Supplementary Material for Complex oscillatory yielding of model hard sphere glasses

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COMPUTER SIMULATIONS

Brownian dynamics (BD) simulations were conducted according to [1], with the addition of an oscillatory shear field and the incorporation of a moderate polydispersity in the particles in order to avoid shear induced crystallization.

In general since colloidal particles are much larger than solvent molecules the clear separation of time and length scales allow us to treat the fluid as a continuum; however colloids are still small enough to be affected by collisions with the fluid molecules and are thus still Brownian. BD can be described as a simplification of SD, where hydrodynamic interactions between particles are neglected. For N rigid particles of radius R and density ρ in a medium of viscosity η moving with velocity U, we examine states where the Reynolds number (the dimensionless ratio of inertial forces $\rho U^2/R$ to viscous forces $\eta U/R^2$) is $Re << 1$. The motion of the particles is described by the N-body Langevin equation:

$$\mathbf{m}(d\mathbf{U}/dt) = \mathbf{F}^H + \mathbf{F}^B + \mathbf{F}^P$$

where $\mathbf{m}$ is the generalized mass/moment tensor, $\mathbf{U}$ is the particle translational/rotational velocity vector, $\mathbf{F}^H$ is the hydrodynamic force vector, $\mathbf{F}^B$ is the stochastic force vector that gives rise to Brownian motion, and $\mathbf{F}^P$ is the deterministic non-hydrodynamic force vector. Since inertia is not important in colloidal dispersions ($Re << 1$) the equation reduces to $\mathbf{F}^H + \mathbf{F}^B + \mathbf{F}^P = 0$. The Brownian forces due to thermal fluid fluctuations are random so their ensemble average is $\overline{\mathbf{F}^B} = 0$, and follow the fluctuation-dissipation theorem so that $\overline{\mathbf{F}^B(0)\mathbf{F}^B(t)} = 2k_BT(6\pi\eta R)\mathbf{I}\delta(t)$ with $\delta(t)$ the delta function and $\mathbf{I}$ the unit tensor. Here we choose to use BD simulations were Hydrodynamic Interactions (HI) between particles are ignored [1] instead of the much more computational demanding Stokesian Dynamics (SD) method where the full HIs between particles are explicitly computed. In this case the hydrodynamic force reduces to Stokes drag $\mathbf{F}^H = -6\pi\eta R\mathbf{U}$, allowing the study of larger and more concentrated systems, in a reasonable computation time.

The non-hydrodynamic force vector for a simple hard sphere system becomes the hard sphere interaction occurring at contact $\mathbf{F}^P = \mathbf{F}^{HS}$. This is calculated through the *potential-free* algorithm of [1, 2] in which the overlap between pairs of particles is corrected by moving the particles with equal force along the line of centres, back to contact. In order to calculate the stress, the algorithm directly calculates the pairwise interparticle forces that would have resulted in the hard sphere displacements during the course of a time step [1]. Therefore

$$\mathbf{F}^{HS} = -6\pi\eta R(\Delta x^{HS}/\Delta t)$$

i.e. the average Stokes drag on the particle during the course of the hard-sphere displacement. Once the interparticle forces from each collision are known, they can be used to calculate the stress matrix[1] according to:

$$\langle\ \mathbf{\Sigma}\rangle = -N\left\langle \mathbf{x}\mathbf{F}^{P}\right\rangle$$

We should note that at rest and for relatively low Pe, Brownian Dynamics simulations qualitatively capture experimental stresses and particle motions, even with the absence of hydrodynamics [1], although stresses cannot be quantitatively compared. We can further note that at at high volume fractions long range hydrodynamics can be partly screened and that lubrication effects leading to shear thickening may become important. However, the fact that shear thickening is absent in our experiments (in the regime studied), further supports our observation that BD simulations describe well the experiments.

In order to have greater clarity of the structural information and avoid crystallization under shear [3], polydispersity was added to the simulations, which is represented by a Gaussian distribution of radii with a rms value of 10%. Runs with $N = 1005$ and 4860 particles were examined by averaging data sets over multiple oscillations (30-100) after reaching a steady state (typically 10 oscillations). We use a time step of $10^{-4}\tau_B$ for $Pe < 1$ (and rest), which scales to 10^{-4} per unit strain for $Pe > 1$ [1]. Initial configurations were constructed by quenching from a dilute liquid state by appropriately increasing the particle size. The system was then properly equilibrated at rest allowing for a steady state to be reached by following the osmotic pressure and particle mean square displacements until the both remained stable (typically after about $50\tau_B$). However, steady states under non-linear shear were found to be generally independent of the initial conditions.

MICROSCOPIC ANALYSIS

Using the positions of the particles from simulations, we are able to calculate structural and dynamic properties. We use the radial pair distribution function, $g(r)$, for the description of the microscopic structure. In the main text, we quantify the structural anisotropy under shear by taking the projection of the radial distribution function, $g(r)$, in the velocity-

gradient (xy) plane of the applied shear. In order to highlight the distortions, the projection is restricted to a distance of 0.7 radii from the plane.

The Mean Squared Displacement (MSD) describes the single particle dynamics. For example in the x axis:

$$\langle \Delta x^2(\tau) \rangle_{N,t} = \frac{1}{N} \left\langle \sum_{i=1}^{N} \left[x_i(t+\tau) - x_i(t) \right]^2 \right\rangle_t$$

with x_i is the position of a particle i in the x axis and N the total number of particles. In our case, x_i is the position the particle calculated after subtraction of affine motion due to shear. In the text we show and discuss the displacements only the vorticity (z) direction, however the velocity (x) and velocity gradient (y) give similar results. An effective diffusion coefficient defined within the period as $D_{eff} = \langle \Delta z^2(T) \rangle_{N,t} / T$ (see fig 4) may convey the changes in microscopic motions during the period of a single oscillation. Note that since during an oscillation period shear rate varies, the displacements vary as well and therefore D_{eff} cannot be described as a simple diffusivity.

TIME-SCALES

We have used a combination of experimental oscillatory shear rheometry and Brownian Dynamics (BD) simulations in a wide range of frequencies, ω, non-dimensionalized in the dilute regime by $Pe^0_\omega = \omega \tau_B$, with $\tau_B = R^2/D_0$ and $D_0 = k_B T / 6\pi\eta R$ the free Stokes-Einstein-Sutherland diffusion coefficient. However, the short time diffusion slows down with volume fraction due to HIs and thus we use a φ dependent short-time self diffusion coefficient, $D_s(\varphi)$, [4] in a $Pe_\omega = \omega R^2 / D_s(\varphi)$. Since in the BD simulations HI are excluded, the oscillation frequency is non-dimesionalized by Pe_ω.

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