control parameters. Like the results of BD presented in this work, in this more rigorous computational study the TEZ is again identified and its evolution as a function of shear rate is identical to that of experiment. The qualitative feature of TEZ remains intact. Only quantitative difference is observed.

S4. Calculation of Stress Components

In this section we give the equations for calculating the stress components for the charged colloids as well as the hard spheres.

The Brownian contribution to the stress $\sigma^{(B)}$ for a hard-sphere suspension can be calculated if $g(\mathbf{r})$ is known (S12, S18, S19):

$$\sigma^{(B)} \approx -n^2 k_B T \frac{d}{2} \iint_{r=d} \hat{r} \hat{r} g(\vec{r}) dS$$
(S38)

where *n* is the number density of particles, *d* is the diameter of the colloidal particle and \hat{r} is the unit vector along the passing through the two particle centers. For the shear geometry, the *xy* component is the shear stress:

$$\sigma_{xy}^{(B)} \approx -n^2 k_B T \frac{d}{2} \iint_{r=d} \hat{r}_x \hat{r}_y g(\vec{r}) dS$$
(S39)

In practice, the following form has been suggested to calculate $\sigma^{(B)}$ to account for the polydispersity of particles (*S19*):

$$\sigma_{xy}^{(B)} \approx -n^2 k_B T \frac{\langle d \rangle}{2} \frac{c}{\varepsilon_1 + \varepsilon_2} \int_{r=\langle d \rangle - \varepsilon_1}^{\langle d \rangle + \varepsilon_2} dr \iint \hat{r}_x \hat{r}_y g(\vec{r}) dS$$
(S40)

where $\langle d \rangle$ is the average diameter of particle, ε_1 and ε_2 indicate the integral range around $\langle d \rangle$, and *C* is a dimensionless factor that accounts for the difference between the above two equations. Using the manner suggested in (*S19*), we set $d - \varepsilon_1$ to be 0.79*d* and $d + \varepsilon_2$ to be 1.15*d*. For the hard-sphere suspension, *C* can be determined by the following two physical constraints:

(i) The calculated $\sigma_{xy}^{(B)}$ should be smaller than $\sigma_{tot} - \sigma_{sol}$, where σ_{tot} is the total stress measured by rheometry and σ_{sol} is the solvent contribution to the stress: $\sigma_{sol} = \eta_{sol}\dot{\gamma}$.

(ii) The hydrodynamic contribution to the viscosity, $\eta_{HS}^{(H)}$ (= $\eta_{tot} - \eta_{HS}^{(B)} - \eta_{sol}$), should monotonically increase as a function of $\dot{\gamma}$.

The constraint (ii) can be justified as follows: 1) the total viscosity of the hard-sphere suspension is composed of the Brownian and hydrodynamic contributions (*S12, S19*), and 2) the hydrodynamic contribution to the viscosity monotonically increases with increasing the shear rate (*S11*).

The range of *C* determined by the above two constraints is 9.1-12.2. Notice that, this value is different from the value used in another study (*S19*), which may be due to the differences on the particle size and solvent. We adopt the value of C = 9.1 here.

The Brownian contribution to the stress for the charged colloids can be estimated by the following equation (*S12*):

$$\sigma_{xy}^{(B)} \approx -n^2 k_B T \frac{d}{2} C \int \hat{r}_x \hat{r}_y g(\vec{r}) W(r) d\vec{r}$$
(S41)

where W(r) is a function that depends on the interparticle potential (S12, S18). It exhibits a sharp peak around the peak position of g(r).

We evaluate the Brownian stress of the charged colloidal suspension using both Eqs. (S40) and (S41). The results are of the same order. In any case, we can conclude that in the charged colloidal suspension, the Brownian contribution to the stress is much smaller than the contribution from the TEZ. This is consistent with the theoretical prediction that in charged colloids the potential contribution to the stress is much larger than the Brownian contribution to the stress (*S12*).

Knowing $\sigma_{xy}^{(B)}$, we can calculate the Brownian contribution to the viscosity by $\eta^{(B)} = \sigma_{xy}^{(B)}/\dot{\gamma}$.

The hydrodynamic viscosity contribution for the hard spheres can be directly obtained by:

$$\eta_{HS}^{(H)} = \eta_{HS} - \eta_{HS}^{(B)} - \eta_{sol}$$
(S42)

The hydrodynamic contribution to the stress for the charged colloids can be estimated by (S12):

$$\frac{\sigma_{CC}^{(H)}}{\dot{\gamma}\eta_{sol}} = 2.5\phi + 2.5\phi^2 + \frac{15}{4\pi}\phi^2 \int \left[M(r) \left(\hat{\boldsymbol{r}} \cdot \hat{\boldsymbol{E}} \cdot \hat{\boldsymbol{r}} \right) \left(\hat{\boldsymbol{r}}\hat{\boldsymbol{r}} - \frac{I}{3} \right) + L(r) \right] \left(\hat{\boldsymbol{r}}\hat{\boldsymbol{E}} \cdot \hat{\boldsymbol{r}} + \hat{\boldsymbol{r}}\hat{\boldsymbol{r}}: \hat{\boldsymbol{E}} - \frac{2}{3}I \left(\hat{\boldsymbol{r}} \cdot \hat{\boldsymbol{E}} \cdot \hat{\boldsymbol{r}} \right) + K(r) \hat{\boldsymbol{E}} \right) g(\boldsymbol{r}) d\boldsymbol{r}$$
(S43)

where E is the bulk strain rate tensor, M(r), L(r) and K(r) are tabulated functions. The theoretical and computational studies (S12) have shown that the integral term in the above equation is not important in the charged colloids, since the electrostatic repulsion can substantially reduce the many-body contribution to hydrodynamic stress by suppressing the near-contact lubrication. Therefore, the above equation can be roughly simplified to (S12):

$$\frac{\eta_{CC}^{(H)}}{\eta_{sol}} = \frac{\sigma_{CC}^{(H)}}{\dot{\gamma}\eta_{sol}} \approx 2.5\phi + 2.5\phi^2 \tag{S44}$$

In this study, the $\eta_{CC}^{(H)}$ is found to be even below 0.1 Pa.s. This value is well below the TEZ contribution at measured shear rates.

References

- S1. H. Watanabe, M.-L. Yao, A. Yamagishi, K. Osaki, T. Shitata, H. Niwa, Y. Morishima, *Rheol. Acta* **35** 433 (1996).
- S2. J. Vermant, M. J. Solomon, J. Phys.: Condens. Matter 17 R187 (2005).
- S3. A. K. Gurnon, P. D. Godfrin, N. J. Wagner, A. P. R. Eberle, P. Butler, L. Porcar, *J. Vis. Exp.* **84** e51068 (2014).
- S4. L. Porcar, D. Pozzo, G. Langenbucher, J. Moyer, P. D. Butler, *Rev. Sci. Instrum.* 82 083902 (2011).
- S5. M. Heinen, P. Holmqvist, A. J. Banchio, G. Nägele, J. Chem. Phys. 134 044532 (2011).
- S6. D. J. Evans, H. J. M. Hanley, S. Hess, Phys. Today 37 26 (1984).
- S7. D. L. Ermark, J. A. McCammon, J. Chem. Phys. 69 1352 (1978).
- S8. A. W. Lees, S. F. Edwards, J. Phys. C 5 1921 (1972).
- S9. S. R. Rastogi, N. J. Wagner, S. R. Lustig, J. Chem. Phys. 104 9234 (1996).
- S10. G. Rickayzen, J. G. Powles, D. M. Heyes, J. Chem. Phys. 118 24 (2003).
- S11. D. R. Foss, J. F. Brady, J. Fluid Mech. 407 167 (2000).
- S12. E. Nazockdast, J. F. Morris, Soft Matter 8 4223 (2012).
- S13. J. Bender, N. J. Wagner, J. Rheol. 40 899 (1996).
- S14. J. F. Brady, Chem. Eng. Sci. 56 2921 (2001).
- S15. T. Iwashita, R. Yamamoto, Phys. Rev. E 80 061402 (2009).
- S16. H. Kobayashi, R. Yamamoto, J. Chem. Phys. 134 064110 (2011).
- S17. J. J. Molina, K. Otomura, H. Shiba, H. Kobayashi, M. Sano, R. Yamamoto, J. Fluid Mech. **792** 590 (2016).
- S18. J. F. Brady, J. Chem. Phys. 99 567 (1993).
- S19. X. Cheng, J. H. McCoy, J. N. Israelachvili, I. Cohen, Science 333 1276 (2011)