Stress-structure relation in dense colloidal melt under forward and instantaneous reversal of shear

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Dense supercooled colloidal melt in forward shear from a quiescent state shows overshoot in shear stress at 10\% strain with an unchanged fluid structure at equal stress before and after overshoot. In addition, we find overshoot in normal stress with a monotonic increase in osmotic pressure at an identical strain. The first and second normal stress become comparable in magnitude and opposite in sign. Functional dependence of the steady state stress and osmotic pressure with Peclet number demonstrate signature of crossover between Newtonian and nearly-Newtonian regime. Moreover, instantaneous shear reversal from steady state exhibit Bauschinger effect, where strong history dependence is observed depending on the time of flow reversal. The distribution of particulate stress and osmotic pressure at the point of flow reversal is shown to be a signature of the subsequent response. We link the history dependence of the stress-strain curves to changes in the fluid structure measured through the angular components of the radial distribution function. A uniform compression in transition from forward to reversed flowing state is found.

I. INTRODUCTION

The mechanical and structural response of dense colloidal dispersion under external forces are intriguing due to the interplay of associated single particle relaxation time scale $\tau_0$ and the structural relaxation time scale $\tau$, many orders of magnitude slower than the previous. A rich behaviour of amorphous solid like and non-Newtonian fluid like behaviour is seen in experiments and simulations when perturbed on a timescale $1/\dot{\gamma}$ with $\tau_0 \ll \dot{\gamma}^{-1} \ll \tau$ \cite{1}. Fluid like behaviour is exemplified by an increase in the shear viscosity referred as shear thinning or thickening, while the solid like behaviour through the finite yield stress and nonzero elastic constants of the media \cite{2}. Non-Newtonian fluids also exhibit nonzero normal stress components, signs of them lead to compression or propulsion of fluid mass leading to fascinating phenomena \textit{e.g.} rotating rod flows \cite{3} and rod climbing effects in attractive colloids \cite{4}. The flowing steady state response is not only characterized as a nonlinear function of $\dot{\gamma}$ by the macroscopic shear stress $\sigma_{xy}$, but also of first, second normal stresses and osmotic pressure \textit{viz.} $N_1(\dot{\gamma})$, $N_2(\dot{\gamma})$ and $P(\dot{\gamma})$. Nonlinear functional form of shear and normal stresses with Peclet number as well as a positive first normal stress and a sign reversed second normal stress for monodisperse colloidal suspensions at lower and moderately high volume fractions had been reported in Stokesian dynamics simulation of concentrated colloidal suspension \cite{5} as well as molecular dynamics (MD) simulation of non-Brownian spheres \cite{6}. Similar results are reported in system with charge-stabilized dispersion \cite{7}, however the functional dependence in vicinity of glass transition are not known.

In addition to the study of steady state properties, rigorous theoretical, experimental as well as simulational emphasis has been employed in past couple of decades to study the transient response of various systems in external shear to understand the kinetic pathway through which these systems evolve to steady flowing state. As a constant strain rate is applied to a quiescent, stress-free state at $t = 0$, shear stress increase from zero to a steady-state value with an intermediate hump at a 10\% strain amplitude for dense colloids, known in the literature as stress overshoot. These overshoot phenomena is found in the MD simulations and experiments of gels \cite{8}, dense polymeric melts \cite{9}, liquid crystalline polymers \cite{10} and charged as well as uncharged dense colloidal melt \cite{11,12}. The last example is reasonably well understood within the mode coupling theory (MCT) framework. An internal connection between superdiffusive particulate motion and jump in the local stress variances has been attributed to the stress overshoot. Considerable emphasis has also been exercised to understand the shear-deformed structure and it’s connection to the macroscopic stresses \cite{13,14}. A universal flow-induced structure at equal stresses have emerged at the elastic and plastic branch of the stress-strain curve. Application of shear deformation at constant rate leads to a modification of the stress overshoot in a system quenched into its glassy state: after startup flow, shear is reversed in the steady state leading to a vanishing of the maximum in the stress-strain curve known as the Bauschinger effect \cite{15,16}. The effect has been analyzed in terms of anisotropic athermal elastic constants that arise since the initially isotropic amorphous state acquires anisotropy under the initial deformation. A gradual disappearance of the stress overshoot as well as ceasing superdiffusion is found by the successive flow reversal from intermediate states to the steady flowing state. The transient and steady state properties of osmotic pressure is difficult to measure in experiments and recently been computed in computer simulations \cite{17}. To our knowledge, the tran-
sient or steady state response in terms of these macroscopic quantities and their relation to the shear-deformed structure under various flow history is yet to be sought.

Here we investigate the nonlinear rheology under start up flow from equilibrated quiescent state as well as in instantaneous flow reversal from intermediate and steady flowing states, without referring to the athermal variant. The issues that we address here can be categorized into (a) the transient and steady state response of the stresses and osmotic pressure to steady shear and response to instantaneous reversal of shear, (b) connection between the mechanical response to the fluid and the particulate stresses and (c) the flow-induced structural response of the melt in transient and steady flowing states and their relation with the macroscopic stresses. Functional dependence of stresses and osmotic pressure to Peclet number is sought to understand the steady state response of the mixture. At flow startup from a quiescent state, a stress overshoot in first and second normal stresses is found that resembles the overshoot in shear stress at equal strain, while gradual disappearance of the overshoot is found by investigating the effect of flow reversal applied at various times during the initial evolution from equilibrium to steady state. We link these response to the single particle stress fluctuations and pressure to seek a connection between the microscopic reason behind the macroscopic response. Also a relation between the flow-induced structure and it’s connection to the macroscopic stresses are sought that has been employed to understand the transient and steady state structural responses to shear reversal. Agreement in the steady state structure in opposite directed flowing states are found that resulted into the same magnitude of the macroscopic stresses. A continuous structural evolution with an exchange in compression-extension axis in shear reversal is found in the angular dependence of the pair correlator.

The paper is organized as follows: Section II gives a concise overview of the simulation method while Sec. III pre-empt the results through establishment of the connection between the mechanical response to the fluid structure. We discuss the central results in Sec IV and Sec. V concludes.

II. SIMULATION METHODS

We simulate a model system of dense supercooled colloidal suspension through nonequilibrium molecular dynamics simulations. An additive binary mixture of size ratio 1.2 is chosen to avoid crystallization as well as artifacts due to large size disparity. The components interact within a cutoff distance \( r < r_{c,\alpha\beta} (= 2^{1/6} \sigma_{\alpha\beta}) \) through a purely-repulsive soft-sphere WCA potential \[ V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{6} + \frac{1}{4} \right] S_{\alpha\beta}(r) \] where \( \sigma \) denotes the particle diameter and \( \alpha, \beta \) the particle species. \( S_{\alpha\beta}(r) = (r - r_{c,\alpha\beta})^{4} / [h^{4} + (r - r_{c,\alpha\beta})^{4}] \) with \( h = 10^{-2} \sigma_{\alpha\beta} \) is a smoothing function applied to ensure continuity of force and conservation of total energy in the NVE ensemble. Both species are assigned equal masses for convenience. Units of energy \( \epsilon_{\alpha\beta} = 1 \) and units of length are chosen so that \( \sigma_{AA} = 1 \) and the unit of time is \( \tau = \sqrt{m_A \sigma_{AA}^{2} / \epsilon_{AA}} \) where \( m_A \) is the mass of A-species of particles. The simulation consisted of \( N = 2N_A = 1300 \) particles in a three-dimensional box with linear dimension \( L = 10 \sigma_{AA} \), corresponding to a number density \( \rho = 1.3 / \sigma_{AA}^{3} \).

Colloidal property is incorporated in the mixture by coupling to a dissipative particle dynamics (DPD) thermostat where the dissipative force, proportional to the relative velocity of two species of particles, ensures Galilean invariance thereby local conservation of momentum. The random force satisfying fluctuation dissipation relation ensures Boltzmann distribution in equilibrium. These two competing force sets uniquely the temperature of the system. The cut off radius for the thermostat is chosen to be \( 1.7r_{c,AA} \) and the controlling parameter for frictional forces is set to \( \zeta = 10 \).

The Langevin equation of motion are integrated with a generalized velocity Verlet algorithm with a time increment of \( \delta t = 5 \times 10^{-4} \tau \). Our estimation of the glass transition point according to MCT description is \( T_c \approx 0.347 \) and we focus our work on the equilibrated fluid at \( T = 0.4 \). Initial equilibration is proceeded by step increments of \( \delta t = 10^{-3} \tau \), assigning new velocities on every 50 integration time steps. The simulation runs were long enough to observe the decay of the incoherent intermediate scattering function to zero for a wave number corresponding to a typical interparticle separation. A set of 200 independently equilibrated configurations served as initial configurations for the forward shear runs, while 200 pre-sheared configurations for three separate strains are chosen for shear reversal runs employing the DPD thermostat.

Shear is applied from strain-free configurations in the \( x \)-direction with a gradient in the \( y \)-direction at a fixed strain rate \( \dot{\gamma} = 5 \times 10^{-3} \) initially for \( 3 \times 10^{7} \) steps resulting to steady state with strain \( \gamma = 75 \). Shear is reversed and proceeded from three pre-sheared states, denoted with strain \( -\gamma_{w}^{cl} = 3.5 \times 10^{-2}, -\gamma_{w}^{max} = 8.6 \times 10^{-2} \) and \( -\gamma_{w}^{c} = 75 \) for \( 3 \times 10^{7} \) simulation steps, resulting to steady states with accumulated strain \( -74.965, -74.914 \) and 0. For all these cases, planar Couette flow is imposed by periodic Lees-Edwards boundary conditions and an establishment of linear velocity profile is achieved within a few iterations (see [12] and the references therein for more detailed description).

III. CONNECTION BETWEEN STRESSES AND STRUCTURE

The amount of stresses developed by the application of steady shear to a quiescent unsheared state or pre-sheared states are measured through the nonzero components of the stress tensor \( \sigma_{\mu\nu} \). Kirkwood formula defines
a combination of kinematic and virial contribution to the stress tensor by [14],
\[
\sigma_{\mu\nu} = \langle \delta_{\mu\nu} \rangle = -\frac{1}{V} \left\langle \sum_{i=1}^{N} \left( m_i v_i,\mu v_i,\nu + \sum_{j\neq i} r_{ij,\mu} F_{ij,\nu} \right) \right\rangle
\]
where the angular brackets are indicative of canonical averaging, \(i, j\) denote the particle index and \(\mu, \nu\) the Cartesian component. In a specified coordinate system having shear along \(x\) direction with a gradient along \(y\) direction, the dominant contribution to the shear stress is the off-diagonal \(xy\)-element and the normal stresses are the combination of the diagonal \(xx, yy\) and \(zz\)-element of the stress tensor. The first and second normal stresses are the differences in the diagonal components as [2],
\[
N_1 = \langle \sigma_{xx} - \sigma_{yy} \rangle; \quad N_2 = \langle \sigma_{yy} - \sigma_{zz} \rangle.
\]
and the third normal stress \(N_3\) is the sum of the two. The osmotic pressure is the sum of the diagonal elements of the stress tensor,
\[
P = -\frac{1}{3} \left( \sigma_{xx} + \sigma_{yy} + \sigma_{zz} \right).
\]

The virial part of the stress tensor can be expressed in terms of pair distribution function \(g^{\alpha\beta}(r) = V/N_{\alpha}N_{\beta} \times \left( \sum_{i=1}^{N_{\alpha}} \sum_{j=1}^{N_{\beta}} \delta(r - |r_i^{\alpha} - r_j^{\beta}|) \right)\) by rewriting the equation and substituting expressions for pairwise force in the following manner [14],
\[
\sigma = -\frac{1}{2V} \left\langle \sum_{i=1}^{N_{\alpha}} \sum_{j=1}^{N_{\beta}} r_{ij} F_{ij} \right\rangle,
\]
\[
= -\frac{1}{2V} \left\langle \sum_{\alpha, \beta} \sum_{i=1}^{N_{\alpha}} \sum_{j=1}^{N_{\beta}} \delta(r - |r_i^{\alpha} - r_j^{\beta}|) r F_{ij} \right\rangle,
\]
\[
= \frac{1}{2V} \left\langle \sum_{\alpha, \beta} \sum_{i=1}^{N_{\alpha}} \sum_{j=1}^{N_{\beta}} \delta(r - |r_i^{\alpha} - r_j^{\beta}|) \frac{r}{r} \partial V_{\alpha\beta}(r) \right\rangle,
\]
\[
= \frac{1}{2V} \left\langle \sum_{\alpha, \beta} \sum_{i=1}^{N_{\alpha}} \sum_{j=1}^{N_{\beta}} 
\frac{r}{r} \partial V_{\alpha\beta}(r) \right\rangle,
\]
\[
= \frac{\rho^2}{2} \left\langle \sum_{\alpha, \beta} \frac{N_{\alpha} N_{\beta}}{N^2} \frac{r}{r} \partial V_{\alpha\beta}(r) \right\rangle
\]
where \(\rho = N/V\) is the average density and \(N_{\alpha}, N_{\beta}\) correspond to the number of particles of the respective species index.

Shear induced pair distribution function for either forward or backward directed sheared states does not exhibit any significant structural change compared to the quiescent state. A more relevant quantity sensitive to shear is constructed [14][15], where the three dimensional pair correlation function is expanded into spherical harmonics as, \(g^{\alpha\beta}(r) = \sum_{l=0}^\infty \sum_{m=-l}^{l} g^{\alpha\beta}_{lm}(r) Y_{lm}(\theta, \phi)\). Here \(Y_{lm}(\theta, \phi) = (-1)^m \sqrt{2l+1/4\pi} P_{lm}(\cos\theta) e^{im\phi}\) are the spherical harmonics of degree \(l\) and order \(m\), \(\theta\) and \(\phi\) are the polar and azimuthal angle and \(P_{lm}(\cos\theta)\) are the associated Legendre polynomial [20]. From symmetry considerations, only even numbers in \(l\) is existent and the most relevant terms in the expansion are associated to \(l = 2, m = 0, \pm 2\). Here we look for in-plane structural changes to shear and the relevant expansion coefficients associated to \(g(r)\) are,
\[
Re[g^{\alpha\beta}_{22}(r)] = \sqrt{\frac{15}{16\pi}} \frac{V}{N_{\alpha}N_{\beta}} \left\langle \sum_{i=1}^{N_{\alpha}} \sum_{j=1}^{N_{\beta}} \delta(r - |r_i^{\alpha} - r_j^{\beta}|) \right\rangle
\]
\[
\times \left\langle \frac{2\alpha^2 - \beta^2}{r^4} \frac{(x_i^\alpha - x_j^\beta)^2}{r^4} \right\rangle
\]
\[
Im[g^{\alpha\beta}_{22}(r)] = \sqrt{\frac{15}{8\pi}} \frac{V}{N_{\alpha}N_{\beta}} \left\langle \sum_{i=1}^{N_{\alpha}} \sum_{j=1}^{N_{\beta}} \delta(r - |r_i^{\alpha} - r_j^{\beta}|) \right\rangle
\]
\[
\times \left\langle \frac{2\alpha^2 - \beta^2}{r^4} \frac{(y_i^\alpha - y_j^\beta)^2}{r^4} \right\rangle
\]
where \(Re\) and \(Im\) represent the real and imaginary part. Both these components are non existent in the quiescent state while they accumulate values in the sheared states. Integrating the algebraic combination of these functions together with the interparticle force yields the first normal stress [21] as well as the shear stress [16][21],
\[
N_1 = \rho^2 \sqrt{\frac{2\pi}{15}} \sum_{\alpha, \beta} \frac{N_{\alpha} N_{\beta}}{N^2} \int_0^\infty drr^3 \frac{\partial V_{\alpha\beta}(r)}{\partial r} \left( Re[g^{\alpha\beta}_{22}(r)] \right),
\]
\[
\sigma_{xy} = -\rho^2 \sqrt{\frac{2\pi}{15}} \sum_{\alpha, \beta} \frac{N_{\alpha} N_{\beta}}{N^2} \int_0^\infty drr^3 \frac{\partial V_{\alpha\beta}(r)}{\partial r} \left( Im[g^{\alpha\beta}_{22}(r)] \right).
\]

IV. RESULTS

Fig. (11) shows the flow curve that is the steady state scaling of the shear stress, first and second normal stresses and the osmotic pressure with the corresponding Peclet number \(Pe\) in forward shear at fixed temperature \(T = 0.4\). The structural relaxation timescale of the supercooled melt at this temperature is computed to be \(\tau_s = 1.8 \times 10^3\) which is slower by a factor of \(10^4\) than the single-particle relaxation time. Panel (a) depicts an increase in \(\sigma_{xy}\) with increasing \(Pe\) which is atypical mechanical response of the melt, with a crossover from Newtonian to sub-Newtonian scaling regime for \(Pe > 0.1\) that corresponds to strain rates higher than \(\dot{\gamma} = 10^{-4}\). It is to notice that above \(T_c\), there exists no finite yield stress and the low \(Pe\) response is always Newtonian as been expected in a dense liquid mixture. However, we find that both first and second normal stresses remain in the sub-Newtonian regime for \(Pe \geq 1\). As seen in Panel (b), the dimensionless number \(G_{\infty}N_{1,2}/\sigma_{xy}^2\), where \(G_{\infty}\)
denotes the elastic shear modulus, is not independent of $P_e$ and reaches a value $\sim 2$ for higher values of $P_e$, as also been predicted in the nonlinear shear-thinning Maxwell model [22].

The osmotic pressure decreases with decreasing $P_e$ and saturates for $P_e < 0.1$. Similar behaviour is also reported in the simulation of hard-sphere glass [23].

Next we draw our attention in studying the transient response of the melt under forward and instantaneous reversal of the direction of applied shear. Fig. 2 depicts the shear stress as a function of strain $\gamma = \dot{\gamma} t$ for fixed strain rate $\dot{\gamma}$ and time $t$ as obtained after application of the strain rate to equilibrated configurations with zero stress and reversal from three different flowing state as mentioned in Section I. In forward shear at a strain around $\gamma \approx 10\%$, a profound stress overshoot from the steady state stress value is observed, discussed earlier in studies of binary colloidal melt with long range interaction [11].

State-of-the-art explanation of this behaviour follows as the enhancement of energies, transferred by the shearing forces to the particles caged within their immediate neighbours with a characteristic length: the Lindemann length. At any strain lower than the denoted strain, the mechanical response of the mixture is that of an elastic solid with finite $G_\infty$ ($\sigma_{xy} \sim G_\infty \gamma$). Considering the time scales involved, the initial part of the $\sigma_{xy}(\gamma)$ curve for low strain rates is dominated by the long-time or low-frequency plateau modulus $G_\infty$ rather than the instantaneous modulus $G_0$ [11]. At large strains however, the response is that of a viscous fluid where $\sigma_{xy}$ is not a function of $\gamma$, but of $\dot{\gamma}$. Strains of order unity appear sufficient to drive the system into this state of steady flow. This is consistent with the expectation that the flow-induced decay of correlations occurs on a time scale set by $1/\dot{\gamma}$. The argument leading to this state follows as the release of elastic energy from the breaking of local cages, that leads also to superdiffusive particle motion in between the ballistic and diffusive motion, as found earlier in the mean squared particle displacement [11, 12].

Reversing the direction of the applied shear at times corresponding to various strains along the stress-strain curve results in an accumulated strain that first decreases to zero. After that, $|\gamma|$ grows linearly as a function of time. In steady flowing state, $|\gamma| \rightarrow \infty$ asymptote is $-\sigma_s(|\gamma|)$. Hence in Fig. 2, different $\sigma_{xy}(|\gamma|)$ curves coincide at large strains.

Comparing with the initial startup curve, the most striking difference is the complete absence of a stress overshoot. This agrees with the findings of Ref. [17] where the same phenomenon was reported for a system quenched into the glassy state initially. As a consequence, the steady-state value of the stress is reached much earlier, already at accumulated strains of $|\gamma| \approx 0.1$. This is somewhat surprising, since one might expect the pre-sheared state to bear structural anisotropies that accommodate flow in the $+x$ direction and hence oppose that in the $-x$ direction more than the isotropic equilibrium structure. This appears to be not the case in our simulation, that we elaborate more while discussing on the local structure. This is corroborated also by looking at the instantaneous effective elastic modulus,
FIG. 3. (Color online) Semilog plot of the normal stress-strain relation $N_1(\gamma)$ and $N_2(\gamma)$ at fixed temperature and strain rate for two different flow histories: panel (a): shear start up from a quiescent state and panel (b): instantaneous shear reversal from a steady flowing state. For comparison, the shear stresses in both situations are depicted. Total of 1000 independent configurations are averaged to obtain the graphics.

$G_{\text{eff}} = d\sigma / d\gamma|_{\gamma - \gamma_0} = 0.025$ ($\gamma_0$ being the strain when stress first decreases to zero): a lower value is found following flow reversal than the one characterizing the initial startup from the equilibrium configuration [12]. Flow reversal inside the elastic transient results in a stress-strain curve that exhibits a stress overshoot (a minimum in the convention that the initial pre-strain is in the positive coordinate direction). The magnitude of that overshoot is almost identical to that observed in the initial startup.

This exemplifies that during the elastic part, strain-induced rearrangements are essentially reversible, unlike in the plastic regime of viscous flow. Fig. (3) also depicts the case of flow reversal once the initial stress-strain curve has reached its maximum (curve labeled with $-\gamma_{\text{max}}$). This intermediate case still exhibits a pronounced overshoot, albeit lower than the $-\gamma_{\text{el}}$ case. Thus, up to the stress overshoot, the response of the system to the initial flow is mainly reversible. This is consistent with the notion that the overshoot marks the nontrivial breaking of nearest-neighbor cages due to the imposed flow. Recall that an overshoot in $\sigma_{xy}(\gamma)$ implies a dynamic shear modulus or microscopic stress autocorrelation function, that exhibits overrelaxation: stresses do not simply decorrelate but, during breaking of cages, are released in such a way that they briefly become anti-correlated during the process.

To complete the discussion on stresses, we study the transient and steady state response of normal stresses, defined in Eq. (2) as a function of strain. Panel (a) of fig. (3) depicts $N_1$ and $N_2$ as a function of strain $\gamma$ for the startup shear from equilibrium configuration while panel (b) shows results in shear reversal from the steady state, after the shear-stress becomes negative. The magnitude of the normal stress is noted approximately $1/10^6$ of order smaller than that of the shear stress, which can be anticipated to the quadratic scaling of normal stress with Peclet number. For startup case, $N_1$ builds up to reach steady state value after exhibiting an overshoot around $10\%$ of strain, very similar to the shear stress-strain response. As also noted, the amount of overshoot in shear or normal stresses stay constant compared to the steady state value. $N_2$ exhibits a negative stress overshoot with a crossover from transient to steady state. Surprisingly we find $N_1 \sim -N_2$ and $N_2 \sim N_1 + N_2 \sim 0$. Once the steady state is reached, we find unchanged response of the normal stresses after shear reversal. The transient shear stress response is also plotted in both panels for comparison. Nonzero values of $N_2$ indicates that in forward shear, the stress overshoot phenomena is not limited only to the shear direction but also has signature in two perpendicular directions to it which is atypical behaviour of a complex fluid. Unchanged magnitude and sign of normal stresses at shear reversal from steady state indicate of uniform normal forces devoid of the flowing direction. The distinction of history dependent response in flow reversal is not primarily due to the swapped flow direction, but due to whether the microscopic structure is still close to its equilibrium configuration (and hence only deformed reversibly), or whether it is sufficiently close to the flowing configuration.

Further support for this hypothesis comes from a study...
of the local stress fluctuations, initially suggested by Zausch et al.\cite{16}. Defining a local stress element as 
\( \sigma_{xy}^i = -(1/V) \sum_{j \neq i} \gamma_{ij,xy} F_{ij,xy} \) such that \( \langle \sigma \rangle = \sigma_{pot} \) is the potential part of the macroscopic stress, the distribution of these local stresses around their average value is studied. The upper panel (a) in Fig.\( \text{[4]} \) depicts the variance of \( \sigma_{xy}^i \) as a function of strain \( |\gamma| \) in forward shear from quiescent state and instantaneous reversal from a steady flowing state. As already noted in ref. \( \text{[16]} \), the initial equilibrium configuration is characterized by a variance that is significantly lower than that in the flowing steady state. A steep increase in \( \text{var}(\sigma_{xy}^i) \) around \( \gamma \approx 0.1 \) is found that coincides with the stress overshoot, separating the reversible elastic regime from the irreversible plastic counterpart. Reversing the shear flow from the steady-state regime (denoted with \( -\gamma_0^c \)), \( \text{var}(\sigma_{xy}^i) \) essentially remains at the previously reached level, exhibiting a small dip below \( \gamma \leq 0.1 \). A plausible explanation for the dip in stress variance can be sought by an argument that instantaneous shear reversal interrupts the planar Couette flow that eventually lower the fluctuations. The variance reaches the forward steady state value as soon as the linear flow profile is re-established in the other direction. In Figure\( \text{[4]} \) (b), the osmotic pressure defined in Eq.\( \text{[3]} \) is depicted for the flow startup and reversal from steady state. For the startup case, the increase in the pressure from one state to another is found without any overshoot at strain \( \approx 0.1 \) while for the reversal there is a slight lowering from a higher value as reached at the forward steady state. Similar response of osmotic pressure and the fluctuation in particulate stress with strain indicate of an interconnection between these seemingly different quantities.

To understand the shear induced anisotropy in the local fluid structure, we measure the angle dependent radial distribution function \( g(r, \theta) \) on shear-gradient (x,y)-plain. Fig.\( \text{[5]} \) shows the extra contribution of shear to the structure from the homogeneous and isotropic quiescent state, denoted with \( g_{eq} \). In forward shear as shown in panel (a-d), the homogeneous state is steadily deformed with development of anisotropies along the extensional-compression axis. This feature of the shear induced structural deformation that pushes more particles around the compressional axis while pulling the particles apart along the extensional axis are also reported in molecular simulations \( \text{[15, 24]} \). As could be anticipated from the stress-strain relationship, the amount of compression-extension is the maximum at the point of overshoot in stresses, shown in panel (c). Panel (e-h) shows the time evolution of the structure at backward flowing state. Because of an instantaneous reversal of shear from the steady state, the extensional and compressional axis exchange direction with an intermediate uniformly compressed state as seen in panel (c). This clearly indicate of an absence of force chains or jamming of colloidal particles \( \text{[25]} \) in the considered shear-rate. The vanishing of the stress overshoot attributes to ceasing of maximal anisotropy along the compression-extension axis, present in the forward shear depicted in panel (c). Endly, panel(d) and panel (h) confirms the equivalence of steady state structure in two flowing directions without any memory of the flow history.

To conclude the discussion on structure, we calculate the steady state structure observed in the local projected quantities \( Re[g_{22}^{\alpha}(r)] \) and \( Im[g_{22}^{\alpha}(r)] \) defined in Eq.\( \text{[6]} \), that can be related to the macroscopic stresses via Eq.\( \text{[7]} \). The upper panel(a) of Fig.\( \text{[6]} \) compares the steady state structure \( Re[g_{22}^{\alpha}(r)] \) for the shear startup from a quiescent state as well as the shear reversal from the steady state for \( \alpha \in A \)-species. We find excellent agreement between the structure in steady state for both directions, indicative of a homogeneously flowing state.
with equal planar anisotropy within statistical accuracy, devoid of any memory of the quiescent or pre-sheared configuration. The most important contribution to first normal stress is attributed to the nearest neighbour distance structure of the pair correlator. As seen for nearest neighbour distances, particles are squeezed along the compressional axis in the plain and extended along the extensional axis. This results to a positive $N_1$ at the considered strain rate. Panel(b) compares the positional dependence of $\text{Im}[g^{AA}_{22}(r)]$ for $\alpha \in A$ -species at steady state for two different shear reversal states denoted by $-\gamma_w^{cl}$ and $-\gamma_w^s$ to the forward directed steady state. The correlator (sign reversed) in forward shear agrees well with the steady reversed flowing state correlators. This result coincides with an earlier claim [16] that at equal moduli of shear stress, the projected structure retains it’s shape devoid of flow history. We found this claim to hold for reverse flowing states. Also we extend this claim for first normal stress-structure relation at steady state, thus validating Eq. (7).

V. CONCLUSIONS AND OUTLOOK

By employing a dissipative particle dynamics scheme in conjunction to Lees-Edwards boundary condition to soft repulsive colloids, in this article we have discussed the nonlinear rheology of dense colloidal suspension under shear flow, specifically the property of the elements in the stress tensor after a sudden application of steady strain rate $\dot{\gamma}$, starting from either a quiescent equilibrium configuration or various configurations that have been pre-sheared in the opposite direction. Functional dependence of Peclet number to shear and normal stresses as well as osmotic pressure is sought to understand the steady state response. A crossover from Newtonian to sub-Newtonian regime is found in shear-stress for $Pe > 0.1$ while the normal stresses remain in the sub-Newtonian regime throughout the range of $Pe$ numbers considered. The osmotic pressure is found to saturate for lower $Pe$. In the considered range of $Pe$ numbers, the binary melt exhibit shear thinning and for much higher rates can result into a shear thickening behaviour with a negative $N_2$ [20]. Stress-strain curves of the pre-sheared configurations are measured along with shear start-up. In addition to the overshoot in shear stress, overshoot in first and second normal stresses is observed at 10% strain amplitude with a step jump in the osmotic pressure as well as in the particulate stress variances. However, once attained the steady state, no overshoot is found in any of the stresses while unchanged state of pressure and particulate stress variance emerge in response to shear reversal. This validates the earlier conjecture of shear induced nearest-neighbour cage breaking at start-up flow, having a steady state with weak cages that ceases to play any dramatic role when the direction of flow is reversed. An interesting connection can be sought between the fluctuations of the particulate shear and normal stresses with the osmotic pressure, which is beyond the work presented here.

Angle dependent pair correlation function depicts that a uniform exchange of compression-extension axis occurs with a continuous evolution of structure, obtaining a steady Couette flow in relatively short span of time without clustering or formation of force chains which are atypical signature in athermal systems. We also do not find any shear induced crystallization in the considered shear rate. Maximal anisotropy is exhibited at a strain where stress-overshoot appears in forward shear while such maxima cease to exist in the shear reversed states. The steady state structure in both direction containing equal anisotropy confirms absence of flow history in steady state. The agreement in shear induced structure at steady flowing state validates the relationship between various components of the pair correlator and macroscopic stresses. The change of sign in shear direction attributes to an exchange of extension-compression axis as noted in the imaginary component of the pair distribution function while unchanged structure of the real component of the pair correlator confirms of a positive $N_2$ for both direction of shear. At equal stresses, the projected structures retain the functional form and thus establishing the stress-structure relationship. In a similar spirit to Eq. (7-8), the functional dependency of $N_2$ and $P$ to the components of pair correlator can be obtained [21] and an unchanged structure at equal stresses
can be found. However, clear conclusion can be drawn at larger strain rates applied to the melt quenched deep into the glassy state below $T_c$, which is outside the scope of this work. We seek for novel experimental measurement in dense supercooled melt to verify the claims presented here.

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