**Supplemental Materials: Self-assembly and rheology of dipolar colloids in simple shear - studied by multi-particle collision dynamics**

1 **Simulation parameters**

The choice of the simulation parameters preserves the hierarchy of the physical and simulation timescales as described previously\(^1\), to ensure consistency with typical colloidal systems: the ratio of the mass of the colloid \(M_p\) to the mass of the MPCD particle \(m_f\) is 79, the nominal number of the MPCD particles per bin is \((n_f) = 6\). The extent of the collision environment \(a\) defines the spatial accuracy of the hydrodynamic flow\(^2\) and is set to \(a = 0.5\sigma\) to properly resolve the flow on the scale of the aggregates \(n \geq 2\), whose contribution to the viscosity scales as \(\propto n^3\). The mean free path of the MPCD particles is \(\lambda_{mpcd} = \Delta t_{mpcd}(\sqrt{\beta M_f})^{-1} \approx 0.3\sigma\) ensuring Galilean invariance\(^1,3\).

The time between the multi-particle collisions is \(\Delta t_{mpcd} = 0.034\tau\), where \(\tau = \sqrt{\beta M_f}\). The simulations are performed with LAMMPS\(^4,5\) in a rheometric slit channel of extent \(L_x, L_y, L_z\) (volume \(V = L_xL_yL_z\)). For zero-field simulations \(L_x = L_y - L_z = 24\sigma\), whereas, for simulations with an applied field (in \(y\) direction) the size of the box is increased for larger interaction parameters: \(L_x = L_y - 16\sigma\) \((\lambda < 4\) or \(24\sigma\) \((\lambda \geq 4)\) and \(L_z = 32\sigma\) \((\lambda < 4\), \(48\sigma\) \((\lambda = 4\), \(72\sigma\) \((\lambda \geq 5)\)) to accommodate the growing microstructure. Periodic BCs are used in the \(x\) (flow) and \(z\) (vorticity) directions, in the \(y\) (gradient) direction the channel is bounded by the free-slip walls realizing reflections \(v_y \rightarrow -v_y\) of the incoming MPCD particles and a short-range repulsive potential of the form (4) (Main text) is applied to the approaching colloids to prevent percolation of the microstructure at larger \(\lambda\). The colloids are randomly dispersed at a predefined volume fraction \(\phi\) (in all simulations \(\phi = 5\text{vol.}\%\) except when \(\phi\) itself is varied) with the total number \(N_p = \phi v_p^{-1}V\), where \(V = L_xL_yL_z\) is the volume of the simulation box and \(v_p = \frac{1}{3} \pi \sigma^3\) is the volume of a colloidal particle. The total number of the MPCD particles is \(N_{mpcd} = a^{-3}V(1-\phi)(n_f)\). In the flow simulations the shearing is induced by adjusting the streaming velocities \(\nu_j\) of the MPCD particles in the bins nearest to the channel walls. After a brief limit run the system was equilibrated for \(t_{eq} = 4,000\tau\) \((\lambda < 8\) \(4,000\tau\) \((\lambda = 4\) or \(20,000\tau\) \((\lambda \geq 5)\)) followed by a production run of \(4,000\tau - 20,000\tau\), depending on the size of the system and the shear rate. Bin-wise sampling was used to measure the flow profile and determine the actual shear rate \(\dot{\gamma}\). Every simulation was repeated between \(4\) and \(32\) times to produce statistically independent trajectories and reduce scatter in the measured observables. The error is reported in terms of the standard deviation.

2 **Equilibrium partition function**

Accounting for just the nearest neighbor interactions the partition function of a self-assembled chain is\(^6\)

\[
Z_n = \int e^{-\beta \sum_{i=1}^{n} U_{dd}(\mathbf{r}_i, \mathbf{r}_{i+1}) + U_{eq}(\mathbf{r}_{i+1})} \prod_{i=1}^{n} \frac{d\mathbf{r}_i}{4\pi} \prod_{i} d\mathbf{r}_{i+1}
\]

(S1)

whereas the interactions beyond the directly adjacent particles along the chain lead to the renormalization of the bond strength \(\lambda \rightarrow \lambda \zeta(3)\), \(\zeta(3) = 1.202\).\(^7,8\) The pair partition function \(Z_2\) in zero and infinite field\(^8\)

\[
H \rightarrow 0: Z_2(0) = 8\lambda \int_{0.5}^{1} \frac{d\lambda}{T^3} \int_{0}^{1} dx \sinh \left( \frac{1}{2} \frac{3\lambda^2}{3-\lambda^2} \right) L_0 \left( \frac{3}{2} \frac{1-x^2}{2} \right)
\]

(S2)

\[
H \rightarrow \infty: Z_2(\infty) = 4\lambda \int_{0.5}^{1} \frac{d\lambda}{T^3} \int_{0}^{1} dx \left( \frac{3}{2} \right)
\]

(S3)

3 **Chain deviation angle**

Tallying the dipolar \((\mathbf{F}^m)\) and hydrodynamic \((\mathbf{F}^h)\) force couples starting from the center \((i = 1)\) of the chain\(^1,12\) in Fig. S1: \(\mathbf{F}^m = 2 \sum_{i=1}^{n} i \sigma e_i \times \mathbf{F}^{h,i}\) where \(e_i\) is the director vector of the chain and \(v_n = \frac{\mathbf{r}_n}{\sigma}\). The energy of the magnetic bond \(U_{dd}(\mathbf{r}_i, \mathbf{r}_{i+1}) = -\lambda kT \left( 3\cos^2 \theta_i - 1 \right)\)

\((\mathbf{e}_i\) is the unit vector in the vertical \((y)\) direction) produces a magnetic force couple: \(\mathbf{F}^0_{i,j} = -\frac{1}{\sigma} \frac{d\mathbf{r}_{i,j}}{dr} \mathbf{e}_j - 6\lambda kT \sigma^{-1} \cos \theta_i \sin \theta_i \mathbf{e}_i \times \mathbf{e}_j\) acting on the \(i\)th and \((i+1)\)th particles \(\theta_i\) is the unit vector in the direction of increasing deviation angle \(\theta_i\). Summing the individual contributions along the chain, a realigning torque is provided by the end particles, where the magnetic force couples are not compensated \(\Gamma^m = -6(n-1) \lambda kT \cos \theta_i \sin \theta_i \mathbf{e}_i \times \mathbf{e}_j\). In turn, assuming the free draining limit, the hydrodynamic force acting on the \(i\)th particle of the \(n\)-particle chain in simple shear \(\mathbf{F}^h_i = 6 \pi n \eta \sigma \gamma^2 \cos \theta_i \mathbf{e}_i\)

\((\mathbf{e}_i\) is the unit vector in the \(x\) direction, \(\eta \) is the viscosity of the solvent) and the deviating torque \(\Gamma^h_j = \frac{1}{2} n(n-1) \pi \eta \gamma \sigma^2 \cos \theta_i \mathbf{e}_i \times \mathbf{e}_j\). The torque equilibrium \(\Gamma^m + \Gamma^h = 0\) yields the deviation angle \(\theta_i\) of the \(n\)-mer

\[
\tan \theta_i = \frac{1}{12} \left( n^2 + n \right) Mn
\]

(S4)

4 **Critical chain length**

Considering the radial force balance of a rigid chain\(^1,12\) (Fig. S1): the \(n\)-particle chain is broken, when the strength of the bond \(\mathbf{F}^m_i = -\frac{d\mathbf{r}_{i,j}}{dr} - 3 \lambda kT \sigma^{-1} \left( 3\cos^2 \theta_i - 1 \right)\) is overcome by the overall shear force extending the chain \(\mathbf{F}^h_i + \mathbf{F}^h_j = -\frac{1}{2} \left( n^2 - 1 \right) \pi n \eta \sigma \gamma \cos \theta_i \sin \theta_i\).

The equation for the maximum length of a stable chain is produced from the radial mechanical balance of the bonding force versus the hydrodynamic erosive force \(F^m_i + F^h_j = 0\) accounting for eq. (S4): \(n^2 + 5n^2 - 2n^2 - 3n - \frac{28}{Mn} = 0\). To a leading order in \(n\) the critical length is

\[
n_{crit} n = \sqrt{\frac{6\sqrt{2}}{Mn}}
\]

(S5)
5 Geometrical coefficients of an n-particle chain

The geometrical coefficients used in eq. (26) are

\[ \alpha_n = \frac{1}{n\alpha_n^0}, \quad \beta_n = \frac{2(n^2-1)}{n(n^2\alpha_0 + \beta_0)} \]
\[ \xi_n = \frac{4}{(n^2+1)n\beta_0^2} - \frac{2}{n\alpha_n^0} \] (S6)

\[ \lambda_n = \frac{n^2-1}{n^2+1}, \quad \chi_n = \frac{2\alpha_n''}{n\alpha_n\beta_0^2} - \frac{8}{(n^2+1)\beta_0^2} + \frac{2}{n\alpha_n^0} \] (S7)

where the elliptic integrals for the case of an ellipsoid of revolution are

\[ \alpha_0 = \int_0^\infty \frac{ds}{(n^2+s)Q_n(s)}, \quad \beta_0 = \int_0^\infty \frac{ds}{(1+s)Q_n(s)} \]
\[ \alpha_0' = \int_0^\infty \frac{ds}{(1+s)^2Q_n(s)}, \quad \beta_0' = \int_0^\infty \frac{ds}{(n^2+s)(1+s)Q_n(s)} \]
\[ \alpha_0'' = \int_0^\infty \frac{sds}{(1+s)^2Q_n(s)}, \quad \beta_0'' = \int_0^\infty \frac{sds}{(n^2+s)(1+s)Q_n(s)} \] (S10)

with \( Q_n(s) = (1+s)\sqrt{n^2+s} \).

References


Figure S2 (a) - simulation snapshot (box size $24\sigma \times 24\sigma \times 24\sigma$) of spontaneous association of dipolar particles without an applied field at a volume fraction $\phi = 5\%$ and dipole interaction parameter $\lambda = 4$. Blue background depicts a sea of MPCD point particles representing the solvent. Simulation snapshots for varying strength of dipolar interactions: (b) $\lambda = 3$, (c) $\lambda = 4$, (d) $\lambda = 5$. Substantial lengthening and branching of the particle chains is observed at larger $\lambda$. Particles color-coded by chain length $n$: monomers ($n = 1$) are blue, $n \geq 10$ - red.

Figure S3 Simulation snapshots (box size $24\sigma \times 48\sigma \times 24\sigma$) with strong vertical external field at a volume fraction $\phi = 5\%$ and dipole interaction parameter $\lambda = 4$ in equilibrium (left - (a), (c)) and under shear (right - (b), (d)) show chains of various length aligned in the direction of the field and deviated by imposed shear flow at $Mn = 0.012$. Side view - (c), (d) along the vorticity direction. Top view - (a), (b) along the direction of the applied field showing that the chains are uniformly dispersed within the layer in either case. Particles color-coded by chain length $n$: monomers ($n = 1$) are blue, $n \geq 10$ - red.
Figure S4 Calculated positional probability density distribution functions $P(r)$ corresponding to the simulations in Figure S3 ($\lambda = 4$, $\phi = 5\%$, note: free-floating monomer contributions are subtracted). Left - 3D PDF $P(r)$ in equilibrium. Right - projection of the PDF $P(x, y) = \int P(r) \, dz$ onto the shear (velocity-vorticity) plane for the same system in equilibrium and at a shear rate $Mn = 0.012$. The deviation of the $n$-particle chains by the angle $\theta_i$ from the direction of the field is visible in the PDF. The bars show the average chain length $\langle n \rangle$ for comparison.
**Figure S5** Chain length distributions $g_n$ in simple shear (with reduced shear rate $Mn$) and strong external field for $\phi = 5\%$ and $\lambda = 4$; $v_p = \frac{1}{6} \pi \sigma^3$ is the particle volume. The inset shows a detailed view of the initial region. The recovery of the tail of the chain length distribution is observed at approx. $0.03 < Mn < 0.15$ signifying a transition into a shear-banded state.

**Figure S6** Scaling factors $\alpha_{Mn}$ and $\beta_{Mn}$ used to collapse the non-equilibrium simulation data in Figure 6 (Main text) as a function of the Mason number $Mn$ for $\lambda = 2$ (●), $\lambda = 3$ (▲), $\lambda = 4$ (□), $\lambda = 5$ (●). For lower shear rates $Mn < 10^{-2} \alpha_{Mn} = 1$ and $\alpha_{Mn} = 1 - \beta_{Mn}$. The lines are intended to guide the eye.

**Figure S7** Projection of the non-equilibrium PDF $P(\mathbf{r})$ onto the shear (velocity-vorticity) plane without an applied field at a volume fraction $\phi = 5\%$, dipole interaction parameter $\lambda = 4$ and $Mn = 0.016$, showing the deformation of the conformations ellipsoid in simple shear.
Figure S8  Intrinsic viscosity $[\eta]$ as a function of the Mason number $M_n$ for varying fraction of dipolar particles $\phi = 1\% - 9\%$ at $\lambda = 4$. A series of calculations has been performed with varying volume fractions $\phi = 1\% - 9\%$ of the colloidal particles to check whether the intrinsic viscosity (28) provides an appropriate scaling for a self-assembled system, where the contributions of the individual colloidal particles should not be additive. The figure shows that for all considered volume fractions the shear thinning regions satisfactorily collapse onto a single curve, which is supported by the chain model. In turn, the model predicts that the plateau region scales as $[\eta] \propto \phi^2$. The simulation data also shows some dispersion in the vicinity of plateau, however, much smaller than the theoretically predicted. Thus, the intrinsic viscosity provides a satisfactory scaling with respect to the concentration $\phi$ of the colloidal particles along the whole viscometric curve.