A structural analysis of concentrated, aggregated colloids under flow

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Using both instantaneous snapshots and simulation generated scattering data, the steady-state flow behaviour of a concentrated aggregated colloidal suspension is analysed in terms of its structure factor \(S(k)\). We find that in the shear thinning regime, unlike model hard sphere results, \(S(k)\) exhibits pre-peaks at small \(k\), which we interpret as indicative of intermediate range order in the shear induced melt. The pre-peak disappears upon the onset of an ordered state of flow at high shear rates, which, like hard sphere results, exhibit Bragg-like peaks in \(S(k)\). These ordered states are associated with the so-called string phases.

1. Introduction

Colloidal suspensions show a variety of flow properties. It is well known, both experimentally \([1]\) and through computer modelling \([2, 3]\) that concentrated (for colloid concentration above 30\%) model hard sphere systems (hard core colloids with steric coats) undergo mild shear thinning and then order (before the onset of shear thickening \([4]\)) with increasing shear rate. Similarly, a suspension of aggregating colloids (a similar system that also includes attractive forces between the particles) at the same volume fraction, will exhibit extreme shear thinning whereby the viscosity changes by orders of magnitude with shear rate \([5, 6]\), though the onset of the disorder-order transition is inhibited in the presence of the aggregating forces.

The studies referred to above assume that the different viscous responses between non-aggregating and aggregating systems are due to structural changes in the colloid microstructure. However, this assumption has never been established clearly. Here we address this problem by studying the changes observed in the structure factor \(S'(k)\) generated from simulations of flowing colloids.

Recent progress in computer simulation techniques have enabled the computation of \(S(k)\) from Brownian dynamics simulations of colloidal fluids \([7]\). Heyes and Mitchell \([7]\) were able to show the qualitative similarities in \(S'(k)\) between atomic and (hard-sphere-like) colloidal fluids under shear, although each system is governed by different kinetics: Newton's equations for the atomic system and Langevin's equations for the colloidal system. Both systems exhibit liquid-like short range order in the shear thinning regime until the onset of the ordered string phase at high shear rates. Differences between the two classes of system normally show up in the dynamic structure factor and in their transport properties.

Here we are concerned with the correlation of behaviour between the shear viscosity \(\eta\), as a function of the shear rate, and \(S(k)\). In this work we attempt to provide deeper insight into the simple shear flow behaviour of concentrated aggregated colloidal suspensions by providing a qualitative description of the associated structural characteristics of these systems and comparing these results with similar hard sphere systems. We aim qualitatively to relate the observed structural data to the rheology that these systems are known to possess \([6]\). This is achieved by analysing the computed static structure factor generated from flow simulations that include hydrodynamic interactions, plus configuration snapshots to characterize qualitatively and visualize structures in the particle configurations induced by shear.

Ideally we would also like to present data on the radial distribution function \(g(r)\). However, due to orientational and other difficulties this is not possible. Whereas the simulated \(S(k)\) can be defined along specific directions, for \(g(r)\) we would have to calculate the angular dependent pair distribution function \(g(r, \theta, \phi)\). Work continues along these lines.

We describe briefly in the next section the important data and simulation techniques. A detailed account of

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both methodology and techniques is available elsewhere [6, 8]. In section 3 we present the results of our simulations. We also include a brief summary of the rheology data, relevant to this work, from our previous flow simulations on concentrated and aggregated systems [6, 8]. These data help us to emphasize the qualitative and quantitative differences between aggregating and non-aggregating systems. In the case of $S(k)$ for aggregating systems, there is clear evidence of the existence of intermediate range order (IRO) in the shear thinning regime which is not present in the $S(k)$ of non-aggregating systems in the same regime.

We also present $S(k)$ for the aggregating system over a range covering decades of shear rate, both in the shear thinning and the high shear rate regimes. We complete these results with instantaneous microstructural snapshots of the aggregating suspension at various shear rates.

2. Simulation method

2.1. Equations of motion

The simulation modelling essentially comprises a version [8] of Stokesian dynamics [10, 11] which makes possible the study of concentrated colloidal systems by incorporating Lees–Edwards boundary conditions [12] on arbitrarily large, defined by the box volume $\Omega$, periodic cells. In considering timescales long with respect to the viscous momentum relaxation time of the suspension, we treat the particles at the Langevin/Smoluchowski level and the fluid by the creeping flow equations. Stick boundary conditions are imposed on the fluid at the particle surfaces.

For $N$ such particles of diameter $d$ immersed in a Newtonian fluid with viscosity $\mu$, the equations of motion are described by the coupled $N$-body Langevin equation expressing force balance:

$$ F^H + F^P + F^B = 0. $$

(1)

The $6N$ force/torque vectors are: (i) hydrodynamic forces $F^H$, exerted on the particles due to their relative motions in the presence of the solvent; (ii) colloidal forces $F^P$ (the sum of repulsive and attractive terms); and (iii) Brownian forces $F^B$.

The terms $F^H$ and $F^B$ have approximate representations and their detailed expressions are available elsewhere [6, 8, 9, 13]. Here $F^H$ is approximated by lubrication hydrodynamic terms acting at the pairwise level in the resistance formalism that leads to a correct many-body and long range mobility term upon inversion [8].

The colloid force term $F^P$ contains both attractive (hence the term ‘aggregated’) colloids and repulsive contributions: $F^P = f^{\text{dep}} + f^{\text{rep}}$. These forces are defined by a

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colloid volume fraction $\phi_c$</td>
<td>0.50</td>
</tr>
<tr>
<td>Number of particles $N$</td>
<td>200, 700</td>
</tr>
<tr>
<td>Spring coat thickness $\delta_t/d$</td>
<td>0.005</td>
</tr>
<tr>
<td>Size ratio $R_g/d$</td>
<td>0.10</td>
</tr>
<tr>
<td>Polymer volume fraction $\phi_p$</td>
<td>0.70</td>
</tr>
<tr>
<td>Spring stiffness $F_0$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>Potential well-depth $U_{\text{min}}/k_BT$</td>
<td>9.0</td>
</tr>
</tbody>
</table>

We choose to model depletion aggregated colloids; that is colloids in a mixture with non-adsorbing polymers of size $R_g$ at volume fraction $\phi_p$ (which sets the depth of the attractive well). We assume a size ratio 10:1 for the colloid to polymer diameters (this sets the range of the attractive force), and therefore model the aggregating forces $f^{\text{dep}}$ on the Asakura–Oosawa depletion potential [14]. This has been measured recently for the case of colloid–polymer mixtures near a wall [15], though recent work has highlighted the limitations of the Asakura–Oosawa potential [16].

A very short range repulsive force $f^{\text{rep}}$ is included also at the surface of the spheres. This takes on the form of a short Hookean spring force mimicking the osmotic part of an attached/adsorbed polymer layer. The spring coat thickness $\delta_t$ sets how much the thermodynamic size of the particle exceeds the hydrodynamic size, and the strength of the spring (which sets the maximal force the spring can supply before collapse) is parametrized by the dimensionless stiffness $F_0$, which is given the value $10^4$ throughout this study. We emphasize the physical significance of the Hookean spring coat in the context of our flow simulations. For the case of sterically stabilized or depletion aggregating colloidal systems, the colloid particles include some form of steric barrier to avoid irreversible coagulation in the deep van der Waals primary minima. Perfectly smooth particles do not exist, although simulations of this pathological case of bare hard spheres have been carried out [17]. Such systems never reach a steady state flow and jam after finite strain [18].

The interaction potential is shown in figure 1, and may be thought of as the colloidal equivalent of a Lennard-Jones system. The size of the cubic simulation box has side length $L$. To provide a reasonable study of structure, most of our studies are done on 700-particle
systems, with $L \approx 9d$, though we occasionally refer to smaller systems ($N = 200$). We find that some fine detail is lost with the smaller systems (particularly in $S(k)$). However, trends seen in the larger systems ($N = 700$, and our ongoing studies at $N = 4000$) are seen in the smaller systems.

2.2. Computation of the stress tensor

In the simulation, the viscosity is obtained from the $xy$ element of the stress tensor $\sigma$ (recall that in simple shear: $\sigma_{xy} = \eta(\dot{\gamma})\dot{\gamma}$) which is computed as the sum over nearest-neighbour (for which a criterion exists [9]) interacting particle pairs $i$ and $j$, and is given by

$$\sigma = -\frac{1}{\Omega} \sum_{\alpha} \sum_{ij} f_{ij,\alpha} r_{ij} + \sigma^B,$$

where $r_{ij}$ is the centre–centre vector separation from particle $i$ to its neighbour $j$, and the sum over $\alpha$ is the sum over the various colloid and dissipative forces $f_{ij,\alpha}$. The Brownian contribution to the stress $\sigma^B$ is detailed elsewhere [8, 13]. Normalization is with respect to the volume of the computational box $\Omega$.

We measure the imposed shear rate in terms of the non-dimensional shear rate the Péclet number. In the simulations, the units are chosen so that the particle diameter $d$, the solvent viscosity $\mu$, and the thermal energy $k_B T$, Boltzmann’s constant times the absolute temperature, are numerically equal to unity. We define the Péclet number, $Pe$, as

$$Pe = \frac{\gamma d \dot{\gamma}}{k_B T}. \quad (3)$$

In these units, therefore, $Pe$ is the shear rate. Consequently, time is measured in units of $d \dot{\gamma}/k_B T$ and force in units of $k_B T / d$.

Although most of our structural analyses are made on systems that do not include Brownian forces, nevertheless we insist on measuring the shear rate in units of $Pe$, although it is not strictly correct to do so. Our previous studies [6] on model variations that compare systems with and without Brownian forces show that the inclusion of Brownian forces plays no qualitative role in determining the rheology of such systems.

2.3. Scattering by simulation

In the analysis of the simulation-generated structure factor the approach we take is that the particles are, by definition of the simulation model, spherical and monodisperse. Likewise, with an experimental analysis we assume that the Born approximation holds, i.e., that multiple scattering may be neglected. Actually, multiple scattering does become increasingly problematic, in the analysis of experimental data, with increasing concentration. Moreover, and again by analogy with experiment, we assume that the colloidal particles are the only finite objects present in solution, with the suspending medium and stabilizing polymers forming a neutral background.

Experimentally, specifically for light scattering, this is achieved by index matching the suspending medium to
the colloids, along with density matching to minimize buoyancy effects. For example, usually PMMA particles are suspended in a mix of organic solvents to achieve the best matching conditions. This amounts to regarding the scattered intensity of this neutral background to be negligible compared with that scattered by the colloidal particles.

For the simulation studies presented in this work the problem reduces to calculating the scattering from a one-component macrofluid in which the particles interact via a specified pair potential. In the simulations we can write down a snapshot of the structure factor, at a given value of the wavenumber \( k = |\mathbf{k}| \), as

\[
S(k) = \frac{1}{N} \sum_{i \neq j} \exp \left[ i \mathbf{k} \cdot \left( \mathbf{r}_i - \mathbf{r}_j \right) \right]
\]

where the sum \( i \) is over all \( N \) particles. At each shear rate, ensemble averages are then taken such that the structure factor

\[
S(k) = \langle S(k) \rangle
\]

where \( \langle \ldots \rangle \) denotes an ensemble average over many (\( > 50 \)) particle configurations (snapshots). We are assuming we are entitled to take this average because we take the averages only after the system has reached its steady-state rheology.

In the simulations the periodic box distorts along with the shear flow, therefore the reciprocal lattice vectors vary also. Calculating \( S(k) \) from a distorted box complicates the computation. However, if we start with a rectangular system then at each unit strain the reciprocal lattice vectors are commensurate with the original lattice vectors; hence, for the sake of consistency, the post analysis of \( S(k) \) is restricted to the set of vectors for an undistorted box from configurations sheared at unit strains. The resolution in \( k \) space is restricted also by the periodic boundary conditions such that the allowed \( k \)-vectors are integer multiples of \( 2\pi/L \) (\( L \) is the length of the computational box), with \( k = 2\pi/L \) the lowest value allowed.

3. Results

3.1. Rheology and snapshots

In our previous rheological studies \([6]\) we showed that our concentrated aggregating systems exhibit power law shear thinning behaviour over many decades in shear rate, and also over a range in \( \phi_c \) in the concentrated regime. During this particular regime, the viscosity of the aggregating systems is greatly enhanced over an equivalent non-aggregating system. We summarize this in figure 2, which shows the computed rheology curves of two 200-particle systems: one with aggregating forces (with \( U_{\text{min}} = -9k_B T \), the other without aggregating forces (i.e., a hard sphere suspension), at 50% colloid volume fraction that includes hydrodynamic interactions, Brownian forces, and Hookean spring surface forces. We also plot additional points, at \( \text{Pe} = 1.0 \), where we have varied the strength (but not the range) of the attractive forces: \( U_{\text{min}} = -5.2k_B T \) and \(-2.6k_B T \).

In an analysis of the contributions to the viscosity \([6]\), we find that the Hookean spring forces dominate the computed viscosity (cf. equation (2)) in all systems.
This must come about from mild compression of these spring coats of closely approaching surfaces (though not so close that the hydrodynamic lubrication forces diverge). However, as the depth of the attractive well increases, the magnitude of the Hookean viscosity term likewise increases. Therefore, the mechanism(s) that give(s) rise to the enhanced viscous response experienced by those systems that include aggregating forces, arises from a complex interplay between the aggregating forces and the surface spring coats.

These data suppose an evolving structural mechanism that becomes increasingly important as the attractive forces become stronger. In typically heuristic fashion, instantaneous snapshots of particle configurations viewed in the gradient–vorticity plane (i.e., looking down the flow direction) are shown in figure 3. We choose this direction as ordering is best visualized in this plane. We picture images of particles (which are drawn half-size for clarity) whose centres lie within the central box of the periodic system. These snapshots are of 200-particle systems, sheared at $\text{Pe} = 1.0$, that have reached a steady state flow, and we compare between (a) the non-aggregating system (effectively $U_{\text{min}} = 0.0$), and the weakly aggregating systems (b) $U_{\text{min}} = -2.6k_B T$ and (c) $U_{\text{min}} = -5.2k_B T$, and then (d) a mildly aggregating system ($U_{\text{min}} = -9.0k_B T$). It is apparent that although we are studying a variation in parameter space of the aggregating forces, the microstructural configurations appear qualitatively similar.

There is no obvious ordering, nor any fractal-type clustering usually associated with shear thinning suspensions (of systems at lower volume fractions than of...
interest here) [19, 20], and so in this first instance we are unable to differentiate between the various systems. Besides, a snapshot is a picture configuration at an instant in time and does not take into account any time-averaged behaviour. Therefore, in an attempt to provide further insight into these structural questions, we plot the corresponding static structure factor $S(k)$, directed along the flow direction, in figure 4. We note that there are important differences in the $S(k)$s plotted in figure 4. Although in all cases the structure factor exhibits liquid-like short range order, the principal peak of $S(k)$ for the aggregating systems is higher and shifted towards larger values of $k$ compared with the structure of the hard sphere colloidal system. Moreover, the highest principal peak of $S(k)$ for the aggregating system corresponds to a deeper potential well. There is, moreover, a fundamental difference between $S(k)$ values for aggregating and non-aggregating systems at small values of $k$. $S(k)$ for the hard sphere colloid decreases asymptotically (as $k^2$) to its long wavelength limit. However, for the aggregating systems a pre-peak (at $k \approx 1.0$) emerges: the signature of intermediate range order in the fluid. The main figure, which shows the results of the simulations with 200 particles, can show only the changes for small $k$, and clearly these are more pronounced with increasing values of the potential well $U_{\min}$. With larger systems of 700 particles, which probe smaller values of $k$, the inset shows the actual pre-peak for one aggregating system, with $U_{\min} = -9.0 k_B T$, with the hard sphere result also shown for comparison. We note that the actual position of the pre-peak may be dependent on system size. Nonetheless there is no doubt of the presence of the pre-peak, the inclusion of aggregating forces induces a significant difference in the structure of the systems, and the difference is the emergence of longer range correlations in the form of intermediate range order.

### 3.2. Structural analysis

It is apparent that the qualitative differences in the rheology during shear thinning are necessarily due to some modified structural mechanism that shows up as pre-peaks in $S(k)$ of the aggregating system. Yet, although there exist several studies on the structural evolution of flowing model hard spheres [1, 2, 3], similar results for concentrated aggregated colloids are not presently available. It is precisely these results which are presented below, specifically studying the effects on the structure of varying shear rates in aggregating systems.

In the following analysis we ignore Brownian forces, in order to ease computational burden. At the well depth we have carried out the following simulations (fixed at $U_{\min} = -9 k_B T$) with Brownian forces negligible in comparison with the aggregating forces. We have shown, during studies over a parameter space of model variations [6], that Brownian forces play no qualitative role in determining the rheology.

Figures 5 and 6 show $S(k)$ as 2-dimensional plots viewed in both the flow–vorticity and flow–gradient...
planes. The former is the plane that is most accessible to experiment. The latter we believe is the plane that is most relevant to structure in simple shear flow (the compression and extensional directions are the diagonal directions in the flow gradient plane). We note, in passing, that experimental results usually are given in terms of the scattering intensity $I(k)$ from which $S(k)$ may be deduced. The wavelength is given, in all figures, in the non-dimensional form $kd$, with $d$ the particle diameter (which is set to unity in the simulations). The results below are at the shear rates, $\text{Pe} = 0.01, 1.0, 10.0, \text{and} 100.0$.

Figures 5 and 6 (a, b) show $S(k)$ viewed in both the flow–vorticity and flow–gradient planes in the shear thinning regime, $\text{Pe} = 0.01$ and 1.0. Besides the pre-peaks at $k \approx 1.0$, signalling intermediate range order, the behaviour of $S(k)$ is fluid-like. At intermediate shear rates, $\text{Pe} = 10.0$, where the system is nearing the end of the shear thinning regime (figures 5 (c) and 6 (c)), there is a significant decrease in the amplitude of the pre-peaks in $S(k)$. This implies that the structural mechanisms responsible for the correlations that give rise to IRO, and hence the enhanced viscous response in the aggregating systems, are being disrupted with increasing shear rate. Moreover, we note that the near-neighbour ring correlations are enhanced from their shear thinning values, indicating stronger short range correlations.

At high shear rates, $\text{Pe} = 100.0$, other correlation (Bragg-like) peaks appear, as seen in figures 5 (d) and 6 (d). Here the circular rings of the subsequent figures...
appear to be sliced by the longer \( k \) correlations due to the emergence of the string phase ordering, which was observed first in hard sphere systems, although the presence of the aggregating forces inhibits this transition in structure, which occurs at lower shear rates for equivalent non-aggregating systems. The peaks are now due to inter- and intra-string correlations. However, liquid-like short range order persists to some degree.

4. Discussion and conclusion

The structure factor \( S(k) \) of aggregating and non-aggregating concentrated colloidal suspensions in the shear thinning regime has been shown to differ qualitatively, particularly at small values of the wavenumber \( k \). This mirrors the different rheological behaviour of the two classes of system in the same regime. We propose that the differences are due to a structural mechanism that enhances the viscous response of the aggregating system. At the level of the static structure factor \( S(k) \), this mechanism is manifested as intermediate range order arising from correlations between particle clusters, as yet ill defined, within the bulk suspension. The correlations giving rise to IRO do not appear to be long lived in our simulations, although their relaxation times must be longer than collision times in the colloid suspension.

In atomic systems, pre-peaks, and features associated with IRO, have been observed in some liquid alloys in thermodynamic equilibrium that, for instance, exhibit specific types of covalent bonding [22]. However, no liquid binary mixture of hard-sphere-like systems in thermodynamic equilibrium are known to exhibit IRO. Single-component atomic systems in thermodynamic

Figure 6. \( S(k) \) viewed in the flow–gradient plane with increasing shear rate: (a) \( \text{Pe} = 0.01 \); (b) \( \text{Pe} = 1.0 \); (c) \( \text{Pe} = 10.0 \); and (d) \( \text{Pe} = 100.0 \).
equilibrium are known to exhibit IRO in their total static structure factor only when the liquid is made up by actual molecules, c.f. liquid CCl$_4$ [23].

The calculations presented in this work are the first to exhibit IRO for a pseudo single-component system of colloidal particles interacting via an effective pair potential. Since effective pair potentials in single component atomic systems are unlikely to induce intermediate range order, we have to look for an explanation of this behaviour elsewhere. We suggest that the pre-peaks in our simulations come about as the result of some complex interplay between the colloid forces in the presence of imposed shear. We are at present trying to unravel the mechanisms of this interplay and will report on our conclusions in due course. Moreover, it may be an interesting exercise to study whether an atomic system under shear which includes attractive forces, say a Lennard-Jones like fluid, does exhibit intermediate range order in some shear regime. Although there are in the literature many studies of Lennard-Jones fluids under shear, none, to our knowledge, has looked at the behaviour of the static structure factor.

Beyond the shear thinning regime, $\text{Pe} \geq 10.0$, pre-peaks give way to an emerging pseudo-crystalline phase. Ordered structures have been observed previously in high shear studies of concentrated colloids [21]. There is broken symmetry in going from a homogeneous liquid-like dispersion to a crystalline-like dispersion, yet whether this transition is continuous or not is still unclear.

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